Handout 1

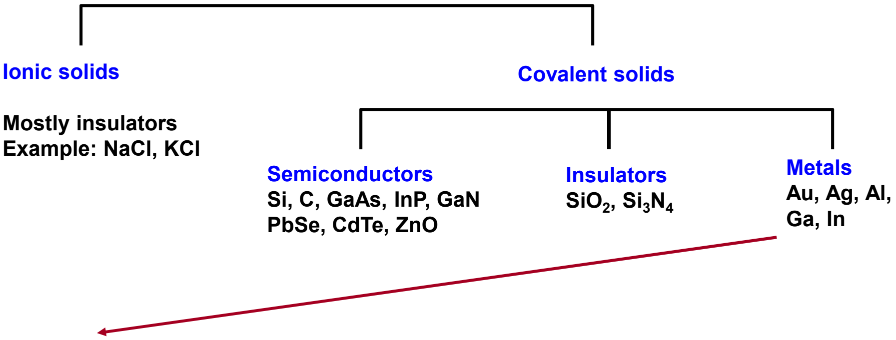
Drude Model for Metals

In this lecture you will learn:

- Metals, insulators, and semiconductors
- Drude model for electrons in metals
- Linear response functions of materials

Paul Drude (1863-1906)

Inorganic Crystalline Materials



Ionic solids

Mostly insulators
Example: NaCl, KCl

Covalent solids

Semiconductors
Si, C, GaAs, InP, GaN
PbSe, CdTe, ZnO

Insulators
SiO_2, Si_3N_4

Metals
Au, Ag, Al,
Ga, In

Metals

1- Metals are usually very conductive

2- Metals have a large number of “free electrons” that can move in response to an applied electric field and contribute to electrical current

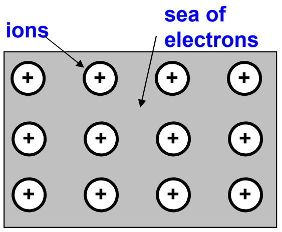
3- Metals have a shiny reflective surface

Properties of Metals: Drude Model

Before ~1900 it was known that most conductive materials obeyed Ohm's law (i.e. *I* =*V/R*).

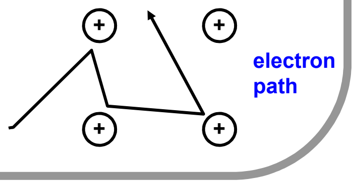
In 1897 J. J. Thompson discovers the electron as the smallest charge carrying constituent of matter with a charge equal to "-*e*"

$$e = 1.6 \times 10^{-19}\ \text{C}$$



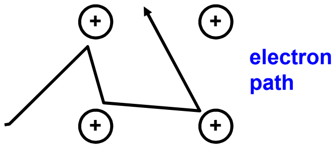
In 1900 P. Drude formulated a theory for conduction in metals using the electron concept. The theory assumed:

1) Metals have a large density of "free electrons" that can move about freely from atom to atom ("sea of electrons")
2) The electrons move according to Newton's laws until they scatter from ions, defects, etc.
3) After a scattering event the momentum of the electron is completely random (i.e. has no relation to its momentum before scattering)



Drude Model - I

Applied Electric Field:



In the presence of an applied external electric field $\vec{E}$ the electron motion, on average, can be described as follows:

Let τ be the scattering time and $1/\tau$ be the scattering rate

This means that the probability of scattering in small time interval time *dt* is: $\dfrac{dt}{\tau}$

The probability of not scattering in time *dt* is then: $\left(1-\dfrac{dt}{\tau}\right)$

Let $\vec{p}(t)$ be the average electron momentum at time *t* , then we have:

$$\vec{p}(t+dt) = \underbrace{\left(1-\frac{dt}{\tau}\right)\left(\vec{p}(t) - e\,\vec{E}(t)\,dt\right)}_{\text{If no scattering happens then Newton's law}} + \underbrace{\left(\frac{dt}{\tau}\right)(0)}_{\text{If scattering happens then average momentum after scattering is zero}}$$

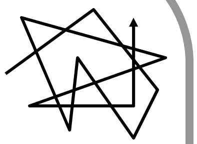
$$\boxed{\Rightarrow \frac{d\vec{p}(t)}{dt} = -e\,\vec{E}(t) - \frac{\vec{p}(t)}{\tau}}$$

Drude Model - II

Case I: No Electric Field

$$\frac{d\vec{p}(t)}{dt} = -\frac{\vec{p}(t)}{\tau}$$

Steady state solution: $\vec{p}(t) = 0$



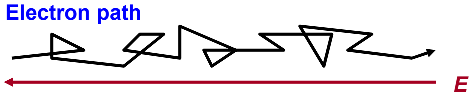
Electron path

Case II: Constant Uniform Electric Field

Steady state solution is:

$$\vec{p}(t) = -e\,\tau\,\vec{E}$$

Electron path



Electron "drift" velocity is defined as:

$$\vec{v} = \frac{\vec{p}(t)}{m} = -\frac{e\,\tau}{m}\vec{E} = -\mu\,\vec{E}$$

$\mu = e\tau/m$ = electron mobility
(units: $\mathrm{cm^2/V\text{-}sec}$)

Electron current density $\vec{J}$ (units: $\mathrm{Amps/cm^2}$) is:

$$\vec{J} = n\,(-e)\,\vec{v} == n\,e\,\mu\,\vec{E} = \sigma\,\vec{E}$$

Where: n = electron density (units : $\#/\mathrm{cm}^3$)

$$\sigma = \text{electron conductivity (units : Siemens/cm)} = ne\mu = \frac{ne^2\tau}{m}$$

Drude Model - III

Case III: Time Dependent Sinusoidal Electric Field

$$\Rightarrow \quad \frac{d\vec{p}(t)}{dt} = -e\,\vec{E}(t) - \frac{\vec{p}(t)}{\tau}$$

There is no steady state solution in this case. Assume the E-field, average momentum, and currents are all sinusoidal with phasors given as follows:

$$\vec{E}(t) = \mathrm{Re}\left[\vec{E}(\omega)\,e^{-i\,\omega\,t}\right] \qquad \vec{p}(t) = \mathrm{Re}\left[\vec{p}(\omega)\,e^{-i\,\omega\,t}\right] \qquad \vec{J}(t) = \mathrm{Re}\left[\vec{J}(\omega)\,e^{-i\,\omega\,t}\right]$$

$$\frac{d\vec{p}(t)}{dt} = -e\,\vec{E}(t) - \frac{\vec{p}(t)}{\tau} \quad \Rightarrow \quad -i\omega\vec{p}(\omega) = -e\vec{E}(\omega) - \frac{\vec{p}(\omega)}{\tau}$$

$$\Rightarrow \quad \vec{p}(\omega) = -\frac{e\,\tau}{1 - i\,\omega\,\tau}\vec{E}(\omega) \quad \Rightarrow \quad \vec{v}(\omega) = \frac{\vec{p}(\omega)}{m} = -\frac{e\,\tau/m}{1 - i\,\omega\,\tau}\vec{E}(\omega)$$

Electron current density:

$$\vec{J}(\omega) = n\,(-e)\,\vec{v}(\omega) = \sigma(\omega)\,\vec{E}(\omega)$$

Where:

$$\boxed{\sigma(\omega) = \frac{\frac{ne^2\tau}{m}}{1 - i\,\omega\,\tau} = \frac{\sigma(\omega = 0)}{1 - i\,\omega\,\tau}}$$

Drude's famous result !!

Linear Response Functions - I

The relationship:

$$\vec{J}(\omega) = \sigma(\omega)\,\vec{E}(\omega)$$

is an example of a relationship between an applied stimulus (the electric field in this case) and the resulting system/material response (the current density in this case). Other examples include:

$$\vec{P}(\omega) = \varepsilon_o\,\chi_e(\omega)\,\vec{E}(\omega)$$

electric polarization density — **electric susceptibility** — **electric field**

$$\vec{M}(\omega) = \chi_m(\omega)\,\vec{H}(\omega)$$

magnetic polarization density — **magnetic susceptibility** — **magnetic field**

The response function (conductivity or susceptibility) must satisfy some fundamental conditions …. (see next few pages)

Linear Response Functions - II

Case III: Time Dependent Non-Sinusoidal Electric Field

For general time-dependent (not necessarily sinusoidal) e-field one can always use Fourier transforms:

$$\vec{E}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\vec{E}(\omega)\,e^{-i\,\omega\,t} \quad \Leftrightarrow \quad \vec{E}(\omega) = \int_{-\infty}^{\infty} dt\;\vec{E}(t)\,e^{i\,\omega\,t} \longrightarrow (1)$$

Then employ the already obtained result in frequency domain:

$$\vec{J}(\omega) = \sigma(\omega)\,\vec{E}(\omega)$$

And convert back to time domain:

$$\vec{J}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\vec{J}(\omega)\,e^{-i\,\omega\,t} = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\sigma(\omega)\,\vec{E}(\omega)\,e^{-i\,\omega\,t}$$

Now substitute from (1) into the above equation to get:

$$\vec{J}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\sigma(\omega)\,\vec{E}(\omega)\,e^{-i\,\omega\,t} = \int_{-\infty}^{\infty} dt' \left[\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\sigma(\omega)\,e^{-i\,\omega(t-t')}\right]\vec{E}(t')$$

$$\Rightarrow \vec{J}(t) = \int_{-\infty}^{\infty} dt'\,\sigma(t-t')\,\vec{E}(t')$$

Linear Response Functions - III

$$\Rightarrow \vec{J}(t) = \int_{-\infty}^{\infty} dt' \, \sigma(t-t') \, \vec{E}(t') \qquad \text{Where:} \quad \sigma(t-t') = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \sigma(\omega) \, e^{-i\,\omega(t-t')}$$

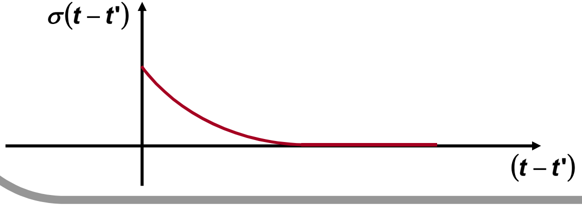
The current at time *t* is a convolution of the conductivity response function and the applied time-dependent E-field

Drude Model: $\sigma(\omega) = \dfrac{\sigma(\omega=0)}{1 - i\,\omega\,\tau}$

$$\sigma(t-t') = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \sigma(\omega) \, e^{-i\,\omega(t-t')} = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \frac{\sigma(\omega=0)}{1 - i\,\omega\,\tau} \, e^{-i\,\omega(t-t')}$$

$$\Rightarrow \sigma(t-t') = \frac{\sigma(\omega=0)}{\tau} \, e^{-\frac{(t-t')}{\tau}} \, \theta(t-t')$$

step function



Linear Response Functions - IV

The linear response functions in time and frequency domain must satisfy the following two conditions:

1) Real inputs must yield real outputs:

Since we had: $$\vec{J}(t) = \int_{-\infty}^{\infty} dt' \left[\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \sigma(\omega) \, e^{-i\,\omega(t-t')} \right] \vec{E}(t')$$

This condition can only hold if:

$$\sigma(-\omega) = \sigma^{*}(\omega)$$

2) Output must be causal (i.e. output at any time cannot depend on future input):

Since we had: $$\vec{J}(t) = \int_{-\infty}^{\infty} dt' \, \sigma(t-t') \, \vec{E}(t')$$

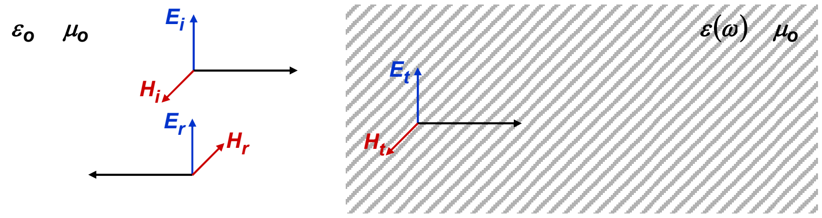
This condition can only hold if:

$$\sigma(t-t') = 0 \quad \text{for} \quad t < t'$$

Both these conditions are satisfied by the Drude model

Drude Model and Metal Reflectivity - I

When E&M waves are incident on a air-metal interface there is a reflected wave:



The reflection coefficient is:

$$\Gamma = \frac{E_r}{E_i} = \frac{\sqrt{\varepsilon_o} - \sqrt{\varepsilon(\omega)}}{\sqrt{\varepsilon_o} + \sqrt{\varepsilon(\omega)}}$$

Question: what is $\varepsilon(\omega)$ for metals?

Drude Model and Metal Reflectivity - II

From Maxwell's equation:

Ampere's law: $\nabla \times \vec{H}(\vec{r},t) = \vec{J}(\vec{r},t) + \varepsilon_o \frac{\partial \vec{E}(\vec{r},t)}{\partial t}$

Phasor form:
$$\begin{aligned} \nabla \times \vec{H}(\vec{r}) &= \vec{J}(\vec{r}) - i\,\omega\,\varepsilon_o\,\vec{E}(\vec{r}) \\ &= \sigma(\omega)\vec{E}(\vec{r}) - i\,\omega\,\varepsilon_o\,\vec{E}(\vec{r}) \\ &= -i\,\omega\,\varepsilon_{eff}(\omega)\,\vec{E}(\vec{r}) \end{aligned}$$

Effective dielectric constant of metals

$$\varepsilon_{eff}(\omega) = \varepsilon_o\left(1 + i\frac{\sigma(\omega)}{\omega\,\varepsilon_o}\right)$$

Metal reflection coefficient becomes:

$$\Gamma = \frac{E_r}{E_i} = \frac{\sqrt{\varepsilon_o} - \sqrt{\varepsilon_{eff}(\omega)}}{\sqrt{\varepsilon_o} + \sqrt{\varepsilon_{eff}(\omega)}}$$

Using the Drude expression: $\sigma(\omega) = \frac{\sigma(\omega = 0)}{1 - i\,\omega\,\tau}$

the frequency dependence of the reflection coefficient of metals can be explained adequately all the way from RF frequencies to optical frequencies

Drude Model and Plasma Frequency of Metals

For metals: $\varepsilon_{eff}(\omega) = \varepsilon_o \left(1 + i\,\dfrac{\sigma(\omega)}{\omega\,\varepsilon_o}\right)$ and $\sigma(\omega) = \dfrac{ne^2\tau/m}{1 - i\,\omega\,\tau} = \dfrac{\sigma(\omega = 0)}{1 - i\,\omega\,\tau}$

For small frequencies $(\omega\tau << 1)$:

$$\sigma(\omega) \approx \sigma(\omega = 0) = \frac{ne^2\tau}{m} \qquad \Rightarrow \quad \varepsilon_{eff}(\omega) \approx \varepsilon_o \left(1 + i\,\frac{\sigma(\omega = 0)}{\omega\,\varepsilon_o}\right)$$

For large frequencies $(\omega\tau >> 1)$ (collision-less plasma regime):

$$\sigma(\omega) \approx \frac{\sigma(\omega = 0)}{-i\omega\,\tau} = i\,\frac{ne^2}{m\omega} \qquad \Rightarrow \quad \varepsilon_{eff}(\omega) \approx \varepsilon_o \left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

where the plasma frequency is: $\omega_p = \sqrt{\dfrac{ne^2}{\varepsilon_o m}}$

For most good metals this frequency is in the UV to visible range

Electrons behave like a collision-less plasma

Note that for $\omega_p > \omega >> \dfrac{1}{\tau}$ the dielectric constant is real and negative

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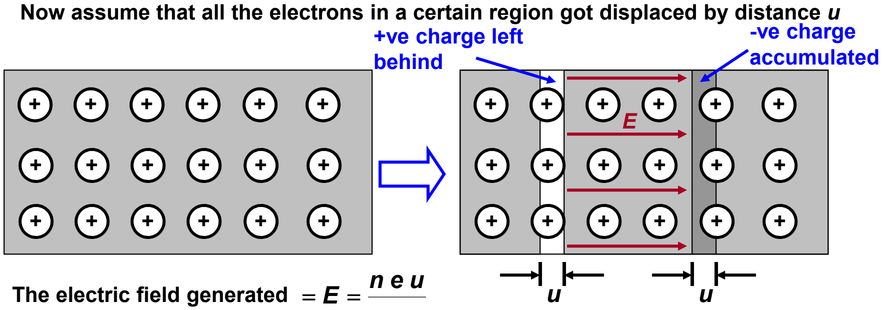
Plasma Oscillations in Metals

Consider a metal with electron density *n*
Now assume that all the electrons in a certain region got displaced by distance *u*



The electric field generated $= E = \dfrac{n\,e\,u}{\varepsilon_o}$

Force on the electrons $= F = -eE = -\dfrac{n\,e^2\,u}{\varepsilon_o}$

As a results of this force electron displacement *u* will obey Newton's second law:

$$m\frac{d^2u(t)}{dt^2} = F = -eE = -\frac{n\,e^2\,u(t)}{\varepsilon_o} \qquad \Rightarrow \quad \frac{d^2u(t)}{dt^2} = -\omega_p^2\,u(t)$$

← second order system

Solution is: $u(t) = A\cos(\omega_p t) + B\sin(\omega_p t)$

Plasma oscillations are charge density oscillations

Plasma Oscillations in Metals – with Scattering

From Drude model, we know that in the presence of scattering we have:

$$\frac{d\vec{p}(t)}{dt} = -e\,\vec{E}(t) - \frac{\vec{p}(t)}{\tau} \quad\Rightarrow\quad m\frac{d^2u(t)}{dt^2} = -e\,E(t) - \frac{m}{\tau}\frac{du(t)}{dt} \qquad \longrightarrow \quad (1)$$

As before, the electric field generated $= E(t) = \dfrac{n\,e\,u(t)}{\varepsilon_o} \qquad \longrightarrow \quad (2)$

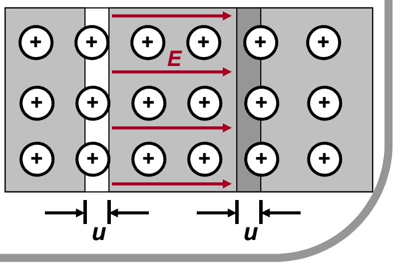
Combining (2) with (1) we get the differential equation:

$$\frac{d^2u(t)}{dt^2} = -\omega_p^2\,u(t) - \frac{1}{\tau}\frac{du(t)}{dt} \longrightarrow \left\{ \omega_p = \sqrt{\frac{ne^2}{\varepsilon_o m}} \right.$$

Or:

$$\frac{d^2u(t)}{dt^2} + \frac{1}{\tau}\frac{du(t)}{dt} + \omega_p^2\,u(t) = 0$$

second order system with damping



Plasma Oscillations in Metals – with Scattering

Case I (underdamped case): $\omega_p > \dfrac{1}{2\tau}$

Solution is:

$$u(t) = e^{-\gamma\,t}\left[A\cos(\Omega_p t) + B\sin(\Omega_p t)\right] \longleftarrow$$

Damped plasma oscillations

Where:

$$\gamma = \frac{1}{2\tau} \qquad \Omega_p = \sqrt{\omega_p^2 - \gamma^2}$$

Case II (overdamped case): $\omega_p < \dfrac{1}{2\tau}$

Solution is:

$$u(t) = A\,e^{-\gamma_1\,t} + B\,e^{-\gamma_2\,t} \longleftarrow$$

No oscillations

Where:

$$\gamma_1 = \frac{1}{2\tau} + \sqrt{\frac{1}{4\tau^2} - \omega_p^2} \qquad \gamma_1 = \frac{1}{2\tau} - \sqrt{\frac{1}{4\tau^2} - \omega_p^2}$$

Appendix: Fourier Transforms in Time OR Space

Fourier transform in time:

$$f(\omega)=\int_{-\infty}^{\infty}dt\;\; f(t)\,e^{i\,\omega\,t}$$

Inverse Fourier transform:

$$f(t)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,f(\omega)\,e^{-i\,\omega\,t}$$

Fourier transform in space:

$$g(k)=\int_{-\infty}^{\infty}dx\;\; g(x)\,e^{-i\,k\,x}$$

Inverse Fourier transform:

$$g(x)=\int_{-\infty}^{\infty}\frac{dk}{2\pi}\,g(k)\,e^{i\,k\,x}$$

Appendix: Fourier Transforms in Time AND Space

Fourier transform in time and space:

$$h(k,\omega)=\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dt\;\;h(x,t)\;\;e^{-i\,k\,x}\;e^{i\,\omega\,t}$$

Inverse Fourier transform:

$$h(x,t)=\int_{-\infty}^{\infty}\frac{dk}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\;\;h(k,\omega)\;\;e^{i\,k\,x}\;e^{-i\,\omega\,t}$$

Appendix: Fourier Transforms in Multiple Space Dimensions

Fourier transform in space:

$$h(k_x,k_y,k_z)=\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dz\quad h(x,y,z)\ e^{-i\,k_x\,x}\ e^{-i\,k_y\,y}e^{-i\,k_z\,z}$$

Need a better notation!

Let:

$$\vec{k}=k_x\hat{x}+k_y\hat{y}+k_z\,\hat{z} \qquad \int d^3\vec{r}=\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dz$$

$$\vec{r}=x\ \hat{x}+y\ \hat{y}+z\ \hat{z}$$

$$\Rightarrow \qquad h(\vec{k})=\int d^3\vec{r}\ \ h(\vec{r})\ e^{-i\,\vec{k}\,.\,\vec{r}}$$

Inverse Fourier transform:

$$h(\vec{r})=\int\frac{d^3\vec{k}}{(2\pi)^3}\ h(\vec{k})\ e^{i\,\vec{k}\,.\,\vec{r}}$$

Handout 2

Sommerfeld Model for Metals – Free Fermion Gas

In this lecture you will learn:

- Sommerfeld theory of metals

Arnold Sommerfeld (1868-1951)

Problems with the Drude Theory

$$\frac{d\vec{p}(t)}{dt} = m\frac{d\vec{v}(t)}{dt} = \vec{F} - \frac{m\vec{v}(t)}{\tau}$$

$$= -e\left[\vec{E} + \vec{v}(t)x\vec{B}\right] - \frac{m\vec{v}(t)}{\tau}$$

- Does not say anything about the electron energy distribution in metals
  - Are all electrons moving around with about the same energy?

- Does not take into account Pauli's exclusion principle

To account for these shortcomings Sommerfeld in 1927 developed a model for electrons in metals that took into consideration the Fermi-Dirac statistics of electrons

Note added:

Six of Sommerfeld's students - Werner Heisenberg, Wolfgang Pauli, Peter Debye, Hans Bethe, Linus Pauling, and Isidor I. Rabi - went on to win Nobel prize in Physics.

Sommerfeld himself was nominated 81 times (more than any other person) but was never awarded the Nobel prize.

Quantum Mechanics and the Schrodinger Equation

The quantum state of an electron is described by the Schrodinger equation:

$$\hat{H}\,\psi(\vec{r},t) = i\hbar\,\frac{\partial\,\psi(\vec{r},t)}{\partial t}$$

Where the Hamiltonian operator is: $\hat{H} = \dfrac{\hat{P}^2}{2m} + V\left(\hat{\vec{r}}\right) = \dfrac{\hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2}{2m} + V\left(\hat{\vec{r}}\right)$

Suppose: $\psi(\vec{r},t) = \psi(\vec{r})\,e^{-i\frac{E}{\hbar}t}$ **then we get:** $\hat{H}\,\psi(\vec{r}) = E\,\psi(\vec{r})$

(Time independent form)

The momentum operator is: $\hat{\vec{P}} = \dfrac{\hbar}{i}\nabla$

Therefore: $\dfrac{\hat{P}^2}{2m} = \dfrac{\hat{\vec{P}}\,.\,\hat{\vec{P}}}{2m} = \dfrac{1}{2m}\dfrac{\hbar}{i}\nabla\,.\,\dfrac{\hbar}{i}\nabla = -\dfrac{\hbar^2}{2m}\nabla^2 = -\dfrac{\hbar^2}{2m}\left[\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}\right]$

The time independent form of the Schrodinger equation is:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\,\psi(\vec{r})$$

Schrodinger Equation for a Free Electron

The time independent form of the Schrodinger equation is:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\,\psi(\vec{r})$$

For a free-electron: $V(\vec{r}) = 0$

We have:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = E\,\psi(\vec{r})$$

Solution is a plane wave (i.e. plane wave is an energy eigenstate):

$$\psi_{\vec{k}}(\vec{r}) = \sqrt{\frac{1}{V}}\;e^{i\,\vec{k}\,.\,\vec{r}} = \sqrt{\frac{1}{V}}\;e^{i\left(k_x x + k_y y + k_z z\right)} \longrightarrow \left\{\int d^3\vec{r}\;\left|\psi_{\vec{k}}(\vec{r})\right|^2 = 1\right.$$

Energy:

The energy of the free-electron state is: $E = \dfrac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2m} = \dfrac{\hbar^2 k^2}{2m}$

Note: The energy is entirely kinetic (due to motion)

Momentum:

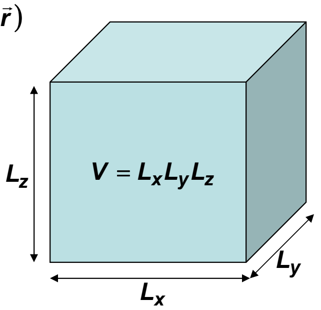
The energy eigenstates are also momentum eigenstates:

$$\hat{\vec{p}} = \frac{\hbar}{i}\nabla \quad\Rightarrow\quad \hat{\vec{p}}\,\psi_{\vec{k}}(\vec{r}) = \frac{\hbar}{i}\nabla\psi_{\vec{k}}(\vec{r}) = \hbar\vec{k}\,\psi_{\vec{k}}(\vec{r})$$

Electrons in Metals: The Free Electron Model

The quantum state of an electron is described by the time-independent Schrodinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})+V(\vec{r})\psi(\vec{r})=E\,\psi(\vec{r})$$



Consider a large metal box of volume $V = L_x L_y L_z$:

In the Sommerfeld model:

- **The electrons inside the box are confined in a three-dimensional infinite potential well with zero potential inside the box and infinite potential outside the box**

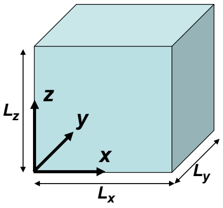
$$V(\vec{r})=0 \quad \text{for } |\vec{r}| \text{ inside the box}$$
$$V(\vec{r})=\infty \quad \text{for } |\vec{r}| \text{ outside the box}$$

free electrons (experience no potential when inside the box)

- **The electron states inside the box are given by the Schrodinger equation**

Electrons in Metals: The Free Electron Model

Need to solve: $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})=E\,\psi(\vec{r})$



$V = L_x L_y L_z$

With the boundary condition that the wavefunction $\psi(\vec{r})$ is zero at the boundary of the box

Solution is: $\psi_{\vec{k}}(\vec{r})=\sqrt{\frac{8}{V}}\sin(k_x x)\sin(k_y y)\sin(k_z z)$

Where: $k_x = n\frac{\pi}{L_x} \qquad k_y = m\frac{\pi}{L_y} \qquad k_z = p\frac{\pi}{L_z}$

And *n*, *m*, and *p* are non-zero positive integers taking values 1, 2, 3, 4, …….

Normalization:

The wavefunction is properly normalized: $\int d^3\vec{r}\;\left|\psi_{\vec{k}}(\vec{r})\right|^2=1$

Energy:

The energy of the electron states is: $E=\frac{\hbar^2\left(k_x^2+k_y^2+k_z^2\right)}{2m}=\frac{\hbar^2k^2}{2m}$

Note: The energy is entirely kinetic (due to motion)

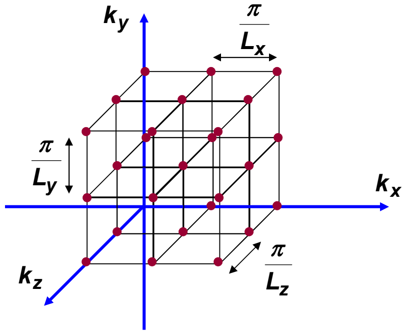
Electrons in Metals: The Free Electron Model

Labeling Scheme:

All electron states and energies can be labeled by the corresponding k-vector

$$\psi_{\vec{k}}(\vec{r}) = \sqrt{\frac{8}{V}}\sin(k_x x)\sin(k_y y)\sin(k_z z)$$

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m}$$



k-space Visualization:

The allowed quantum states can be visualized as a 3D grid of points in the first quadrant of the "k-space"

$$k_x = n\frac{\pi}{L_x} \qquad k_y = m\frac{\pi}{L_y} \qquad k_z = p\frac{\pi}{L_z}$$

n, m, p = 1, 2, 3, 4, …….

Problems:

- The "sine" solutions are difficult to work with – need to choose better solutions
- The "sine" solutions come from the boundary conditions – and most of the electrons inside the metal hardly ever see the boundary

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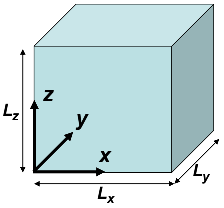
Born Von Karman Periodic Boundary Conditions

Solve: $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = E\,\psi(\vec{r})$



Instead of using the boundary condition: $\psi(\vec{r})\big|_{\text{boundary}} = 0$

Use periodic boundary conditions:

$$\left.\begin{aligned}\psi(x+L_x,y,z)&=\psi(x,y,z)\\ \psi(x,y+L_y,z)&=\psi(x,y,z)\\ \psi(x,y,z+L_z)&=\psi(x,y,z)\end{aligned}\right\}$$

These imply that each facet of the box is folded and joined to the opposite facet

Solution is: $\psi_{\vec{k}}(\vec{r}) = \sqrt{\frac{1}{V}}\,e^{i\,\vec{k}\,.\,\vec{r}} = \sqrt{\frac{1}{V}}\,e^{i\,(k_x x + k_y y + k_z z)}$

The boundary conditions dictate that the allowed values of k_x, k_y, and k_z, are such that:

$$e^{i\,k_x(x+L_x)} = e^{i\,(k_x x)} \;\Rightarrow\; e^{i\,(k_x L_x)} = 1 \;\Rightarrow\; k_x = n\frac{2\pi}{L_x} \qquad n = 0, \pm1, \pm2, \ldots.$$

$$e^{i\,k_y(y+L_y)} = e^{i\,(k_y y)} \;\Rightarrow\; e^{i\,(k_y L_y)} = 1 \;\Rightarrow\; k_y = m\frac{2\pi}{L_y} \qquad m = 0, \pm1, \pm2, \ldots.$$

$$e^{i\,k_z(z+L_z)} = e^{i\,(k_z z)} \;\Rightarrow\; e^{i\,(k_z L_z)} = 1 \;\Rightarrow\; k_z = p\frac{2\pi}{L_z} \qquad p = 0, \pm1, \pm2, \ldots.$$

Born Von Karman Periodic Boundary Conditions

Labeling Scheme:

All electron states and energies can be labeled by the corresponding k-vector

$$\psi_{\vec{k}}(\vec{r}) = \sqrt{\frac{1}{V}}\; e^{i\,\vec{k}\,.\,\vec{r}} \qquad\qquad E(\vec{k}) = \frac{\hbar^2 k^2}{2\,m}$$

Normalization: The wavefunction is properly normalized: $\int d^3\vec{r}\;\left|\psi_{\vec{k}}(\vec{r})\right|^2 = 1$

Orthogonality: Wavefunctions of two different states are orthogonal:

$$\int d^3\vec{r}\;\psi^*_{\vec{k}'}(\vec{r})\,\psi_{\vec{k}}(\vec{r}) = \int d^3\vec{r}\;\frac{e^{i\left(\vec{k}-\vec{k}'\right).\,\vec{r}}}{V} = \delta_{\vec{k}',\vec{k}}$$

Momentum Eigenstates:

Another advantage of using the plane-wave energy eigenstates (as opposed to the "sine" energy eigenstates) is that the plane-wave states are also momentum eigenstates

Momentum operator: $\hat{\vec{p}} = \frac{\hbar}{i}\nabla \quad\Rightarrow\quad \hat{\vec{p}}\,\psi_{\vec{k}}(\vec{r}) = \frac{\hbar}{i}\nabla\psi_{\vec{k}}(\vec{r}) = \hbar\vec{k}\,\psi_{\vec{k}}(\vec{r})$

Velocity:

Velocity of eigenstates is: $\vec{v}(\vec{k}) = \frac{\hbar\vec{k}}{m} = \frac{1}{\hbar}\nabla_{\vec{k}}\,E(\vec{k})$

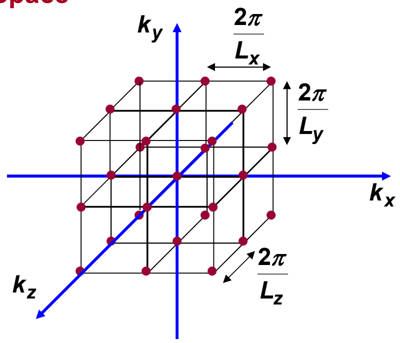
States in k-Space

k-space Visualization:

The allowed quantum states states can be visualized as a 3D grid of points in the entire "k-space"

$$k_x = n\frac{2\pi}{L_x} \qquad k_y = m\frac{2\pi}{L_y} \qquad k_z = p\frac{2\pi}{L_z}$$

$n, m, p = 0, \pm1, \pm2, \pm3, \ldots\ldots$



Density of Grid Points in k-space:

Looking at the figure, in k-space there is only one grid point in every small volume of size:

$$\left(\frac{2\pi}{L_x}\right)\left(\frac{2\pi}{L_y}\right)\left(\frac{2\pi}{L_z}\right) = \frac{(2\pi)^3}{V}$$

$\Rightarrow$ There are $\frac{V}{(2\pi)^3}$ grid points per unit volume of k-space $\Big\}$ Very important result

Electron Spin

Electron Spin:

Electrons also have spin degrees of freedom. An electron can have spin up or down.

So we can write the full quantum state of the electron as follows:

$$\psi_{\vec{k}\uparrow}(\vec{r}) = \sqrt{\frac{1}{V}}\; e^{i\,\vec{k}\,.\,\vec{r}}\left|\uparrow\right\rangle \qquad \text{or} \qquad \psi_{\vec{k}\downarrow}(\vec{r}) = \sqrt{\frac{1}{V}}\; e^{i\,\vec{k}\,.\,\vec{r}}\left|\downarrow\right\rangle$$

The energy does not depend on the spin (at least for the case at hand) and therefore

$$E\left(\vec{k}\uparrow\right) = E\left(\vec{k}\downarrow\right) = \frac{\hbar^2 k^2}{2m}$$

For the most part in this course, spin will be something extra that tags along and one can normally forget about it provided it is taken into account when counting all the available states

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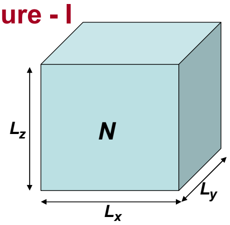
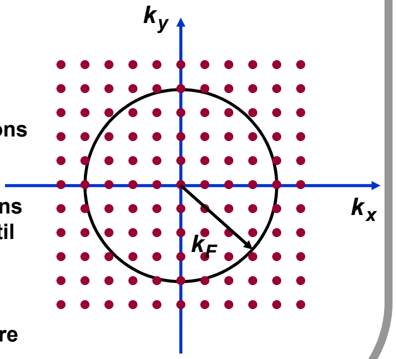
The Electron Gas at Zero Temperature - I



- Suppose we have *N* electrons in the box.
- Then how do we start filling the allowed quantum states?
- Suppose *T*~0K and we are interested in a filling scheme that gives the lowest total energy.

The energy of a quantum state is:

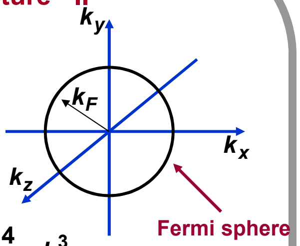
$$E\left(\vec{k}\right) = \frac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2m} = \frac{\hbar^2 k^2}{2m}$$



Strategy:

- Each grid-point can be occupied by two electrons (spin up and spin down)
- Start filling up the grid-points (with two electrons each) in spherical regions of increasing radii until you have a total of *N* electrons
- When we are done, all filled (i.e. occupied) quantum states correspond to grid-points that are inside a spherical region of radius k_F

The Electron Gas at Zero Temperature - II



- Each grid-point can be occupied by two electrons (spin up and spin down)

- All filled quantum states correspond to grid-points that are inside a spherical region of radius k_F

Volume of the spherical region $= \frac{4}{3}\pi\, k_F^3$

Number of grid-points in the spherical region = $\frac{V}{(2\pi)^3} \times \frac{4}{3}\pi\, k_F^3$

Number of quantum states (including spin) inside the spherical shell = $2 \times \frac{V}{(2\pi)^3} \times \frac{4}{3}\pi\, k_F^3 = \frac{V}{3\pi^2} k_F^3$

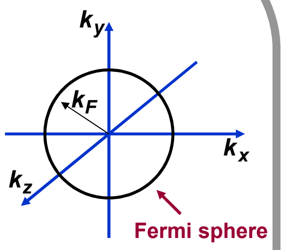
But the above must equal the total number *N* of electrons inside the box:

$$N = \frac{V}{3\pi^2} k_F^3$$

$$\Rightarrow \quad n = \text{electron density} = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$$

$$\Rightarrow \quad k_F = \left(3\pi^2 n\right)^{\frac{1}{3}}$$

The Electron Gas at Zero Temperature - III



- All quantum states inside the Fermi sphere are filled (i.e. occupied by electrons)
- All quantum states outside the Fermi sphere are empty

Fermi Momentum:
The largest momentum of the electrons is: $\hbar k_F$
This is called the Fermi momentum
Fermi momentum can be found if one knows the electron density:

$$k_F = \left(3\pi^2 n\right)^{\frac{1}{3}}$$

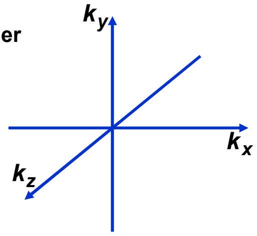
Fermi Energy:
The largest energy of the electrons is: $\frac{\hbar^2 k_F^2}{2m}$

This is called the Fermi energy E_F : $E_F = \frac{\hbar^2 k_F^2}{2m}$

Also: $E_F = \frac{\hbar^2 \left(3\pi^2 n\right)^{\frac{2}{3}}}{2m}$ or $n = \frac{1}{3\pi^2}\left(\frac{2m\, E_F}{\hbar^2}\right)^{\frac{3}{2}}$

Fermi Velocity:
The largest velocity of the electrons is called the Fermi velocity v_F : $v_F = \frac{\hbar k_F}{m}$

The Electron Gas at Non-Zero Temperature - I



- Since T≠0K, the filling scheme used for T=0K will no longer work

- For T≠0K one can only speak of the “probability” that a particular quantum state is occupied

Suppose the probability that the quantum state of wavevector $\vec{k}$ is occupied by an electron is $f(\vec{k})$

Then the total number N of electrons must equal the following sum over all grid-points in k-space:

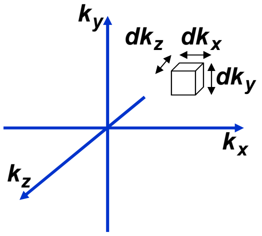
$$N = 2 \times \sum_{\text{all } \vec{k}} f(\vec{k})$$

spin

- By assumption $f(\vec{k})$ does not depend on the spin. That is why spin is taken into account by just adding the factor of 2 outside the sum

- $f(\vec{k})$ can have any value between 0 and 1

The Electron Gas at Non-Zero Temperature - II



Recall that there are $\dfrac{V}{(2\pi)^3}$ grid points per unit volume of k-space

⇒ So in volume $dk_x\, dk_y\, dk_z$ of k-space the number of grid points is:

$$\frac{V}{(2\pi)^3} dk_x\, dk_y\, dk_z = \frac{V}{(2\pi)^3} d^3\vec{k}$$

⇒ The summation over all grid points in k-space can be replaced by a volume integral

$$\sum_{\text{all } \vec{k}} \rightarrow V \int \frac{d^3\vec{k}}{(2\pi)^3}$$

Therefore:

$$N = 2 \times \sum_{\text{all } \vec{k}} f(\vec{k}) = 2 \times V \int \frac{d^3\vec{k}}{(2\pi)^3} f(\vec{k})$$

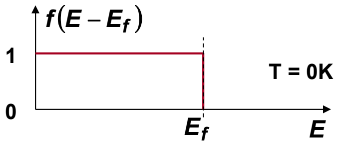
Question: What is $f(\vec{k})$?

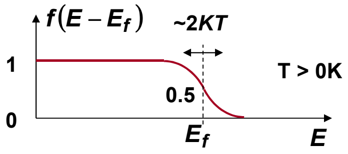
The Fermi-Dirac Distribution - I

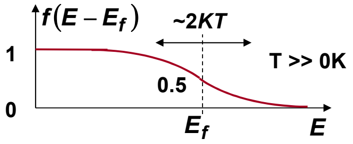
A fermion (such as an electron) at temperature T occupies a quantum state with energy E with a probability $f(E-E_f)$ given by the Fermi-Dirac distribution function:

$$f(E-E_f) = \frac{1}{1+e^{(E-E_f)/KT}}$$

E_f = chemical potential or the Fermi level (do not confuse Fermi energy with Fermi level)
K = Boltzmann constant = 1.38×10^{-23} Joules/Kelvin







The Fermi level E_f is determined by invoking some physical argument …(as we shall see)

Distribution Functions: Notation

The following notation will be used in this course:

- The notation $f(\vec{k})$ will be used to indicate a general k-space distribution function (not necessarily an equilibrium Fermi-Dirac distribution function)

- The notation $f(E-E_f)$ will be used to indicate an equilibrium Fermi-Dirac distribution function with Fermi-level E_f. Note that the Fermi-level is explicitly indicated. Note also that the Fermi-Dirac distribution depends only on the energy and not on the exact point in k-space

- Sometimes the notations $f_o(E-E_f)$ or $f_o(E)$ or $f_o(\vec{k})$ are also used to indicate equilibrium Fermi-Dirac distribution functions

The Electron Gas at Non-Zero Temperature - III

The probability $f(\vec{k})$ that the quantum state of wavevector $\vec{k}$ is occupied by an electron is given by the Fermi-Dirac distribution function:

$$f(\vec{k}) = \frac{1}{1+e^{\left(E(\vec{k})-E_f\right)/KT}} = f\left(E(\vec{k})-E_f\right)$$

Where: $E(\vec{k}) = \frac{\hbar^2\left(k_x^2+k_y^2+k_z^2\right)}{2m} = \frac{\hbar^2 k^2}{2m}$

Therefore:

$$N = 2\times V \int \frac{d^3\vec{k}}{(2\pi)^3}\, f(\vec{k}) = 2\times V \int \frac{d^3\vec{k}}{(2\pi)^3}\, \frac{1}{1+e^{\left(E(\vec{k})-E_f\right)/KT}}$$

Density of States:

The k-space volume integral is cumbersome. We need to convert into a simpler form – an energy space integral – using the following steps:

$$d^3\vec{k} = 4\pi\, k^2\, dk \qquad \text{and} \qquad E = \frac{\hbar^2 k^2}{2m} \Rightarrow dE = \frac{\hbar^2 k}{m} dk$$

Therefore:

$$d^3\vec{k} = 4\pi\, k^2\, dk = 4\pi \frac{m\,k}{\hbar^2} dE \qquad \text{But:} \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

It follows that:

$$d^3\vec{k} = 4\pi \frac{m\,k}{\hbar^2} dE = \frac{4\pi}{\hbar^3}\sqrt{2m^3E}\, dE$$

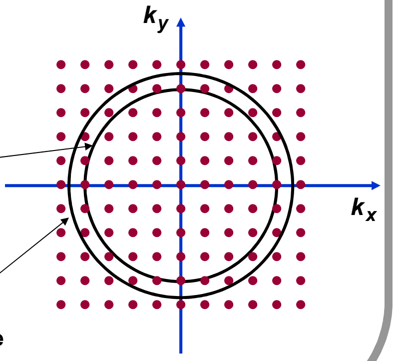
The Electron Gas at Non-Zero Temperature - IV

$$N = 2\times V \int \frac{d^3\vec{k}}{(2\pi)^3}\, \frac{1}{1+e^{\left(E(\vec{k})-E_f\right)/KT}} = V\int_0^\infty dE\;\; g(E)\; \frac{1}{1+e^{(E-E_f)/KT}}$$

Where: $g(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E}$ ← **Density of states function**

$g(E)$ has units: # / Joule-cm^3

The product $g(E)\, dE$ represents the number of quantum states available in the energy interval between E and $(E+dE)$ per cm^3 of the metal



Suppose E corresponds to the inner spherical shell from the relation:

$$E = \frac{\hbar^2 k^2}{2m}$$

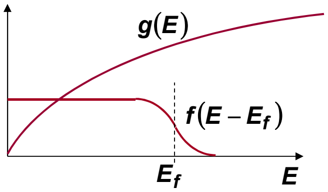
And suppose $(E+dE)$ corresponds to the outer spherical shell, then $g(E)\, dE$ corresponds to twice the number of the grid points between the two spherical shells

The Electron Gas at Non-Zero Temperature - V

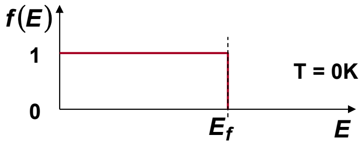
$$N = V\int_0^\infty dE \;\; g(E)\;\frac{1}{1+e^{(E-E_f)/KT}} = V\int_0^\infty dE \;\; g(E)\;\; f(E-E_f)$$

Where: $g(E) = \dfrac{1}{2\pi^2}\left(\dfrac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E}$

The expression for *N* can be visualized as the integration over the product of the two functions:



Check: Suppose *T*=0K:



$$N = V\int_0^\infty dE \;\; g(E)\;\; f(E-E_f) = V\int_0^{E_f} dE \;\; g(E)$$

$$= V\,\frac{1}{3\pi^2}\left(\frac{2m\,E_f}{\hbar^2}\right)^{\frac{3}{2}}$$

$$\Rightarrow \quad n = \frac{1}{3\pi^2}\left(\frac{2m\,E_f}{\hbar^2}\right)^{\frac{3}{2}}$$

Compare with the previous result at *T*=0K:

$$n = \frac{1}{3\pi^2}\left(\frac{2m\,E_F}{\hbar^2}\right)^{\frac{3}{2}} \quad \Rightarrow$$

At *T*=0K (and only at *T*=0K) the Fermi level E_f is the same as the Fermi energy E_F

The Electron Gas at Non-Zero Temperature - VI

For *T* ≠ 0K:

Since the carrier density is known, and does not change with temperature, the Fermi level at temperature *T* is found from the expression

$$n = \int_0^\infty dE \;\; g(E)\;\frac{1}{1+e^{(E-E_f)/KT}}$$

In general, the Fermi level E_f is a function of temperature and decreases from E_F as the temperature increases

$$E_f(T=0) = E_F$$
$$\& \quad E_f(T>0) < E_F$$

For small temperatures ($KT \ll E_F$), a useful approximation is:

$$E_f(T) \approx E_F\left[1-\frac{1}{3}\left(\frac{\pi\,K\,T}{2\,E_F}\right)^2\right]$$

Total Energy of the Fermion Gas

The total energy *U* of the electron gas can be written as:

$$U = 2\times \sum_{\text{all } \vec{k}} f(\vec{k})\,E(\vec{k}) = 2\times V \int \frac{d^3\vec{k}}{(2\pi)^3}\, f(\vec{k})\,E(\vec{k})$$

Convert the k-space integral to energy integral: $U = V\int_0^{\infty} dE\;\; g(E)\;\; f(E - E_f)\,E$

The energy density *u* is: $u = \dfrac{U}{V} = \int_0^{\infty} dE\;\; g(E)\;\; f(E - E_f)\,E$

Suppose *T*=0K:

$$u = \int_0^{E_F} dE\;\; g(E)\;\; E = \frac{1}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} (E_F)^{\frac{5}{2}}$$

Since: $n = \dfrac{1}{3\pi^2}\left(\dfrac{2m\,E_F}{\hbar^2}\right)^{\frac{3}{2}}$

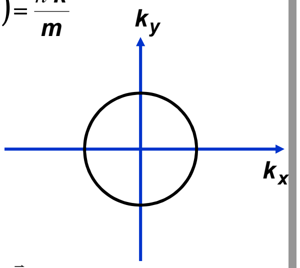
We have: $u = \dfrac{3}{5}\,n\,E_F$

Equilibrium Current Density of the Electron Gas

In the Drude model we had:

$$\vec{J} = n\,(-e)\,\vec{v}$$

- But now we have a Fermi gas in which electrons move with different velocities
- The velocity of the electron with wavevector $\vec{k}$ is: $\vec{v}(\vec{k}) = \dfrac{\hbar\,\vec{k}}{m}$



So the current density expression can be written as:

$$\vec{J} = (-e)\frac{2}{V}\times \sum_{\text{all } \vec{k}} f(\vec{k})\,\vec{v}(\vec{k}) = -2\,e\times \int \frac{d^3\vec{k}}{(2\pi)^3}\, f(\vec{k})\,\vec{v}(\vec{k})$$

$$\vec{J} = -2\,e\times \int \frac{d^3\vec{k}}{(2\pi)^3}\, f(\vec{k})\;\frac{\hbar\,\vec{k}}{m}$$

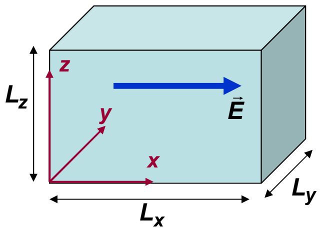
In the sum, for every occupied state $\vec{k}$ there is a state $-\vec{k}$ occupied with exactly the same probability. Therefore:

$$\vec{J} = -2\,e\times \int \frac{d^3\vec{k}}{(2\pi)^3}\, f(\vec{k})\;\frac{\hbar\,\vec{k}}{m} = 0$$

Makes sense - metals do not have net current densities flowing in equilibrium

Electron Gas in an Applied Electric Field - I

- Now suppose there is an electric field inside the metal
- Also assume, as in the Drude model, that the scattering time of the electrons is τ and the scattering rate is $1/\tau$
- The time-independent Schrodinger equation is a good point to start:



$$\hat{H}\,\psi(\vec{r},t) = i\hbar\,\frac{\partial\,\psi(\vec{r},t)}{\partial t}$$

Where: $\hat{H} = \frac{\hat{P}^2}{2m} + V(\hat{\vec{r}}) = \frac{\hat{P}^2}{2m} + e\,\vec{E}\,.\,\vec{r} = -\frac{\hbar^2}{2m}\nabla^2 + e\,\vec{E}\,.\,\vec{r}$

Assume a solution: $\psi(\vec{r},t) = \sqrt{\frac{1}{V}}\;e^{i\left(\vec{k}-\frac{e\,\vec{E}}{\hbar}t\right).\,\vec{r}}\;e^{-i\frac{\int_{-\infty}^{t}E(t')\,dt'}{\hbar}}$ and plug it in to get:

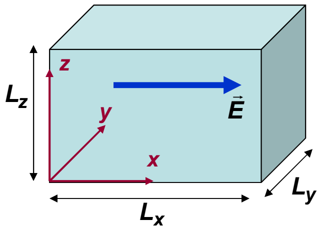
$$E(t) = \frac{\hbar^2\left|\vec{k}-\frac{e\,\vec{E}}{\hbar}t\right|^2}{2m}$$

The energy of the electron shows that its wavevector (and momentum) is increasing with time

The wavevector is now time dependent!

Electron Gas in an Applied Electric Field - II

- An equation for the time-dependent electron wavevector can be written as:



$$\frac{d\;\hbar\vec{k}(t)}{dt} = -e\,\vec{E}$$

Now we need to add the effect of electron scattering. As in the Drude model, assume that scattering adds damping:

$$\frac{d\;\hbar\vec{k}(t)}{dt} = -e\,\vec{E} - \frac{\hbar\left[\vec{k}(t)-\vec{k}\right]}{\tau}$$

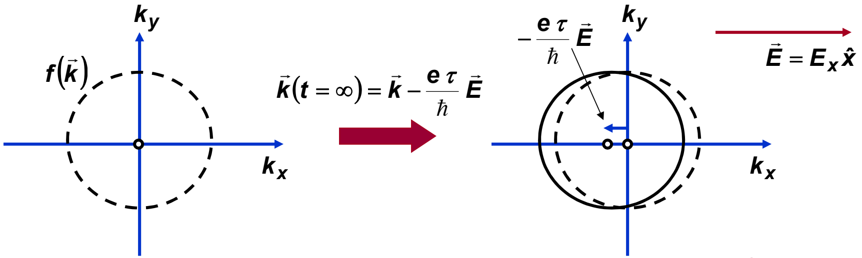
The boundary condition is that: $\vec{k}(t=0) = \vec{k}$

Note: the damping term ensures that when the field is turned off, the wavevector of the electron goes back to its original value

Steady State Solution: $\vec{k}(t=\infty) = \vec{k} - \frac{e\,\tau}{\hbar}\vec{E}$

In the presence of an electric field, the wavevector of every electron is shifted by an equal amount that is determined by the scattering time and the field strength

Electron Gas in an Applied Electric Field - III



$$\vec{k}(t=\infty) = \vec{k} - \frac{e\,\tau}{\hbar}\vec{E}$$

Electron distribution in k-space when E-field is zero

Distribution function: $f(\vec{k})$

Electron distribution is shifted in k-space when E-field is not zero

Distribution function: $f\left(\vec{k} + \frac{e\,\tau}{\hbar}\vec{E}\right)$

Since the wavevector of each electron is shifted by the same amount in the presence of the E-field, the net effect in k-space is that the entire electron distribution is shifted as shown

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Electron Gas in an Applied Electric Field - IV

Current Density:

$$\vec{J} = -2\,e \times \int \frac{d^3\vec{k}}{(2\pi)^3}\, f\left(\vec{k} + \frac{e\,\tau}{\hbar}\vec{E}\right)\vec{v}(\vec{k})$$

Do a shift in the integration variable:

$$\vec{J} = -2\,e \times \int \frac{d^3\vec{k}}{(2\pi)^3}\, f(\vec{k})\,\vec{v}\left(\vec{k} - \frac{e\,\tau}{\hbar}\vec{E}\right)$$

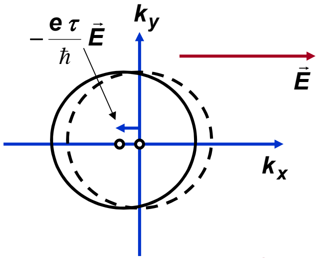
$$\vec{J} = -2\,e \times \int \frac{d^3\vec{k}}{(2\pi)^3}\, f(\vec{k})\,\frac{\hbar\left(\vec{k} - \frac{e\,\tau}{\hbar}\vec{E}\right)}{m}$$

$$\vec{J} = \frac{e^2\tau}{m}\left[2 \times \int \frac{d^3\vec{k}}{(2\pi)^3}\, f(\vec{k})\right]\vec{E}$$

electron density = n

$$\vec{J} = \frac{n\,e^2\tau}{m}\vec{E} = \sigma\,\vec{E}$$

Where: $\sigma = \frac{n\,e^2\tau}{m}$ → Same as the Drude result!



Electron distribution is shifted in k-space when E-field is not zero

Distribution function: $f\left(\vec{k} + \frac{e\,\tau}{\hbar}\vec{E}\right)$

Handout 3

Free Electron Gas in 2D and 1D

In this lecture you will learn:

- Free electron gas in two dimensions and in one dimension
- Density of States in k-space and in energy in lower dimensions

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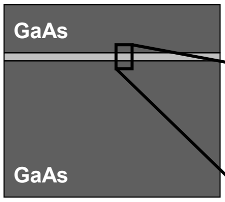
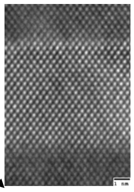
Electron Gases in 2D

- In several physical systems electron are confined to move in just 2 dimensions
- Examples, discussed in detail later in the course, are shown below:

Semiconductor Quantum Wells:



InGaAs quantum well (1-10 nm)

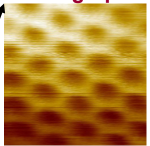


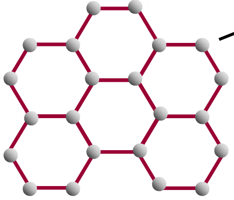
TEM micrograph

Semiconductor quantum wells can be composed of pretty much any semiconductor from the groups II, III, IV, V, and VI of the periodic table

Graphene:

STM micrograph



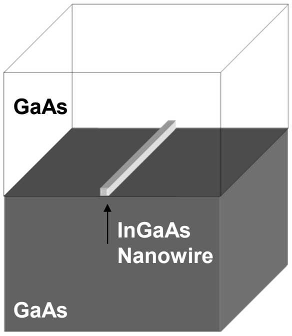


Graphene is a single atomic layer of carbon atoms arranged in a honeycomb lattice

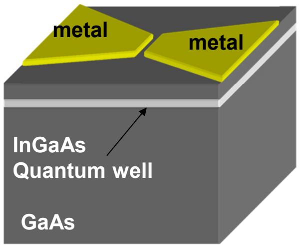
Electron Gases in 1D

- In several physical systems electron are confined to move in just 1 dimension
- Examples, discussed in detail later in the course, are shown below:

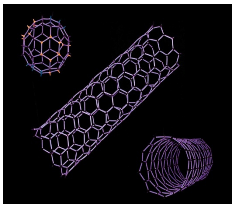
Semiconductor Quantum Wires (or Nanowires):



Semiconductor Quantum Point Contacts (Electrostatic Gating):



Carbon Nanotubes (Rolled Graphene Sheets):

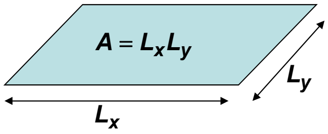


Electrons in 2D Metals: The Free Electron Model

The quantum state of an electron is described by the time-independent Schrodinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})+V(\vec{r})\psi(\vec{r})=E\,\psi(\vec{r})$$

Consider a large metal sheet of area $A= L_x L_y$:



Use the Sommerfeld model:

- The electrons inside the sheet are confined in a two-dimensional infinite potential well with zero potential inside the sheet and infinite potential outside the sheet

$$V(\vec{r})=0 \quad \text{for } \vec{r} \text{ inside the sheet}$$
$$V(\vec{r})=\infty \quad \text{for } \vec{r} \text{ outside the sheet}$$

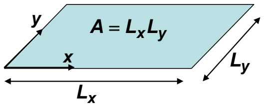
free electrons (experience no potential when inside the sheet)

- The electron states inside the sheet are given by the Schrodinger equation

Born Von Karman Periodic Boundary Conditions in 2D

Solve: $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = E\,\psi(\vec{r})$

Use periodic boundary conditions:



$$\left.\begin{aligned}\psi(x+L_x,y,z) &= \psi(x,y,z)\\ \psi(x,y+L_y,z) &= \psi(x,y,z)\end{aligned}\right\}$$

These imply that each edge of the sheet is folded and joined to the opposite edge

Solution is: $\psi(\vec{r}) = \sqrt{\frac{1}{A}}\; e^{i\,\vec{k}\,.\,\vec{r}} = \sqrt{\frac{1}{A}}\; e^{i\,(k_x x + k_y y)}$

The boundary conditions dictate that the allowed values of k_x, and k_y are such that:

$$e^{i\,(k_x L_x)} = 1 \quad\Rightarrow\quad k_x = n\frac{2\pi}{L_x} \qquad n = 0, \pm1, \pm2, \pm3, \ldots\ldots.$$

$$e^{i\,(k_y L_y)} = 1 \quad\Rightarrow\quad k_y = m\frac{2\pi}{L_y} \qquad m = 0, \pm1, \pm2, \pm3, \ldots\ldots.$$

Born Von Karman Periodic Boundary Conditions in 2D

Labeling Scheme:

All electron states and energies can be labeled by the corresponding k-vector

$$\psi_{\vec{k}}(\vec{r}) = \sqrt{\frac{1}{A}}\; e^{i\,\vec{k}\,.\,\vec{r}} \qquad\qquad E(\vec{k}) = \frac{\hbar^2 k^2}{2\,m}$$

Normalization: The wavefunction is properly normalized: $\int d^2\vec{r}\;\left|\psi_{\vec{k}}(\vec{r})\right|^2 = 1$

Orthogonality: Wavefunctions of two different states are orthogonal:

$$\int d^2\vec{r}\;\psi^*_{\vec{k}'}(\vec{r})\,\psi_{\vec{k}}(\vec{r}) = \int d^2\vec{r}\;\frac{e^{i\,(\vec{k}-\vec{k}')\,.\,\vec{r}}}{A} = \delta_{\vec{k}',\,\vec{k}}$$

Momentum Eigenstates:

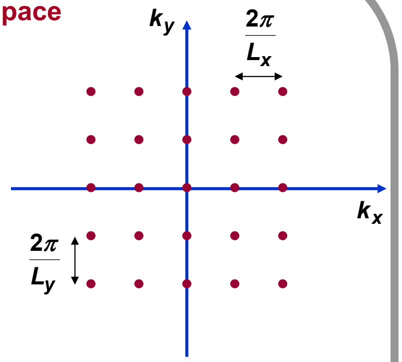
Another advantage of using the plane-wave energy eigenstates (as opposed to the “sine” energy eigenstates) is that the plane-wave states are also momentum eigenstates

Momentum operator: $\hat{\vec{p}} = \frac{\hbar}{i}\nabla \quad\Rightarrow\quad \hat{\vec{p}}\,\psi_{\vec{k}}(\vec{r}) = \frac{\hbar}{i}\nabla\psi_{\vec{k}}(\vec{r}) = \hbar\vec{k}\,\psi_{\vec{k}}(\vec{r})$

Velocity:

Velocity of eigenstates is: $\vec{v}(\vec{k}) = \frac{\hbar\vec{k}}{m} = \frac{1}{\hbar}\nabla_{\vec{k}}\,E(\vec{k})$

States in 2D k-Space



k-space Visualization:

The allowed quantum states states can be visualized as a 2D grid of points in the entire “k-space”

$$k_x = n\frac{2\pi}{L_x} \qquad k_y = m\frac{2\pi}{L_y}$$

$$n, m = 0, \pm 1, \pm 2, \pm 3, \ldots\ldots$$

Density of Grid Points in k-space:

Looking at the figure, in k-space there is only one grid point in every small area of size:

$$\left(\frac{2\pi}{L_x}\right)\left(\frac{2\pi}{L_y}\right) = \frac{(2\pi)^2}{A}$$

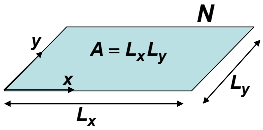
$\Rightarrow$ There are $\frac{A}{(2\pi)^2}$ grid points per unit area of k-space $\Big\}$ Very important result

The Electron Gas in 2D at Zero Temperature - I

- Suppose we have *N* electrons in the sheet.

- Then how do we start filling the allowed quantum states?

- Suppose *T*~0K and we are interested in a filling scheme that gives the lowest total energy.



The energy of a quantum state is:

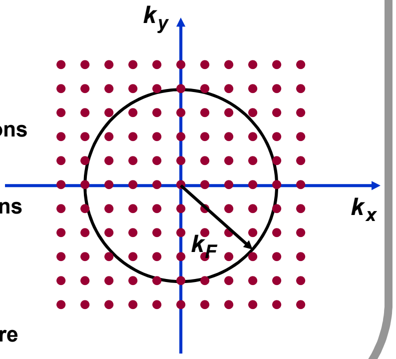
$$E(\vec{k}) = \frac{\hbar^2\left(k_x^2 + k_y^2\right)}{2m} = \frac{\hbar^2 k^2}{2m}$$

Strategy:

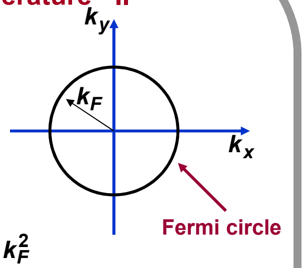
- Each grid-point can be occupied by two electrons (spin up and spin down)

- Start filling up the grid-points (with two electrons each) in circular regions of increasing radii until you have a total of *N* electrons

- When we are done, all filled (i.e. occupied) quantum states correspond to grid-points that are inside a circular region of radius k_F



The Electron Gas in 2D at Zero Temperature - II



- Each grid-point can be occupied by two electrons (spin up and spin down)

- All filled quantum states correspond to grid-points that are inside a circular region of radius k_F

Area of the circular region = $\pi\, k_F^2$

Number of grid-points in the circular region = $\dfrac{A}{(2\pi)^2}\times\pi\, k_F^2$

Number of quantum states (including spin) in the circular region = $2\times\dfrac{A}{(2\pi)^2}\times\pi\, k_F^2 = \dfrac{A}{2\pi}k_F^2$

But the above must equal the total number *N* of electrons inside the box:

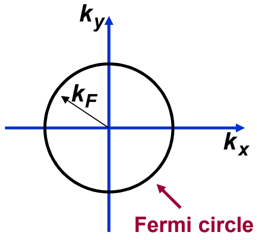
$$N = \frac{A}{2\pi}k_F^2$$

$$\Rightarrow \quad n = \text{electron density} = \frac{N}{A} = \frac{k_F^2}{2\pi}$$

$$\Rightarrow \quad k_F = (2\pi\, n)^{\frac{1}{2}}$$

$\Big\{$ Units of the electron density *n* are #/cm^2

The Electron Gas in 2D at Zero Temperature - III



- All quantum states inside the Fermi circle are filled (i.e. occupied by electrons)
- All quantum states outside the Fermi circle are empty

Fermi Momentum:

The largest momentum of the electrons is: $\hbar k_F$

This is called the Fermi momentum

Fermi momentum can be found if one knows the electron density:

$$k_F = (2\pi\, n)^{\frac{1}{2}}$$

Fermi Energy:

The largest energy of the electrons is: $\dfrac{\hbar^2 k_F^2}{2m}$

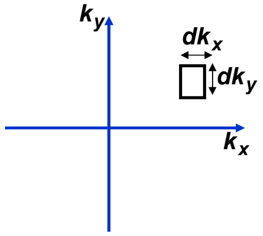
This is called the Fermi energy E_F : $\quad E_F = \dfrac{\hbar^2 k_F^2}{2m}$

Also: $\quad E_F = \dfrac{\hbar^2 \pi\, n}{m} \quad$ or $\quad n = \dfrac{m}{\pi\,\hbar^2}E_F$

Fermi Velocity:

The largest velocity of the electrons is called the Fermi velocity v_F : $\quad v_F = \dfrac{\hbar k_F}{m}$

The Electron Gas in 2D at Non-Zero Temperature - I



Recall that there are $\frac{A}{(2\pi)^2}$ grid points per unit area of k-space

⇒ So in area $dk_x\, dk_y$ of k-space the number of grid points is:

$$\frac{A}{(2\pi)^2} dk_x\, dk_y = \frac{A}{(2\pi)^2} d^2\vec{k}$$

⇒ The summation over all grid points in k-space can be replaced by an area integral

$$\sum_{\text{all } \vec{k}} \rightarrow A \int \frac{d^2\vec{k}}{(2\pi)^2}$$

Therefore:

$$N = 2 \times \sum_{\text{all } \vec{k}} f(\vec{k}) = 2 \times A \int \frac{d^2\vec{k}}{(2\pi)^2} f(\vec{k})$$

$f(\vec{k})$ is the occupation probability of a quantum state

The Electron Gas in 2D at Non-Zero Temperature - II

The probability $f(\vec{k})$ that the quantum state of wavevector $\vec{k}$ is occupied by an electron is given by the Fermi-Dirac distribution function:

$$f(\vec{k}) = \frac{1}{1 + e^{\left(E(\vec{k}) - E_f\right)/KT}} \qquad \text{Where:} \qquad E(\vec{k}) = \frac{\hbar^2\left(k_x^2 + k_y^2\right)}{2m} = \frac{\hbar^2 k^2}{2m}$$

Therefore:

$$N = 2 \times A \int \frac{d^2\vec{k}}{(2\pi)^2} f(\vec{k}) = 2 \times A \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{1}{1 + e^{\left(E(\vec{k}) - E_f\right)/KT}}$$

Density of States:

The k-space integral is cumbersome. We need to convert into a simpler form – an energy space integral – using the following steps:

$$d^2\vec{k} = 2\pi\, k\, dk \qquad \text{and} \qquad E = \frac{\hbar^2 k^2}{2m} \Rightarrow dE = \frac{\hbar^2 k}{m} dk$$

Therefore:

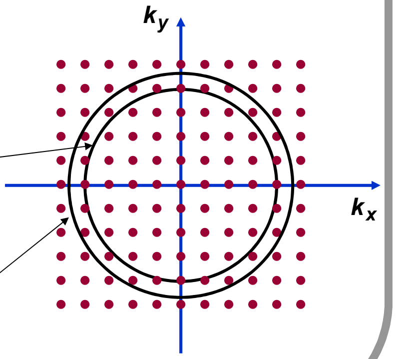
$$2 \times A \int \frac{d^2\vec{k}}{(2\pi)^2} \rightarrow A \int_0^\infty \frac{k\, dk}{\pi} \rightarrow A \int_0^\infty \frac{m}{\pi \hbar^2} dE$$

The Electron Gas in 2D at Non-Zero Temperature - III

$$N = 2\times A\int \frac{d^2\vec{k}}{(2\pi)^2}\;\frac{1}{1+e^{\left(E(\vec{k})-E_f\right)/KT}} = A\int_0^\infty dE\;\; g_{2D}(E)\;\frac{1}{1+e^{(E-E_f)/KT}}$$

Where: $g_{2D}(E) = \frac{m}{\pi\hbar^2}$ ← **Density of states function is constant (independent of energy) in 2D**

$g_{2D}(E)$ has units: # / Joule-cm^2



The product $g(E)\,dE$ represents the number of quantum states available in the energy interval between E and $(E+dE)$ per cm^2 of the metal

Suppose E corresponds to the inner circle from the relation:

$$E = \frac{\hbar^2 k^2}{2m}$$

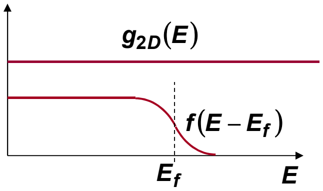
And suppose $(E+dE)$ corresponds to the outer circle, then $g_{2D}(E)\,dE$ corresponds to twice the number of the grid points between the two circles

The Electron Gas in 2D at Non-Zero Temperature - IV

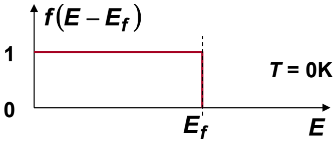
$$N = A\int_0^\infty dE\;\; g_{2D}(E)\;\frac{1}{1+e^{(E-E_f)/KT}} = A\int_0^\infty dE\;\; g_{2D}(E)\;\; f(E-E_f)$$

Where: $g_{2D}(E) = \frac{m}{\pi\hbar^2}$

The expression for N can be visualized as the integration over the product of the two functions:



Check: Suppose T=0K:



$T = 0\text{K}$

$$N = A\int_0^\infty dE\;\; g_{2D}(E)\;\; f(E-E_f) = A\int_0^{E_f} dE\;\; g_{2D}(E)$$

$$= A\,\frac{m}{\pi\hbar^2}E_f$$

$$\Rightarrow\quad n = \frac{m}{\pi\hbar^2}E_f$$

Compare with the previous result at T=0K:

$$n = \frac{m}{\pi\hbar^2}E_F \quad\Rightarrow$$

At T=0K (and only at T=0K) the Fermi level E_f is the same as the Fermi energy E_F

The Electron Gas in 2D at Non-Zero Temperature - V

For $T \neq 0$K:

Since the carrier density is known, and does not change with temperature, the Fermi level at temperature T is found from the expression

$$n = \int_0^\infty dE \;\; g_{2D}(E) \; \frac{1}{1+e^{(E-E_f)/KT}} = \frac{m}{\pi \hbar^2} KT \log\left[1+e^{\frac{E_f}{KT}}\right]$$

In general, the Fermi level E_f is a function of temperature and decreases from E_F as the temperature increases. The exact relationship can be found by inverting the above equation and recalling that:

$$n = \frac{m}{\pi \hbar^2} E_F$$

to get:

$$E_f(T) = KT \log\left[e^{\frac{E_F}{KT}} - 1\right]$$

Total Energy of the 2D Electron Gas

The total energy U of the electron gas can be written as:

$$U = 2 \times \sum_{\text{all } \vec{k}} f(\vec{k}) E(\vec{k}) = 2 \times A \int \frac{d^2\vec{k}}{(2\pi)^2} f(\vec{k}) E(\vec{k})$$

Convert the k-space integral to energy integral: $U = A \int_0^\infty dE \;\; g_{2D}(E) \;\; f(E-E_f)\, E$

The energy density u is $u = \frac{U}{A} = \int_0^\infty dE \;\; g_{2D}(E) \;\; f(E-E_f)\, E$

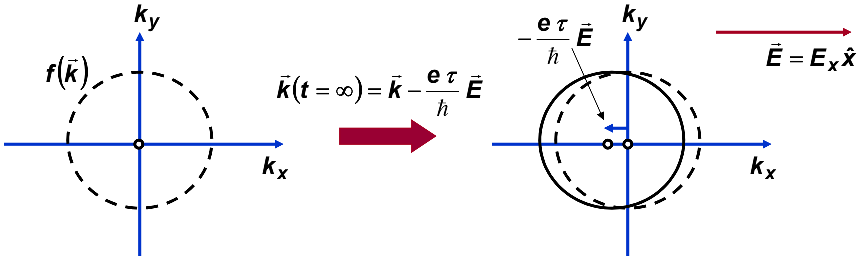
Suppose T=0K:

$$u = \int_0^{E_F} dE \;\; g_{2D}(E) \;\; E = \frac{m}{2\pi \hbar^2} E_F^2$$

Since: $n = \frac{m}{\pi \hbar^2} E_F$

We have: $u = \frac{1}{2} n E_F$

2D Electron Gas in an Applied Electric Field - I



$$\vec{k}(t=\infty) = \vec{k} - \frac{e\,\tau}{\hbar}\vec{E}$$

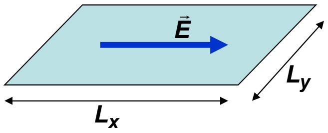
Electron distribution in k-space when E-field is zero

Distribution function: $f(\vec{k})$

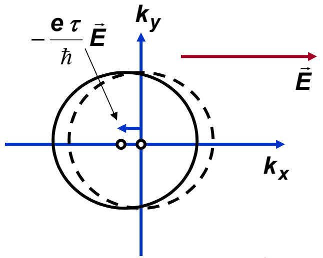
Electron distribution is shifted in k-space when E-field is not zero

Distribution function: $f\left(\vec{k} + \frac{e\,\tau}{\hbar}\vec{E}\right)$

Since the wavevector of each electron is shifted by the same amount in the presence of the E-field, the net effect in k-space is that the entire electron distribution is shifted as shown



2D Electron Gas in an Applied Electric Field - II



Electron distribution is shifted in k-space when E-field is not zero

Distribution function: $f\left(\vec{k} + \frac{e\,\tau}{\hbar}\vec{E}\right)$

Current density (units: A/cm)

$$\vec{J} = -2\,e \times \int \frac{d^2\vec{k}}{(2\pi)^2} f\left(\vec{k} + \frac{e\,\tau}{\hbar}\vec{E}\right)\vec{v}(\vec{k})$$

Do a shift in the integration variable:

$$\vec{J} = -2\,e \times \int \frac{d^2\vec{k}}{(2\pi)^2} f(\vec{k})\,\vec{v}\left(\vec{k} - \frac{e\,\tau}{\hbar}\vec{E}\right)$$

$$\vec{J} = -2\,e \times \int \frac{d^2\vec{k}}{(2\pi)^2} f(\vec{k})\frac{\hbar\left(\vec{k} - \frac{e\,\tau}{\hbar}\vec{E}\right)}{m}$$

$$\vec{J} = \frac{e^2\tau}{m}\left[\underbrace{2 \times \int \frac{d^2\vec{k}}{(2\pi)^2} f(\vec{k})}_{}\right]\vec{E}$$

electron density = n (units: #/cm^2)

$$\vec{J} = \frac{n\,e^2\tau}{m}\vec{E} = \sigma\,\vec{E}$$

Where: $\sigma = \frac{n\,e^2\tau}{m}$ →

Same as the Drude result - but units are different. Units of σ are Siemens in 2D

Electrons in 1D Metals: The Free Electron Model

The quantum state of an electron is described by the time-independent Schrodinger equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)+V(x)\psi(x)=E\,\psi(x)$$

Consider a large metal wire of length *L* :

Use the Sommerfeld model:

- **The electrons inside the wire are confined in a one-dimensional infinite potential well with zero potential inside the wire and infinite potential outside the wire**

$$V(x)=0 \quad \text{for } x \text{ inside the wire}$$
$$V(x)=\infty \quad \text{for } x \text{ outside the wire}$$

free electrons (experience no potential when inside the wire)

- **The electron states inside the wire are given by the Schrodinger equation**

Born Von Karman Periodic Boundary Conditions in 1D

Solve: $$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)=E\,\psi(x)$$

Use periodic boundary conditions:

$$\left.\psi(x+L,y,z)=\psi(x,y,z)\right\}$$

These imply that each facet of the sheet is folded and joined to the opposite facet

Solution is: $$\psi(x)=\sqrt{\frac{1}{L}}\,e^{i(k_x x)}$$

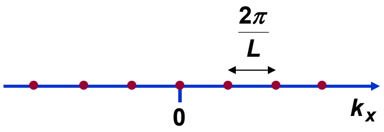
The boundary conditions dictate that the allowed values of k_x are such that:

$$e^{i(k_x L)}=1 \quad\Rightarrow\quad k_x=n\frac{2\pi}{L} \qquad n=0,\pm1,\pm2,\pm3,\ldots\ldots$$

States in 1D k-Space

k-space Visualization:

The allowed quantum states states can be visualized as a 1D grid of points in the entire "k-space"



$$k_x = n\frac{2\pi}{L}$$

$n = 0, \pm 1, \pm 2, \pm 3, \ldots\ldots.$

Density of Grid Points in k-space:

Looking at the figure, in k-space there is only one grid point in every small length of size:

$$\left(\frac{2\pi}{L}\right)$$

$\Rightarrow$ There are $\frac{L}{2\pi}$ grid points per unit length of k-space $\Big\}$ Very important result

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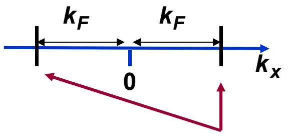
The Electron Gas in 1D at Zero Temperature - I

- Each grid-point can be occupied by two electrons (spin up and spin down)
- All filled quantum states correspond to grid-points that are within a distance k_F from the origin



Fermi points

Length of the region = $2k_F$

Number of grid-points in the region = $\frac{L}{2\pi} \times 2k_F$

Number of quantum states (including spin) in the region = $2 \times \frac{L}{2\pi} \times 2k_F$

But the above must equal the total number N of electrons in the wire:

$$N = L\frac{2k_F}{\pi}$$

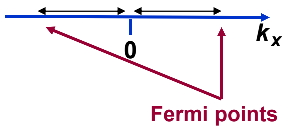
$$\Rightarrow \quad n = \text{electron density} = \frac{N}{L} = \frac{2k_F}{\pi}$$

$$\Rightarrow \quad k_F = \frac{\pi\, n}{2}$$

$\Big\{$ Units of the electron density n are #/cm

The Electron Gas in 1D at Zero Temperature - II

- All quantum states between the Fermi points are filled (i.e. occupied by electrons)
- All quantum states outside the Fermi points are empty



Fermi Momentum:

The largest momentum of the electrons is: $\hbar k_F$

This is called the Fermi momentum

Fermi momentum can be found if one knows the electron density:

$$k_F = \frac{\pi n}{2}$$

Fermi Energy:

The largest energy of the electrons is: $\frac{\hbar^2 k_F^2}{2m}$

This is called the Fermi energy E_F : $E_F = \frac{\hbar^2 k_F^2}{2m}$

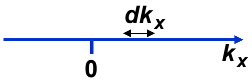
Also: $E_F = \frac{\hbar^2 \pi^2 n^2}{8 m}$ or $n = \frac{\sqrt{8m}}{\pi \hbar} \sqrt{E_F}$

Fermi Velocity:

The largest velocity of the electrons is called the Fermi velocity v_F : $v_F = \frac{\hbar k_F}{m}$

The Electron Gas in 1D at Non-Zero Temperature - I

Recall that there are $\frac{L}{2\pi}$ grid points per unit length of k-space



⇒ So in length dk_x of k-space the number of grid points is:

$$\frac{L}{2\pi} dk_x$$

⇒ The summation over all grid points in k-space can be replaced by an integral

$$\sum_{\text{all } \vec{k}} \rightarrow L \int_{-\infty}^{\infty} \frac{dk_x}{2\pi}$$

Therefore:

$$N = 2 \times \sum_{\text{all } \vec{k}} f(k_x) = 2 \times L \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} f(k_x)$$

$f(k_x)$ is the occupation probability of a quantum state

The Electron Gas in 1D at Non-Zero Temperature - II

The probability $f(k_x)$ that the quantum state of wavevector k_x is occupied by an electron is given by the Fermi-Dirac distribution function:

$$f(k_x) = \frac{1}{1+e^{(E(k_x)-E_f)/KT}} \qquad \text{Where:} \qquad E(\vec{k}) = \frac{\hbar^2 k_x^2}{2m}$$

Therefore:

$$N = 2\times L \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} f(k_x) = 2\times L \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} \frac{1}{1+e^{(E(k_x)-E_f)/KT}}$$

Density of States:

The k-space integral is cumbersome. We need to convert into a simpler form – an energy space integral – using the following steps:

$$2\times L \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} \rightarrow 2\times L \times 2 \int_{0}^{\infty} \frac{dk}{2\pi} \qquad \text{and} \qquad E = \frac{\hbar^2 k^2}{2m} \Rightarrow dE = \frac{\hbar^2 k}{m} dk$$

Therefore:

$$2\times L \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} \rightarrow L\int_{0}^{\infty} dE \; \frac{\sqrt{2m}}{\pi\,\hbar} \frac{1}{\sqrt{E}}$$

The Electron Gas in 1D at Non-Zero Temperature - III

$$N = 2\times L \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} \frac{1}{1+e^{(E(k_x)-E_f)/KT}} = L\int_{0}^{\infty} dE \;\; g_{1D}(E) \frac{1}{1+e^{(E-E_f)/KT}}$$

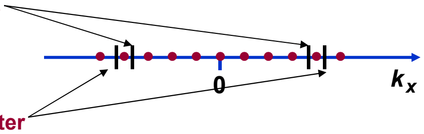
Where: $g_{1D}(E) = \frac{\sqrt{2m}}{\pi\,\hbar} \frac{1}{\sqrt{E}}$ ← Density of states function in 1D

$g_{1D}(E)$ has units: # / Joule-cm

The product $g(E)\,dE$ represents the number of quantum states available in the energy interval between E and $(E+dE)$ per cm of the metal

Suppose E corresponds to the inner points from the relation:

$$E = \frac{\hbar^2 k^2}{2m}$$

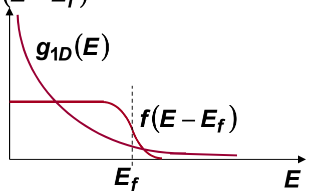


And suppose $(E+dE)$ corresponds to the outer points, then $g_{1D}(E)\,dE$ corresponds to twice the number of the grid points between the points (adding contributions from both sides)

The Electron Gas in 1D at Non-Zero Temperature - IV

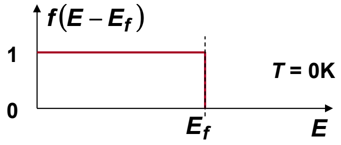
$$N = L\int_0^\infty dE\;\; g_{1D}(E)\;\frac{1}{1+e^{(E-E_f)/KT}} = L\int_0^\infty dE\;\; g_{1D}(E)\;\; f(E-E_f)$$

Where: $g_{1D}(E) = \frac{\sqrt{2m}}{\pi\,\hbar}\frac{1}{\sqrt{E}}$



The expression for *N* can be visualized as the integration over the product of the two functions:

Check: Suppose *T*=0K:



$$N = L\int_0^\infty dE\;\; g_{1D}(E)\;\; f(E-E_f) = L\int_0^{E_f} dE\;\; g_{1D}(E)$$

$$= L\frac{\sqrt{8m}}{\pi\,\hbar}\sqrt{E_f}$$

$$\Rightarrow\quad n = \frac{\sqrt{8m}}{\pi\,\hbar}\sqrt{E_f}$$

Compare with the previous result at *T*=0K:

$$n = \frac{\sqrt{8m}}{\pi\,\hbar}\sqrt{E_F}\quad\Rightarrow$$

At *T*=0K (and only at *T*=0K) the Fermi level E_f is the same as the Fermi energy E_F

The Electron Gas in 1D at Non-Zero Temperature - V

For *T* ≠ 0K:

Since the carrier density is known, and does not change with temperature, the Fermi level at temperature *T* is found from the expression

$$n = \int_0^\infty dE\;\; g_{1D}(E)\;\frac{1}{1+e^{(E-E_f)/KT}}$$

In general, the Fermi level E_f is a function of temperature and decreases from E_F as the temperature increases.

Total Energy of the 1D Electron Gas

The total energy *U* of the electron gas can be written as:

$$U = 2\times \sum_{\text{all }\vec{k}} f(k_x)\,E(k_x) = 2\times L\int_{-\infty}^{\infty}\frac{dk_x}{2\pi}\,f(k_x)\,E(k_x)$$

Convert the k-space integral to energy integral: $U = L\int_0^{\infty} dE\;\; g_{1D}(E)\;\; f(E-E_f)\,E$

The energy density *u* is: $u = \frac{U}{L} = \int_0^{\infty} dE\;\; g_{1D}(E)\;\; f(E-E_f)\,E$

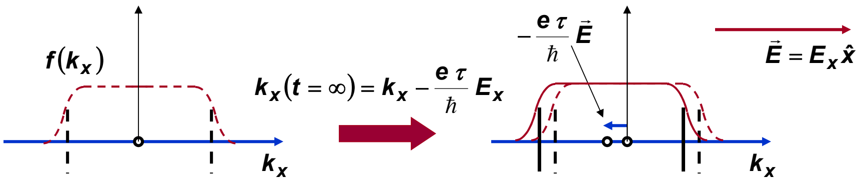
Suppose *T*=0K:

$$u = \int_0^{E_F} dE\;\; g_{1D}(E)\;\; E = \frac{\sqrt{8m}}{\pi\hbar}\frac{E_F^{3/2}}{3}$$

Since: $n = \frac{\sqrt{8m}}{\pi\hbar}\sqrt{E_F}$

We have: $u = \frac{1}{3}n\,E_F$

1D Electron Gas in an Applied Electric Field - I



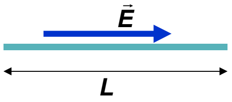
Electron distribution in k-space when E-field is zero

Distribution function: $f(k_x)$

Electron distribution is shifted in k-space when E-field is not zero

Distribution function: $f\left(k_x + \frac{e\,\tau}{\hbar}E_x\right)$

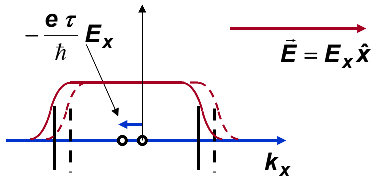
Since the wavevector of each electron is shifted by the same amount in the presence of the E-field, the net effect in k-space is that the entire electron distribution is shifted as shown



1D Electron Gas in an Applied Electric Field - II

Current (units: A)

$$I = -2\,e \times \int_{-\infty}^{\infty} \frac{dk_x}{2\pi}\, f\!\left(k_x + \frac{e\,\tau}{\hbar}E_x\right) v(k_x)$$



Electron distribution is shifted in k-space when E-field is not zero

Distribution function: $f\!\left(k_x + \frac{e\,\tau}{\hbar}E_x\right)$

Do a shift in the integration variable:

$$I = -2\,e \times \int_{-\infty}^{\infty} \frac{dk_x}{2\pi}\, f(k_x)\, v\!\left(k_x - \frac{e\,\tau}{\hbar}E_x\right)$$

$$I = -2\,e \times \int_{-\infty}^{\infty} \frac{dk_x}{2\pi}\, f(k_x)\, \frac{\hbar\left(k_x - \frac{e\,\tau}{\hbar}E_x\right)}{m}$$

$$I = \frac{e^2\tau}{m}\left[2 \times \int_{-\infty}^{\infty} \frac{dk_x}{2\pi}\, f(k_x)\right] E_x$$

electron density = *n* (units: #/cm)

$$I = \frac{n\,e^2\tau}{m}\vec{E} = \sigma\,\vec{E}$$

Where: $\sigma = \frac{n\,e^2\tau}{m}$

Same as the Drude result - but units are different. Units of σ are Siemens-cm in 1D

Handout 4

Lattices in 1D, 2D, and 3D

In this lecture you will learn:

- Bravais lattices
- Primitive lattice vectors
- Unit cells and primitive cells
- Lattices with basis and basis vectors

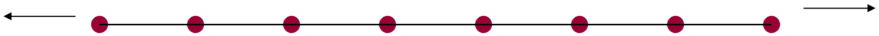
August Bravais (1811-1863)

Bravais Lattice

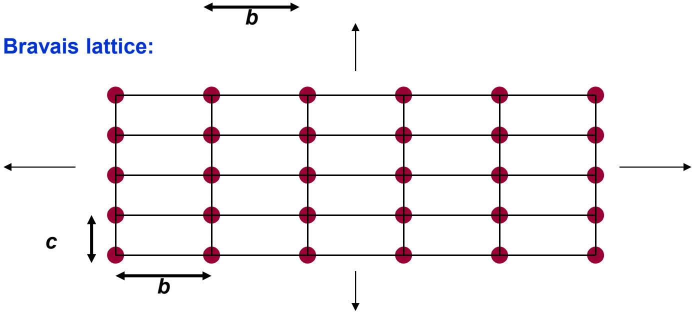
A fundamental concept in the description of crystalline solids is that of a "Bravais lattice". A Bravais lattice is an infinite arrangement of points (or atoms) in space that has the following property:

The lattice looks exactly the same when viewed from any lattice point

A 1D Bravais lattice:

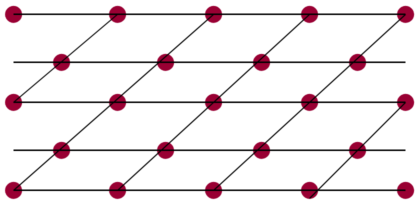


A 2D Bravais lattice:

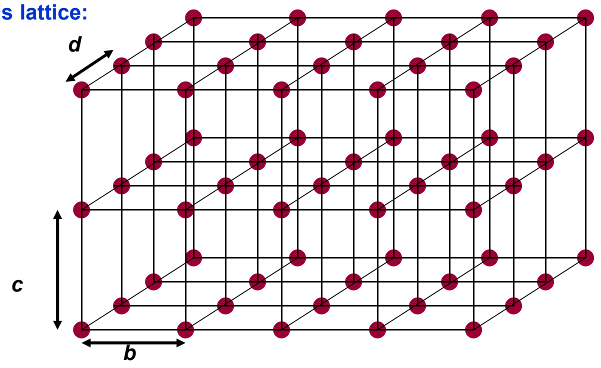


Bravais Lattice

A 2D Bravais lattice:



A 3D Bravais lattice:



Bravais Lattice

A Bravais lattice has the following property:

The position vector of all points (or atoms) in the lattice can be written as follows:

1D $\vec{R} = n\,\vec{a}_1$

2D $\vec{R} = n\,\vec{a}_1 + m\,\vec{a}_2$

3D $\vec{R} = n\,\vec{a}_1 + m\,\vec{a}_2 + p\,\vec{a}_3$

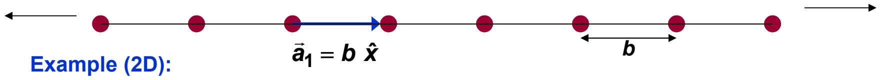
Where n, m, p = 0, ±1, ±2, ±3, …….

And the vectors,

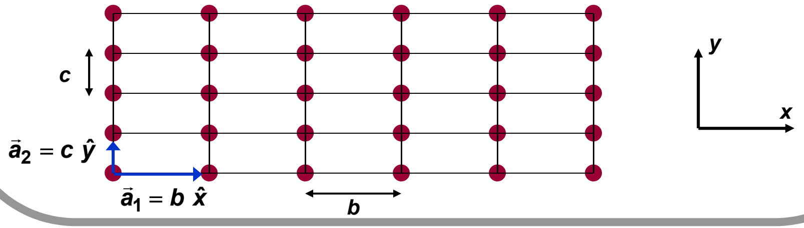
$\vec{a}_1$, $\vec{a}_2$, **and** $\vec{a}_3$

are called the “primitive lattice vectors” and are said to span the lattice. These vectors are not parallel.

Example (1D):

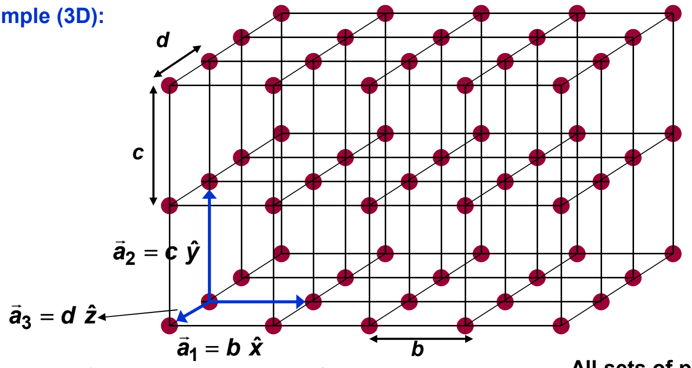


Example (2D):

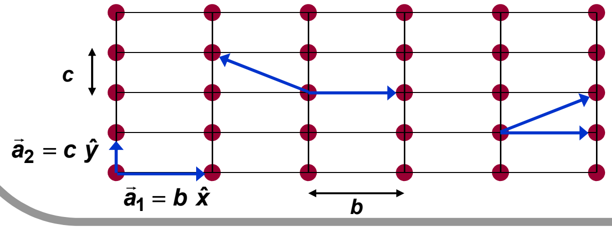


Bravais Lattice

Example (3D):



The choice of primitive vectors is NOT unique:



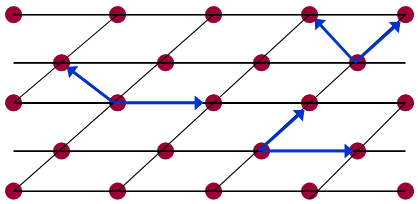
All sets of primitive vectors shown will work for the 2D lattice

$\vec{a}_2 = b\,\hat{x} + c\,\hat{y}$

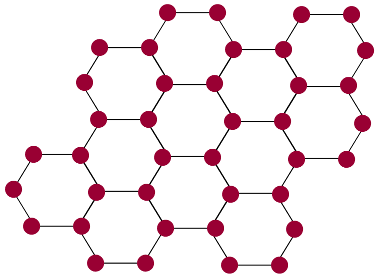
$\vec{a}_1 = b\,\hat{x}$

Bravais Lattice

Example (2D):



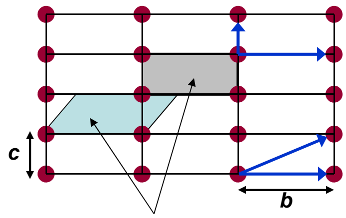
All lattices are not Bravais lattices:



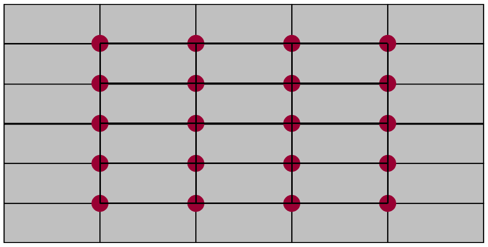
The honeycomb lattice

The Primitive Cell

- A primitive cell of a Bravais lattice is the smallest region which when translated by all different lattice vectors can "tile" or "cover" the entire lattice without overlapping



Two different choices of primitive cell



Tiling of the lattice by the primitive cell

- The primitive cell is not unique
- The volume (3D), area (2D), or length (1D) of a primitive cell can be given in terms of the primitive vectors, and is independent of the choice of the primitive vectors or of the primitive cells

1D $\Omega_1 = |\vec{a}_1|$

2D $\Omega_2 = |\vec{a}_1 \times \vec{a}_2|$

3D $\Omega_3 = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$

Example, for the 2D lattice above:

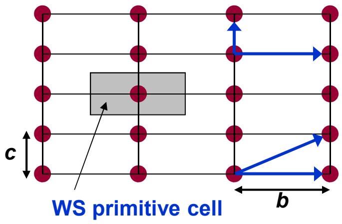
$$\vec{a}_1 = b\,\hat{x} \qquad \vec{a}_2 = c\,\hat{y} \qquad \Omega_2 = |\vec{a}_1 \times \vec{a}_2| = bc$$

or

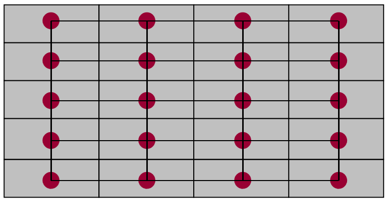
$$\vec{a}_1 = b\,\hat{x} \qquad \vec{a}_2 = b\,\hat{x} + c\,\hat{y} \qquad \Omega_2 = |\vec{a}_1 \times \vec{a}_2| = bc$$

The Wigner-Seitz Primitive Cell

- The Wigner-Seitz (WS) primitive cell of a Bravais lattice is a special kind of a primitive cell and consists of region in space around a lattice point that consists of all points in space that are closer to this lattice point than to any other lattice point



WS primitive cell



Tiling of the lattice by the WS primitive cell

- The Wigner-Seitz primitive cell is unique
- The volume (3D), area (2D), or length (1D) of a WS primitive cell can be given in terms of the primitive vectors, and is independent of the choice of the primitive vectors

1D $\Omega_1 = |\vec{a}_1|$

2D $\Omega_2 = |\vec{a}_1 \times \vec{a}_2|$

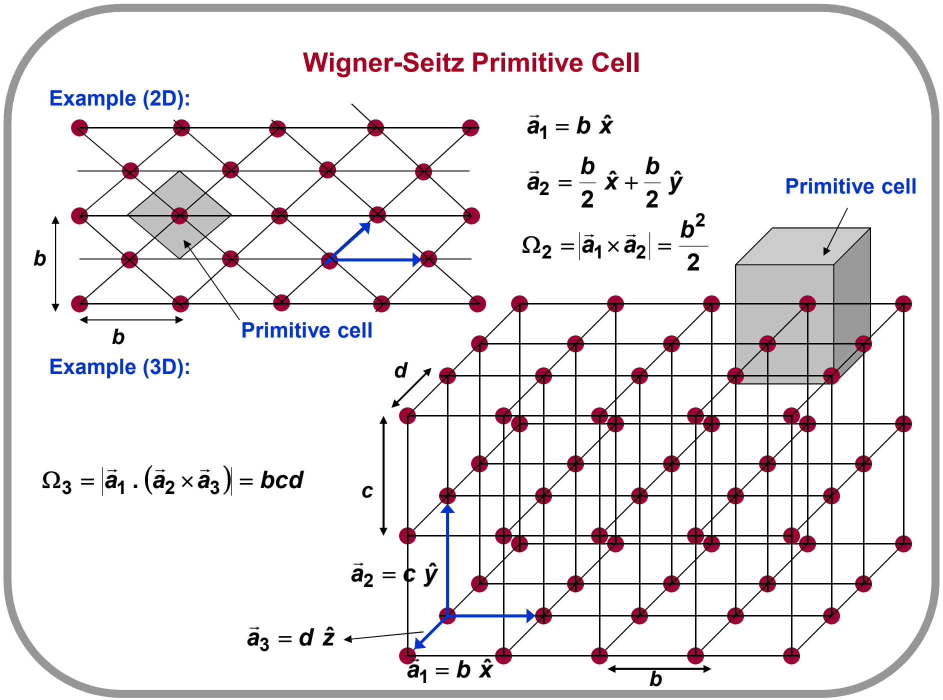
3D $\Omega_3 = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$

Example, for the 2D lattice above:

$$\vec{a}_1 = b\,\hat{x} \qquad \vec{a}_2 = c\,\hat{y} \qquad \Omega_2 = |\vec{a}_1 \times \vec{a}_2| = bc$$

or

$$\vec{a}_1 = b\,\hat{x} \qquad \vec{a}_2 = b\,\hat{x} + c\,\hat{y} \qquad \Omega_2 = |\vec{a}_1 \times \vec{a}_2| = bc$$



Wigner-Seitz Primitive Cell

Example (2D):

$$\vec{a}_1 = b\,\hat{x}$$

$$\vec{a}_2 = \frac{b}{2}\,\hat{x} + \frac{b}{2}\,\hat{y}$$

$$\Omega_2 = \left|\vec{a}_1 \times \vec{a}_2\right| = \frac{b^2}{2}$$

Primitive cell

Example (3D):

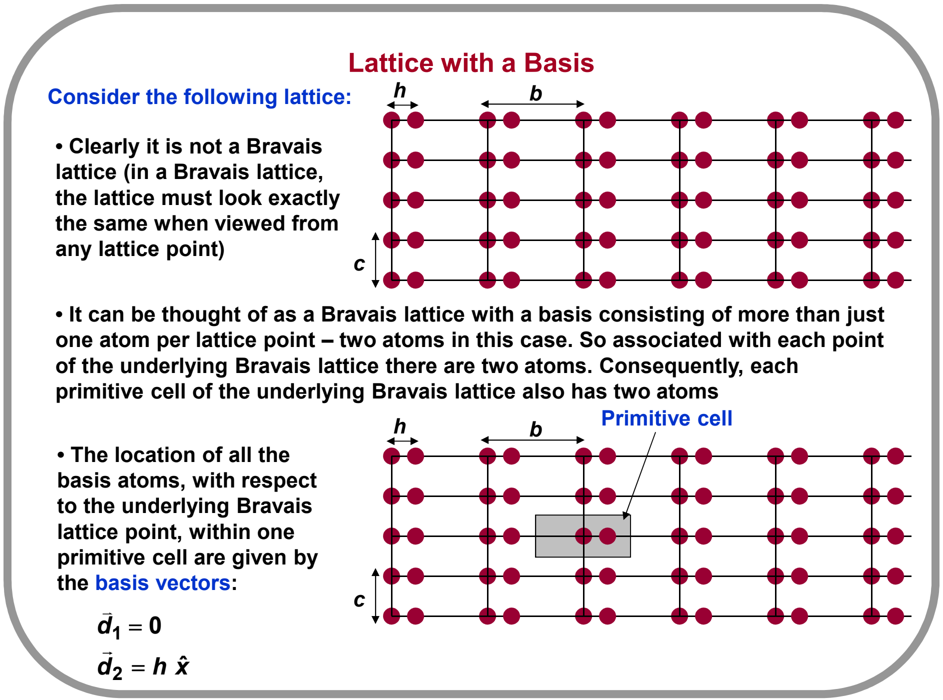
$$\Omega_3 = \left|\vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3\right)\right| = bcd$$

$$\vec{a}_2 = c\,\hat{y}$$

$$\vec{a}_3 = d\,\hat{z}$$

$$\vec{a}_1 = b\,\hat{x}$$

Primitive cell



Lattice with a Basis

Consider the following lattice:

- Clearly it is not a Bravais lattice (in a Bravais lattice, the lattice must look exactly the same when viewed from any lattice point)

- It can be thought of as a Bravais lattice with a basis consisting of more than just one atom per lattice point – two atoms in this case. So associated with each point of the underlying Bravais lattice there are two atoms. Consequently, each primitive cell of the underlying Bravais lattice also has two atoms

- The location of all the basis atoms, with respect to the underlying Bravais lattice point, within one primitive cell are given by the **basis vectors**:

$$\vec{d}_1 = 0$$

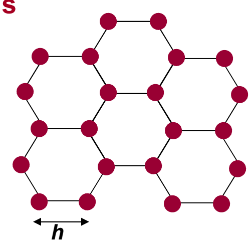
$$\vec{d}_2 = h\,\hat{x}$$

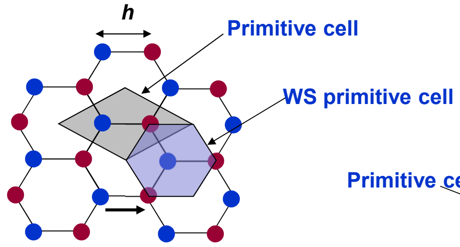
Primitive cell

Lattice with a Basis

Consider the Honeycomb lattice:

It is not a Bravais lattice, but it can be considered a Bravais lattice with a two-atom basis



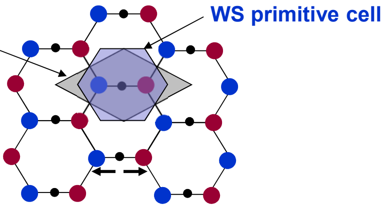


I can take the "blue" atoms to be the points of the underlying Bravais lattice that has a two-atom basis - "blue" and "red" - with basis vectors:

$$\vec{d}_1 = 0 \qquad \vec{d}_2 = h\,\hat{x}$$

Note: "red" and "blue" color coding is only for illustrative purposes. All atoms are the same.

Primitive cell



Or I can take the small "black" points to be the underlying Bravais lattice that has a two-atom basis - "blue" and "red" - with basis vectors:

$$\vec{d}_1 = -\frac{h}{2}\,\hat{x} \qquad \vec{d}_2 = \frac{h}{2}\,\hat{x}$$

Lattice with a Basis

Now consider a lattice made up of two different atoms: "red" and "black", as shown

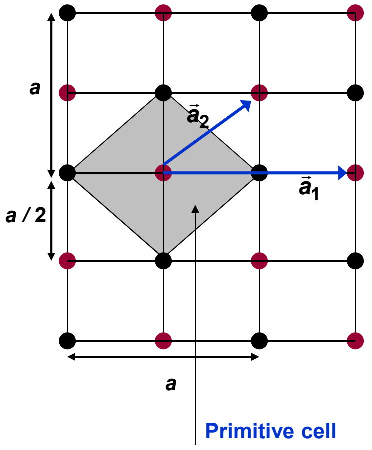
- It is clearly not a Bravais lattice since two different types of atoms occupy lattice positions
- The lattice define by the "red" atoms can be taken as the underlying Bravais lattice that has a two-atom basis: one "red" and one "black"
- The lattice primitive vectors are:

$$\vec{a}_1 = a\,\hat{x} \qquad \vec{a}_2 = \frac{a}{2}\,\hat{x} + \frac{a}{2}\,\hat{y}$$

- The two basis vectors are:

$$\vec{d}_1 = 0$$

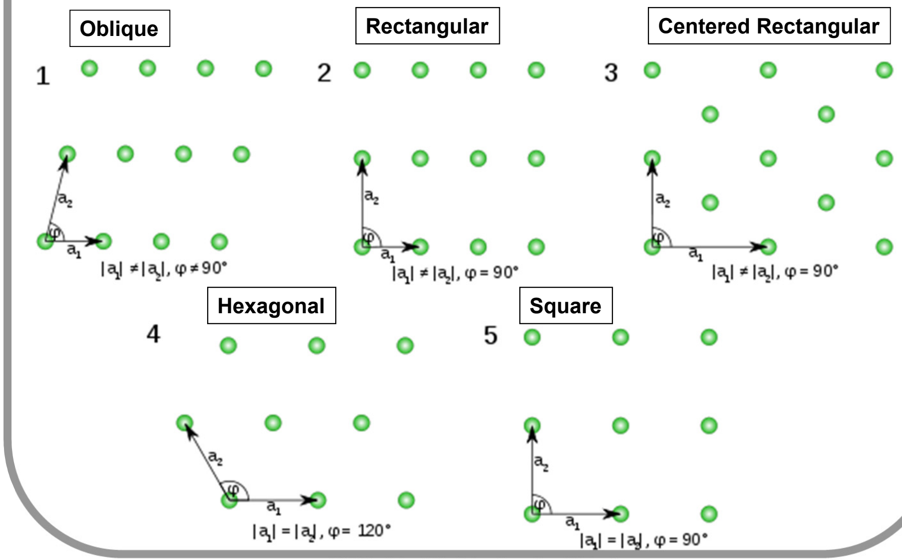
$$\vec{d}_2 = \frac{a}{2}\,\hat{x}$$



The primitive cell has the two basis atoms: one "red" and one "black" (actually one-fourth each of four "black" atoms)

Bravais Lattices in 2D

There are only 5 Bravais lattices in 2D



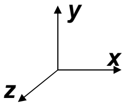
Lattices in 3D and the Unit Cell

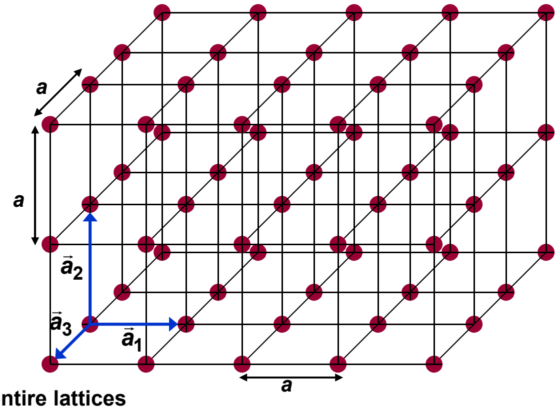
Simple Cubic Lattice:

$\vec{a}_1 = a\,\hat{x}$

$\vec{a}_2 = a\,\hat{y}$

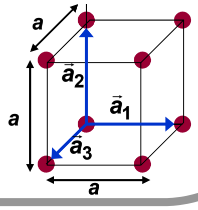
$\vec{a}_3 = a\,\hat{z}$





Unit Cell:

It is very cumbersome to draw entire lattices in 3D so some small portion of the lattice, having full symmetry of the lattice, is usually drawn. This small portion when repeated can generate the whole lattice and is called the "unit cell" and it could be larger than the primitive cell

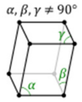


Unit cell of a cubic lattice

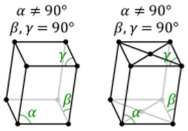
Bravais Lattices in 3D

There are 14 different Bravais lattices in 3D that are classified into 7 different crystal systems (only the unit cells are shown below)

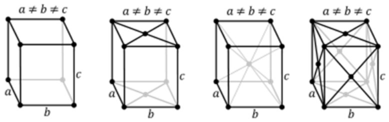
1) Triclinic:



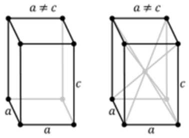
2) Monoclinic:



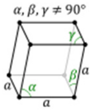
3) Orthorhombic:



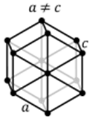
4) Tetragonal:



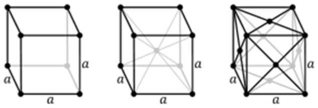
5) Rhombohedral:



6) Hexagonal:



7) Cubic:



Simple Cubic

Body Centered Cubic

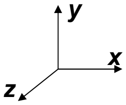
Face Centered Cubic

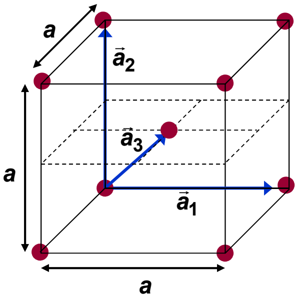
BCC and FCC Lattices

Body Centered Cubic (BCC) Lattice:

$$\vec{a}_1 = a\,\hat{x} \quad \vec{a}_2 = a\,\hat{y}$$

$$\vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})$$





Unit Cell

Or a more symmetric choice is:

$$\vec{a}_1 = \frac{a}{2}(-\hat{x} + \hat{y} + \hat{z})$$

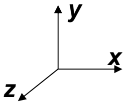
$$\vec{a}_2 = \frac{a}{2}(\hat{x} - \hat{y} + \hat{z}) \qquad \vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z})$$

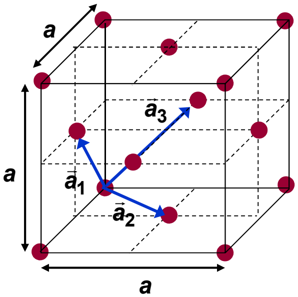
Face Centered Cubic (FCC) Lattice:

$$\vec{a}_1 = \frac{a}{2}(\hat{y} + \hat{z})$$

$$\vec{a}_2 = \frac{a}{2}(\hat{x} + \hat{z})$$

$$\vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{y})$$



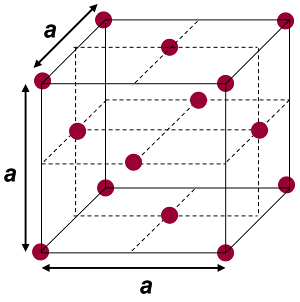


Unit Cell

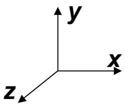
BCC and FCC Lattices

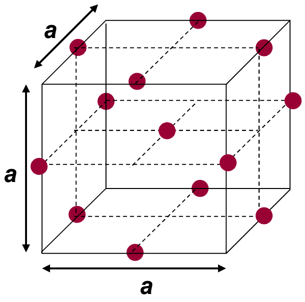
The choice of unit cell is not unique

Shown are two different unit cells for the FCC lattice



FCC Unit Cell

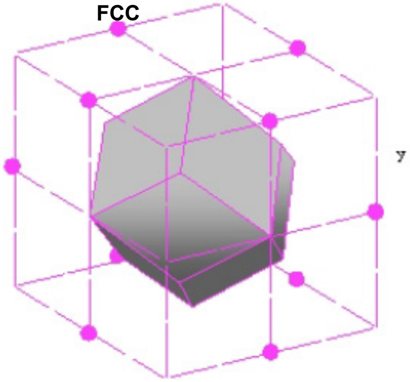


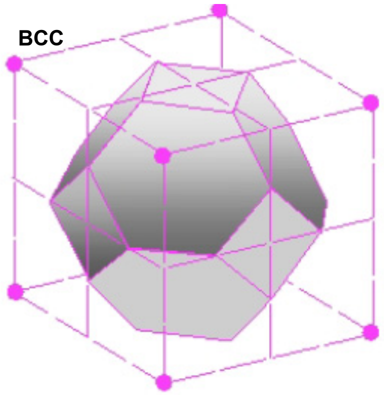


FCC Unit Cell

BCC and FCC Lattices

The (Wigner-Seitz) primitive cells of FCC and BCC Lattices are shown:





Materials with FCC lattices:

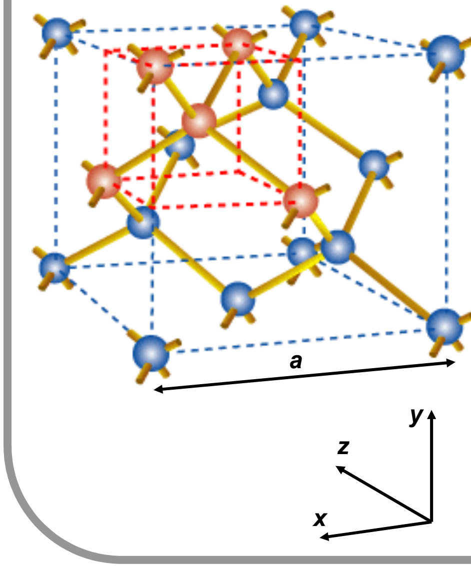
Aluminum, Nickel, Copper, Platinum, Gold, Lead, Silver, Silicon, Germanium, Diamond, Gallium Arsenide, Indium Phosphide

Materials with BCC lattices:

Lithium, Sodium, Potassium, Chromium, Iron, Molybdenum, Tungsten, Manganese

Lattices of Silicon, Germanium, and Diamond

Diamond Lattice



- Each atom is covalently bonded to four other atoms via sp3 bonds in a tetrahedral configuration
- The lattice defined by the position of the atoms is not a Bravais lattice
- The underlying lattice is an FCC lattice with a two-point (or two-atom) basis
- The lattice constant "*a*" usually found in the literature is the size of the unit cell, as shown. The primitive lattice vectors are:

$$\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z}) \quad \vec{a}_2 = \frac{a}{2}(\hat{x}+\hat{z})$$

$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y})$$

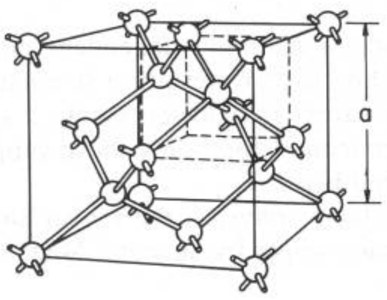
Same as for a FCC lattice

- The two basis vectors are:

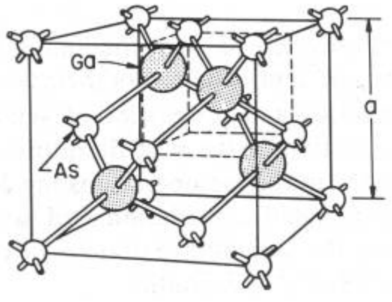
$$\vec{d}_1 = 0 \qquad \vec{d}_2 = \frac{a}{4}(\hat{x}+\hat{y}+\hat{z})$$

Lattices of III-V Binaries (GaAs, InP, GaP, InAs, AlAs, InSb, etc)

Diamond lattice (Si, Ge, Diamond)



Zincblende lattice (GaAs, InP, InAs)



- Each Group III atom is covalently bonded to four other group V atoms (and vice versa) via sp3 bonds in a tetrahedral configuration
- The underlying lattice is an FCC lattice with a two-point (or two-atom) basis. In contrast to the diamond lattice, the two atoms in the basis of zincblende lattice are different

Handout 5

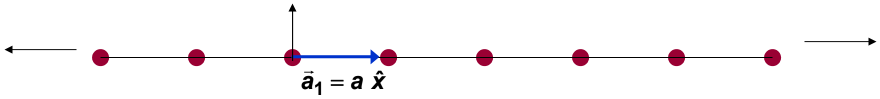
The Reciprocal Lattice

In this lecture you will learn:

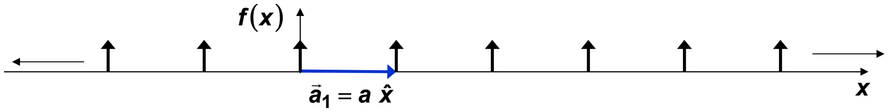
- Fourier transforms of lattices
- The reciprocal lattice
- Brillouin Zones
- X-ray diffraction
- Fourier transforms of lattice periodic functions

Fourier Transform (FT) of a 1D Lattice

Consider a 1D Bravais lattice:



Now consider a function consisting of a "lattice" of delta functions – in which a delta function is placed at each lattice point:



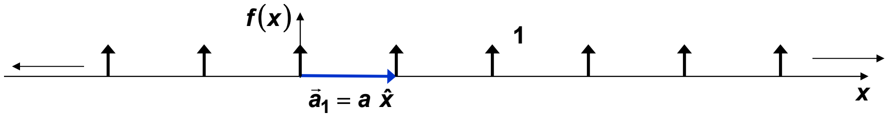
$$f(x) = \sum_{n=-\infty}^{\infty} \delta(x - n\,a)$$

The FT of this function is (as you found in your homework):

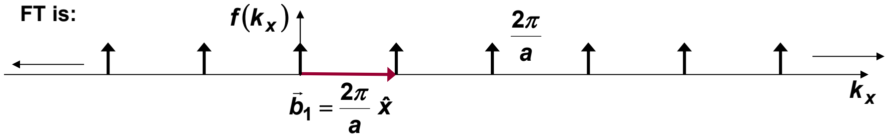
$$f(k_x) = \int_{-\infty}^{+\infty} dx \sum_{n=-\infty}^{\infty} \delta(x - n\,a)\, e^{-i\,k_x\,x} = \sum_{n=-\infty}^{\infty} e^{i\,k_x\,n\,a} = \frac{2\pi}{a} \sum_{m=-\infty}^{\infty} \delta\left(k_x - m\,\frac{2\pi}{a}\right)$$

The FT of a train of delta functions is also a train of delta functions in k-space

Reciprocal Lattice as FT of a 1D Lattice

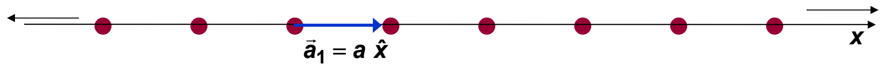


FT is:

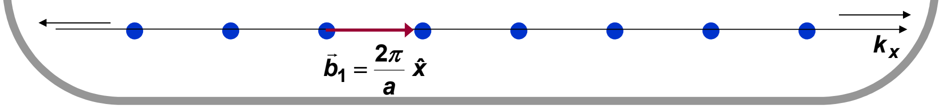


The reciprocal lattice is defined by the position of the delta-functions in the FT of the actual lattice (also called the direct lattice)

Direct lattice (or the actual lattice):

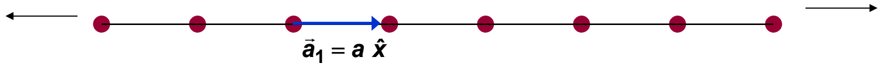


Reciprocal lattice:

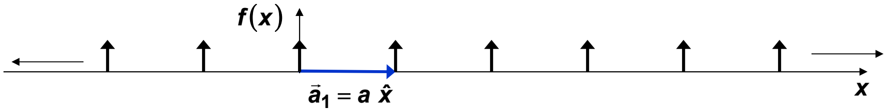


Reciprocal Lattice of a 1D Lattice

For the 1D Bravais lattice,



The position vector $\vec{R}_n$ of any lattice point is given by: $\vec{R}_n = n\,\vec{a}_1$



$$f(x) = \sum_{n=-\infty}^{\infty} \delta\left(\vec{x} - \vec{R}_n\right)$$

The FT of this function is: $f(k_x) = \int_{-\infty}^{+\infty} dx \sum_{n=-\infty}^{\infty} \delta\left(\vec{x} - \vec{R}_n\right) e^{-i\,k_x\,x} = \sum_{n=-\infty}^{\infty} e^{i\,\vec{k}.\vec{R}_n}$

The reciprocal lattice in k-space is defined by the set of all points for which the k-vector satisfies,

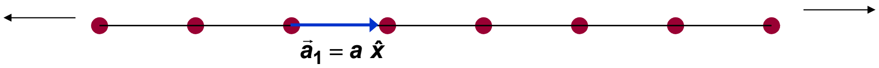
$$e^{i\,\vec{k}\,.\,\vec{R}_n} = 1$$

for ALL $\vec{R}_n$ of the direct lattice

For the points in k-space belonging to the reciprocal lattice the summation $\sum_{n=-\infty}^{\infty} e^{i\,\vec{k}.\vec{R}_n}$ becomes very large!

Reciprocal Lattice of a 1D Lattice

For the 1D Bravais lattice,



The position vector $\vec{R}_n$ of any lattice point is given by: $\vec{R}_n = n\,\vec{a}_1$

The reciprocal lattice in k-space is defined by the set of all points for which the k-vector satisfies,

$$e^{i\,\vec{k}\,.\,\vec{R}_n} = 1$$

for ALL $\vec{R}_n$ of the direct lattice

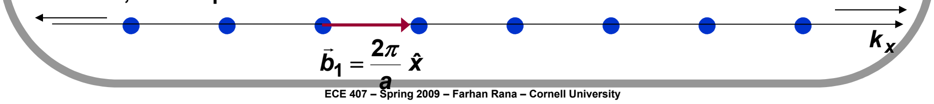
For $\vec{k}$ to satisfy $e^{i\,\vec{k}\,.\,\vec{R}_n} = 1$, it must be that for all $\vec{R}_n$:

$$\vec{k}\,.\,\vec{R}_n = 2\pi \times \{\text{integer}\}$$

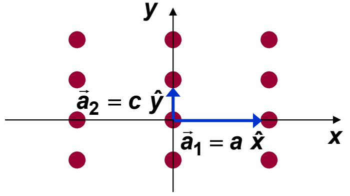
$$\Rightarrow k_x\; na = 2\pi \times \{\text{integer}\}$$

$$\Rightarrow k_x = m\frac{2\pi}{a} \quad \Big\{ \text{ where } m \text{ is any integer}$$

Therefore, the reciprocal lattice is:



Reciprocal Lattice of a 2D Lattice



Consider the 2D rectangular Bravais lattice:

If we place a 2D delta function at each lattice point we get the function:

$$f(x,y) = \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} \delta(x - n\,a)\,\delta(y - m\,c)$$

The above notation is too cumbersome, so we write it in a simpler way as:

$$f(\vec{r}) = \sum_{j} \delta^2\left(\vec{r} - \vec{R}_j\right) \longrightarrow$$ The summation over "*j*" is over all the lattice points

A 2D delta function has the property: $\int d^2\vec{r}\;\; \delta^2(\vec{r} - \vec{r}_o)\, g(\vec{r}) = g(\vec{r}_o)$
and it is just a product of two 1D delta functions corresponding to the *x* and *y* components of the vectors in its arguments: $\delta^2(\vec{r} - \vec{r}_o) = \delta(x - \vec{r}_o.\hat{x})\,\delta(y - \vec{r}_o.\hat{y})$

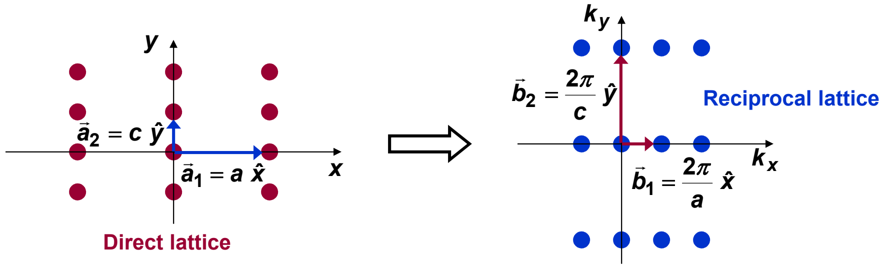
Now we Fourier transform the function $f(\vec{r})$:

$$f(\vec{k}) = \int d^2\vec{r}\;\; f(\vec{r})\; e^{-i\,\vec{k}\,.\,\vec{r}} = \int d^2\vec{r}\;\; \sum_j \delta^2\left(\vec{r} - \vec{R}_j\right)\, e^{-i\,\vec{k}\,.\,\vec{r}}$$

$$= \sum_j e^{-i\,\vec{k}\,.\,\vec{R}_j} = \frac{(2\pi)^2}{ac}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} \delta\left(k_x - n\frac{2\pi}{a}\right)\delta\left(k_y - m\frac{2\pi}{c}\right)$$

Reciprocal Lattice of a 2D Lattice

$$f(\vec{k}) = \sum_j e^{-i\,\vec{k}\,.\,\vec{R}_j} = \frac{(2\pi)^2}{ac}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\delta\left(k_x - n\frac{2\pi}{a}\right)\delta\left(k_y - m\frac{2\pi}{c}\right)$$



- Note also that the reciprocal lattice in k-space is defined by the set of all points for which the k-vector satisfies,

$$e^{i\,\vec{k}\,.\,\vec{R}_j} = 1$$

for all $\vec{R}_j$ of the direct lattice

- Reciprocal lattice as the FT of the direct lattice or as set of all points in k-space for which $\exp\left(i\,\vec{k}\,.\,\vec{R}_j\right) = 1$ for all $\vec{R}_j$, are equivalent statements

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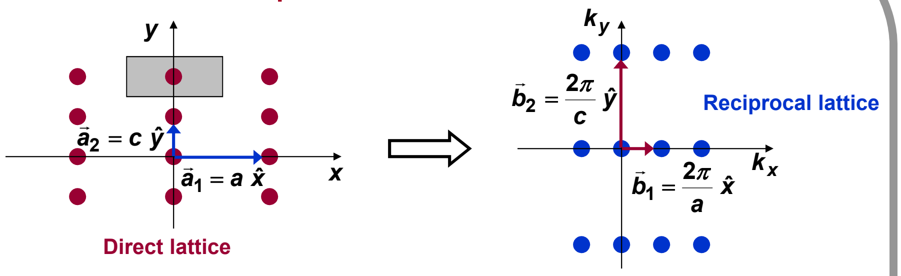
Reciprocal Lattice of a 2D Lattice



- The reciprocal lattice of a Bravais lattice is always a Bravais lattice and has its own primitive lattice vectors, for example, $\vec{b}_1$ and $\vec{b}_2$ in the above figure

- The position vector $\vec{G}$ of any point in the reciprocal lattice can be expressed in terms of the primitive lattice vectors:

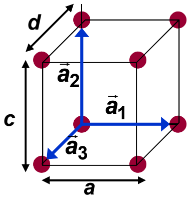
$$\vec{G} = n\,\vec{b}_1 + m\,\vec{b}_2 \qquad \Big\{ \text{For } m \text{ and } n \text{ integers}$$

So we can write the FT in a better way as:

$$f(\vec{k}) = \frac{(2\pi)^2}{ac}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\delta\left(k_x - n\frac{2\pi}{a}\right)\delta\left(k_y - m\frac{2\pi}{c}\right) = \frac{(2\pi)^2}{\Omega_2}\sum_j \delta^2\left(\vec{k} - \vec{G}_j\right)$$

where $\Omega_2 = ac$ is the area of the direct lattice primitive cell

Reciprocal Lattice of a 3D Lattice



Consider a orthorhombic direct lattice:

$$\vec{R} = n\,\vec{a}_1 + m\,\vec{a}_2 + p\,\vec{a}_3 \qquad \text{where } n, m, \text{ and } p \text{ are integers}$$

Then the corresponding delta-function lattice is:

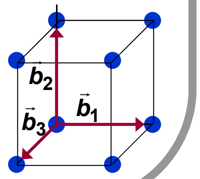
$$f(\vec{r}) = \sum_j \delta^3\left(\vec{r} - \vec{R}_j\right)$$

A 3D delta function has the property: $\int d^3\vec{r}\;\; \delta^3(\vec{r} - \vec{r}_o)\, g(\vec{r}) = g(\vec{r}_o)$

The reciprocal lattice in k-space is defined by the set of all points for which the k-vector satisfies: $\exp\left(i\,\vec{k}\,.\,\vec{R}_j\right) = 1$ for all $\vec{R}_j$ of the direct lattice. The above relation will hold if $\vec{k}$ equals $\vec{G}$:

$$\vec{G} = n\,\vec{b}_1 + m\,\vec{b}_2 + p\,\vec{b}_3 \qquad \text{and} \qquad \vec{b}_1 = \frac{2\pi}{a}\,\hat{x} \qquad \vec{b}_2 = \frac{2\pi}{c}\,\hat{y} \qquad \vec{b}_3 = \frac{2\pi}{d}\,\hat{z}$$

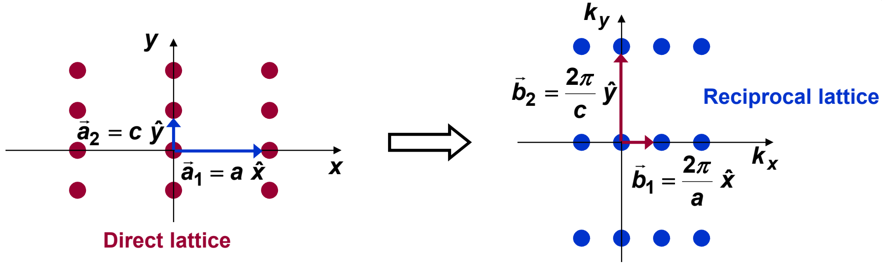
Finally, the FT of the direct lattice is:



$$f(\vec{k}) = \int d^3\vec{r}\;\; f(\vec{r})\; e^{-i\,\vec{k}\,.\,\vec{r}} = \int d^3\vec{r}\;\; \sum_j \delta^3\left(\vec{r} - \vec{R}_j\right)\; e^{-i\,\vec{k}\,.\,\vec{r}}$$

$$= \sum_j e^{-i\,\vec{k}\,.\,\vec{R}_j} = \frac{(2\pi)^3}{acd}\sum_j \delta^3\left(\vec{k} - \vec{G}_j\right) = \frac{(2\pi)^3}{\Omega_3}\sum_j \delta^3\left(\vec{k} - \vec{G}_j\right)$$

Direct Lattice Vectors and Reciprocal Lattice Vectors



$$\vec{R} = n\,\vec{a}_1 + m\,\vec{a}_2 \qquad\qquad \vec{G} = n\,\vec{b}_1 + m\,\vec{b}_2$$

Remember that the reciprocal lattice in k-space is defined by the set of all points for which the k-vector satisfies,

$$e^{i\,\vec{k}\,.\,\vec{R}} = 1$$

for all $\vec{R}$ of the direct lattice

So for all direct lattice vectors $\vec{R}$ and all reciprocal lattice vectors $\vec{G}$ we must have:

$$\boxed{e^{i\,\vec{G}\,.\,\vec{R}} = 1}$$

Reciprocal Lattice of General Lattices in 1D, 2D, 3D

More often that not, the direct lattice primitive vectors, $\vec{a}_1, \vec{a}_2$, and $\vec{a}_3$, are not orthogonal

Question: How does one find the reciprocal lattice vectors in the general case?

ID lattice:

If the direct lattice primitive vector is: $\vec{a}_1 = a\,\hat{x}$
and length of primitive cell is: $\Omega_1 = a$
Then the reciprocal lattice primitive vector is: $\vec{b}_1 = \frac{2\pi}{a}\,\hat{x}$

$$f(\vec{r}) = \sum_j \delta\left(\vec{r} - \vec{R}_j\right) \Longleftrightarrow f(\vec{k}) = \frac{2\pi}{\Omega_1}\sum_j \delta\left(\vec{k} - \vec{G}_j\right)$$

Note:

$$\vec{a}_1 . \vec{b}_1 = 2\pi$$

$$e^{i\,\vec{G}_p . \vec{R}_m} = 1$$

2D lattice:

If the direct lattice is in the *x-y* plane and the primitive vectors are: $\vec{a}_1$ and $\vec{a}_2$
and area of primitive cell is: $\Omega_2 = \left|\vec{a}_1 \times \vec{a}_2\right|$
Then the reciprocal lattice primitive vectors are: $\vec{b}_1 = 2\pi\frac{\vec{a}_2 \times \hat{z}}{\Omega_2}$ $\quad \vec{b}_2 = 2\pi\frac{\hat{z} \times \vec{a}_1}{\Omega_2}$

$$f(\vec{r}) = \sum_j \delta^2\left(\vec{r} - \vec{R}_j\right) \Longleftrightarrow f(\vec{k}) = \frac{(2\pi)^2}{\Omega_2}\sum_j \delta^2\left(\vec{k} - \vec{G}_j\right)$$

Note: $\vec{a}_j . \vec{b}_k = 2\pi\,\delta_{jk}$ and $e^{i\,\vec{G}_p . \vec{R}_m} = 1$

Reciprocal Lattice of General Lattices in 1D, 2D, 3D

3D lattice:

If the direct lattice primitive vectors are: $\vec{a}_1, \vec{a}_2$, and $\vec{a}_3$
and volume of primitive cell is: $\Omega_3 = \left|\vec{a}_1 . \left(\vec{a}_2 \times \vec{a}_3\right)\right|$

Then the reciprocal lattice primitive vectors are:

$$\vec{b}_1 = 2\pi\frac{\vec{a}_2 \times \vec{a}_3}{\Omega_3} \quad \vec{b}_2 = 2\pi\frac{\vec{a}_3 \times \vec{a}_1}{\Omega_3} \quad \vec{b}_3 = 2\pi\frac{\vec{a}_1 \times \vec{a}_2}{\Omega_3}$$

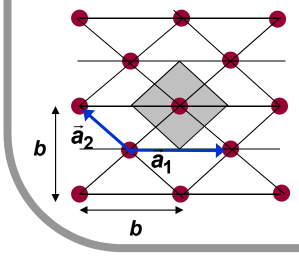
$$f(\vec{r}) = \sum_j \delta^3\left(\vec{r} - \vec{R}_j\right) \Longleftrightarrow f(\vec{k}) = \frac{(2\pi)^3}{\Omega_3}\sum_j \delta^3\left(\vec{k} - \vec{G}_j\right)$$

Note:

$$\vec{a}_j . \vec{b}_k = 2\pi\,\delta_{jk}$$

$$e^{i\,\vec{G}_p . \vec{R}_m} = 1$$

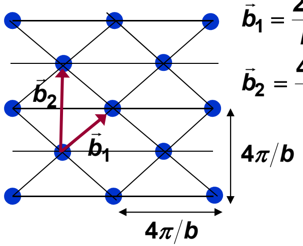
Example 2D lattice:



$$\vec{a}_1 = b\,\hat{x}$$

$$\vec{a}_2 = -\frac{b}{2}\,\hat{x} + \frac{b}{2}\,\hat{y}$$

$$\Omega_2 = \left|\vec{a}_1 \times \vec{a}_2\right| = \frac{b^2}{2}$$

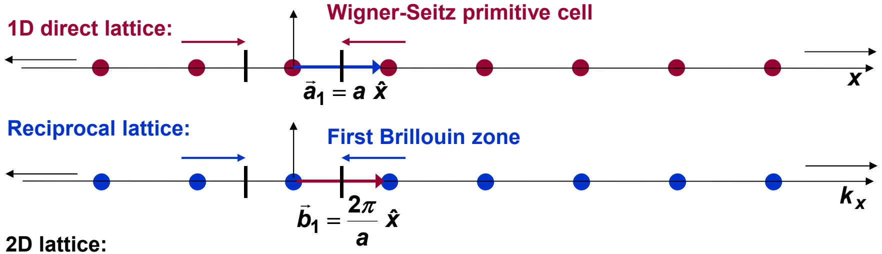


$$\vec{b}_1 = \frac{2\pi}{b}\left(\hat{x} + \hat{y}\right)$$

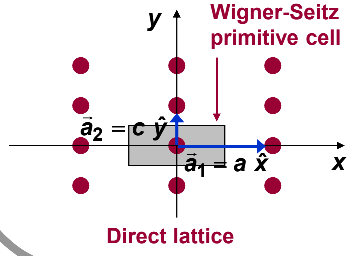
$$\vec{b}_2 = \frac{4\pi}{b}\,\hat{y}$$

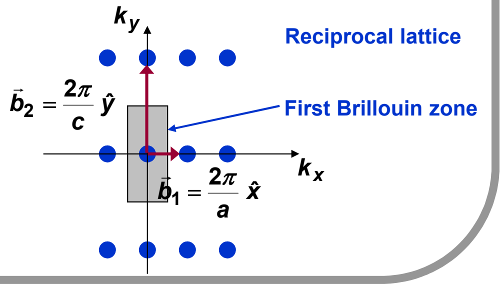
The Brillouin Zone

The Wigner-Seitz primitive cell of the reciprocal lattice centered at the origin is called the Brillouin zone (or the first Brillouin zone or FBZ)



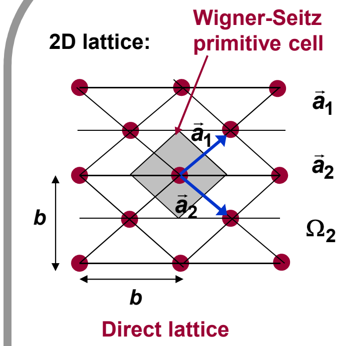
2D lattice:





The Brillouin Zone

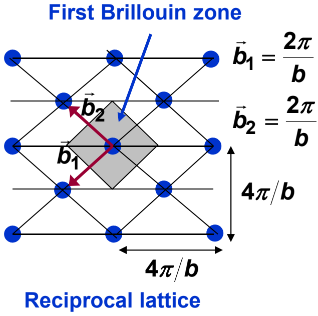
2D lattice:



$$\vec{a}_1 = \frac{b}{2}\,\hat{x} + \frac{b}{2}\,\hat{y}$$

$$\vec{a}_2 = \frac{b}{2}\,\hat{x} - \frac{b}{2}\,\hat{y}$$

$$\Omega_2 = \left|\vec{a}_1 \times \vec{a}_2\right| = \frac{b^2}{2}$$



$$\vec{b}_1 = \frac{2\pi}{b}\left(-\hat{x} - \hat{y}\right)$$

$$\vec{b}_2 = \frac{2\pi}{b}\left(-\hat{x} + \hat{y}\right)$$

Volume/Area/Length of the first Brillouin zone:

The volume (3D), area (2D), length (1D) of the first Brillouin zone is given in the same way as the corresponding expressions for the primitive cell of a direct lattice:

1D $\Pi_1 = \left|\vec{b}_1\right|$

2D $\Pi_2 = \left|\vec{b}_1 \times \vec{b}_2\right|$

3D $\Pi_3 = \left|\vec{b}_1 \cdot \left(\vec{b}_2 \times \vec{b}_3\right)\right|$

Note that in all dimensions (*d*) the following relationship holds between the volumes, areas, lengths of the direct and reciprocal lattice primitive cells:

$$\Pi_d = \frac{(2\pi)^d}{\Omega_d}$$

Direct Lattice Planes and Reciprocal Lattice Vectors

There is an intimate relationship between reciprocal lattice vectors and planes of points in the direct lattice captured by this theorem and its converse

Theorem:

If there is a family of parallel lattice planes separated by distance "d" and $\hat{n}$ is a unit vector normal to the planes then the vector given by,

$$\vec{G} = \frac{2\pi}{d}\hat{n}$$

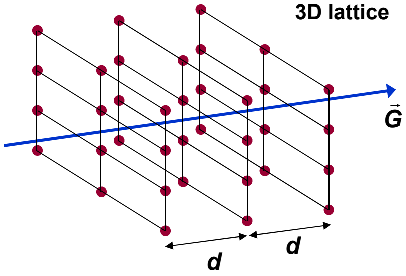
is a reciprocal lattice vector and so is:

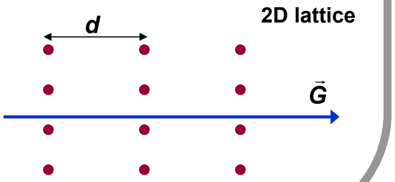
$$m\frac{2\pi}{d}\hat{n} \qquad \{ \quad m = \text{integer}$$

Converse:

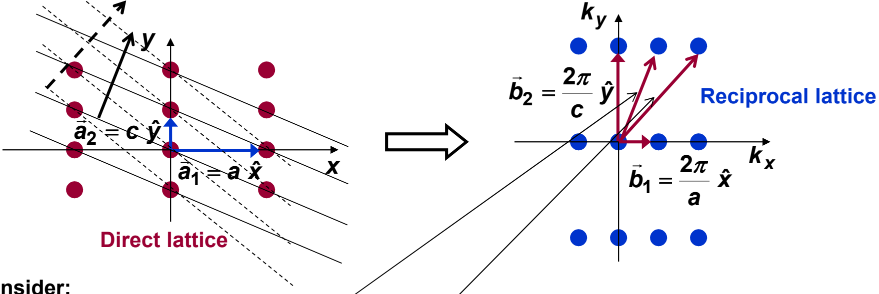
If $\vec{G}_1$ is any reciprocal lattice vector, and $\vec{G}$ is the reciprocal lattice vector of the smallest magnitude parallel to $\vec{G}_1$, then there exist a family of lattice planes perpendicular to $\vec{G}_1$ and $\vec{G}$, and separated by distance "d" where:

$$d = \frac{2\pi}{|\vec{G}|}$$





Example: Direct Lattice Planes and Reciprocal Lattice Vectors



Consider:

$$\vec{G} = \vec{b}_1 + \vec{b}_2 = 2\pi\left(\frac{\hat{x}}{a} + \frac{\hat{y}}{c}\right)$$

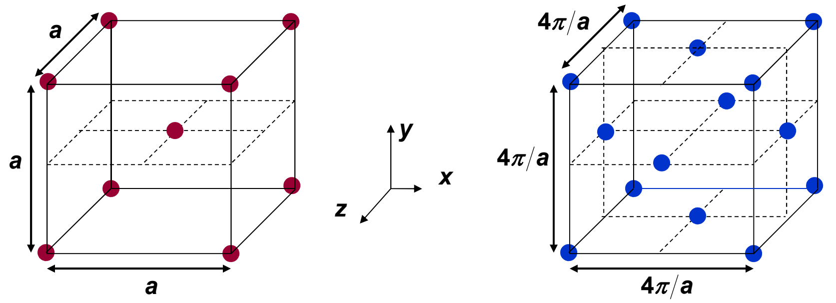
There must be a family of lattice planes normal to $\vec{G}$ and separated by: $\frac{2\pi}{|\vec{G}|} = \frac{ac}{\sqrt{a^2 + c^2}}$

Now consider:

$$\vec{G} = 2\vec{b}_1 + \vec{b}_2 = 2\pi\left(\frac{2\hat{x}}{a} + \frac{\hat{y}}{c}\right)$$

There must be a family of lattice planes normal to $\vec{G}$ and separated by: $\frac{2\pi}{|\vec{G}|} = \frac{ac}{\sqrt{a^2 + 4c^2}}$

The BCC Direct Lattice



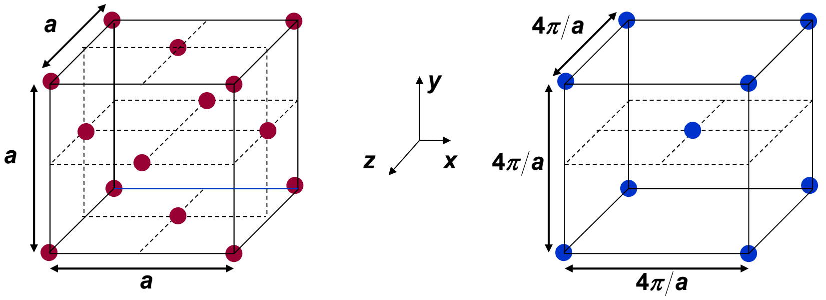
Direct lattice: BCC

Reciprocal lattice: FCC

The direct and the reciprocal lattices are not necessarily always the same!

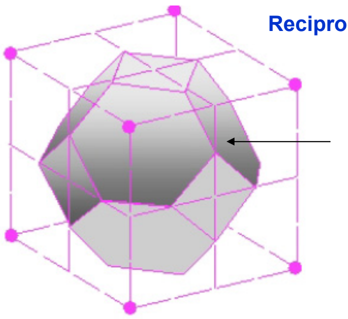
a

The FCC Direct Lattice



Direct lattice: FCC

Reciprocal lattice: BCC



First Brillouin zone of the BCC reciprocal lattice for an FCC direct lattice

The Reciprocal Lattice and FTs of Periodic Functions

The relationship between delta-functions on a "*d*" dimensional lattice and its Fourier transform is:

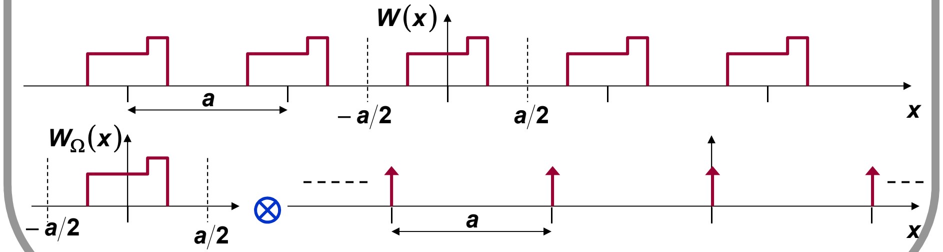
$$f(\vec{r})=\sum_{j}\delta^{d}\left(\vec{r}-\vec{R}_{j}\right) \Longleftrightarrow f(\vec{k})=\frac{(2\pi)^{d}}{\Omega_{d}}\sum_{j}\delta^{d}\left(\vec{k}-\vec{G}_{j}\right)$$

Supper $W(\vec{r})$ is a periodic function with the periodicity of the direct lattice then by definition:

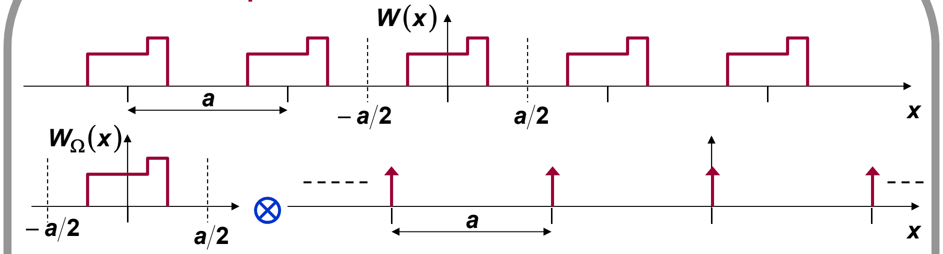
$$W\left(\vec{r}+\vec{R}_{j}\right)=W(\vec{r})$$

for all $\vec{R}_{j}$ of the direct lattice

One can always write a periodic function as a convolution of its value in the primitive cell and a lattice of delta functions, as shown for 1D below:



The Reciprocal Lattice and FTs of Periodic Functions



Mathematically:

$$W(x)=W_{\Omega}(x)\otimes\sum_{n=-\infty}^{\infty}\delta(x-n\,a)$$

And more generally in "*d*" dimensions for a lattice periodic function $W(\vec{r})$ we have:

$$W(\vec{r})=W_{\Omega}(\vec{r})\otimes\sum_{j}\delta^{d}\left(\vec{r}-\vec{R}_{j}\right)$$

Value of the function in one primitive cell

Lattice of delta functions

The Reciprocal Lattice and FTs of Periodic Functions

For a periodic function we have:

$$W(\vec{r}) = W_{\Omega}(\vec{r}) \otimes \sum_{j} \delta^{d}\left(\vec{r} - \vec{R}_{j}\right)$$

Its FT is now easy given that we know the FT of a lattice of delta functions:

$$f(\vec{r}) = \sum_{j} \delta^{d}\left(\vec{r} - \vec{R}_{j}\right) \Longleftrightarrow f\left(\vec{k}\right) = \frac{(2\pi)^{d}}{\Omega_{d}} \sum_{j} \delta^{d}\left(\vec{k} - \vec{G}_{j}\right)$$

We get:

$$W\left(\vec{k}\right) = W_{\Omega}\left(\vec{k}\right) \times \frac{(2\pi)^{d}}{\Omega_{d}} \sum_{j} \delta^{d}\left(\vec{k} - \vec{G}_{j}\right) = \frac{(2\pi)^{d}}{\Omega_{d}} \sum_{j} \delta^{d}\left(\vec{k} - \vec{G}_{j}\right) W_{\Omega}\left(\vec{G}_{j}\right)$$

The FT looks like reciprocal lattice of delta-functions with unequal weights

If we now take the inverse FT we get:

$$W(\vec{r}) = \int \frac{d^{d}\vec{k}}{(2\pi)^{d}} W\left(\vec{k}\right) e^{i\,\vec{k}\,.\,\vec{r}} = \int \frac{d^{d}\vec{k}}{(2\pi)^{d}} \frac{(2\pi)^{d}}{\Omega_{d}} \sum_{j} \delta^{d}\left(\vec{k} - \vec{G}_{j}\right) W_{\Omega}\left(\vec{G}_{j}\right) e^{i\,\vec{k}\,.\,\vec{r}}$$

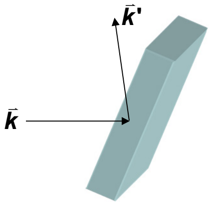
$$= \sum_{j} \frac{W_{\Omega}\left(\vec{G}_{j}\right)}{\Omega_{d}} e^{i\,\vec{G}_{j}\,.\,\vec{r}} \longrightarrow$$

A lattice periodic function can always be written as a Fourier series that only has wavevectors belonging to the reciprocal lattice

The Reciprocal Lattice and X-Ray Diffraction

X-ray diffraction is the most commonly used method to study crystal structures

In this scheme, X-rays of wavevector $\vec{k}$ are sent into a crystal, and the scattered X-rays in the direction of a different wavevector, say $\vec{k}'$, are measured



If the position dependent dielectric constant of the medium is given by $\varepsilon(\vec{r})$ then the diffraction theory tells us that the amplitude of the scattered X-rays in the direction of $\vec{k}'$ is proportional to the integral:

$$S\left(\vec{k} \rightarrow \vec{k}'\right) \propto \int d^{3}\vec{r}\;\; e^{-i\,\vec{k}'\,.\,\vec{r}}\;\; \varepsilon(\vec{r})\, e^{i\,\vec{k}\,.\,\vec{r}}$$

For X-ray frequencies, the dielectric constant is a periodic function with the periodicity of the lattice. Therefore, one can write:

$$\varepsilon(\vec{r}) = \sum_{j} \varepsilon\left(\vec{G}_{j}\right) e^{i\,\vec{G}_{j}\,.\,\vec{r}}$$

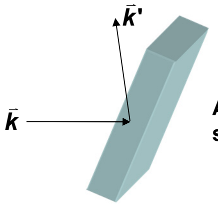
Plug this into the integral above to get: $S\left(\vec{k} \rightarrow \vec{k}'\right) \propto \sum_{j} \varepsilon\left(\vec{G}_{j}\right)(2\pi)^{3}\delta\left(\vec{k} + \vec{G}_{j} - \vec{k}'\right)$

$\Rightarrow$ X-rays will scatter in only those directions for which:

$\vec{k}' = \vec{k} + \vec{G}$ where $\vec{G}$ is some reciprocal lattice vector

Or: $\vec{k}' = \vec{k} \pm \vec{G}$ Because $-\vec{G}$ is also a reciprocal vector whenever $\vec{G}$ is a reciprocal vector

The Reciprocal Lattice and X-Ray Diffraction



⇒ X-rays will scatter in only those directions for which:

$$\vec{k}' = \vec{k} \pm \vec{G} \longrightarrow (1)$$

Also, the frequency of the incident and diffracted X-rays is the same so:

$$\omega' = \omega$$

$$\Rightarrow |\vec{k}'|c = |\vec{k}|c$$

$$\Rightarrow |\vec{k}'| = |\vec{k}|$$

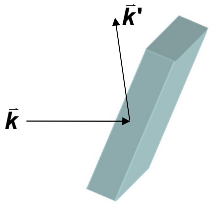
(1) gives: $|\vec{k}'|^2 = |\vec{k}|^2 + |\vec{G}|^2 \pm 2\,\vec{k}\,.\,\vec{G}$

$$\Rightarrow |\vec{k}'|^2 = |\vec{k}|^2 + |\vec{G}|^2 \pm 2\,\vec{k}\,.\,\vec{G}$$

$$\Rightarrow |\vec{k}|^2 = |\vec{k}|^2 + |\vec{G}|^2 \pm 2\,\vec{k}\,.\,\vec{G}$$

$$\Rightarrow \pm\,\vec{k}\,.\,\vec{G} = \frac{|\vec{G}|^2}{2} \qquad \Big\{ \text{ Condition for X-ray diffraction}$$

The Reciprocal Lattice and X-Ray Diffraction



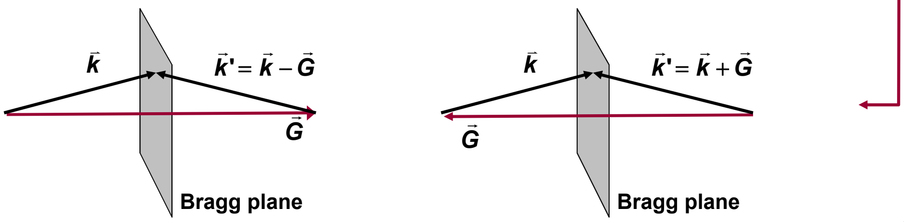
The condition,

$$\vec{k}\,.\,\vec{G} = \pm\frac{|\vec{G}|^2}{2}$$

is called the Bragg condition for diffraction

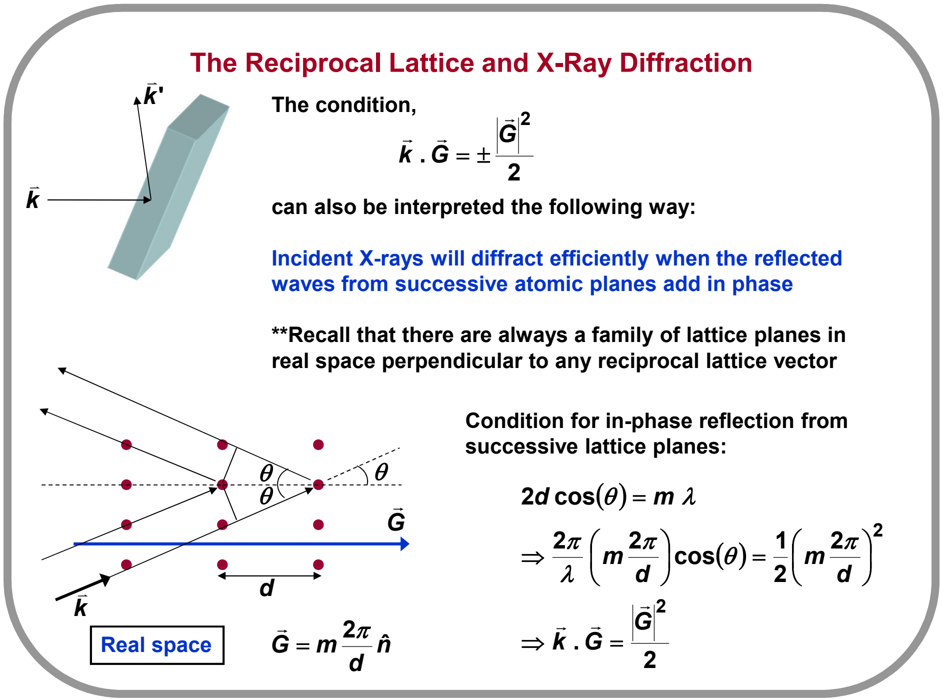
Incident X-rays will diffract efficiently provided the incident wavevector satisfies the Bragg condition for some reciprocal lattice vector $\vec{G}$

A graphical way to see the Bragg condition is that the incident wavevector lies on a plane in k-space (called the Bragg plane) that is the perpendicular bisector of some reciprocal lattice vector $\vec{G}$



k-space

k-space



The Reciprocal Lattice and X-Ray Diffraction

The condition,

$$\vec{k}\,.\,\vec{G} = \pm\frac{|\vec{G}|^2}{2}$$

can also be interpreted the following way:

Incident X-rays will diffract efficiently when the reflected waves from successive atomic planes add in phase

**Recall that there are always a family of lattice planes in real space perpendicular to any reciprocal lattice vector

Condition for in-phase reflection from successive lattice planes:

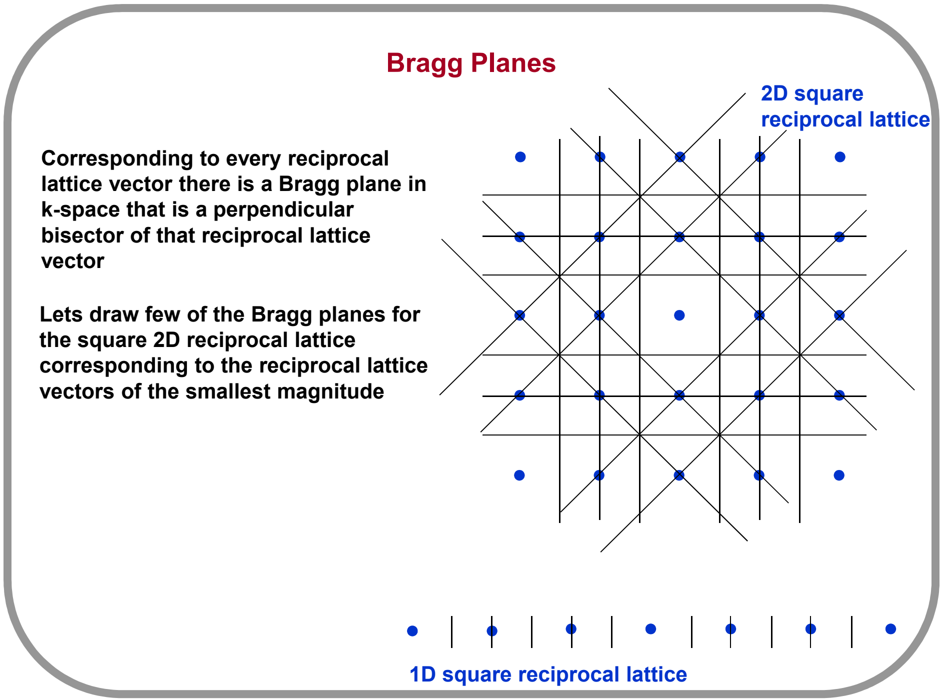
$$2d\cos(\theta) = m\,\lambda$$

$$\Rightarrow \frac{2\pi}{\lambda}\left(m\frac{2\pi}{d}\right)\cos(\theta) = \frac{1}{2}\left(m\frac{2\pi}{d}\right)^2$$

$$\Rightarrow \vec{k}\,.\,\vec{G} = \frac{|\vec{G}|^2}{2}$$

Real space

$$\vec{G} = m\frac{2\pi}{d}\hat{n}$$



Bragg Planes

Corresponding to every reciprocal lattice vector there is a Bragg plane in k-space that is a perpendicular bisector of that reciprocal lattice vector

Lets draw few of the Bragg planes for the square 2D reciprocal lattice corresponding to the reciprocal lattice vectors of the smallest magnitude

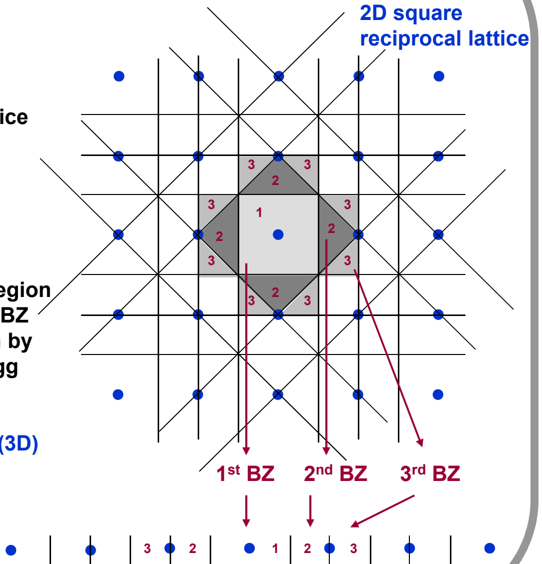
Bragg Planes and Higher Order Brillouin Zones

Bragg planes are shown for the square 2D reciprocal lattice corresponding to the reciprocal lattice vectors of the smallest magnitude

Higher Order Brillouin Zones

The nth BZ can be defined as the region in k-space that is not in the (n-1)th BZ and can be reached from the origin by crossing at the minimum (n-1) Bragg planes

The length (1D), area (2D), volume (3D) of BZ of any order is the same



Appendix: Proof of the General Lattice FT Relation in 3D

This appendix gives proof of the FT relation:

$$f(\vec{r}) = \sum_j \delta^3(\vec{r} - \vec{R}_j) \iff f(\vec{k}) = \frac{(2\pi)^3}{\Omega_3} \sum_j \delta^3(\vec{k} - \vec{G}_j)$$

for the general case when the direct lattice primitive vectors are not orthogonal

Let: $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$

Define the reciprocal lattice primitive vectors as:

$$\vec{b}_1 = 2\pi \frac{\hat{a}_2 \times \hat{a}_3}{\Omega_3} \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\Omega_3} \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\Omega_3}$$

Note: $\vec{a}_j \,.\, \vec{b}_k = 2\pi\, \delta_{jk}$

Now we take FT:

$$f(\vec{k}) = \int d^3\vec{r}\; f(\vec{r})\; e^{-i\vec{k}.\vec{r}} = \int d^3\vec{r}\; \sum_j \delta^3(\vec{r} - \vec{R}_j)\; e^{-i\vec{k}.\vec{r}}$$

$$= \sum_j e^{-i\vec{k}.\vec{R}_j}$$

Appendix: Proof

One can expand $\vec{k}$ in any suitable basis. Instead of choosing the usual basis:

$$\vec{k} = k_x \hat{x} + k_y \hat{y} + k_z \hat{z}$$

I choose the basis defined by the reciprocal lattice primitive vectors:

$$\vec{k} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3$$

Given that: $\vec{a}_j \cdot \vec{b}_k = 2\pi \, \delta_{jk}$

I get:

$$f(\vec{k}) = \sum_j e^{-i\,\vec{k}\,.\,\vec{R}_j} = \sum_{n_1\, n_2\, n_3} e^{-i\,\vec{k}\,.\,(n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3)}$$
$$= \sum_{m_1\, m_2\, m_3} \delta(k_1 - m_1)\,\delta(k_2 - m_2)\,\delta(k_3 - m_3)$$

Now:

$$\delta(k_1 - m_1)\,\delta(k_2 - m_2)\,\delta(k_3 - m_3) \propto \delta^3(\vec{k} - \vec{G})$$

where: $\vec{G} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3$

But we don't know the exact weight of the delta function $\delta^3(\vec{k} - \vec{G})$

Appendix: Proof

Since: $\vec{k} = k_x \hat{x} + k_y \hat{y} + k_z \hat{z}$ and $\vec{k} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3$

This implies:

$$\begin{bmatrix} k_x \\ k_y \\ k_z \end{bmatrix} = \begin{bmatrix} b_{1x} & b_{2x} & b_{3x} \\ b_{2x} & b_{2y} & b_{2z} \\ b_{3x} & b_{3y} & b_{3z} \end{bmatrix} \begin{bmatrix} k_1 \\ k_2 \\ k_3 \end{bmatrix} \quad \text{———} \quad (1)$$

Any integral over k-space in the form: $\int_{-\infty}^{\infty} dk_1 \int_{-\infty}^{\infty} dk_2 \int_{-\infty}^{\infty} dk_3$

can be converted into an integral in the form: $\int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} dk_z$

by the Jacobian of the transformation:

$$\int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} dk_z \;\rightarrow\; \left| \frac{\partial(k_x, k_y, k_z)}{\partial(k_1, k_2, k_3)} \right| \int_{-\infty}^{\infty} dk_1 \int_{-\infty}^{\infty} dk_2 \int_{-\infty}^{\infty} dk_3$$

Therefore:

$$\delta(k_1 - m_1)\,\delta(k_2 - m_2)\,\delta(k_3 - m_3) = \left| \frac{\partial(k_x, k_y, k_z)}{\partial(k_1, k_2, k_3)} \right| \delta^3(\vec{k} - \vec{G})$$

Appendix: Proof

From (1) on previous slide:

$$\left|\frac{\partial(k_x,k_y,k_z)}{\partial(k_1,k_2,k_3)}\right| = \left|\vec{b}_1 \,.\, (\vec{b}_2 \times \vec{b}_3)\right| = \Pi_3 = \frac{(2\pi)^3}{\Omega_3}$$

Therefore:

$$f(\vec{k}) = \sum_j e^{-i\,\vec{k}\,.\,\vec{R}_j} = \sum_{m_1\, m_2\, m_3} \delta(k_1 - m_1)\,\delta(k_2 - m_2)\,\delta(k_3 - m_3)$$

$$= \frac{(2\pi)^3}{\Omega_3} \sum_j \delta^3\left(\vec{k} - \vec{G}_j\right)$$

Review Handout

Time Independent Perturbation Theory in Quantum Mechanics

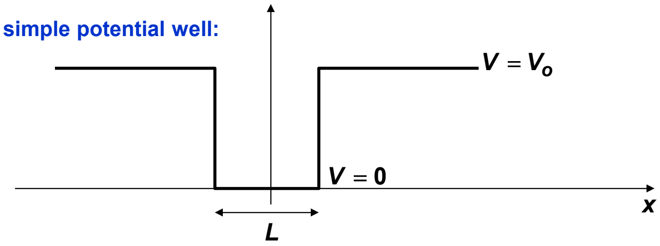
In this lecture you will learn:

- First and Second Order Time Independent Perturbation Theory in Quantum Mechanics

Werner Heisenberg (1901-1976)

Motivation: A Potential Well Problem

Consider a simple potential well:



Suppose one has found all the eigenvalues and the eigenstates by solving the Schrodinger equation:

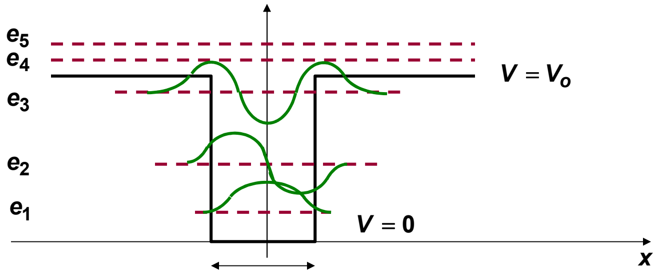
$$-\frac{\hbar^2}{2m}\nabla^2\phi(x)+V(x)\phi(x)=E\,\phi(x)$$

The eigenenergies are labeled as: e_n $\{\, n = 1,2,3,\ldots\ldots$

The corresponding eigenstates are: $\phi_n(x)$ or $|\phi_n\rangle$ $\{\, n = 1,2,3,\ldots\ldots$

Motivation: A Potential Well Problem

Eigenstates of a simple potential well are as depicted below:

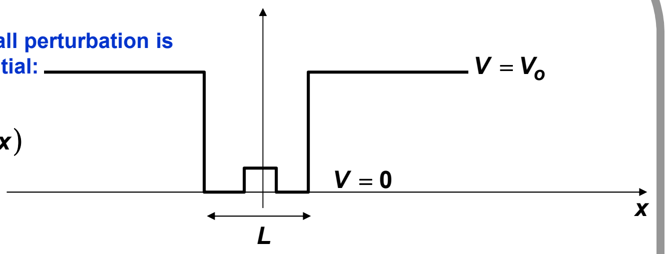


The eigenenergies are labeled as: e_n $\{ n = 1,2,3,\ldots\ldots$

The corresponding eigenstates are: $\phi_n(x)$ or $|\phi_n\rangle$ $\{ n = 1,2,3,\ldots\ldots$

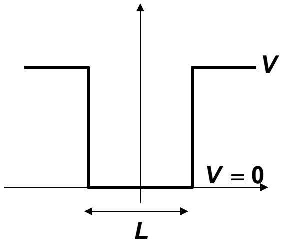
Motivation: Addition of a Small Perturbation

Now assume that a small perturbation is introduced in the potential:



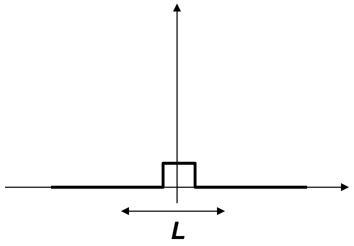
$$U(x) = V(x) + \Delta V(x)$$

$U(x) =$



$V(x)$

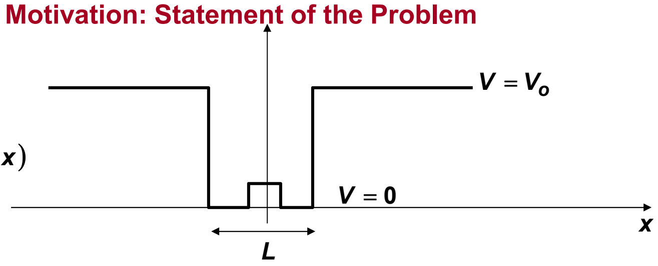
+



$\Delta V(x)$

Motivation: Statement of the Problem

$$U(x) = V(x) + \Delta V(x)$$



How do we find the eigenstates and eigenenergies for the new potential $U(x)$?

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x) + U(x)\psi(x) = E\,\psi(x)$$

Option: Start from scratch again and solve the Schrodinger equation to get:

The new eigenenergies, labeled as: E_n $\{\, n = 1,2,3,\ldots\ldots$

and the corresponding eigenstates: $\psi_n(x)$ or $|\psi_n\rangle$ $\{\, n = 1,2,3,\ldots\ldots$

Luckily, another simpler option is available

Time Independent Perturbation Theory

Lets generalize the potential well problem a little

Suppose for a Hamiltonian $\hat{H}_o$ we have solved the Schrodinger equation and obtained all the eigenenergies and eigenstates:

$\hat{H}_o|\phi_n\rangle = e_n|\phi_n\rangle$ $\{\, n = 1,2,3,\ldots\ldots$ **Orthonormality** → $\langle\phi_n|\phi_p\rangle = \delta_{np}$

We now want to obtain the eigenenergies and the eigenstates for the new hamiltonian $\hat{H}$ where $\hat{H}$ has an added small perturbation,

$\hat{H} = \hat{H}_o + \Delta\hat{H}$ $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ $\{\, n = 1,2,3,\ldots\ldots$

Basic Assumption: If $\Delta\hat{H}$ is not too large a perturbation, the new eigenenergies and eigenstates are likely close to the unperturbed values

Therefore assume:

$$\left.\begin{aligned}|\psi_n\rangle &= |\phi_n\rangle + \underbrace{\sum_{m\neq n}\Delta c_m^n|\phi_m\rangle}_{\text{Some small correction}}\\ E_n &= e_n + \underbrace{\Delta e_n}_{\text{Some small correction}}\end{aligned}\right\}$$

Main idea: Use the old eigenstates to construct the new eigenstates

First Order Perturbation Theory

A Note on the Correction Terms:

$$E_n = e_n + \underbrace{\Delta e_n}_{\text{Correction}} \qquad |\psi_n\rangle = |\phi_n\rangle + \underbrace{\sum_{m\neq n}\Delta c_m^n|\phi_m\rangle}_{\text{Correction}}$$

We expect that the correction terms can be expended in a series where each successive term is proportional to a higher power of $\Delta\hat{H}$. After all, the corrections should approach zero as the perturbation is made smaller, i.e. as $\Delta\hat{H} \to 0$

First Order Corrections to the Eigenenergies:

Take the expressions: $|\psi_n\rangle = |\phi_n\rangle + \sum_{m\neq n}\Delta c_m^n|\phi_m\rangle$ $\qquad E_n = e_n + \Delta e_n$

Plug them into the Schrodinger equation: $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

And multiply both sides from the left by the bra: $\langle\phi_n|$

$$\langle\phi_n|\left(\hat{H}_o+\Delta\hat{H}\right)\left(|\phi_n\rangle+\sum_{m\neq n}\Delta c_m^n|\phi_m\rangle\right) = \langle\phi_n|\left(e_n+\Delta e_n\right)\left(|\phi_n\rangle+\sum_{m\neq n}\Delta c_m^n|\phi_m\rangle\right)$$

First Order Perturbation Theory

$$\langle\phi_n|\left(\hat{H}_o+\Delta\hat{H}\right)\left(|\phi_n\rangle+\sum_{m\neq n}\Delta c_m^n|\phi_m\rangle\right) = \langle\phi_n|\left(e_n+\Delta e_n\right)\left(|\phi_n\rangle+\sum_{m\neq n}\Delta c_m^n|\phi_m\rangle\right)$$

Note that the quantities Δc_m^n and Δe_n , if non-zero, are proportional to some power of $\Delta\hat{H}$ that is equal to or greater than unity

So, as a first order approximation, we keep only those terms in the equation above that are first order in the perturbation $\Delta\hat{H}$. This gives,

$$\Delta e_n = \langle\phi_n|\Delta\hat{H}|\phi_n\rangle$$

As expected, the first order correction to the eigenenergy is proportional to $\Delta\hat{H}$

First Order Corrections to the Eigenstates:

Now take the expressions: $|\psi_n\rangle = |\phi_n\rangle + \sum_{m\neq n}\Delta c_m^n|\phi_m\rangle$ $\qquad E_n = e_n + \Delta e_n$

Plug them into the Schrodinger equation: $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

And multiply both sides from the left by the bra: $\langle\phi_p|$ $\qquad (p \neq n)$

$$\langle\phi_p|\left(\hat{H}_o+\Delta\hat{H}\right)\left(|\phi_n\rangle+\sum_{m\neq n}\Delta c_m^n|\phi_m\rangle\right) = \langle\phi_p|\left(e_n+\Delta e_n\right)\left(|\phi_n\rangle+\sum_{m\neq n}\Delta c_m^n|\phi_m\rangle\right)$$

First Order Perturbation Theory

$$\langle \phi_p | \left(\hat{H}_o + \Delta\hat{H}\right) \left(|\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle \right) = \langle \phi_p | \left(e_n + \Delta e_n\right) \left(|\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle \right)$$

Again, as a first order approximation, we keep only those terms in the equation above that are first order in the perturbation $\Delta\hat{H}$. This gives,

$$\Delta c_p^n = \frac{\langle \phi_p | \Delta\hat{H} | \phi_n \rangle}{e_n - e_p}$$

Summing up the results obtained thus far, we can write the new eigenstates and eigenenergies in the presence of the perturbation as follows,

$$\boxed{\begin{aligned} E_n &= e_n + \langle \phi_n | \Delta\hat{H} | \phi_n \rangle \quad + \quad \text{terms higher order in } \Delta\hat{H} \\ |\psi_n\rangle &= |\phi_n\rangle + \sum_{m\neq n} \frac{\langle \phi_m | \Delta\hat{H} | \phi_n \rangle}{e_n - e_m} |\phi_m\rangle \quad + \quad \text{terms higher order in } \Delta\hat{H} \end{aligned}}$$

Question: What if we want more accurate eiegenenergies and/or eigenstates?

Answer: One can obtain corrections to arbitrary large powers in $\Delta\hat{H}$

Second Order Perturbation Theory

For many interesting perturbations the first order correction term to the energy vanishes, i.e.:

$$\langle \phi_n | \Delta\hat{H} | \phi_n \rangle = 0$$

For the above reason and/or also to obtain more accurate values of the eigenenergies, it is sometimes necessary to obtain corrections to the eigenenergies that are of second order in $\Delta\hat{H}$

Second Order Corrections to the Eigenenergies:

We take the expressions obtained that are accurate to first order in $\Delta\hat{H}$:

$$E_n = e_n + \langle \phi_n | \Delta\hat{H} | \phi_n \rangle + \Delta e_n$$

$$|\psi_n\rangle = |\phi_n\rangle + \sum_{m\neq n} \frac{\langle \phi_m | \Delta\hat{H} | \phi_n \rangle}{e_n - e_m} |\phi_m\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle$$

The terms containing Δc_m^n and Δe_n now represent second order corrections

We plug them into the Schrodinger equation: $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

And multiply both sides from the left by the bra: $\langle \phi_n |$

Second Order Perturbation Theory

$$\langle \phi_n | \left(\hat{H}_o + \Delta\hat{H}\right) \left(|\phi_n\rangle + \sum_{m\neq n} \frac{\langle \phi_m|\Delta\hat{H}|\phi_n\rangle}{e_n - e_m}|\phi_m\rangle + \sum_{m\neq n}\Delta c_m^n |\phi_m\rangle \right) =$$

$$\langle \phi_n | \left(e_n + \langle\phi_n|\Delta\hat{H}|\phi_n\rangle + \Delta e_n\right) \left(|\phi_n\rangle + \sum_{m\neq n} \frac{\langle \phi_m|\Delta\hat{H}|\phi_n\rangle}{e_n - e_m}|\phi_m\rangle + \sum_{m\neq n}\Delta c_m^n |\phi_m\rangle \right)$$

We keep only those terms in the equation above that are second order or first order in the perturbation $\Delta\hat{H}$. The terms first order in $\Delta\hat{H}$ cancel out (as they should since the solution we used was already accurate to the first order) and we get:

$$\Delta e_n = \sum_{m\neq n} \frac{\left|\langle \phi_m|\Delta\hat{H}|\phi_n\rangle\right|^2}{e_n - e_m}$$

The expression for the eigenenergies accurate to second order in $\Delta\hat{H}$ is thus:

$$\boxed{E_n = e_n + \langle\phi_n|\Delta\hat{H}|\phi_n\rangle + \sum_{m\neq n} \frac{\left|\langle \phi_m|\Delta\hat{H}|\phi_n\rangle\right|^2}{e_n - e_m} + \text{terms of higher order in } \Delta\hat{H}}$$

Handout 6

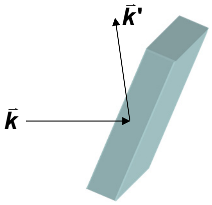
Electrons in Periodic Potentials

In this lecture you will learn:

- Bloch's theorem and Bloch functions
- Electron Bragg scattering and opening of bandgaps
- Free electron bands and zone folding
- Energy bands in 1D, 2D, and 3D lattices

The Reciprocal Lattice and X-Ray Diffraction

⇒ **X-rays will scatter in only those directions for which:**



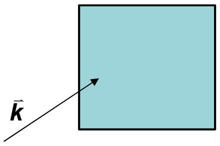
$$\vec{k}' = \vec{k} \pm \vec{G} \qquad \text{and} \qquad |\vec{k}'| = |\vec{k}|$$

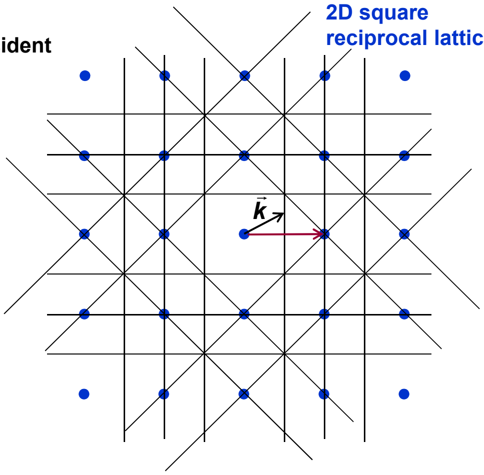
$$\boxed{\pm \vec{k} \cdot \vec{G} = \frac{|\vec{G}|^2}{2}}$$

Bragg condition for X-ray scattering

X-Ray Diffraction and Bragg Planes

Consider x-rays with wavevector $\vec{k}$ incident on a crystal, as shown:





2D square reciprocal lattice

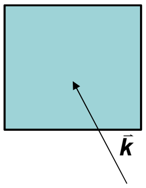
$$\vec{k}' = \vec{k} \pm \vec{G}$$

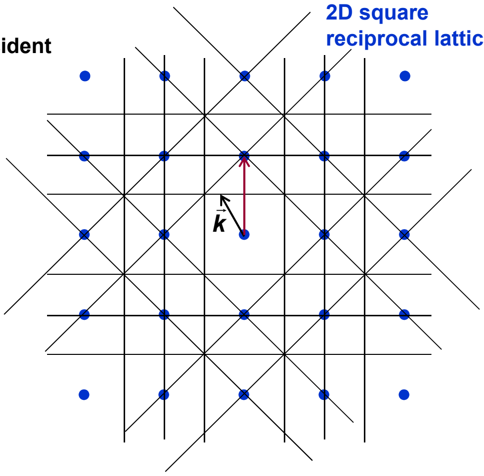
$$|\vec{k}'| = |\vec{k}|$$

What is $\vec{k}'$?

X-Ray Diffraction and Bragg Planes

Consider x-rays with wavevector $\vec{k}$ incident on a crystal, as shown:





2D square reciprocal lattice

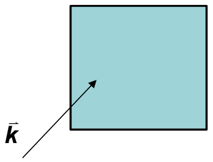
$$\vec{k}' = \vec{k} \pm \vec{G}$$

$$|\vec{k}'| = |\vec{k}|$$

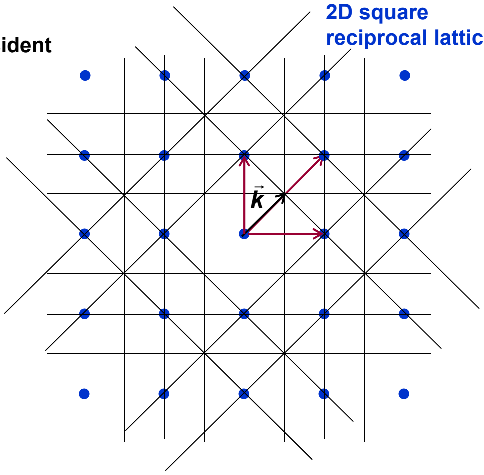
What is $\vec{k}'$?

X-Ray Diffraction and Bragg Planes

Consider x-rays with wavevector $\vec{k}$ incident on a crystal, as shown:



2D square reciprocal lattice



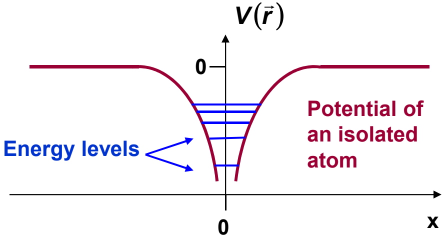
$$\vec{k}' = \vec{k} \pm \vec{G}$$

$$|\vec{k}'| = |\vec{k}|$$

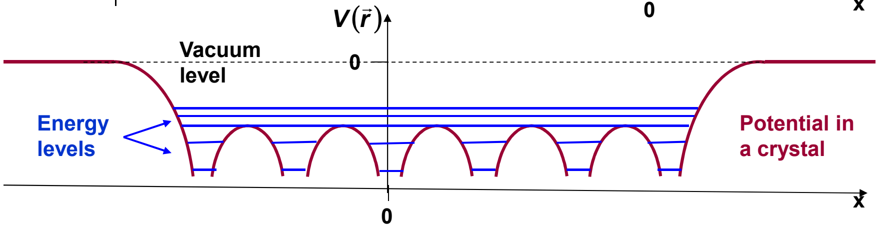
What is $\vec{k}'$?

Atomic Potentials in Crystals

The potential energy of an electron due to a single isolated atom looks like:



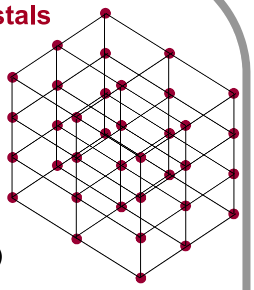
In a crystal, the potential energy due to all the atoms in the lattice looks like:



The lowest energy levels and wavefunctions of electrons remain unchanged when going from an isolated atom to a crystal

The higher energy levels (usually corresponding to the outermost atomic shell) get modified, and the corresponding wavefunctions are no longer localized at individual atoms but become spread over the entire crystal

Properties of Atomic Potentials in Crystals



- The atomic potential is lattice periodic (even for a lattice with a basis):

$$V(\vec{r}+\vec{R}) = V(\vec{r})$$

where $\vec{R}$ is any lattice vector

- Because the atomic potential is lattice periodic, it can be written as a convolution (assuming a lattice in "*d*" dimensions)

$$V(\vec{r}) = V_{\Omega}(\vec{r}) \otimes \sum_j \delta^d(\vec{r}-\vec{R}_j) \qquad \left\{ V_{\Omega}(\vec{r}) = \text{potential in one primitive cell} \right.$$

and expanded in a Fourier series of the type:

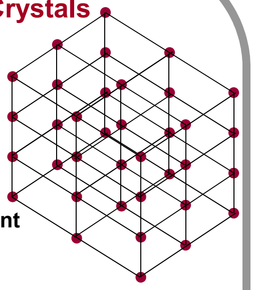
$$V(\vec{r}) = \sum_j \frac{V_{\Omega}(\vec{G}_j)}{\Omega_d} e^{i\,\vec{G}_j\,.\,\vec{r}} = \sum_j V(\vec{G}_j)\, e^{i\,\vec{G}_j\,.\,\vec{r}} \qquad \left\{ \text{Verify that: } V(\vec{r}+\vec{R}) = V(\vec{r}) \right.$$

where only the reciprocal lattice vectors appear in the exponential

⇒ The Fourier components of the periodic potential contain only the reciprocal lattice vectors

---

Properties of Electron Wavefunctions in Crystals



Electrons in a crystal satisfy the Schrodinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\,\psi(\vec{r})$$

Where:

$$V(\vec{r}+\vec{R}) = V(\vec{r})$$

Since the potential is periodic, and one lattice site is no different than any other lattice site, the solutions must satisfy:

$$\left|\psi(\vec{r}+\vec{R})\right|^2 = \left|\psi(\vec{r})\right|^2$$

This implies that the wavefunction at positions separated by a lattice vector can only differ by a phase factor:

$$\psi(\vec{r}+\vec{R}) = e^{i\,\theta(\vec{R})}\,\psi(\vec{r})$$

It follows that both the following relations must hold:

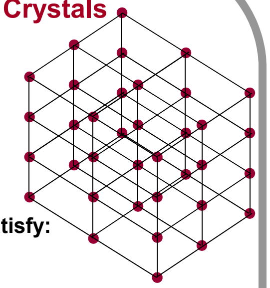
$$\psi(\vec{r}+\vec{R}+\vec{R}') = e^{i\,\theta(\vec{R})}\,\psi(\vec{r}+\vec{R}') = e^{i\,[\theta(\vec{R})+\theta(\vec{R}')]}\,\psi(\vec{r})$$

$$\psi(\vec{r}+\vec{R}+\vec{R}') = e^{i\,\theta(\vec{R}+\vec{R}')}\,\psi(\vec{r})$$

Which implies:

$$\theta(\vec{R}) + \theta(\vec{R}') = \theta(\vec{R}+\vec{R}')$$

Properties of Electron Wavefunctions in Crystals



The simplest, and the only way, that the relation:

$$\theta(\vec{R})+\theta(\vec{R}')=\theta(\vec{R}+\vec{R}')$$

can hold for all lattice vectors is if the phase is a linear scalar function of the vector $\vec{R}$:

$$\theta(\vec{R})=\vec{k}\,.\,\vec{R}$$

where $\vec{k}$ is some vector. It follows that our solutions must satisfy:

$$\psi(\vec{r}+\vec{R})=e^{i\,\vec{k}\,.\,\vec{R}}\,\psi(\vec{r})$$

Bloch's Theorem:

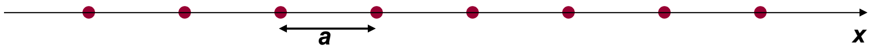
The above is one version of the so called **Bloch's theorem**, which says that associated with every solution of the Schrodinger equation in a periodic potential there is a wavevector $\vec{k}$ such that:

$$\psi(\vec{r}+\vec{R})=e^{i\,\vec{k}\,.\,\vec{R}}\,\psi(\vec{r})$$

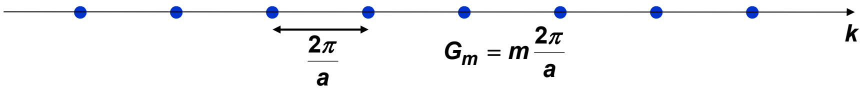
Solutions of the Schrodinger equation for periodic potentials with the above property are called Bloch functions

Case Study: Electron in a 1D Periodic Potential

Consider the 1D Bravais lattice,



The position vector R_n of any lattice point is given by: $R_n = n\,a$
And the reciprocal lattice and reciprocal lattice vectors are:



$$G_m = m\frac{2\pi}{a}$$

Free Electron Approach:

We will suppose that the periodic atomic potential $V(x)$ is small, and that the electrons are essentially free, and we will treat the potential as a perturbation and see how it effects the free electrons. We have:

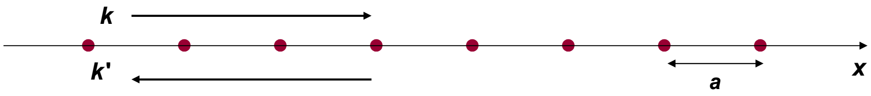
$$V(x+n\,a)=V(x)$$

Consequently, the Fourier series expansion of $V(x)$ will be:

$$V(x)=\sum_m V(G_m)\,e^{i\,G_m\,x} \qquad \text{where :}\;\; V(G_m)=\frac{V_\Omega(k=G_m)}{a}$$

Electron in a 1D Periodic Potential: Bragg Scattering

The key idea is that the electrons will Bragg scatter from the periodic atomic potentials just like X-rays:



For Bragg scattering, the difference between the final and initial wavevector must equal a reciprocal lattice vector:

$$k' - k = \pm G_m$$

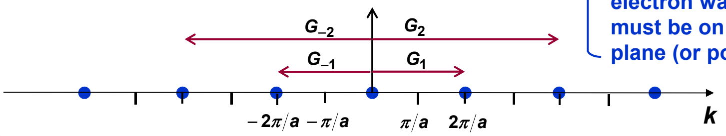
AND the final and initial electron energies must be equal:

$$\frac{\hbar^2 |k'|^2}{2m} = \frac{\hbar^2 |k|^2}{2m}$$

Both the above conditions are satisfied if:

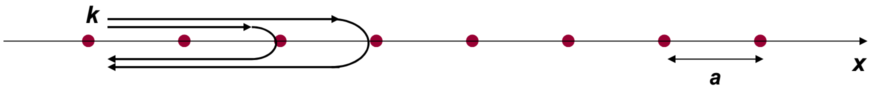
$$k' = -k \qquad \& \qquad k = \pm \frac{G_m}{2}$$

The initial electron wavevector must be one-half of a reciprocal lattice vector OR the initial electron wavevector must be on a Bragg plane (or point in 1D)



Electron in a 1D Periodic Potential: Bragg Scattering

The Bragg condition can also be thought in terms of interference of waves in scattering:



Consider an electron with wavevector k. The electron will "Bragg scatter" from the atoms if the electron wave, with wavelength λ, reflecting off successive atoms adds in phase in the backward direction

This condition gives:

$$2\,a = m\,\lambda$$

$$\Rightarrow 2\frac{2\pi}{\lambda}a = 2\pi\, m$$

$$\Rightarrow 2\,|k| = m\frac{2\pi}{a} = G_m$$

$$\Rightarrow |k| = \frac{G_m}{2}$$

$$\Rightarrow k = \pm\frac{G_m}{2}$$

Perturbation Theory: A Review

Consider a Hamiltonian with eigenfunctions and energies given by:

$$\hat{H}_o|\phi_n\rangle = e_n|\phi_n\rangle$$

In the presence of a perturbing potential, the new eigenfunctions and energies are given by:

$$\left(\hat{H}_o + \hat{V}\right)|\psi_n\rangle = E_n|\psi_n\rangle$$

If the perturbation is small, then the new eigenfunctions are slightly perturbed from the original eigenfunctions and, to first order in the perturbation, can be written as:

$$|\psi_n\rangle \approx |\phi_n\rangle + \sum_{m\neq n} \frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{e_n - e_m}|\phi_m\rangle + \text{higher order terms}$$

Thus, the perturbation "mixes" the eigenfunctions of the original Hamiltonian to generate the eigenfunction of the new Hamiltonian.

Note: The effect of the perturbation is not small, and the perturbation theory breaks down, if for:

$$\langle\phi_m|\hat{V}|\phi_n\rangle \neq 0$$

we have:

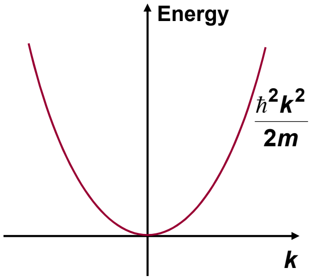
$$e_n - e_m \approx 0$$

Electron in a 1D Periodic Potential: Perturbation Theory

The goal here is to treat the periodic potential as a perturbation to the free electron Hamiltonian. So in the absence of the perturbation we have the free electron case:

$$\hat{H}_o = \frac{\hat{P}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \quad \Rightarrow \quad \phi_k(x) = \sqrt{\frac{1}{L}}\, e^{i\,k\,x} \qquad e(k) = \frac{\hbar^2 k^2}{2m}$$

$$\hat{H}_o|\phi_k\rangle = e(k)\,|\phi_k\rangle$$



The energy dispersion relation of free electrons is parabolic, as shown in the figure

Now assume that the perturbation is the periodic potential of the atoms:

$$V(x)$$

which can also be expressed in a Fourier series as:

$$V(x) = \sum_m V(G_m)\; e^{i\,G_m\,x} \qquad \text{where : } V(G_m) = \frac{V_\Omega(k = G_m)}{a}$$

Electron in a 1D Periodic Potential: Perturbation Theory

So we try perturbation theory and write:

$$\left(\hat{H}_o + \hat{V}(x)\right)|\psi_k\rangle = E(k)|\psi_k\rangle$$

And write the new eigenfunction as:

$$|\psi_k\rangle \approx |\phi_k\rangle + \sum_{k'} \frac{\langle\phi_{k'}|\hat{V}|\phi_k\rangle}{e(k)-e(k')}|\phi_{k'}\rangle + \text{higher order terms}$$

First evaluate the potential matrix element (*L* is the size of the entire 1D crystal):

$$\langle\phi_{k'}|\hat{V}|\phi_k\rangle = \int_{-L/2}^{L/2} dx\, \sqrt{\frac{1}{L}}\, e^{-i\,k'x}\, V(x)\, \sqrt{\frac{1}{L}}\, e^{i\,k\,x}$$

$$= \frac{1}{L}\sum_m V(G_m) \int_{-L/2}^{L/2} dx\, e^{-i\,k'x}\, e^{i\,G_m\,x}\, e^{i\,k\,x}$$

$$= \sum_m V(G_m)\ \delta_{k'-k\,,\,G_m} = 0 \quad \text{unless} \quad k' = k + G_m$$

Electron in a 1D Periodic Potential: Perturbation Theory

The new eigenfunction is:

$$|\psi_k\rangle \approx |\phi_k\rangle + \sum_{k'} \frac{\langle\phi_{k'}|\hat{V}|\phi_k\rangle}{e(k)-e(k')}|\phi_{k'}\rangle + \text{higher order terms} \quad \left\{ \begin{array}{l} \langle\phi_{k'}|\hat{V}|\phi_k\rangle \\ = \sum_m V(G_m)\,\delta_{k'-k\,,\,G_m} \end{array} \right.$$

$$= |\phi_k\rangle + \sum_m \frac{V(G_m)}{e(k)-e(k+G_m)}|\phi_{k+G_m}\rangle + \text{higher order terms}$$

⇒ The new eigenfunction corresponding to the wavevector *k* consists of a superposition of only those plane waves whose wavevectors differ from *k* by reciprocal lattice vectors

The effects of the periodic perturbation will be large for those electron states for which the denominator is zero or is close to zero:

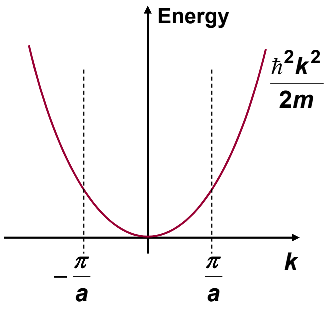
$$e(k) - e(k+G_m) \approx 0 \longrightarrow \left\{ \text{and} \quad V(G_m) \neq 0 \right.$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(G_m^2 + 2kG_m\right) \approx 0$$

$$\Rightarrow k \approx -\frac{G_m}{2} = -m\frac{\pi}{a} \longrightarrow \left\{ \text{Bragg condition} \right.$$

⇒ Perturbation theory breaks down for those electron states that Bragg scatter from the periodic potential!

Electron in a 1D Periodic Potential: Variational Solution



We consider a periodic atomic potential of the form:

$$V(x) = V(G_1)\,e^{i\,G_1\,x} + V(G_{-1})\,e^{i\,G_{-1}\,x}$$

$$G_1 = \frac{2\pi}{a} \qquad G_{-1} = -\frac{2\pi}{a} = -G_1$$

Since the potential is always real: $V(G_{-1}) = V^*(G_1)$

The potential will strongly couple plane wave eigenstates with wavevectors that differ by $\pm G_1$ and the strongest coupling will be between states with wavevectors,

$$\frac{\pi}{a}, -\frac{\pi}{a} = \frac{G_1}{2}, \frac{G_{-1}}{2}$$

because they have equal energy

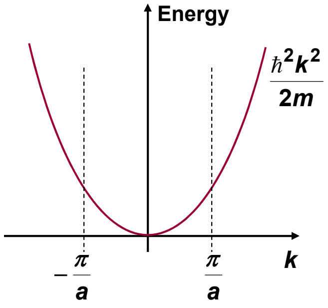
Variational Solution (Finite Basis Expansion):

For states with wavevectors k near $+\pi/a$, we assume a variational solution for the perturbed state:

$$|\psi_k\rangle \approx c(k)\,|\phi_k\rangle + c(k+G_{-1})\,|\phi_{k+G_{-1}}\rangle$$

Or: $$\psi_k(x) \approx c(k)\sqrt{\frac{1}{L}}\,e^{i\,k\,x} + c(k+G_{-1})\sqrt{\frac{1}{L}}\,e^{i\,(k+G_{-1})\,x}$$

Electron in a 1D Periodic Potential: Variational Solution



$$|\psi_k\rangle \approx c(k)\,|\phi_k\rangle + c(k+G_{-1})\,|\phi_{k+G_{-1}}\rangle$$

Plug it into the Schrodinger equation:

$$\left(\hat{H}_o + V(x)\right)|\psi_k\rangle = E(k)|\psi_k\rangle$$

And then take the bra with $\langle\phi_k|$ and then with $\langle\phi_{k+G_{-1}}|$ to get the matrix eigenvalue equation:

$$\begin{bmatrix} e(k) & V(G_1) \\ V(G_{-1}) & e(k+G_{-1}) \end{bmatrix}\begin{bmatrix} c(k) \\ c(k+G_{-1}) \end{bmatrix} = E(k)\begin{bmatrix} c(k) \\ c(k+G_{-1}) \end{bmatrix}$$

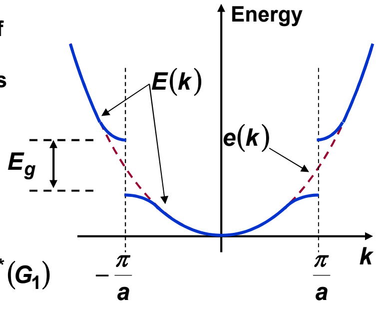
Solution for the energy eigenvalue is:

$$E(k) = \frac{e(k)+e(k+G_{-1})}{2} \pm \sqrt{\left(\frac{e(k)-e(k+G_{-1})}{2}\right)^2 + |V(G_{-1})|^2} \quad \Big\{ \text{ for } k \text{ near } +\pi/a$$

Now, in a similar way, had we started off by trying to find a solution for k near –π/a we would have obtained:

$$E(k) = \frac{e(k)+e(k+G_1)}{2} \pm \sqrt{\left(\frac{e(k)-e(k+G_1)}{2}\right)^2 + |V(G_1)|^2} \quad \Big\{ \text{ for } k \text{ near } -\pi/a$$

Electron in a 1D Periodic Potential: Variational Solution



The obtained solutions $E(k)$ are plotted on top of the free electron energy dispersion $e(k)$ so that you can see the difference. An energy gap opens up!

$$\boxed{E_g = 2|V(G_1)| = 2|V(G_{-1})|}$$

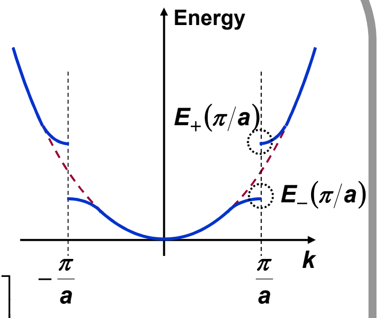
$$V(x) = V(G_1)\,e^{i G_1 x} + V(G_{-1})\,e^{i G_{-1} x}$$

$$G_1 = \frac{2\pi}{a} \qquad G_{-1} = -\frac{2\pi}{a} = -G_1 \qquad V(G_{-1}) = V^*(G_1)$$

$$E(k) = \frac{e(k)+e(k+G_{-1})}{2} \pm \sqrt{\left(\frac{e(k)-e(k+G_{-1})}{2}\right)^2 + |V(G_{-1})|^2} \qquad \Big\{ \text{ for } k \text{ near } +\pi/a$$

$$E(k) = \frac{e(k)+e(k+G_1)}{2} \pm \sqrt{\left(\frac{e(k)-e(k+G_1)}{2}\right)^2 + |V(G_1)|^2} \qquad \Big\{ \text{ for } k \text{ near } -\pi/a$$

Electron in a 1D Periodic Potential: Variational Solution



Lets find the wavefunctions for k=π/a

The matrix equation becomes:

$$\begin{bmatrix} e(\pi/a) & V(G_1) \\ V(G_{-1}) & e(-\pi/a) \end{bmatrix}\begin{bmatrix} c(\pi/a) \\ c(-\pi/a) \end{bmatrix} = E(\pi/a)\begin{bmatrix} c(\pi/a) \\ c(-\pi/a) \end{bmatrix}$$

The two solutions for $V(G_1)$ real are:

$$E_\pm(\pi/a) = e(\pi/a) \pm V(G_1)$$

$$\begin{bmatrix} c(\pi/a) \\ c(-\pi/a) \end{bmatrix}_+ = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix} \qquad \begin{bmatrix} c(\pi/a) \\ c(-\pi/a) \end{bmatrix}_- = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

$$\Rightarrow |\psi_{\pi/a}\rangle \approx c(\pi/a)\,|\phi_{\pi/a}\rangle + c(-\pi/a)\,|\phi_{-\pi/a}\rangle$$

$$\Rightarrow \psi_{\pi/a}(x) \approx \sqrt{\frac{1}{2L}}\left(e^{i\frac{\pi}{a}x} \pm e^{-i\frac{\pi}{a}x}\right) = \begin{cases} \sqrt{\frac{2}{L}}\cos\left(\frac{\pi}{a}x\right) \\ i\sqrt{\frac{2}{L}}\sin\left(\frac{\pi}{a}x\right) \end{cases}$$

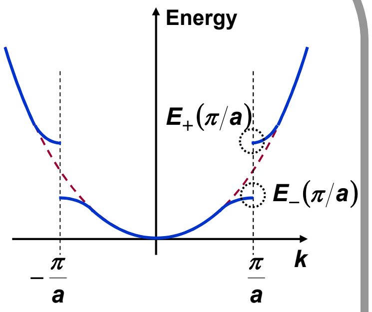
Electron in a 1D Periodic Potential: Origin of the Bandgaps

We have: $E_{\pm}(\pi/a) = e(\pi/a) \pm V(G_1)$

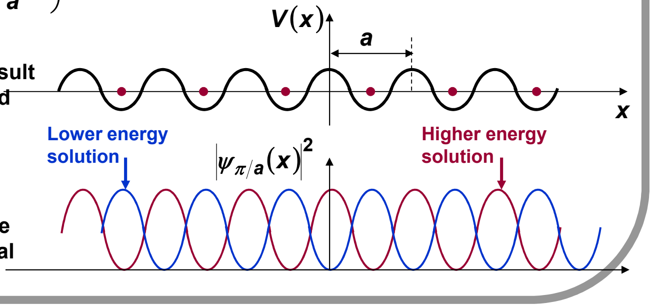
$$\psi_{\pi/a}(x) \approx \sqrt{\frac{1}{2L}}\left(e^{i\frac{\pi}{a}x} \pm e^{-i\frac{\pi}{a}x}\right) = \begin{cases} \sqrt{\frac{2}{L}}\cos\left(\frac{\pi}{a}x\right) \\ i\sqrt{\frac{2}{L}}\sin\left(\frac{\pi}{a}x\right) \end{cases}$$

Note that (for $V(G_1)$ real):

$$V(x) = V(G_1)\,e^{i\,G_1\,x} + V(G_{-1})\,e^{i\,G_{-1}\,x}$$
$$= 2\,V(G_1)\cos\left(\frac{2\pi}{a}x\right)$$



- The solutions are standing waves (as a result of forward and backward Bragg scattering)
- The higher energy solution has larger probability density in the region of higher potential



Electron in a 1D Periodic Potential: Summary

Summary of Findings:

- For a perturbative periodic potential with the following Fourier Series representation,

$$V(x) = V(G_1)\,e^{i\,G_1\,x} + V(G_{-1})\,e^{i\,G_{-1}\,x}$$

the plane wave eigenfunctions of the free electron with wavevector k get coupled with the wavevectors $(k+G_1)$ and $(k+G_{-1})$ as a result of the fact that the potential had wavevectors G_1 and G_{-1} in its Fourier series.

$$G_1 = \frac{2\pi}{a}$$

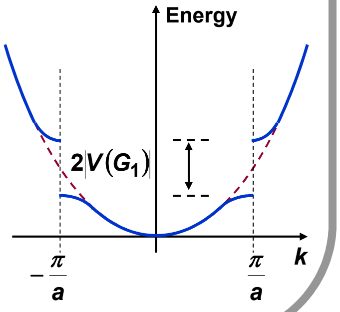
$$G_{-1} = -\frac{2\pi}{a} = -G_1$$

- If the electron wavevector k is such that $e(k)$ and $e(k+G_1)$ have the same energy, or if $e(k)$ and $e(k+G_{-1})$ have the same energy, then a bandgap of magnitude $2|V(G_1)|$ will open up in the free electron dispersion for the wavevector value k

$$e(k) = e(k+G_1) \qquad e(k) = e(k+G_{-1})$$

$$\Rightarrow k = -\frac{G_1}{2} \qquad \Rightarrow k = -\frac{G_{-1}}{2}$$

Bandgap will open for these values of k



Electron in a 1D Periodic Potential: More General Case

Now suppose the potential looks like:

$$V(x) = V(G_1)\,e^{i G_1 x} + V(G_{-1})\,e^{i G_{-1} x} + V(G_2)\,e^{i G_2 x} + V(G_{-2})\,e^{i G_{-2} x}$$

Bandgaps will open at these k-points:

(1) $e(k) = e(k + G_{-1})$

$$\Rightarrow k = -\frac{G_{-1}}{2} = \frac{\pi}{a}$$

(2) $e(k) = e(k + G_1)$

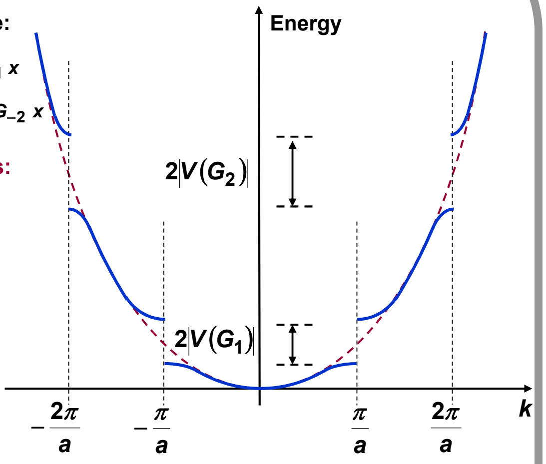
$$\Rightarrow k = -\frac{G_1}{2} = -\frac{\pi}{a}$$

(3) $e(k) = e(k + G_{-2})$

$$\Rightarrow k = -\frac{G_{-2}}{2} = \frac{2\pi}{a}$$

(4) $e(k) = e(k + G_2)$

$$\Rightarrow k = -\frac{G_2}{2} = -\frac{2\pi}{a}$$



$G_1 = \frac{2\pi}{a}$ $G_{-1} = -\frac{2\pi}{a} = -G_1$

$G_2 = \frac{4\pi}{a}$ $G_{-2} = -\frac{4\pi}{a} = -G_2$

Bandgaps and Bragg Planes

Bandgaps will open at these k-points:

(1) $e(k) = e(k + G_{-1})$

$$\Rightarrow k = -\frac{G_{-1}}{2} = \frac{\pi}{a}$$

(2) $e(k) = e(k + G_1)$

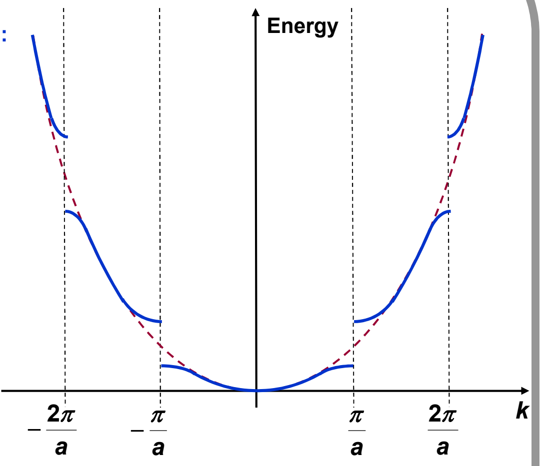
$$\Rightarrow k = -\frac{G_1}{2} = -\frac{\pi}{a}$$

(3) $e(k) = e(k + G_{-2})$

$$\Rightarrow k = -\frac{G_{-2}}{2} = \frac{2\pi}{a}$$

(4) $e(k) = e(k + G_2)$

$$\Rightarrow k = -\frac{G_2}{2} = -\frac{2\pi}{a}$$



Bandgaps open at Bragg points (1D), lines (2D), planes (3D) in the reciprocal space. Recall that a wavevector is on a Bragg point (1D), line (2D), plane (3D) if the following condition holds:

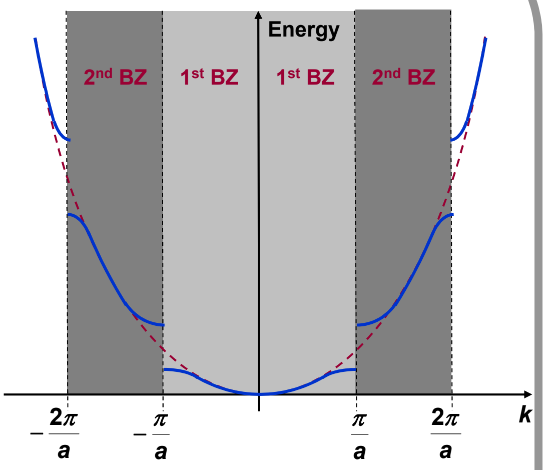
$$\vec{k}\,.\,\vec{G} = \pm\frac{|\vec{G}|^2}{2}$$ and for 1D it becomes: $$k = \pm\frac{G_m}{2}$$

Bandgaps and Brillouin Zone Boundaries

Some very important observations:

- Bandgaps open at Bragg points (1D), lines (2D), planes (3D) in the reciprocal space.
- The Bragg points (1D), lines (2D), planes (3D) define the boundary between Brillouin zones

⇒ Bandgaps open at the Brillouin zone boundaries



The Restricted k-Space Convention and Energy Bands

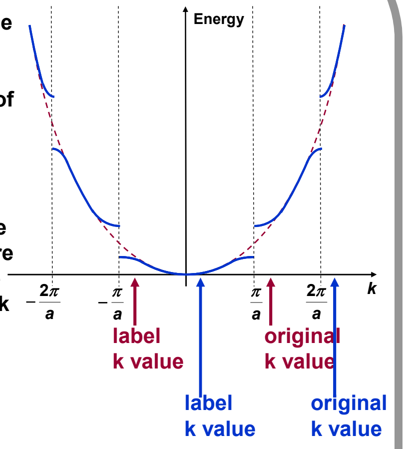
Consider any value of the wavevector outside the FBZ, as shown

The unperturbed solution would be plane wave of wavevector *k*:

$$\phi_k(x) = \sqrt{\frac{1}{L}}\, e^{i\,k\,x}$$

The periodic potential perturbation would couple this plane wave state with all other states that are separated from it in k-space by reciprocal lattice vectors. Therefore the actual solution would look something like:

$$\psi_k(x) = \sum_m c(k+G_m)\sqrt{\frac{1}{L}}\, e^{i\,(k+G_m)\,x}$$



The above is a superposition of plane waves with wavevectors that differ from the unperturbed wavevector by reciprocal lattice vectors

The convention is to label the actual solutions $\psi_k(x)$ not by the k-value of the unperturbed wavefunction but by that wavevector in the superposition solution that falls in the FBZ, as shown

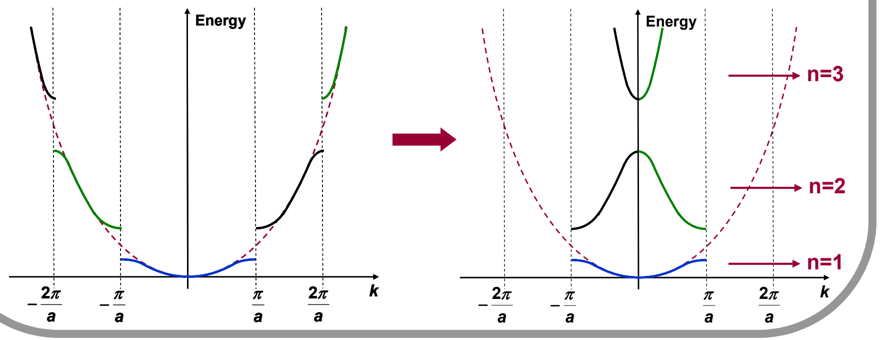
The Restricted k-Space Convention and Energy Bands

In the actual solution: $\psi_k(x) = \sum_m c(k+G_m)\sqrt{\frac{1}{L}}\, e^{i(k+G_m)x}$

The k-value used for labeling is always understood to be in the first BZ

Consequently, the energy-vs-k dispersion relation is always drawn only for the first BZ by translating the energy-vs-k curves lying in higher BZs to the the first BZ by appropriate reciprocal lattice vectors, as shown below:

The resulting different "bands" of energy in the first BZ are called "energy bands" and are labeled as *n*=1,2,3,….



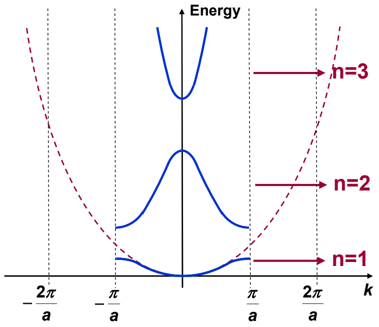
The Restricted k-Space Convention and Energy Bands

Since now we have multiple energy values for the same k-label, we use an additional label "*n*" to indicate the energy band. The final solutions and energy values are then written as follows:

$$\psi_{n,k}(x) \qquad \text{and} \qquad E_n(k)$$

where k-value is understood to be in the first BZ. And the solution can be expanded as:

$$\psi_{n,k}(x) = \sum_m c_n(k+G_m)\sqrt{\frac{1}{L}}\, e^{i(k+G_m)x}$$



Bloch's theorem check:

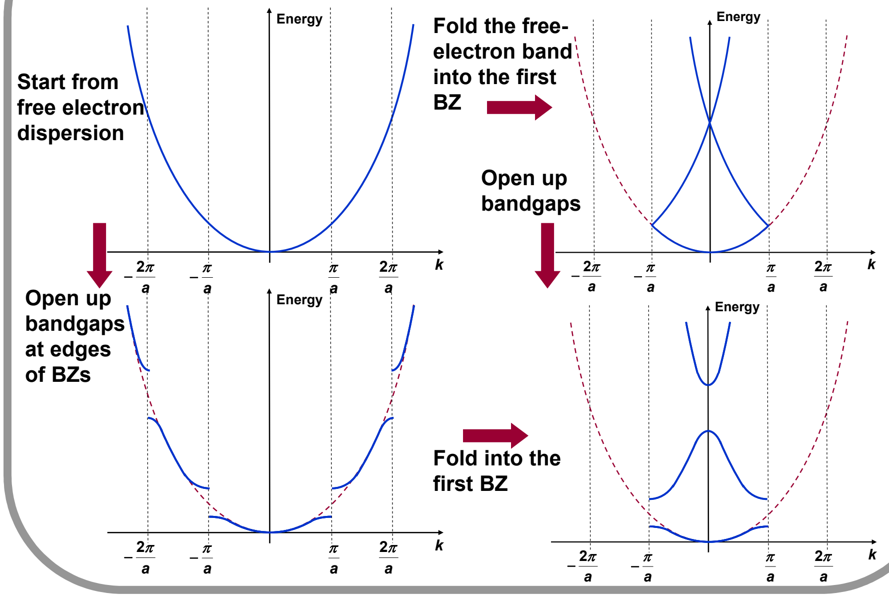
We know that solutions of the Schrodinger equation in periodic potentials (Bloch functions) need to satisfy the Bloch's theorem:

$$\psi(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi(\vec{r})$$

$$\psi_{n,k}(x+R) = \sum_m c_n(k+G_m)\sqrt{\frac{1}{L}}\, e^{i(k+G_m)(x+R)} = e^{i\,k\,R}\sum_m c_n(k+G_m)\sqrt{\frac{1}{L}}\, e^{i(k+G_m)x}$$
$$= e^{i\,k\,R}\psi_{n,k}(x)$$

From Free Electron Dispersion to Energy Bands – 1D

One can always get an approximate idea of how the bands will look:



Start from free electron dispersion

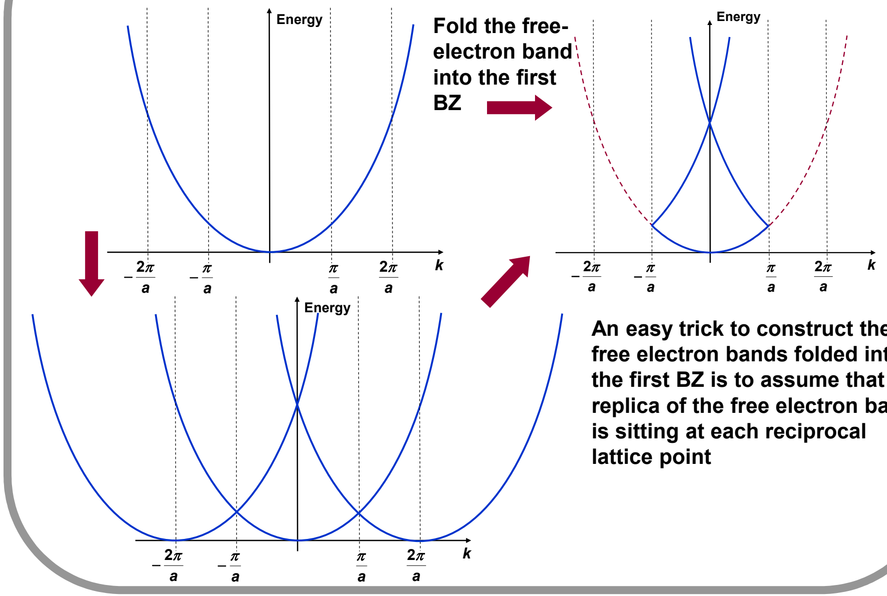
Fold the free-electron band into the first BZ

Open up bandgaps

Open up bandgaps at edges of BZs

Fold into the first BZ

From Free Electron Dispersion to Energy Bands: Zone Folding



Fold the free-electron band into the first BZ

An easy trick to construct the free electron bands folded into the first BZ is to assume that a replica of the free electron band is sitting at each reciprocal lattice point

Generalization to Higher Dimensions - I

Consider a 2D or a 3D crystal with the periodic potential given as:

$$V(\vec{r}) = \sum_j V(\vec{G}_j)\, e^{i\,\vec{G}_j\,.\,\vec{r}}$$

- **The potential will couple the free-electron state with wavevector $\vec{k}$ to all other states with wavevectors $\vec{k}+\vec{G}_j$**
- **The strongest coupling will be with states whose energy $\dfrac{\hbar^2|\vec{k}+\vec{G}_j|^2}{2m}$ equals $\dfrac{\hbar^2|\vec{k}|^2}{2m}$**
- **Therefore, strong coupling will occur if the wavevector $\vec{k}$ satisfies:**

$$\frac{\hbar^2|\vec{k}+\vec{G}_j|^2}{2m} = \frac{\hbar^2|\vec{k}|^2}{2m}$$

$$\Rightarrow 2\vec{G}_j.\vec{k} + |\vec{G}_j|^2 = 0$$

$$\Rightarrow \vec{k}.\vec{G}_j = -\frac{|\vec{G}_j|^2}{2}$$

- **Since, the reciprocal lattice vector $\vec{G}_j$ is arbitrary, one can also write the above condition as:**

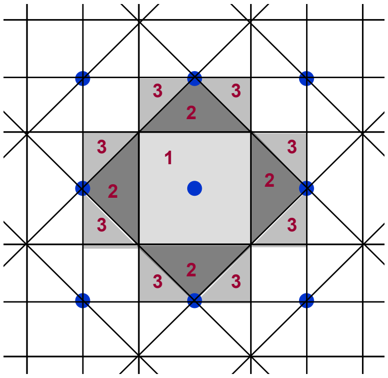
$$\vec{k}\,.\,\vec{G} = \pm\frac{|\vec{G}|^2}{2} \longrightarrow \Big\{\ \text{Bragg condition}$$

Generalization to Higher Dimensions - II

In a 1D lattice, bandgaps opened up at k-values at the Bragg points (edges of BZs):

1D reciprocal lattice

2D square reciprocal lattice



Same thing happens in higher dimensions: bandgaps open up for wavevectors that lie on the Bragg lines (2D), planes (3D).

- **Recall that a wavevector will like on a Bragg line/plane if it satisfies:**

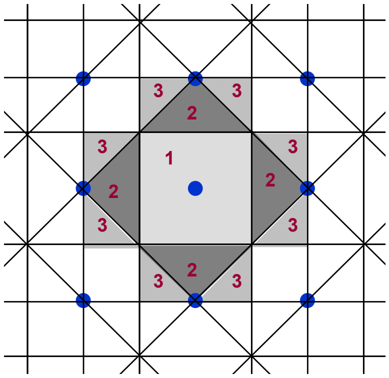
$$\vec{k}\,.\,\vec{G} = \pm\frac{|\vec{G}|^2}{2}$$

for some reciprocal lattice vector $\vec{G}$

- **Bragg lines/planes in k-space are perpendicular bisectors of some reciprocal lattice vector**

Generalization to Higher Dimensions - III

2D square reciprocal lattice



- Bandgaps will open up at the edges of the Brillouin zones
- Wavevector is restricted to the first BZ, and electron energy-vs-k dispersion curves in higher BZs can be translated by appropriate reciprocal lattice vectors to be in the first BZ to obtain energy bands
- Electron energies and solutions are written as:

$$\psi_{n,\vec{k}}(\vec{r}) \qquad \text{and} \qquad E_n(\vec{k})$$

- The solutions satisfy the Bloch's theorem:

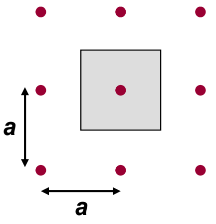
$$\psi(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi(\vec{r})$$

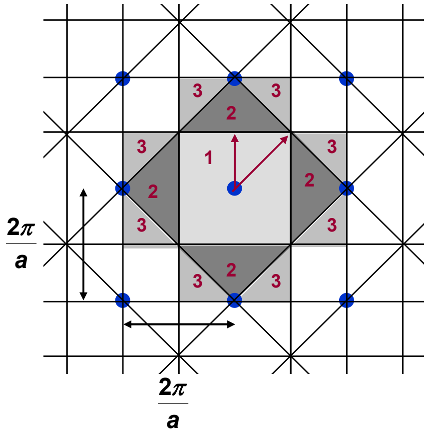
and can be written as a superposition of plane waves, as shown below for 3D:

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_j c_n(\vec{k}+\vec{G}_j)\sqrt{\frac{1}{V}}\,e^{i(\vec{k}+\vec{G}_j).\vec{r}}$$

Energy Bands of a 2D Square Lattice - I

2D square direct lattice





Question: How to draw the free electron bands?

Answer: Assume a free electron band sitting at each reciprocal lattice point and then consider its contribution to the bands in the first BZ

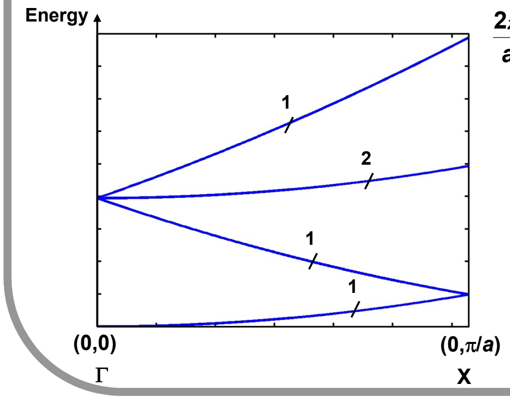
Reciprocal lattice

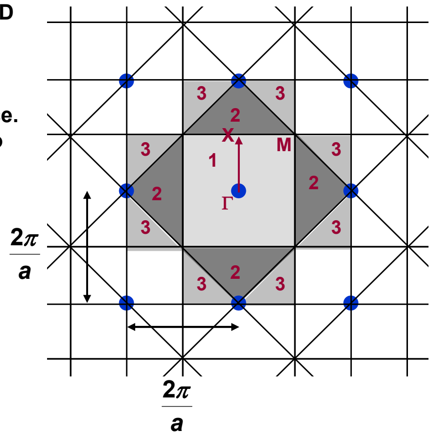
$$\vec{G} = m\frac{2\pi}{a}\hat{x} + n\frac{2\pi}{a}\hat{y}$$

Energy Bands of a 2D Square Lattice - II

- It is obviously difficult to draw bands for 2D or 3D lattices

- The bands are usually drawn along some specific high-symmetry directions in k-space. The figure below shows the bands from Γ to the X point (the numbers indicate the degeneracy of each energy band)

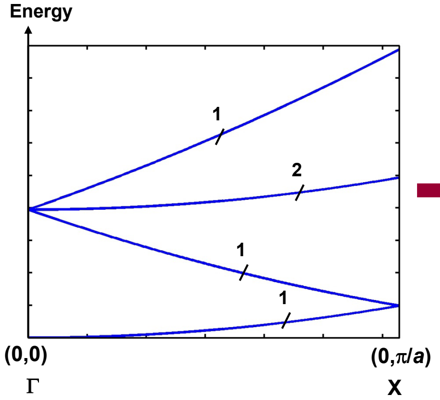


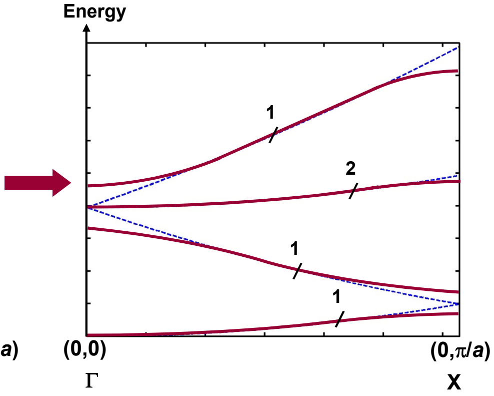


Reciprocal lattice

$$\vec{G} = m\frac{2\pi}{a}\hat{x} + n\frac{2\pi}{a}\hat{y}$$

Energy Bands of a 2D Square Lattice - II

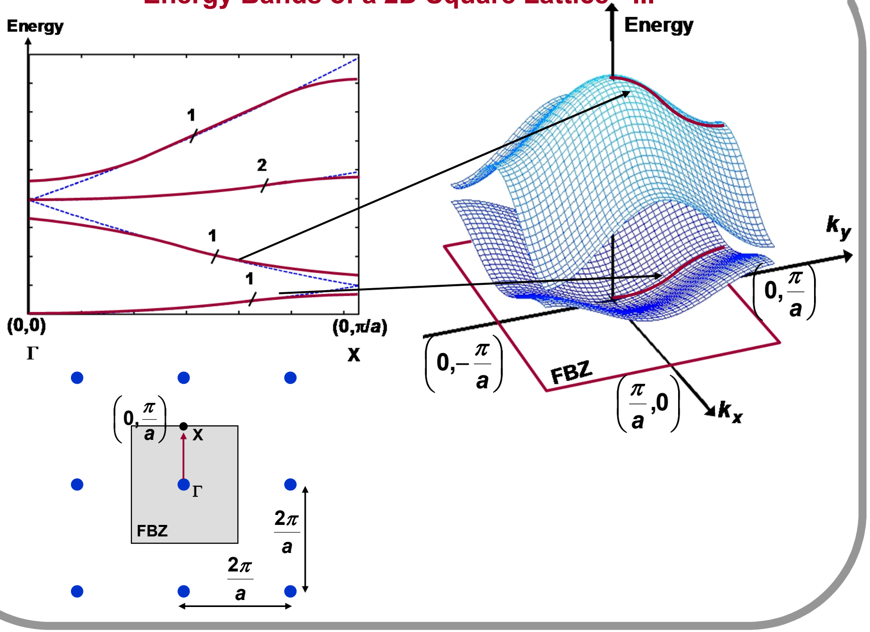




- Once the free electron energy bands have been drawn in the first BZ then the locations where bandgaps are likely to be opened are identified

- A rough sketch of the actual bands can then be made, as shown above

Energy Bands of a 2D Square Lattice - III



Appendix: Obtaining the 2x2 Matrix Equation (On Slide 14)

Remember the matrix element of the periodic potential between the plane wave states:

$$\langle \phi_{k'} | \hat{V} | \phi_k \rangle = \sum_m V(G_m)\ \delta_{k'-k\,,\,G_m}$$

Trial solution for values of *k* near G_1:

$$|\psi_k\rangle \approx c(k)\,|\phi_k\rangle + c(k+G_{-1})\,|\phi_{k+G_{-1}}\rangle$$

Plug it into the Schrodinger equation:

$$\left(\hat{H}_o + V(x)\right)|\psi_k\rangle = E(k)|\psi_k\rangle$$

And then take the bra with $\langle \phi_k|$ to get:

$$\langle \phi_k|\left(\hat{H}_o + \hat{V}(x)\right)|\psi_k\rangle = E(k)\langle \phi_k|\psi_k\rangle$$

$$\Rightarrow \langle \phi_k|\left(\hat{H}_o + \hat{V}(x)\right)\left[c(k)|\phi_k\rangle + c(k+G_{-1})|\phi_{k+G_{-1}}\rangle\right]$$

$$= E(k)\langle \phi_k|\left[c(k)|\phi_k\rangle + c(k+G_{-1})|\phi_{k+G_{-1}}\rangle\right]$$

$$\Rightarrow e(k)\,c(k) + \langle \phi_k|\hat{V}(x)|\phi_{k+G_{-1}}\rangle\, c(k+G_{-1}) = E(k)\,c(k)$$

$$\Rightarrow e(k)\,c(k) + V(G_1)\,c(k+G_{-1}) = E(k)\,c(k) \quad \longleftarrow \text{First result}$$

Appendix: Obtaining the 2x2 Matrix Equation

$$|\psi_k\rangle \approx c(k)\,|\phi_k\rangle + c(k+G_{-1})\,|\phi_{k+G_{-1}}\rangle$$

Plug it into the Schrodinger equation:

$$\left(\hat{H}_o + V(x)\right)|\psi_k\rangle = E(k)|\psi_k\rangle$$

And then take the bra with $\langle\phi_{k+G_{-1}}|$ to get:

$$\langle\phi_{k+G_{-1}}|\left(\hat{H}_o + \hat{V}(x)\right)|\psi_k\rangle = E(k)\langle\phi_{k+G_{-1}}|\psi_k\rangle$$

$$\Rightarrow \langle\phi_{k+G_{-1}}|\left(\hat{H}_o + \hat{V}(x)\right)\left[\,c(k)|\phi_k\rangle + c(k+G_{-1})|\phi_{k+G_{-1}}\rangle\right]$$

$$= E(k)\langle\phi_{k+G_{-1}}|\left[\,c(k)|\phi_k\rangle + c(k+G_{-1})|\phi_{k+G_{-1}}\rangle\right]$$

$$\Rightarrow e(k+G_{-1})\,c(k+G_{-1}) + \langle\phi_{k+G_{-1}}|\hat{V}(x)|\phi_k\rangle\,c(k) = E(k)\,c(k+G_{-1})$$

$$\Rightarrow e(k+G_{-1})\,c(k+G_{-1}) + V(G_{-1})\,c(k) = E(k)\,c(k+G_{-1}) \quad \longleftarrow \text{Second result}$$

Appendix: Obtaining the 2x2 Matrix Equation

We have the two equations:

(1) $$e(k)\,c(k) + V(G_1)\,c(k+G_{-1}) = E(k)\,c(k)$$

(2) $$e(k+G_{-1})\,c(k+G_{-1}) + V(G_{-1})\,c(k) = E(k)\,c(k+G_{-1})$$

which can be written in the matrix form:

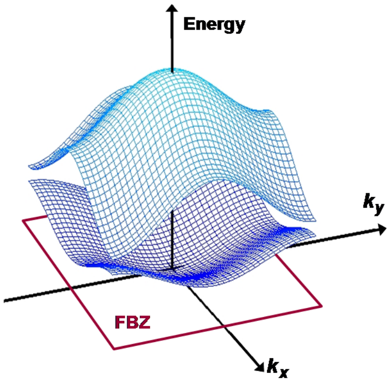
$$\begin{bmatrix} e(k) & V(G_1) \\ V(G_{-1}) & e(k+G_{-1}) \end{bmatrix}\begin{bmatrix} c(k) \\ c(k+G_{-1}) \end{bmatrix} = E(k)\begin{bmatrix} c(k) \\ c(k+G_{-1}) \end{bmatrix}$$

Handout 7

Properties of Bloch States and Electron Statistics in Energy Bands

In this lecture you will learn:

- Properties of Bloch functions
- Periodic boundary conditions for Bloch functions
- Density of states in k-space
- Electron occupation statistics in energy bands



Bloch Functions - Summary

- Electron energies and solutions are written as ($\vec{k}$ is restricted to the first BZ):

$$\psi_{n,\vec{k}}(\vec{r}) \qquad \text{and} \qquad E_n(\vec{k})$$

- The solutions satisfy the Bloch's theorem:

$$\psi_{n,\vec{k}}(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})$$

and can be written as a superposition of plane waves, as shown below for 3D:

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_j c_n(\vec{k}+\vec{G}_j)\sqrt{\frac{1}{V}}\,e^{i\,(\vec{k}+\vec{G}_j)\,.\,\vec{r}}$$

- Any lattice vector and reciprocal lattice vector can be written as:

$$\vec{R} = n_1\,\vec{a}_1 + n_2\,\vec{a}_2 + n_3\,\vec{a}_3 \qquad \vec{G} = m_1\,\vec{b}_1 + m_2\,\vec{b}_2 + m_3\,\vec{b}_3$$

- Volume of the direct lattice primitive cell and the reciprocal lattice first BZ are:

$$\Omega_3 = \left|\,\vec{a}_1\,.\,(\vec{a}_2\times\vec{a}_3)\,\right| \qquad \Pi_3 = \left|\,\vec{b}_1\,.\,(\vec{b}_2\times\vec{b}_3)\,\right|$$

Bloch Function – Product Form Expression

A Bloch function corresponding to the wavevector $\vec{k}$ and energy band "*n*" can always be written as superposition over plane waves in the form:

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_j c_n\left(\vec{k}+\vec{G}_j\right)\sqrt{\frac{1}{V}}\, e^{i\left(\vec{k}+\vec{G}_j\right).\vec{r}}$$

The above expression can be re-written as follows:

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\,\vec{k}\,.\,\vec{r}}\sum_j c_n\left(\vec{k}+\vec{G}_j\right)\sqrt{\frac{1}{V}}\, e^{i\,\vec{G}_j\,.\,\vec{r}}$$

$$= \sqrt{\frac{1}{V}}\, e^{i\,\vec{k}\,.\,\vec{r}}\sum_j c_{n,\vec{k}}\left(\vec{G}_j\right)\, e^{i\,\vec{G}_j\,.\,\vec{r}}$$

$$= \sqrt{\frac{1}{V}}\, e^{i\,\vec{k}\,.\,\vec{r}}\; u_{n,\vec{k}}(\vec{r})$$

Where the function $u_{n,\vec{k}}(\vec{r})$ is lattice periodic:

$$u_{n,\vec{k}}\left(\vec{r}+\vec{R}\right) = \sum_j c_{n,\vec{k}}\left(\vec{G}_j\right)\, e^{i\,\vec{G}_j\,.\left(\vec{r}+\vec{R}\right)} = \sum_j c_{n,\vec{k}}\left(\vec{G}_j\right)\, e^{i\,\vec{G}_j\,.\,\vec{r}}$$

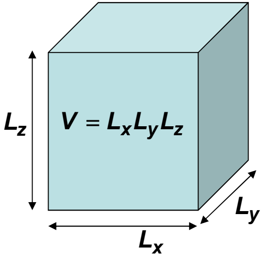
$$= u_{n,\vec{k}}(\vec{r})$$

Note that: $\psi_{n,\vec{k}}(\vec{r}) = \sqrt{\frac{1}{V}}\, e^{i\,\vec{k}\,.\,\vec{r}}\; u_{n,\vec{k}}(\vec{r})$ $\xrightarrow[\text{Bloch's theorem}]{\text{satisfies}}$ $\left\{ \begin{array}{l} \psi_{n,\vec{k}}\left(\vec{r}+\vec{R}\right) \\ = e^{i\,\vec{k}\,.\,\vec{R}}\;\psi_{n,\vec{k}}(\vec{r}) \end{array}\right.$

Allowed Wavevectors for Free-Electrons (Sommerfeld Model)

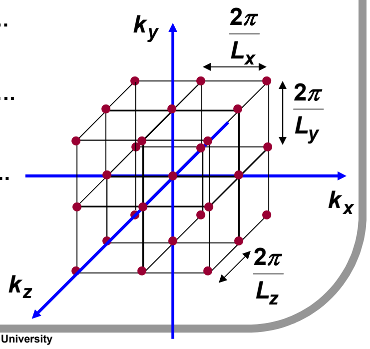
We used periodic boundary conditions:

$$\psi\left(x+L_x,y,z\right)=\psi(x,y,z)$$
$$\psi\left(x,y+L_y,z\right)=\psi(x,y,z)$$
$$\psi\left(x,y,z+L_z\right)=\psi(x,y,z)$$



The boundary conditions dictate that the allowed values of k_x, k_y, and k_z, are such that:

$$\left.\begin{array}{lll} e^{i\left(k_x L_x\right)}=1 & \Rightarrow & k_x = n\dfrac{2\pi}{L_x} \\ e^{i\left(k_y L_y\right)}=1 & \Rightarrow & k_y = m\dfrac{2\pi}{L_y} \\ e^{i\left(k_z L_z\right)}=1 & \Rightarrow & k_z = p\dfrac{2\pi}{L_z} \end{array}\right\} \begin{array}{l} n = 0, \pm 1, \pm 2, \ldots. \\ m = 0, \pm 1, \pm 2, \ldots. \\ p = 0, \pm 1, \pm 2, \ldots. \end{array}$$



$\Rightarrow$ There are $\dfrac{V}{(2\pi)^3}$ grid points per unit volume of k-space

Bloch Functions – Periodic Boundary Conditions

Direct lattice

Reciprocal lattice for a 2D lattice

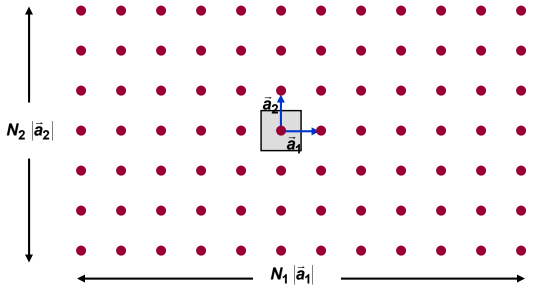
- Any vector $\vec{k}$ in the first BZ can be written as:

$$\vec{k} = \alpha_1\,\vec{b}_1 + \alpha_2\,\vec{b}_2 + \alpha_3\,\vec{b}_3$$

where α_1, α_2, and α_3 range from -1/2 to +1/2:

$$-\frac{1}{2} < \alpha_1 \le \frac{1}{2} \qquad -\frac{1}{2} < \alpha_2 \le \frac{1}{2} \qquad -\frac{1}{2} < \alpha_3 \le \frac{1}{2}$$

Bloch Functions – Periodic Boundary Conditions



For the 2D crystal :

$$A = |\,N_1\vec{a}_1 \times N_2\vec{a}_2\,|$$
$$= N_1 N_2\,\Omega_2$$

- Consider a 3D crystal made up of N_1 primitive cells in the $\vec{a}_1$ direction, N_2 primitive cells in the $\vec{a}_2$ direction and N_3 primitive cells in the $\vec{a}_3$ direction

$\Rightarrow$ Volume of the entire crystal is: $V = \left|\,N_1\vec{a}_1 \,.\, \left(N_2\vec{a}_2 \times N_3\vec{a}_3\right)\right| = N_1 N_2 N_3\,\Omega_3$

Assuming periodic boundary conditions in all three directions we must have:

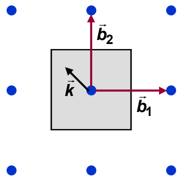
$$\psi\left(\vec{r} + N_1\,\vec{a}_1\right) = e^{i\,\vec{k}\,.\,N_1\,\vec{a}_1}\,\psi\left(\vec{r}\right) = \psi\left(\vec{r}\right)$$

$$\psi\left(\vec{r} + N_2\,\vec{a}_2\right) = e^{i\,\vec{k}\,.\,N_2\,\vec{a}_2}\,\psi\left(\vec{r}\right) = \psi\left(\vec{r}\right)$$

$$\psi\left(\vec{r} + N_3\,\vec{a}_3\right) = e^{i\,\vec{k}\,.\,N_3\,\vec{a}_3}\,\psi\left(\vec{r}\right) = \psi\left(\vec{r}\right)$$

Bloch Functions – Periodic Boundary Conditions

The periodic boundary condition in the $\vec{a}_1$ direction implies:



Reciprocal lattice for a 2D lattice

$$\Rightarrow e^{i\,\vec{k}\,.\,N_1\,\vec{a}_1} = 1 \qquad \left\{ \vec{k} = \alpha_1\,\vec{b}_1 + \alpha_2\,\vec{b}_2 + \alpha_3\,\vec{b}_3 \right.$$

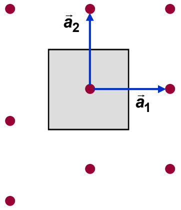
$$\Rightarrow \vec{k}\,.\,N_1\,\vec{a}_1 = 2\pi\,m_1 \qquad \left\{ m_1 \text{ is an integer} \right.$$

$$\Rightarrow 2\pi\,\alpha_1\,N_1 = 2\pi\,m_1 \qquad \left\{ \text{recall that: } \vec{a}_j\,.\,\vec{b}_k = 2\pi\,\delta_{j\,k} \right.$$

$$\Rightarrow \alpha_1 = \frac{m_1}{N_1}$$

Since: $-\frac{1}{2} < \alpha_1 \le \frac{1}{2} \quad \Rightarrow \quad -\frac{N_1}{2} < m_1 \le \frac{N_1}{2}$

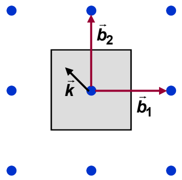
$\Rightarrow$ m_1 can have N_1 different integral values between $-N_1/2$ and $+N_1/2$



Direct lattice

Bloch Functions – Periodic Boundary Conditions

Similarly, the periodic boundary conditions in the directions of $\vec{a}_2$ and $\vec{a}_3$ imply:



Reciprocal lattice for a 2D lattice

$$\Rightarrow e^{i\,\vec{k}\,.\,N_2\,\vec{a}_2} = 1 \quad \& \quad e^{i\,\vec{k}\,.\,N_3\,\vec{a}_3} = 1$$

$$\Rightarrow \vec{k}\,.\,N_2\,\vec{a}_2 = 2\pi\,m_2 \quad \& \quad \vec{k}\,.\,N_3\,\vec{a}_3 = 2\pi\,m_3$$

$$\Rightarrow \alpha_2 = \frac{m_2}{N_2} \quad \& \quad \alpha_3 = \frac{m_3}{N_3}$$

$$\Rightarrow \quad -\frac{N_2}{2} < m_2 \le \frac{N_2}{2} \quad \& \quad -\frac{N_3}{2} < m_3 \le \frac{N_3}{2}$$

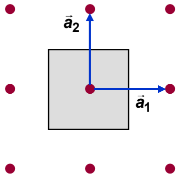
$\Rightarrow$ m_1 can have N_1 different integral values
$\Rightarrow$ m_2 can have N_2 different integral values
$\Rightarrow$ m_3 can have N_3 different integral values

Since any k-vector in the FBZ is given as:

$$\vec{k} = \alpha_1\,\vec{b}_1 + \alpha_2\,\vec{b}_2 + \alpha_3\,\vec{b}_3$$

$\Rightarrow$ there are $N_1\,N_2\,N_3$ different allowed k-values in the FBZ

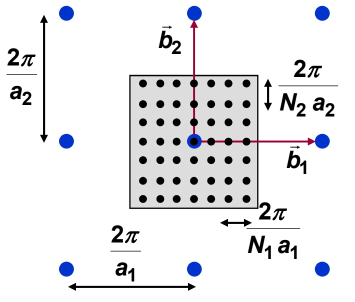
$\Rightarrow$ There are as many different allowed k-values in the FBZ as the number of primitive cells in the crystal



Direct lattice

Density of States in k-Space

Reciprocal lattice for a 2D lattice



$$\vec{k} = \alpha_1 \vec{b}_1 + \alpha_2 \vec{b}_2 + \alpha_3 \vec{b}_3$$

$$\alpha_1 = \frac{m_1}{N_1} \qquad \left\{ -\frac{N_1}{2} < m_1 \le \frac{N_1}{2} \right.$$

$$\alpha_2 = \frac{m_2}{N_2} \qquad \left\{ -\frac{N_2}{2} < m_2 \le \frac{N_2}{2} \right.$$

$$\alpha_3 = \frac{m_3}{N_3} \qquad \left\{ -\frac{N_3}{2} < m_3 \le \frac{N_3}{2} \right.$$

Question: Since $\vec{k}$ is allowed to have only discrete values, how many allowed k-values are there per unit volume of the k-space?

3D Case:

Volume of the first BZ is:

$$\Pi_3 = \left| \vec{b}_1 \cdot \left(\vec{b}_2 \times \vec{b}_3 \right) \right|$$

- In this volume, there are $N_1 \, N_2 \, N_3$ allowed k-values
- The number of allowed k-values per unit volume in k-space are:

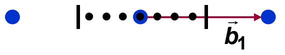
$$= \frac{N_1 N_2 N_3}{\Pi_3}$$

$$= N_1 N_2 N_3 \frac{\Omega_3}{(2\pi)^3}$$

$$= \frac{V}{(2\pi)^3}$$

where V is the volume of the crystal

Density of States in k-Space



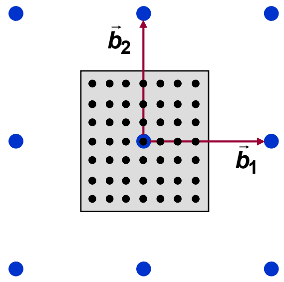
1D Case:

Length of the crystal: $L = N_1 \left| \vec{a}_1 \right| = N_1 \, \Omega_1$

Length of the first BZ is: $\Pi_1 = \left| \vec{b}_1 \right| = \frac{2\pi}{\Omega_1}$

- In the first BZ, there are N_1 allowed k-values
- The number of allowed k-values per unit length in k-space are:

$$= \frac{N_1}{\Pi_1} = N_1 \frac{\Omega_1}{(2\pi)^1} = \frac{L}{(2\pi)}$$



2D Case:

Area of the crystal: $A = \left| N_1 \, \vec{a}_1 \times N_2 \, \vec{a}_2 \right| = N_1 \, N_2 \, \Omega_2$

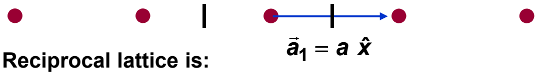
Area of the first BZ is: $\Pi_2 = \left| \vec{b}_1 \times \vec{b}_2 \right| = \frac{(2\pi)^2}{\Omega_2}$

- In the first BZ, there are $N_1 N_2$ allowed k-values
- The number of allowed k-values per unit area in k-space are:

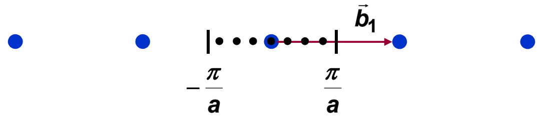
$$= \frac{N_1 N_2}{\Pi_2} = N_1 N_2 \frac{\Omega_2}{(2\pi)^2} = \frac{A}{(2\pi)^2}$$

States in k-Space and Number of Primitive Cells

1D Case:



Reciprocal lattice is:



Length of the crystal: $L = N_1 \left|\vec{a}_1\right| = N_1\,\Omega_1 = N_1\,a$

Length of the first BZ is: $\Pi_1 = \left|\vec{b}_1\right| = \frac{2\pi}{a}$

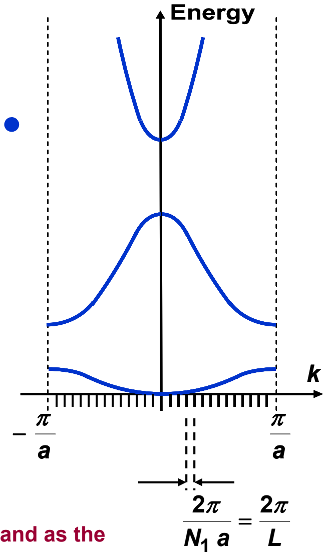
- In the first BZ, there are N_1 allowed k-values
- The number of allowed k-values per unit length in k-space are:

$$= \frac{N_1}{\Pi_1} = N_1 \frac{\Omega_1}{(2\pi)^1} = \frac{L}{(2\pi)}$$

There are N_1 allowed k-values in k-space

⇒There are N_1 allowed k-values per energy band

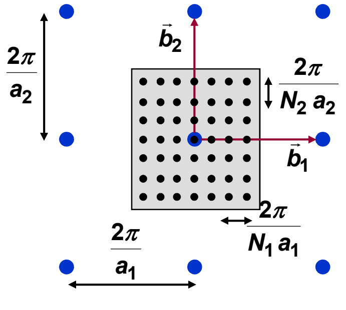
⇒There are as many allowed k-values per energy band as the number of primitive cells in the entire crystal

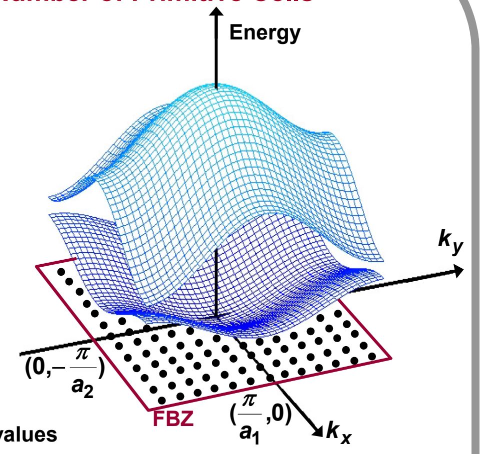


States in k-Space and Number of Primitive Cells

2D Case:

Reciprocal lattice is:



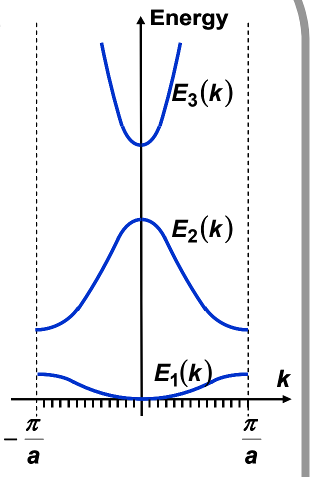


- In the first BZ, there are N_1N_2 allowed k-values

⇒There are N_1N_2 allowed k-values per energy band

⇒There are as many allowed k-values per energy band as the number of primitive cells in the entire crystal

Statistics of Electrons in Energy Bands



Suppose I want to find the total number of electrons in the n-th band – how should I find it?

The probability that the quantum state of wavevector $\vec{k}$ is in the n-th energy band is occupied by an electron is given by the Fermi-Dirac distribution:

$$f_n(\vec{k}) = \frac{1}{1+e^{\left(E_n(\vec{k})-E_f\right)/KT}}$$

Then the total number N of electrons in the n-th band must equal the following sum over all the allowed values in k-space in the first BZ:

$$N = 2\times \sum_{\text{all } \vec{k} \text{ in FBZ}} f_n(\vec{k})$$

spin

1D Case:

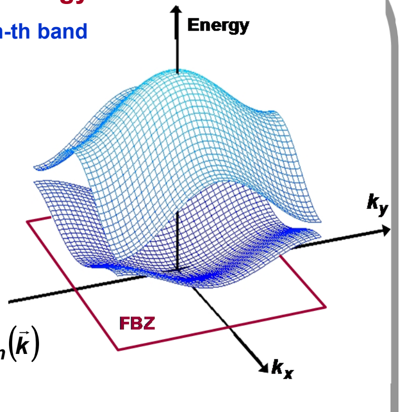
The number of allowed k-values per unit length in k-space is $L/2\pi$, therefore:

$$\Rightarrow \quad N = 2\times \sum_{\text{all } \vec{k} \text{ in FBZ}} f_n(k) = 2\times L \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} f_n(k)$$

Statistics of Electrons in Energy Bands

Need to find the total number of electrons in the n-th band

$$N = 2\times \sum_{\text{all } \vec{k} \text{ in FBZ}} f_n(\vec{k})$$



2D Case:

The number of allowed k-values per unit area in k-space is: $\frac{A}{(2\pi)^2}$

Therefore:

$$N = 2\times \sum_{\text{all } \vec{k} \text{ in FBZ}} f_n(\vec{k}) = 2\times A \int_{FBZ} \frac{d^2\vec{k}}{(2\pi)^2} f_n(\vec{k})$$

3D Case:

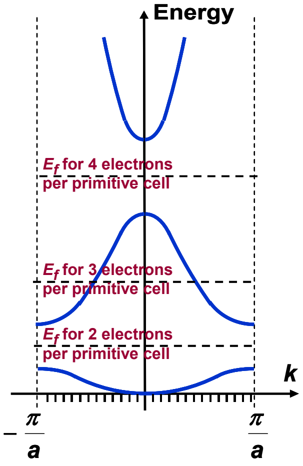
The number of allowed k-values per unit volume in k-space is: $\frac{V}{(2\pi)^3}$

Therefore:

$$N = 2\times \sum_{\text{all } \vec{k} \text{ in FBZ}} f_n(\vec{k}) = 2\times V \int_{FBZ} \frac{d^3\vec{k}}{(2\pi)^3} f_n(\vec{k})$$

Band Filling at $T \approx 0$K for a 1D lattice

Suppose the number of primitive cells = N_1



Question: suppose we have 2 electrons per primitive cell. How will the bands fill up at $T \approx 0$K? Where will be the Fermi level?

2 electrons per primitive cell
$\Rightarrow 2N_1$ total number of electrons

Number of k-values per band = N_1
Number of quantum states per band = $2 \text{x} N_1$
$\overset{\uparrow}{\text{spin}}$

$\Rightarrow$ First band will be completely filled. All higher bands will be empty

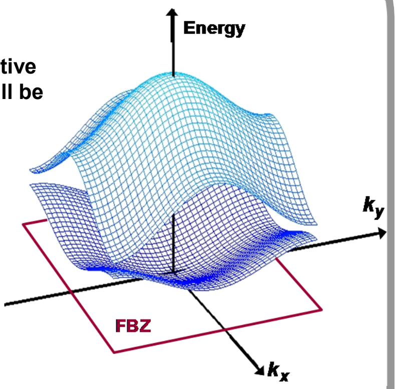
Question: Suppose we have 3 electrons per primitive cell. How will the bands fill up at $T \approx 0$K?

3 electrons per primitive cell
$\Rightarrow 3N_1$ total number of electrons

$\Rightarrow$ First band will be completely filled. Second band will be half filled. All higher bands will be empty

Band Filling at $T \approx 0$K for a 2D lattice

Suppose the number of primitive cells = $N_1 N_2$



Question: suppose we have 2 electrons per primitive cell. How will the bands fill up at $T \approx 0$K? Where will be the Fermi level?

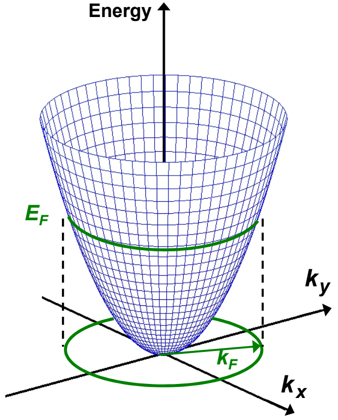
2 electrons per primitive cell
$\Rightarrow 2N_1 N_2$ total number of electrons

Number of k-values per band = $N_1 N_2$
Number of quantum states per band = $2 \text{x} N_1 N_2$
$\overset{\uparrow}{\text{spin}}$

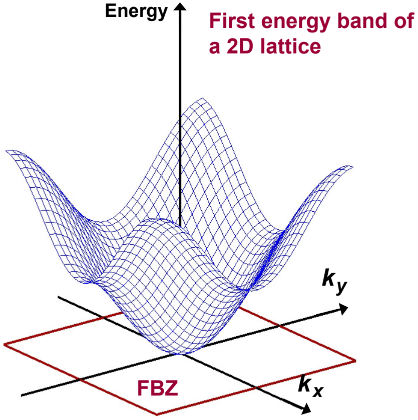
$\Rightarrow$ First band will be completely filled. All higher bands will be empty

Important lesson:
In an energy band (whether in 1D, 2D or 3D) the total number of quantum states available is twice the number of primitive cells in the direct lattice. How the bands get filled depends on the number of electrons per primitive cell.

Fermi Surfaces (3D) and Contours (2D) in Solids



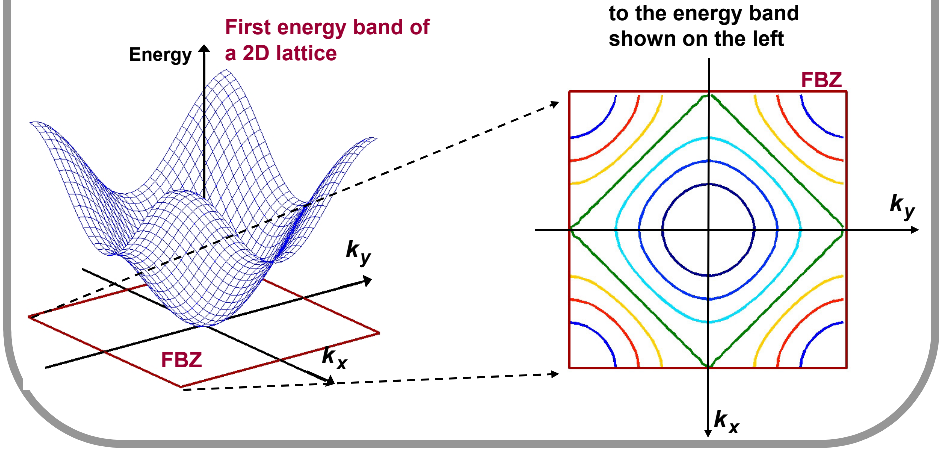
Fermi circle for a free electron gas in 2D



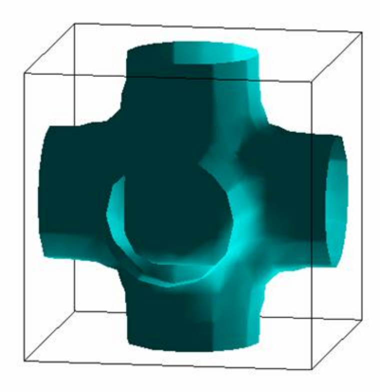
What happens in solids when the energy bands are more complex?

Fermi Surfaces (3D) and Contours (2D) in Solids

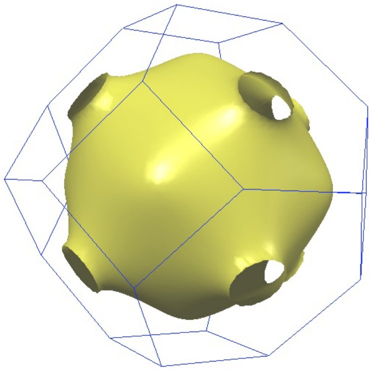
Fermi contours for different electron densities corresponding to the energy band shown on the left



Fermi Surfaces (3D) and Contours (2D) in Solids



Fermi surface of a simple cubic direct lattice shown inside the first BZ



Fermi surface of a FCC lattice shown inside the first BZ (the figure shows the Fermi surface of Copper)

Band Filling at $T \approx 0$K for Silicon

Silicon:

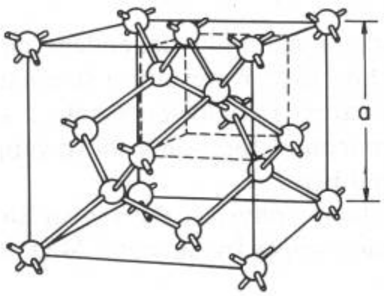
Atomic number: 14

Electron Configuration: $1s^2\ 2s^2 2p^6\ 3s^2\ 3p^2$

Number of electrons in the outermost shell: 4

- The electrons in the outermost shell can move from atom to atom in the lattice – they are not confined to any individual atom. Their energies are described by the energy bands

- The electrons in the inner shells remain confined to individual atoms



- Silicon lattice is FCC

- There are 2 Silicon atoms per primitive cell (2 basis atoms)

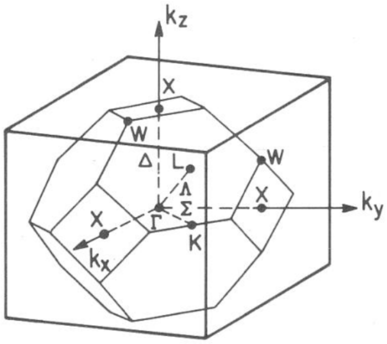
⇒ There are 4 electrons contributed by each Silicon atom and so there are 8 electrons per primitive cell that are available to fill the energy bands

Band Filling at *T*≈0K for Silicon

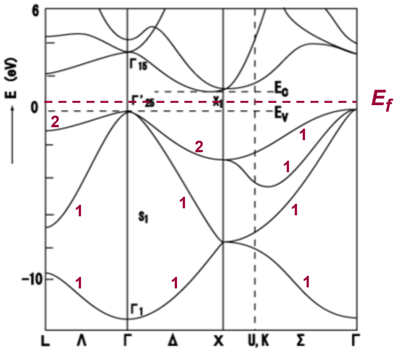
- There are 8 electrons per unit cell available to fill the energy bands

- Recall that in each energy band the number of states available is twice the number of primitive cells in the crystal

- In Silicon, the lowest 4 energy bands will get completely filled at *T*≈0K and all the higher energy bands will be empty



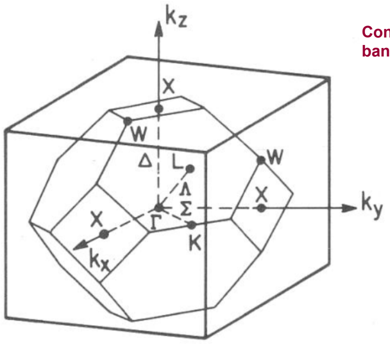
FBZ (for FCC lattice)



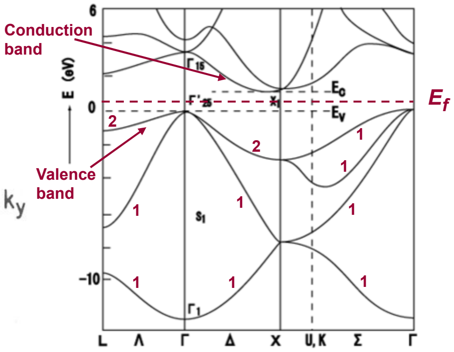
Silicon Energy Bands

Energy Bands in Silicon

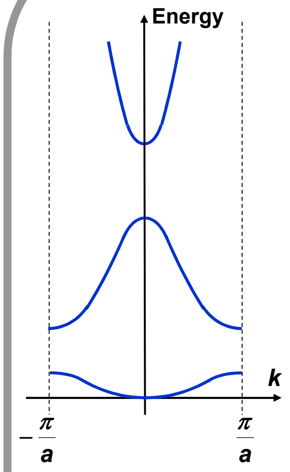
- The highest filled energy band is called the valence band. In silicon the valence band is double degenerate at most points in the first BZ
- The lowest empty energy band is called the conduction band
- In energy, the valence band maximum and the conduction band minimum need not happen at the same point in k-space (as is the case in Silicon)
- The lowest energy of the conduction band is called E_c and the highest energy of the valence band is called E_v

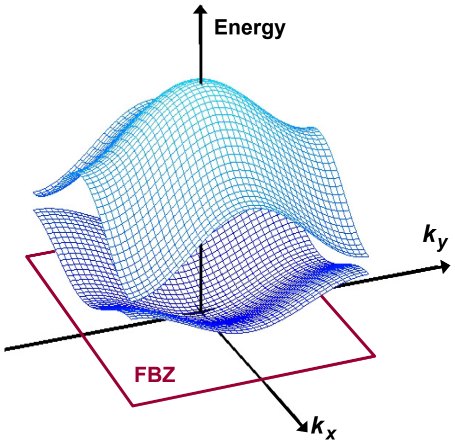


FBZ (for FCC lattice)



Silicon Energy Bands


Energy
k
$-\frac{\pi}{a}$
$\frac{\pi}{a}$

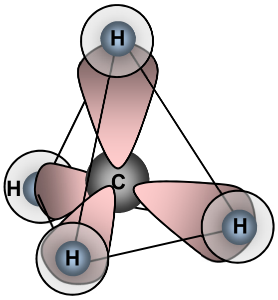

Energy
k_y
FBZ
k_x

Handout 8

Linear Combination of Atomic Orbitals (LCAO)

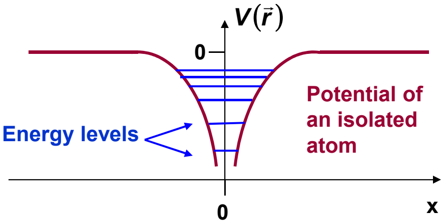
In this lecture you will learn:

- An approach to energy states in molecules based on the linear combination of atomic orbitals

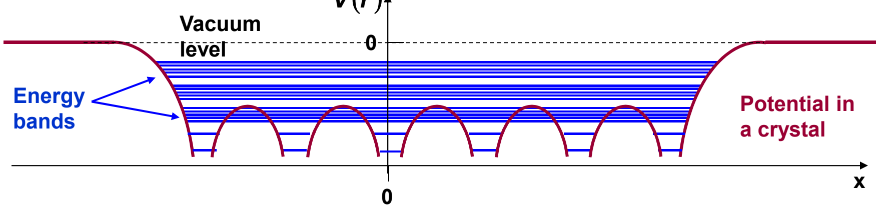


Energy Bands and Atomic Potentials in Crystals

The potential energy of an electron due to a single isolated atom looks like:



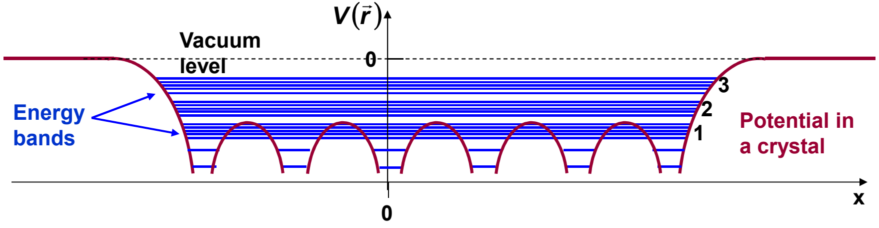
In a crystal, the potential energy due to all the atoms in the lattice looks like:



The lowest energy levels and wavefunctions of electrons remain unchanged when going from an isolated atom to a crystal

The higher energy levels (usually corresponding to the outermost atomic shell) get modified, and the corresponding wavefunctions are no longer localized at individual atoms but become spread over the entire crystal

Failure of the Nearly-Free-Electron Approach



- For energy bands that are higher in energy (e.g. 2 & 3 in the figure above) the periodic potential of the atoms can be taken as a small perturbation

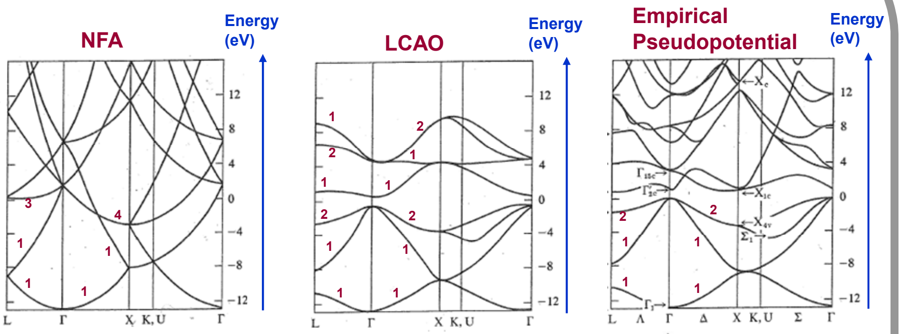
⇒For higher energy bands, the nearly-free-electron approach works well and gives almost the correct results

- For energy bands that are lower in energy (e.g. 1 in the figure above) the periodic potential of the atoms is a strong perturbation

⇒ For lower energy bands, the nearly-free-electron approach does not usually work very well

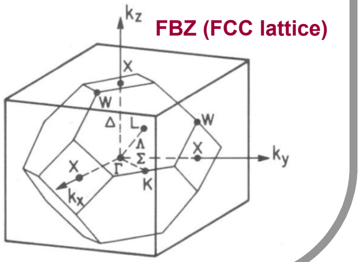
---

Nearly-Free-Electron Approach Vs LCAO for Germanium



- For most semiconductors, the nearly-free-electron approach does not work very well

- LCAO (or tight binding) works much better and provides additional insights



LCAO: From Hydrogen Atom to Hydrogen Molecule

Consider a Hydrogen atom with one electron in the 1s orbital:

One can solve the Schrodinger equation:

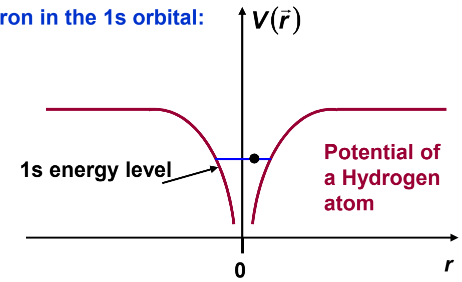
$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})+V(\vec{r})\psi(\vec{r})=E\,\psi(\vec{r})$$

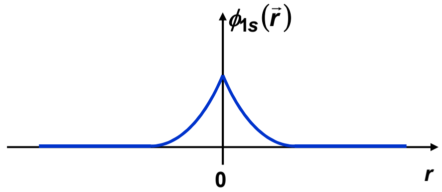
and find the energy of the 1s orbital and its wavefunction

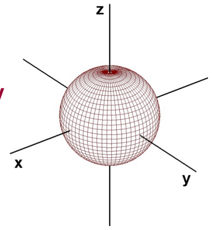
$$\hat{H}_o\,|\phi_{1s}(\vec{r})\rangle=E_{1s}\,|\phi_{1s}(\vec{r})\rangle$$

where:

$$\hat{H}_o=-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})$$







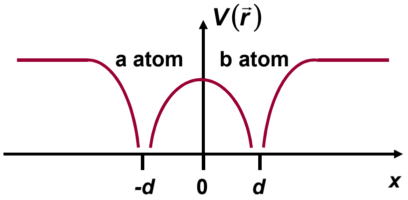
Angular probability distribution for the 1s orbital

$$\phi_{1s}(\vec{r})=\frac{1}{\sqrt{\pi\,a_o^3}}\,e^{-r/a_o}$$

Radial amplitude for the 1s orbital

Linear Combination of Atomic Orbitals (LCAO)

Now consider a Hydrogen molecule made up of two covalently bonded Hydrogen atoms sitting at a distance of 2d from each other, as shown:



Hamiltonian for an electron is:

$$\hat{H}=-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r}-d\hat{x})+V(\vec{r}+d\hat{x})$$

The basic idea behind LCAO approach is to construct a trial variational solution in which the wavefunction is made up of a linear combination (or superposition) of orbitals of isolated atoms:

$$|\psi(\vec{r})\rangle=c_a\,|\phi_{1s}(\vec{r}-d\,\hat{x})\rangle+c_b\,|\phi_{1s}(\vec{r}+d\hat{x})\rangle$$

And then plugging the trial solution into the Schrodinger equation to find the coefficients c_a and c_b and the new eigenenergies:

$$\hat{H}\,|\psi(\vec{r})\rangle=E\,|\psi(\vec{r})\rangle$$

LCAO: From Hydrogen Atom to Hydrogen Molecule

Plug the LCAO solution: $|\psi(\vec{r})\rangle = c_a\,|\phi_{1s}(\vec{r}-d\,\hat{x})\rangle + c_b\,|\phi_{1s}(\vec{r}+d\hat{x})\rangle$

into: $\hat{H}|\psi(\vec{r})\rangle = E\,|\psi(\vec{r})\rangle$ $\qquad \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}-d\hat{x}) + V(\vec{r}+d\hat{x})$

STEP 1: take the bra of the equation first with $\langle\,\phi_{1s}(\vec{r}-d\,\hat{x})|$ to get:

$$\begin{aligned}&\langle\phi_{1s}(\vec{r}-d\,\hat{x})|\,\hat{H}\left[c_a\,|\phi_{1s}(\vec{r}-d\,\hat{x})\rangle + c_b\,|\phi_{1s}(\vec{r}+d\hat{x})\rangle\right]\\ &= E\langle\phi_{1s}(\vec{r}-d\,\hat{x})|\left[c_a\,|\phi_{1s}(\vec{r}-d\,\hat{x})\rangle + c_b\,|\phi_{1s}(\vec{r}+d\hat{x})\rangle\right]\end{aligned}$$

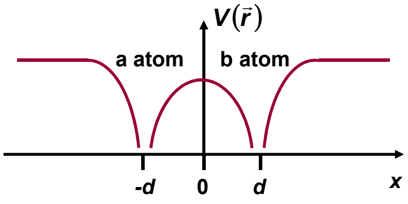
Note that:

$$\langle\phi_{1s}(\vec{r}-d\hat{x})|\hat{H}|\phi_{1s}(\vec{r}-d\hat{x})\rangle \approx E_{1s}$$

Let:

$$\langle\phi_{1s}(\vec{r}-d\hat{x})|\,\hat{H}\,|\phi_{1s}(\vec{r}+d\hat{x})\rangle \approx -V_{ss\sigma}$$

$$\langle\phi_{1s}(\vec{r}-d\hat{x})|\phi_{1s}(\vec{r}+d\hat{x})\rangle \approx 0$$



Not exactly zero – but we will assume so for simplicity

LCAO: From Hydrogen Atom to Hydrogen Molecule

So we get finally:

$$E_{1s}\,c_a - V_{ss\sigma}\,c_b = E\,c_a$$

STEP 2: take the bra of the equation now with $\langle\,\phi_{1s}(\vec{r}+d\,\hat{x})|$ to get:

$$E_{1s}\,c_b - V_{ss\sigma}\,c_a = E\,c_b$$

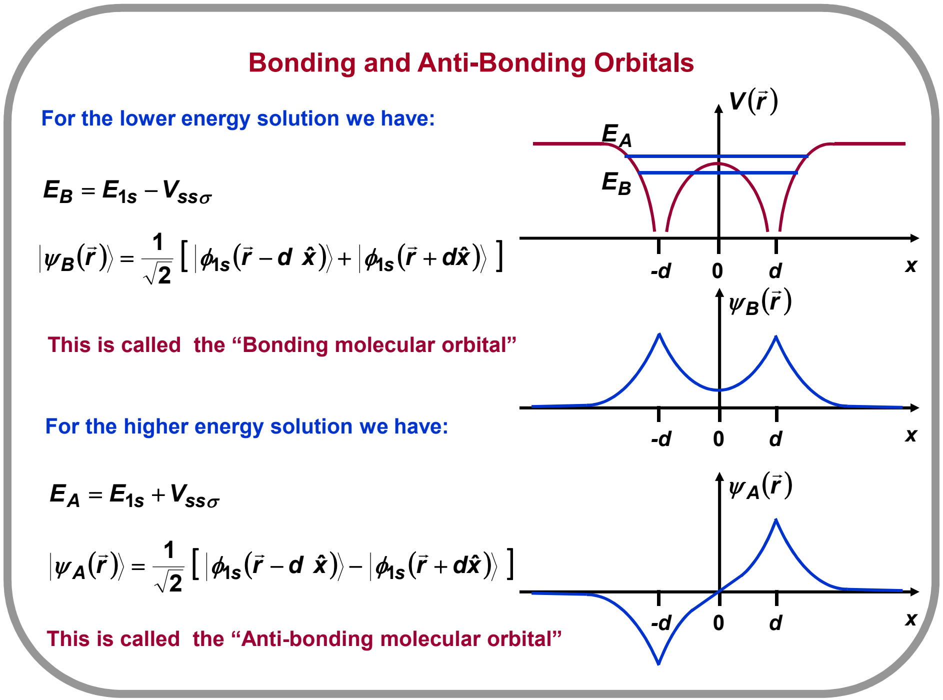
Write the two equations obtained in matrix form:

$$\begin{bmatrix} E_{1s} & -V_{ss\sigma} \\ -V_{ss\sigma} & E_{1s} \end{bmatrix}\begin{bmatrix} c_a \\ c_b \end{bmatrix} = E\begin{bmatrix} c_a \\ c_b \end{bmatrix}$$

This is now an eigenvalue equation and the two solutions are:

$$E = E_{1s} \pm V_{ss\sigma}$$

$$\begin{bmatrix} c_a \\ c_b \end{bmatrix}_+ = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix} \qquad \begin{bmatrix} c_a \\ c_b \end{bmatrix}_- = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}$$



Bonding and Anti-Bonding Orbitals

For the lower energy solution we have:

$$E_B = E_{1s} - V_{ss\sigma}$$

$$|\psi_B(\vec{r})\rangle = \frac{1}{\sqrt{2}}\left[\,|\phi_{1s}(\vec{r}-d\,\hat{x})\rangle + |\phi_{1s}(\vec{r}+d\hat{x})\rangle\,\right]$$

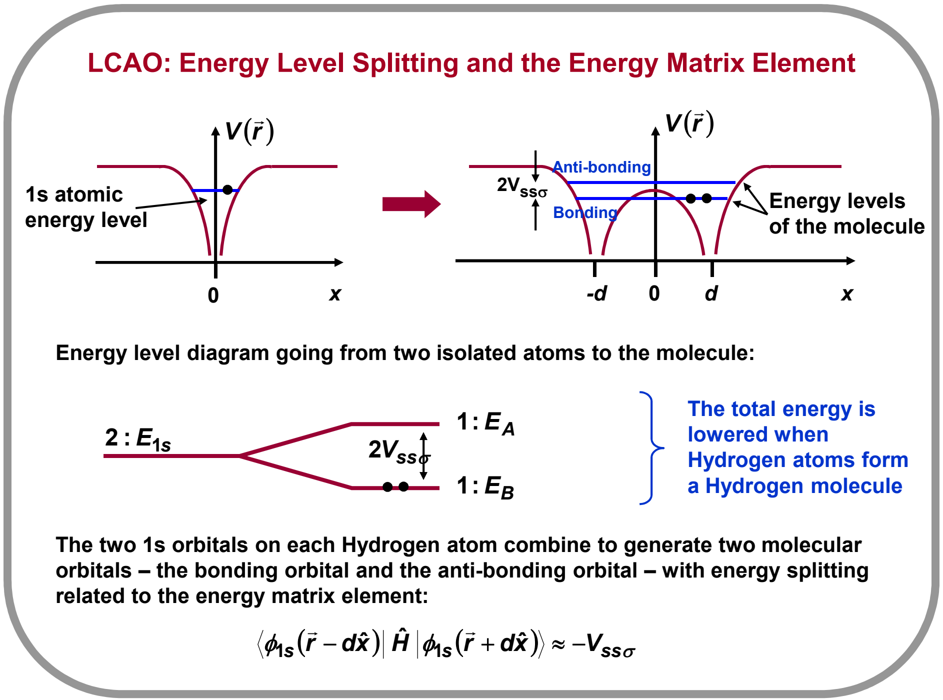
This is called the "Bonding molecular orbital"

For the higher energy solution we have:

$$E_A = E_{1s} + V_{ss\sigma}$$

$$|\psi_A(\vec{r})\rangle = \frac{1}{\sqrt{2}}\left[\,|\phi_{1s}(\vec{r}-d\,\hat{x})\rangle - |\phi_{1s}(\vec{r}+d\hat{x})\rangle\,\right]$$

This is called the "Anti-bonding molecular orbital"



LCAO: Energy Level Splitting and the Energy Matrix Element

Energy level diagram going from two isolated atoms to the molecule:

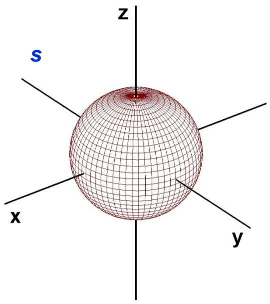
The total energy is lowered when Hydrogen atoms form a Hydrogen molecule

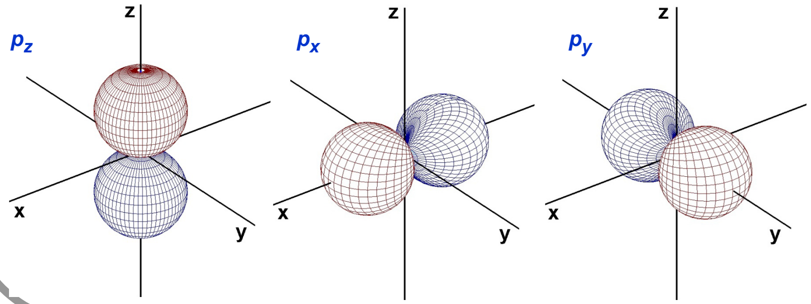
The two 1s orbitals on each Hydrogen atom combine to generate two molecular orbitals – the bonding orbital and the anti-bonding orbital – with energy splitting related to the energy matrix element:

$$\langle\phi_{1s}(\vec{r}-d\hat{x})|\,\hat{H}\,|\phi_{1s}(\vec{r}+d\hat{x})\rangle \approx -V_{ss\sigma}$$

Atomic Orbitals

- Wavefunction amplitudes of the atomic s and p orbitals in the angular directions are plotted
- The s-orbital is spherically symmetric
- The p-orbitals have +ve and –ve lobes and are oriented along x-axis, y-axis, and z-axis

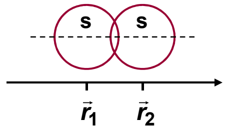




Orbitals and Bonding

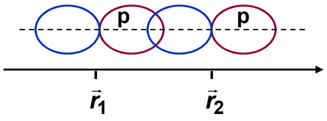
There are two main types of co-valent bonds: sigma bonds (or σ-bonds) and pi-bonds (or π-bonds)

(1) Sigma bonds (or σ-bonds):



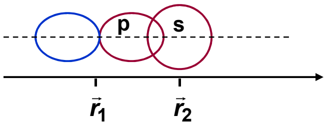
s-s σ-bond
(Example: Hydrogen molecule, semiconductors)

$$\langle \phi_s(\vec{r}-\vec{r}_1)|\,\hat{H}\,|\phi_s(\vec{r}-\vec{r}_2)\rangle \approx -V_{ss\sigma}$$



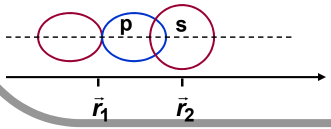
p-p σ-bond
(Example: Semiconductors)

$$\langle \phi_p(\vec{r}-\vec{r}_1)|\,\hat{H}\,|\phi_p(\vec{r}-\vec{r}_2)\rangle \approx V_{pp\sigma}$$



s-p σ-bond
(Example: Semiconductors)

$$\langle \phi_p(\vec{r}-\vec{r}_1)|\,\hat{H}\,|\phi_s(\vec{r}-\vec{r}_2)\rangle \approx -V_{sp\sigma}$$

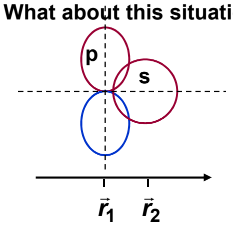


s-p σ-bond
(Example: Semiconductors)

$$\langle \phi_p(\vec{r}-\vec{r}_1)|\,\hat{H}\,|\phi_s(\vec{r}-\vec{r}_2)\rangle \approx V_{sp\sigma}$$

Orbitals and Bonding

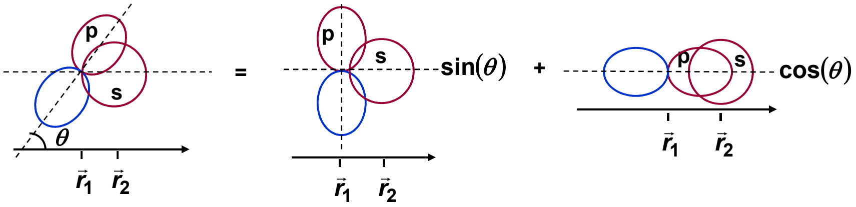
What about this situation?



$$\langle \phi_p(\vec r-\vec r_1)|\,\hat H\,|\phi_s(\vec r-\vec r_2)\rangle \approx 0$$

The Hamiltonian is up-down symmetric
The s-orbital is up-down symmetric
The p-orbital is up-down anti-symmetric
⇒ The matrix element is zero! No bonding possible

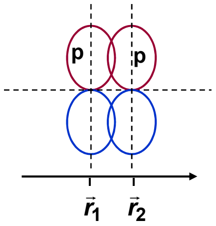
What about this situation? What should be the matrix element?



$$\langle \phi_p(\vec r-\vec r_1)|\,\hat H\,|\phi_s(\vec r-\vec r_2)\rangle \approx 0\,.\,\sin(\theta)+\left(-V_{sp\sigma}\right).\cos(\theta)$$
$$= -V_{sp\sigma}\cos(\theta)$$

Orbitals and Bonding

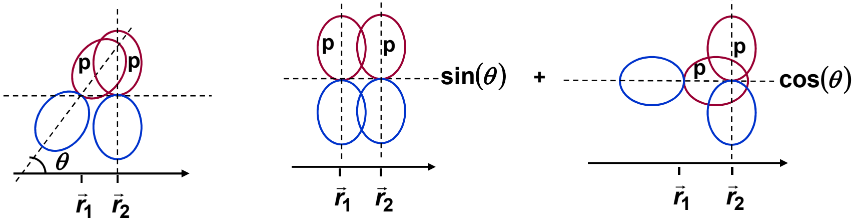
(2) Pi bonds (or π-bonds):



p-p π-bond
(Example: graphene, carbon nanotubes, conjugated conducting molecules)

$$\langle \phi_p(\vec r-\vec r_1)|\,\hat H\,|\phi_p(\vec r-\vec r_2)\rangle \approx -V_{pp\pi}$$

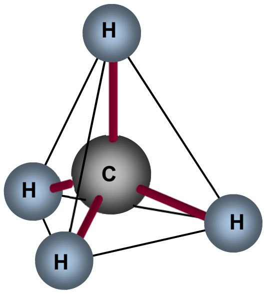
What about this situation? What should be the matrix element?



$$\langle \phi_p(\vec r-\vec r_1)|\,\hat H\,|\phi_p(\vec r-\vec r_2)\rangle \approx \left(-V_{pp\pi}\right).\sin(\theta)+0\,.\cos(\theta)$$
$$= -V_{pp\pi}\sin(\theta)$$

LCAO: Methane Molecule

A methane molecule consists of one carbon atom covalently bonded to 4 hydrogen atoms in a tetrahedral configuration:



Carbon:

Atomic number: 6

Electron Configuration: $1s^2\ 2s^2\ 2p^2$

Number of electrons in the outermost shell: 4

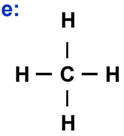
Hydrogen:

Atomic number: 1

Electron Configuration: $1s^1$

Number of electrons in the outermost shell: 1

Methane:



$$\begin{array}{c} H \\ | \\ H - C - H \\ | \\ H \end{array}$$

The four electrons from the outermost shell of the carbon atom and the four electrons from the four hydrogen atoms take part in covalent bonding

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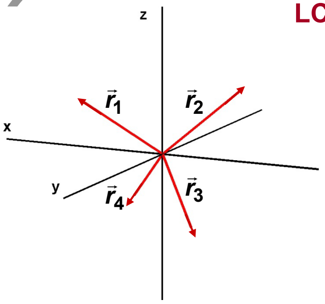
LCAO: Methane Molecule



- **The carbon atom is sitting at the origin**
- **The position vectors of the four hydrogen atoms are:**

$$\vec{r}_1 = \frac{d}{\sqrt{3}}(1,1,1) \quad \vec{r}_2 = \frac{d}{\sqrt{3}}(-1,-1,1) \quad \vec{r}_3 = \frac{d}{\sqrt{3}}(-1,1,-1)$$

$$\vec{r}_2 = \frac{d}{\sqrt{3}}(1,-1,-1) \longrightarrow \text{Tetrahedral configuration}$$

- **The carbon atom has one 2s orbital and three 2p orbitals**
- **Each hydrogen atom has one 1s orbital**
- **One can write the solution for the methane molecule as a linear combination of all available orbitals**

$$|\psi(\vec{r})\rangle = \sum_{j=1}^{4} c_j\, |\phi_{1s}(\vec{r}-\vec{r}_j)\rangle + c_5\, |\phi_{2s}(\vec{r})\rangle + c_6\, |\phi_{2px}(\vec{r})\rangle + c_7\, |\phi_{2py}(\vec{r})\rangle + c_8\, |\phi_{2pz}(\vec{r})\rangle$$

But we will pursue a different, and simpler, approach

LCAO: Methane Molecule – sp$_3$ Hybridization

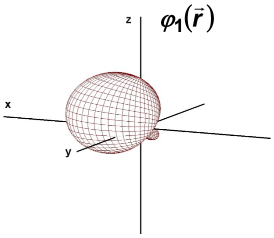
For the carbon atom, do a change of basis and define 4 new sp3 atomic orbitals from the 4 existing (one 2s and three 2p) atomic orbitals

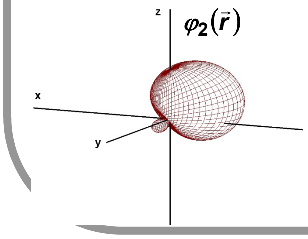
$$|\varphi_1(\vec{r})\rangle = \frac{1}{2}\left[\,|\phi_{2s}(\vec{r})\rangle + |\phi_{2px}(\vec{r})\rangle + |\phi_{2py}(\vec{r})\rangle + |\phi_{2pz}(\vec{r})\rangle\,\right]$$

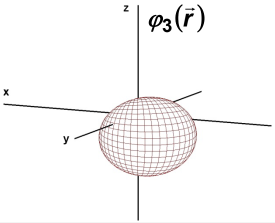
$$|\varphi_2(\vec{r})\rangle = \frac{1}{2}\left[\,|\phi_{2s}(\vec{r})\rangle - |\phi_{2px}(\vec{r})\rangle - |\phi_{2py}(\vec{r})\rangle + |\phi_{2pz}(\vec{r})\rangle\,\right]$$

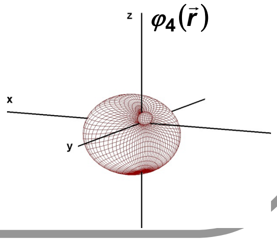
$$|\varphi_3(\vec{r})\rangle = \frac{1}{2}\left[\,|\phi_{2s}(\vec{r})\rangle - |\phi_{2px}(\vec{r})\rangle + |\phi_{2py}(\vec{r})\rangle - |\phi_{2pz}(\vec{r})\rangle\,\right]$$

$$|\varphi_3(\vec{r})\rangle = \frac{1}{2}\left[\,|\phi_{2s}(\vec{r})\rangle + |\phi_{2px}(\vec{r})\rangle - |\phi_{2py}(\vec{r})\rangle - |\phi_{2pz}(\vec{r})\rangle\,\right]$$



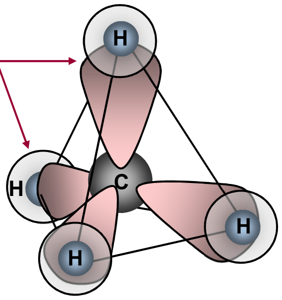






LCAO: Methane Molecule – sp$_3$ Hybridization

- **Each carbon sp3 orbital forms a s-sp3 σ-bond with the 1s orbital of the hydrogen atoms towards which it is pointing:**



s-sp3 σ-bond

Average energy of the sp3 orbital:

$$\Rightarrow \langle\varphi_j(\vec{r})|\,\hat{H}\,|\varphi_m(\vec{r})\rangle = E_{sp3}\,\delta_{j\,m} = \frac{E_{2s}+3E_{2p}}{4}\,\delta_{j\,m}$$

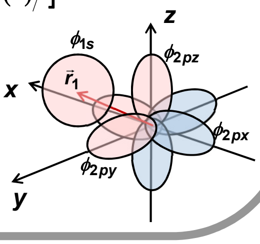
Important matrix element for the s-sp3 bond:

$$\langle\phi_{1s}(\vec{r}-\vec{r}_1)|\,\hat{H}\,|\varphi_1(\vec{r})\rangle$$

$$= \langle\phi_{1s}(\vec{r}-\vec{r}_1)|\,\hat{H}\,\frac{1}{2}\left[\,|\phi_{2s}(\vec{r})\rangle + |\phi_{2px}(\vec{r})\rangle + |\phi_{2py}(\vec{r})\rangle + |\phi_{2pz}(\vec{r})\rangle\,\right]$$

$$= -\frac{1}{2}V_{ss\sigma} - \frac{1}{2}\frac{V_{sp\sigma}}{\sqrt{3}} - \frac{1}{2}\frac{V_{sp\sigma}}{\sqrt{3}} - -\frac{1}{2}\frac{V_{sp\sigma}}{\sqrt{3}}$$

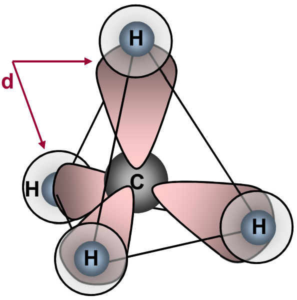
$$= -\left(\frac{V_{ss\sigma}+\sqrt{3}V_{sp\sigma}}{2}\right) = -\eta$$



LCAO: Methane Molecule – sp$_3$ Hybridization

- **Matrix elements for all s-sp3 σ-bonds are the same**

Important matrix elements:



s-sp3
σ-bond

$$\langle \phi_{1s}(\vec{r}-\vec{r}_1)|\,\hat{H}\,|\varphi_1(\vec{r})\rangle = -\left(\frac{V_{ss\sigma}+\sqrt{3}V_{sp\sigma}}{2}\right) = -\eta$$

$$\langle \phi_{1s}(\vec{r}-\vec{r}_2)|\,\hat{H}\,|\varphi_2(\vec{r})\rangle = -\left(\frac{V_{ss\sigma}+\sqrt{3}V_{sp\sigma}}{2}\right) = -\eta$$

$$\langle \phi_{1s}(\vec{r}-\vec{r}_3)|\,\hat{H}\,|\varphi_3(\vec{r})\rangle = -\left(\frac{V_{ss\sigma}+\sqrt{3}V_{sp\sigma}}{2}\right) = -\eta$$

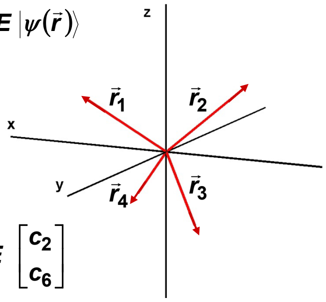
$$\langle \phi_{1s}(\vec{r}-\vec{r}_4)|\,\hat{H}\,|\varphi_4(\vec{r})\rangle = -\left(\frac{V_{ss\sigma}+\sqrt{3}V_{sp\sigma}}{2}\right) = -\eta$$

LCAO: Methane Molecule – sp$_3$ Hybridization

Write the solution for the methane molecule using the sp3 orbitals of the carbon atom:

$$|\psi(\vec{r})\rangle = \sum_{j=1}^{4} c_j\,|\phi_{1s}(\vec{r}-\vec{r}_j)\rangle + c_5\,|\varphi_1(\vec{r})\rangle + c_6\,|\varphi_2(\vec{r})\rangle + c_7\,|\varphi_3(\vec{r})\rangle + c_8\,|\varphi_4(\vec{r})\rangle$$

And plug it into the Schrodinger equation: $\hat{H}\,|\psi(\vec{r})\rangle = E\,|\psi(\vec{r})\rangle$



To a first approximation, 1s orbital on each Hydrogen atom has a large matrix element only with the sp3 orbital pointing towards it, so instead of one giant 8x8 matrix equation one gets a set of four 2x2 matrix equations:

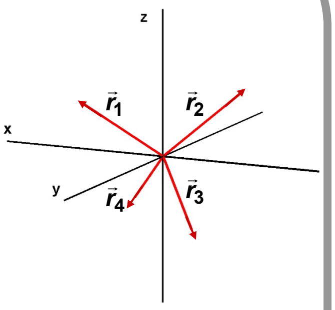
$$\begin{bmatrix} E_{1s} & -\eta \\ -\eta & E_{sp3} \end{bmatrix}\begin{bmatrix} c_1 \\ c_5 \end{bmatrix} = E\begin{bmatrix} c_1 \\ c_5 \end{bmatrix} \qquad \begin{bmatrix} E_{1s} & -\eta \\ -\eta & E_{sp3} \end{bmatrix}\begin{bmatrix} c_2 \\ c_6 \end{bmatrix} = E\begin{bmatrix} c_2 \\ c_6 \end{bmatrix}$$

$$\begin{bmatrix} E_{1s} & -\eta \\ -\eta & E_{sp3} \end{bmatrix}\begin{bmatrix} c_3 \\ c_7 \end{bmatrix} = E\begin{bmatrix} c_3 \\ c_7 \end{bmatrix} \qquad \begin{bmatrix} E_{1s} & -\eta \\ -\eta & E_{sp3} \end{bmatrix}\begin{bmatrix} c_4 \\ c_8 \end{bmatrix} = E\begin{bmatrix} c_4 \\ c_8 \end{bmatrix}$$

Where: $\eta = \left(\frac{V_{ss\sigma}+\sqrt{3}V_{sp\sigma}}{2}\right) = -\langle \phi_{1s}(\vec{r}-\vec{r}_1)|\,\hat{H}\,|\varphi_1(\vec{r})\rangle$

LCAO: Methane Molecule – sp$_3$ Hybridization

$$\begin{bmatrix} E_{1s} & -\eta \\ -\eta & E_{sp3} \end{bmatrix}\begin{bmatrix} c_1 \\ c_5 \end{bmatrix} = E\begin{bmatrix} c_1 \\ c_5 \end{bmatrix}$$



The energy eigenvalues of any one of these four 2x2 equations are:

$$E_A = \left(\frac{E_{1s}+E_{sp3}}{2}\right) + \sqrt{\left(\frac{E_{1s}-E_{sp3}}{2}\right)^2 + \eta^2}$$

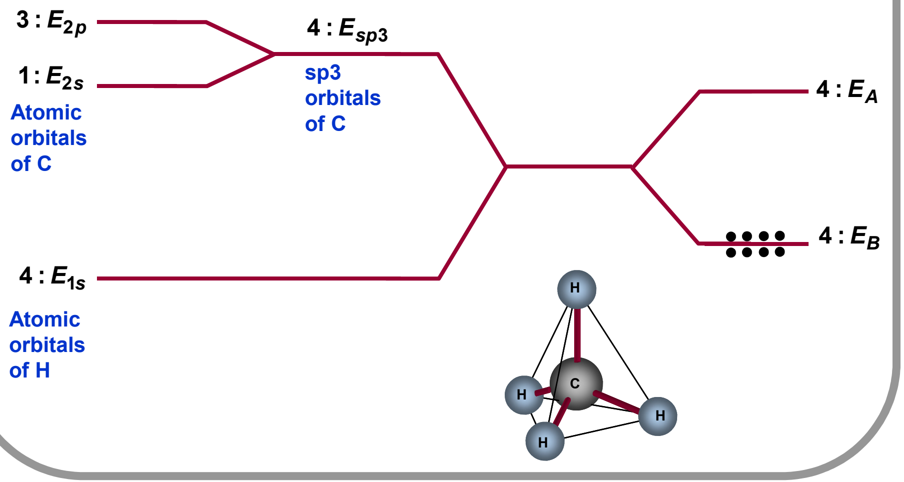
$$E_B = \left(\frac{E_{1s}+E_{sp3}}{2}\right) - \sqrt{\left(\frac{E_{1s}-E_{sp3}}{2}\right)^2 + \eta^2}$$

- **The higher energy corresponds to the anti-bonding state and the lower energy corresponds to the bonding state.**

- **In this case, the bonding and anti-bonding states are made up of a linear combination of the hydrogen 1s state and one of the carbon sp3 state.**

LCAO: Methane Molecule – sp$_3$ Hybridization

Energy level diagram going from isolated hydrogen and carbon atoms to the orbitals of the methane molecule is:



$3: E_{2p}$

$1: E_{2s}$

Atomic orbitals of C

$4: E_{sp3}$

sp3 orbitals of C

$4: E_{1s}$

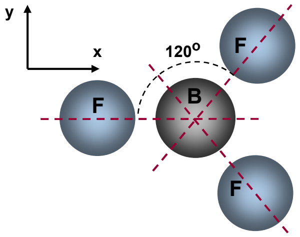
Atomic orbitals of H

$4: E_A$

$4: E_B$

LCAO: Boron Trifluoride Molecule

A BF_3 molecule consists of one boron atom covalently bonded to 3 fluorine atoms and all atoms lie in the same plane



Boron:

Atomic number: 5

Electron Configuration: $1s^2\ 2s^2\ 2p^1$

Number of electrons in the outermost shell: 3

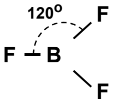
Fluorine:

Atomic number: 9

Electron Configuration: $1s^2\ 2s^2\ 2p^5$

Number of electrons in the outermost shell: 7

BF_3:



All three electrons from the outermost shell of the boron atom and only one of the 7 electrons from each fluorine atom take part in covalent bonding

---

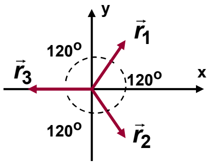
LCAO: BF_3 Molecule – sp_2 Hybridization

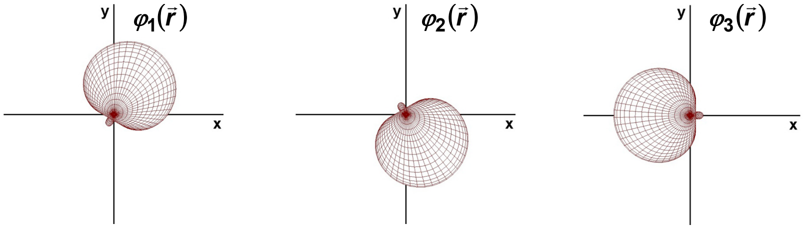
For the boron atom, do a change of basis and define 3 new sp2 atomic orbitals from the 3 existing (one 2s and two 2p) atomic orbitals

$$|\varphi_1(\vec{r})\rangle = \frac{1}{\sqrt{3}}|\phi_{2s}(\vec{r})\rangle + \frac{1}{\sqrt{6}}|\phi_{2px}(\vec{r})\rangle + \frac{1}{\sqrt{2}}|\phi_{2py}(\vec{r})\rangle$$

$$|\varphi_2(\vec{r})\rangle = \frac{1}{\sqrt{3}}|\phi_{2s}(\vec{r})\rangle + \frac{1}{\sqrt{6}}|\phi_{2px}(\vec{r})\rangle - \frac{1}{\sqrt{2}}|\phi_{2py}(\vec{r})\rangle$$

$$|\varphi_3(\vec{r})\rangle = \frac{1}{\sqrt{3}}|\phi_{2s}(\vec{r})\rangle - \sqrt{\frac{2}{3}}|\phi_{2px}(\vec{r})\rangle$$





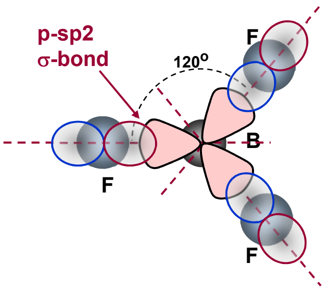
LCAO: BF_3 Molecule – sp_2 Hybridization

- In the fluorine atom, the 2s orbital and the two 2p orbitals that are perpendicular to the line joining the fluorine atom to the boron atom are all filled with 2 electrons each and do not participate in bonding

- The remaining p-orbital in fluorine that is pointing towards the boron atom, and contains one electron, forms a σ-bond with the sp2 orbital pointing towards it

Average energy of the sp2 orbital:

$$\Rightarrow \langle \varphi_j(\vec{r}) | \hat{H} | \varphi_m(\vec{r}) \rangle = E_{sp2}\, \delta_{j\,m} = \frac{E_{2s} + 2E_{2p}}{3}\, \delta_{j\,m}$$



Important matrix elements:

$$\langle \phi_{2p}(\vec{r} - \vec{r}_1) | \hat{H} | \varphi_1(\vec{r}) \rangle = \left(\frac{V_{sp\sigma} + \sqrt{2} V_{pp\sigma}}{\sqrt{3}} \right) = \eta$$

$$\langle \phi_{2p}(\vec{r} - \vec{r}_2) | \hat{H} | \varphi_2(\vec{r}) \rangle = \left(\frac{V_{sp\sigma} + \sqrt{2} V_{pp\sigma}}{\sqrt{3}} \right) = \eta$$

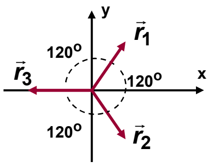
$$\langle \phi_{2p}(\vec{r} - \vec{r}_3) | \hat{H} | \varphi_3(\vec{r}) \rangle = -\left(\frac{V_{sp\sigma} + \sqrt{2} V_{pp\sigma}}{\sqrt{3}} \right) = -\eta$$

LCAO: BF_3 Molecule – sp_2 Hybridization

Write the solution for the BF_3 molecule using the sp2 orbitals of the boron atom:

$$|\psi(\vec{r})\rangle = \sum_{j=1}^{3} c_j \, |\phi_{2p}(\vec{r} - \vec{r}_j)\rangle + c_4 \, |\varphi_1(\vec{r})\rangle + c_5 \, |\varphi_2(\vec{r})\rangle + c_6 \, |\varphi_3(\vec{r})\rangle$$

And plug it into the Schrodinger equation: $\hat{H} |\psi(\vec{r})\rangle = E \, |\psi(\vec{r})\rangle$



To a first approximation, the 2p orbital on each fluorine atom has a large matrix element only with the sp2 orbital pointing towards it, so instead of one giant 6x6 matrix equation one gets a set of three 2x2 matrix equations:

$$\begin{bmatrix} E_{2p} & \eta \\ \eta & E_{sp2} \end{bmatrix} \begin{bmatrix} c_1 \\ c_4 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_4 \end{bmatrix} \qquad \begin{bmatrix} E_{2p} & \eta \\ \eta & E_{sp2} \end{bmatrix} \begin{bmatrix} c_2 \\ c_5 \end{bmatrix} = E \begin{bmatrix} c_2 \\ c_5 \end{bmatrix}$$

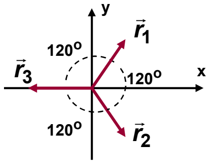
$$\begin{bmatrix} E_{2p} & -\eta \\ -\eta & E_{sp2} \end{bmatrix} \begin{bmatrix} c_3 \\ c_6 \end{bmatrix} = E \begin{bmatrix} c_3 \\ c_6 \end{bmatrix}$$

Where:

$$\eta = \left(\frac{V_{sp\sigma} + \sqrt{2} V_{pp\sigma}}{\sqrt{3}} \right) = \langle \phi_{2p}(\vec{r} - \vec{r}_1) | \hat{H} | \varphi_1(\vec{r}) \rangle$$

LCAO: BF_3 Molecule – sp_2 Hybridization

$$\begin{bmatrix} E_{2p} & \eta \\ \eta & E_{sp2} \end{bmatrix} \begin{bmatrix} c_1 \\ c_4 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_4 \end{bmatrix}$$



The energy eigenvalues of any one of these three 2x2 equations are:

$$E_A = \left(\frac{E_{2p} + E_{sp2}}{2}\right) + \sqrt{\left(\frac{E_{2p} - E_{sp2}}{2}\right)^2 + \eta^2}$$

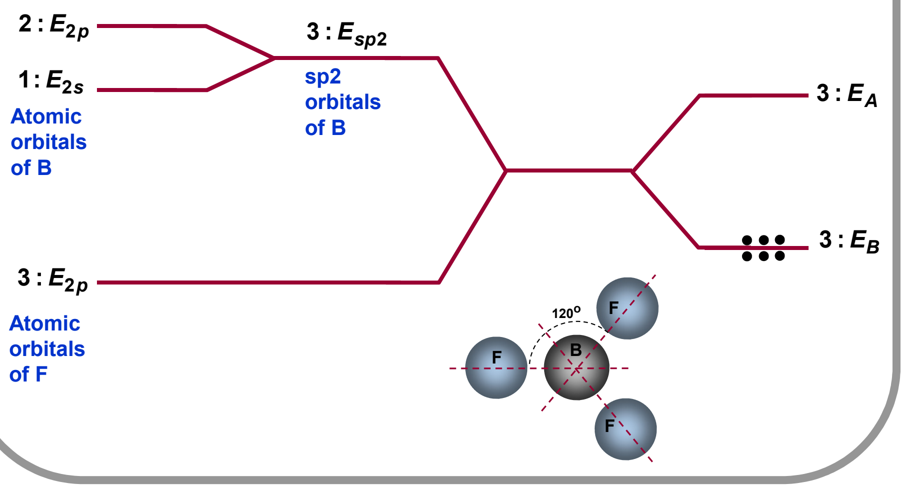
$$E_B = \left(\frac{E_{2p} + E_{sp2}}{2}\right) - \sqrt{\left(\frac{E_{2p} - E_{sp2}}{2}\right)^2 + \eta^2}$$

- **The higher energy corresponds to the anti-bonding state and the lower energy corresponds to the bonding state.**

- **In this case, the bonding and anti-bonding states are made up of a linear combination of the fluorine 2p state and one of the carbon sp2 state.**

LCAO: BF_3 Molecule – sp_2 Hybridization

Energy level diagram going from isolated fluorine and carbon atoms to the orbitals of the BF_3 molecule is:

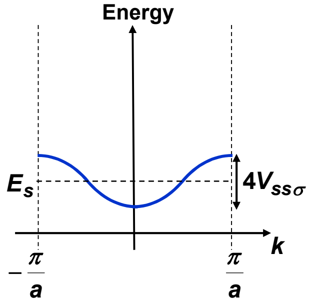


Handout 9

Application of LCAO to Energy Bands in Solids and the Tight Binding Method

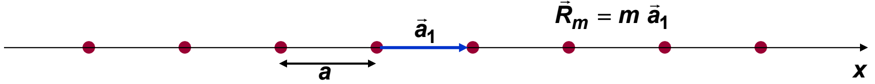
In this lecture you will learn:

- An approach to energy bands in solids using LCAO and the tight binding method



Example: A 1D Crystal with 1 Orbital per Primitive Cell

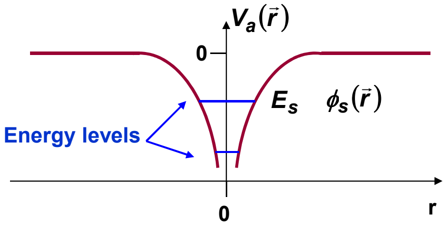
Consider a 1D lattice of atoms:



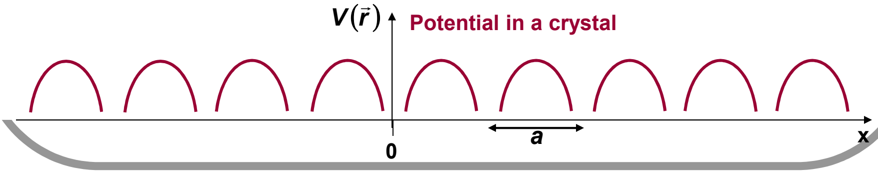
Each atom has the energy levels as shown

- The electrons in the lowest energy level(s) are well localized and do not take part in bonding with neighboring atoms

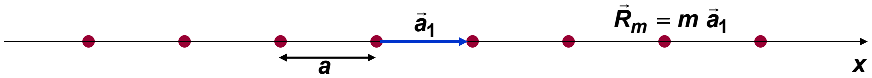
- The electrons in the outermost s-orbital participate in bonding



The crystal has the Hamiltonian: $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \sum_m V_a(\vec{r} - \vec{R}_m)$



Tight Binding Approach for a 1D Crystal



$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \sum_m V_a\left(\vec{r} - \vec{R}_m\right) \longrightarrow \text{Periodic potential}$$

We assume that the solution is of the LCAO form: $\psi(\vec{r}) = \sum_m c_m\,\phi_s\left(\vec{r} - \vec{R}_m\right)$

And assume that orbitals on different atoms are approx. orthogonal:

$$\left\langle \phi_s\left(\vec{r} - \vec{R}_n\right) \middle| \phi_s\left(\vec{r} - \vec{R}_m\right) \right\rangle = \delta_{n\,m}$$

- If we have *N* atoms in the lattice, then our solution is made up of *N* different s-orbitals that are sitting on the *N* atoms

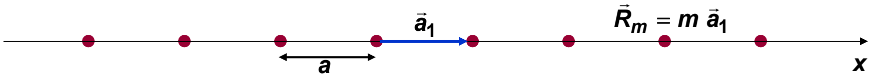
- In principle one can take the assumed solution, as written above, plug it in the Schrodinger equation, get an *N*x*N* matrix and solve it (just as we did in the case of molecules). But one can do better ………..

We know from Bloch's theorem that the solution must satisfy the following:

$$\left|\psi\left(\vec{r} + \vec{R}\right)\right|^2 = \left|\psi(\vec{r})\right|^2$$

$$\psi\left(\vec{r} + \vec{R}\right) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi(\vec{r})$$

Tight Binding Approach for a 1D Crystal



Consideration 1:

For the solution: $\psi(\vec{r}) = \sum_m c_m\,\phi_s\left(\vec{r} - \vec{R}_m\right)$

to satisfy:

$$\left|\psi\left(\vec{r} + \vec{R}\right)\right|^2 = \left|\psi(\vec{r})\right|^2$$

one must have the same value of $\left|c_m\right|^2$ for all *m* (i.e. all coefficients must have the same weight).

So we can write without loosing generality: $c_m = \frac{e^{i\,\theta_m}}{\sqrt{N}} \longrightarrow \int \left|\psi(\vec{r})\right|^2 d^3\vec{r} = 1$

Consideration 2:

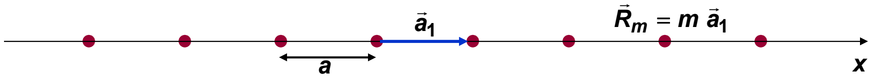
For the solution: $\psi(\vec{r}) = \sum_m \frac{e^{i\,\theta_m}}{\sqrt{N}}\,\phi_s\left(\vec{r} - \vec{R}_m\right)$

to satisfy:

$$\psi\left(\vec{r} + \vec{R}\right) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi(\vec{r})$$

one must have the phase value equal to: $\theta_m = \vec{k}\,.\,\vec{R}_m$

Tight Binding Approach for a 1D Crystal



Consideration 2 (contd…):

Proof:

$$\psi(\vec{r}) = \sum_m \frac{e^{i\theta_m}}{\sqrt{N}}\,\phi_s(\vec{r}-\vec{R}_m) = \sum_m \frac{e^{i\vec{k}.\vec{R}_m}}{\sqrt{N}}\,\phi_s(\vec{r}-\vec{R}_m)$$

For the Bloch condition we get:

$$\psi(\vec{r}+\vec{R}) = \sum_m \frac{e^{i\vec{k}.\vec{R}_m}}{\sqrt{N}}\,\phi_s(\vec{r}+\vec{R}-\vec{R}_m) = \sum_m \frac{e^{i\vec{k}.\vec{R}_m}}{\sqrt{N}}\,\phi_s\big(\vec{r}-(\vec{R}_m-\vec{R})\big)$$

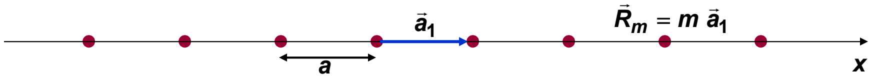
Let:

$$\vec{R}_m - \vec{R} = \vec{R}_p$$

$$\Rightarrow \psi(\vec{r}+\vec{R}) = \sum_p \frac{e^{i\vec{k}.(\vec{R}_p+\vec{R})}}{\sqrt{N}}\,\phi_s(\vec{r}-\vec{R}_p) = e^{i\vec{k}.\vec{R}}\sum_p \frac{e^{i\vec{k}.\vec{R}_p}}{\sqrt{N}}\,\phi_s(\vec{r}-\vec{R}_p)$$

$$= e^{i\vec{k}.\vec{R}}\,\psi(\vec{r})$$

Tight Binding Approach for a 1D Crystal



So we can write the solution as:

$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\vec{k}.\vec{R}_m}}{\sqrt{N}}\,\phi_s(\vec{r}-\vec{R}_m)$$

And we know that it is a Bloch function because:

$$\psi_{\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}.\vec{R}}\,\psi_{\vec{k}}(\vec{r})$$

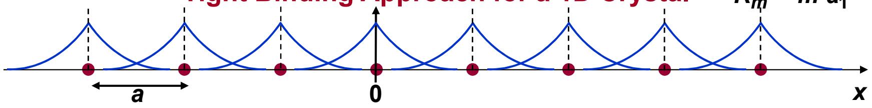
All that remains to be found is the energy of this solution – so we plug it into the Schrodinger equation:

$$\hat{H}\,\left|\psi_{\vec{k}}(\vec{r})\right\rangle = E(\vec{k})\left|\psi_{\vec{k}}(\vec{r})\right\rangle$$

$$\Rightarrow \sum_m \frac{e^{i\vec{k}.\vec{R}_m}}{\sqrt{N}}\,\hat{H}\,\left|\phi_s(\vec{r}-\vec{R}_m)\right\rangle = E(\vec{k})\sum_m \frac{e^{i\vec{k}.\vec{R}_m}}{\sqrt{N}}\,\left|\phi_s(\vec{r}-\vec{R}_m)\right\rangle$$

Tight Binding Approach for a 1D Crystal

$\vec{R}_m = m\,\vec{a}_1$



$$\Rightarrow \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}}\,\hat{H}\,\left|\phi_s\left(\vec{r}-\vec{R}_m\right)\right\rangle = E\left(\vec{k}\right)\sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}}\left|\phi_s\left(\vec{r}-\vec{R}_m\right)\right\rangle$$

Multiply this equation with $\left\langle \phi_s(\vec{r})\right|$ and:

- **keep the energy matrix elements for orbitals that are nearest neighbors and**
- **assume that the orbitals on different atoms are orthogonal**

$$\frac{e^{i\,\vec{k}\,.\,\vec{R}_1}}{\sqrt{N}}\left\langle \phi_s(\vec{r})\right|\hat{H}\left|\phi_s\left(\vec{r}-\vec{R}_1\right)\right\rangle + \frac{1}{\sqrt{N}}\left\langle \phi_s(\vec{r})\right|\hat{H}\left|\phi_s(\vec{r})\right\rangle + \frac{e^{i\,\vec{k}\,.\,\vec{R}_{-1}}}{\sqrt{N}}\left\langle \phi_s(\vec{r})\right|\hat{H}\left|\phi_s\left(\vec{r}-\vec{R}_{-1}\right)\right\rangle$$

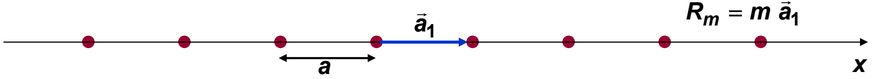
$$= E\left(\vec{k}\right)\frac{1}{\sqrt{N}}\left\langle \phi_s(\vec{r})\middle|\phi_s(\vec{r})\right\rangle$$

$$\Rightarrow -V_{ss\sigma}\frac{e^{i\,\vec{k}\,.\,\vec{a}_1}}{\sqrt{N}} + \frac{1}{\sqrt{N}}E_s - \frac{e^{-i\,\vec{k}\,.\,\vec{a}_1}}{\sqrt{N}}V_{ss\sigma} = E\left(\vec{k}\right)\frac{1}{\sqrt{N}}$$

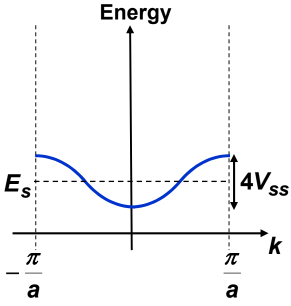
$$\Rightarrow E\left(\vec{k}\right) = E_s - 2V_{ss\sigma}\cos\left(\vec{k}\,.\,\vec{a}_1\right)$$

Tight Binding Approach for a 1D Crystal

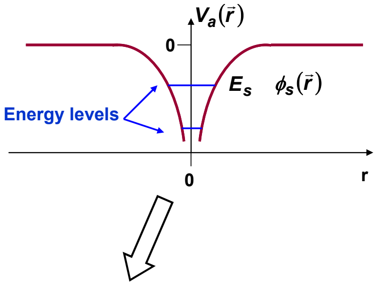
$\vec{R}_m = m\,\vec{a}_1$

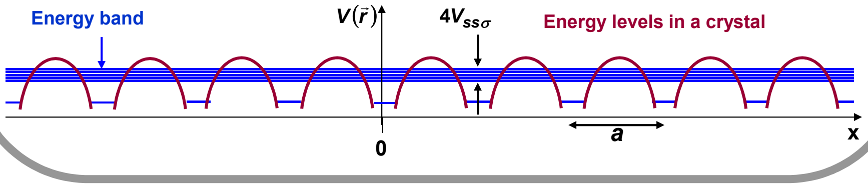


$$E\left(\vec{k}\right) = E_s - 2V_{ss\sigma}\cos\left(\vec{k}\,.\,\vec{a}_1\right)$$

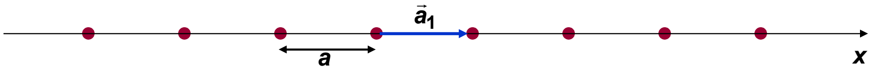


Energy levels in an isolated atom

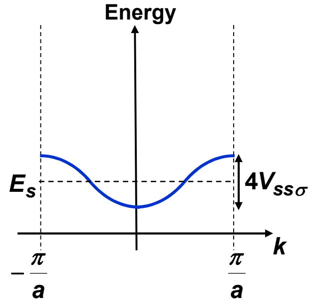




Tight Binding Approach for a 1D Crystal



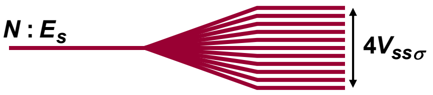
$E(\vec{k}) = E_s - 2V_{ss\sigma}\cos(\vec{k}\,.\,\vec{a}_1)$



- Number of quantum states at the starting point = 2 x number of orbitals used in the LCAO solution = 2*N*

- Number of quantum states at the ending point = 2 x energy levels per band for an *N* atom crystal = 2*N*

⇒ Initial number of quantum states = Final number of quantum states

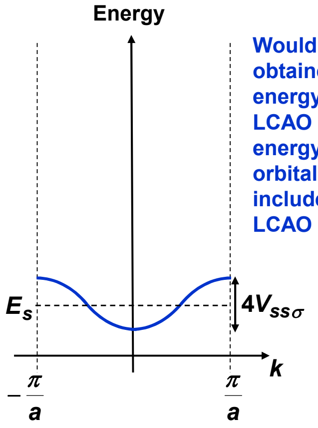


A band of *N* energy levels
2*N* quantum states

Tight Binding vs NFEA for a 1D Crystal

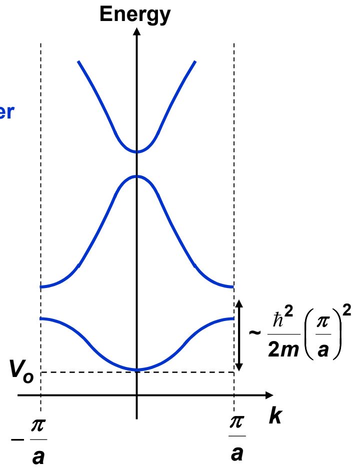
LCAO – Tight Binding

$E(\vec{k}) = E_s - 2V_{ss\sigma}\cos(\vec{k}\,.\,\vec{a}_1)$



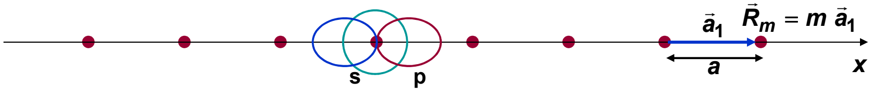
Would have also obtained the higher energy bands in LCAO if higher energy atomic orbitals were also included in the LCAO solution

Nearly Free Electron Approach (NFEA)



The energy matrix elements are of the order of: $V_{ss\sigma} \sim \frac{\hbar^2}{m}\frac{1}{a^2}$

Example: A 1D Crystal with 2 Orbitals per Primitive Cell



Each atoms now has a s-orbital and a p-orbital that contributes to energy band formation

$$\phi_s(\vec{r}) \rightarrow E_s$$
$$\phi_p(\vec{r}) \rightarrow E_p$$

We write the solution in the form:

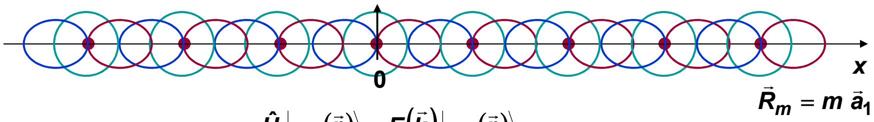
$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}}\left[c_s(\vec{k})\,\phi_s(\vec{r}-\vec{R}_m) + c_p(\vec{k})\,\phi_p(\vec{r}-\vec{R}_m)\right]$$

Verify that it satisfies: $\psi_{\vec{k}}(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\psi_{\vec{k}}(\vec{r})$

And plug it into the Schrodinger equation:

$$\hat{H}\left|\psi_{\vec{k}}(\vec{r})\right\rangle = E(\vec{k})\left|\psi_{\vec{k}}(\vec{r})\right\rangle$$

Tight Binding Approach for a 1D Crystal



$$\hat{H}\left|\psi_{\vec{k}}(\vec{r})\right\rangle = E(\vec{k})\left|\psi_{\vec{k}}(\vec{r})\right\rangle$$

Step 1:

Multiply the equation with $\left\langle\phi_s(\vec{r})\right|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors and
- assume that the orbitals on different atoms are orthogonal

$$\left[E_s - 2V_{ss\sigma}\cos(\vec{k}.\vec{a}_1)\right]c_s(\vec{k}) + 2i\,V_{sp\sigma}\sin(\vec{k}.\vec{a}_1)\,c_p(\vec{k}) = E(\vec{k})\,c_s(\vec{k})$$

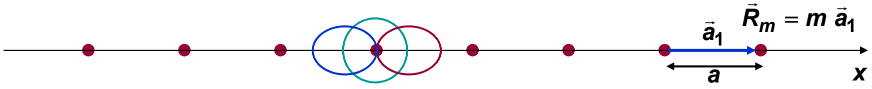
Step 2:

Multiply the equation with $\left\langle\phi_p(\vec{r})\right|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors and
- assume that the orbitals on different atoms are orthogonal

$$\left[E_p + 2V_{pp\sigma}\cos(\vec{k}.\vec{a}_1)\right]c_p(\vec{k}) - 2i\,V_{sp\sigma}\sin(\vec{k}.\vec{a}_1)\,c_s(\vec{k}) = E(\vec{k})\,c_p(\vec{k})$$

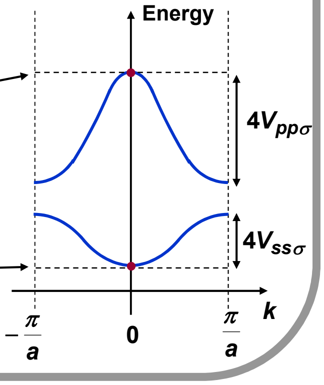
Tight Binding Approach for a 1D Crystal



We can write the two equations in matrix form:

$$\begin{bmatrix} E_s - 2V_{ss\sigma}\cos(\vec{k}.\vec{a}_1) & 2i\,V_{sp\sigma}\sin(\vec{k}.\vec{a}_1) \\ -2i\,V_{sp\sigma}\sin(\vec{k}.\vec{a}_1) & E_p + 2V_{pp\sigma}\cos(\vec{k}.\vec{a}_1) \end{bmatrix} \begin{bmatrix} c_s(\vec{k}) \\ c_p(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_s(\vec{k}) \\ c_p(\vec{k}) \end{bmatrix}$$

For each value of wavevector one obtains two eigenvalues – corresponding to two energy bands



For $\vec{k} = 0$ we get:

$$E(\vec{k} = 0) = E_p + 2V_{pp\sigma}$$

$$\begin{bmatrix} c_s(\vec{k} = 0) \\ c_p(\vec{k} = 0) \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

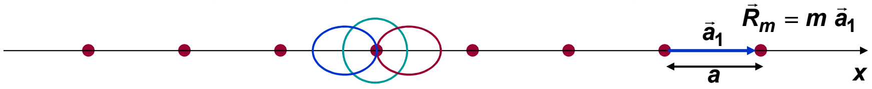
Bloch function is made of only p-orbitals

$$E(\vec{k} = 0) = E_s - 2V_{ss\sigma}$$

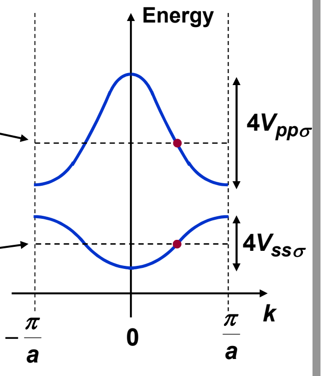
$$\begin{bmatrix} c_s(\vec{k} = 0) \\ c_p(\vec{k} = 0) \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

Bloch function is made of only s-orbitals

Tight Binding Approach for a 1D Crystal



For $\vec{k} = \frac{\pi}{2a}\hat{x}$ we get:



$$E\left(\vec{k} = \frac{\pi}{2a}\hat{x}\right) = ?$$

$$\begin{bmatrix} c_s\left(\vec{k} = \frac{\pi}{2a}\hat{x}\right) \\ c_p\left(\vec{k} = \frac{\pi}{2a}\hat{x}\right) \end{bmatrix} = \begin{bmatrix} ? \\ ? \end{bmatrix}$$

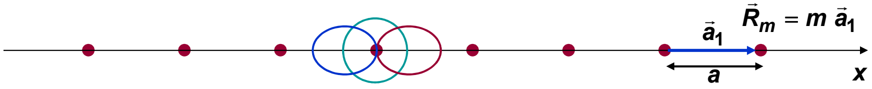
Bloch function is made of both s- and p-orbitals

$$E\left(\vec{k} = \frac{\pi}{2a}\right) = ?$$

$$\begin{bmatrix} c_s\left(\vec{k} = \frac{\pi}{2a}\hat{x}\right) \\ c_p\left(\vec{k} = \frac{\pi}{2a}\hat{x}\right) \end{bmatrix} = \begin{bmatrix} ? \\ ? \end{bmatrix}$$

Bloch function is made of both s- and p-orbitals

Tight Binding Approach for a 1D Crystal



For $\vec{k} = \frac{\pi}{a}\hat{x}$ we get:

$$E\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) = E_p - 2V_{pp\sigma}$$

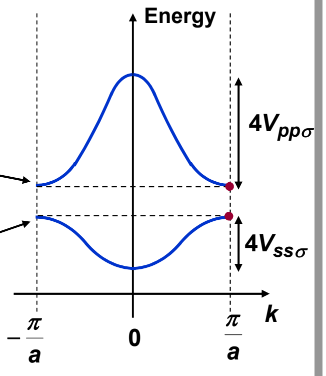
$$\begin{bmatrix} c_s\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) \\ c_p\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

Bloch function is made of only p-orbitals

$$E\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) = E_s + 2V_{ss\sigma}$$

$$\begin{bmatrix} c_s\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) \\ c_p\left(\vec{k} = \frac{\pi}{a}\hat{x}\right) \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

Bloch function is made of only s-orbitals

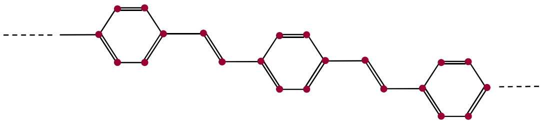


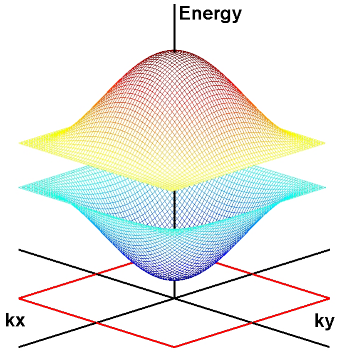
Handout 10

The Tight Binding Method (Contd…)
And
Crystal Symmetries and Energy Bands

In this lecture you will learn:

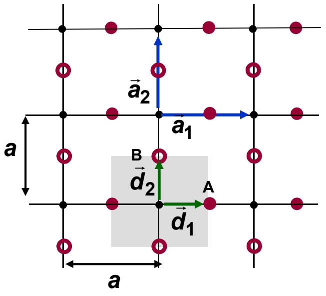
- The tight binding method (contd…)
- The π-bands in conjugated hydrocarbons
- The relationship between symmetries and energy bands





Tight Binding for a Square Lattice with a Two-Atom Basis

Consider a 2D square lattice with a two-atom basis:



- The primitive vectors and basis vectors are as follows:

$$\vec{a}_1 = a\,\hat{x} \qquad \vec{a}_2 = a\,\hat{y}$$

$$\vec{d}_1 = \frac{a}{2}\,\hat{x} \qquad \vec{d}_2 = \frac{a}{2}\,\hat{y}$$

- Each basis atom contributes one s-orbital that participates in bonding

⇒ Each primitive cell contributes two s-orbitals that participate in bonding

$$\phi_{SA}(\vec{r}) \leftrightarrow E_{SA}$$
$$\phi_{SB}(\vec{r}) \leftrightarrow E_{SB}$$

One can write the trial tight-binding solution for wavevector $\vec{k}$ as:

$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \left[c_{SA}(\vec{k})\, e^{i\vec{k}\,.\,\vec{d}_1}\, \phi_{SA}(\vec{r}-\vec{R}_m-\vec{d}_1) + c_{SB}(\vec{k})\, e^{i\vec{k}\,.\,\vec{d}_2}\, \phi_{SB}(\vec{r}-\vec{R}_m-\vec{d}_2) \right]$$

Analysis of the Tight Binding Solution

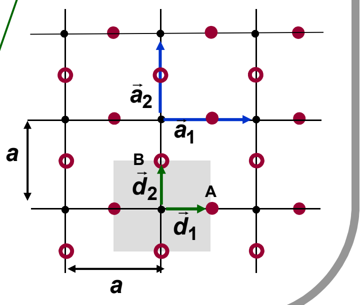
$$\psi_{\vec k}(\vec r)=\sum_m \frac{e^{i\vec k\,.\,\vec R_m}}{\sqrt{N}}\underbrace{\left[c_{SA}(\vec k)\,e^{i\vec k\,.\,\vec d_1}\,\phi_{SA}(\vec r-\vec R_m-\vec d_1)+c_{SB}(\vec k)\,e^{i\vec k\,.\,\vec d_2}\,\phi_{SB}(\vec r-\vec R_m-\vec d_2)\right]}$$

(1) Summation over all primitive cells

(3) Summation over all orbitals within a primitive cell with undetermined coefficients

(2) Common phase factor for each primitive cell

(4) A phase factor for each orbital that is related to the position of the orbital within the primitive cell w.r.t. lattice point



Tight Binding Solution

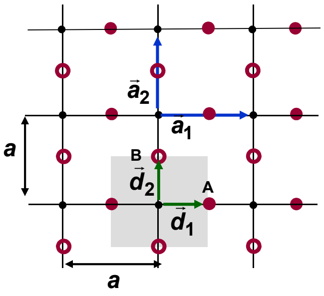
Plug the solution into the Schrodinger equation: $\hat H\,|\psi_{\vec k}(\vec r)\rangle = E(\vec k)\,|\psi_{\vec k}(\vec r)\rangle$

And then, one by one, multiply by from the left by the bra's corresponding to every orbital in one primitive cell to generate as many equations as the number of orbitals per primitive cell

Step 1:

Multiply the equation with $\langle\phi_{SA}(\vec r-\vec d_1)|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors, and
- assume that the orbitals on different atoms are orthogonal



$$E_{SA}\,c_{SA}(\vec k)-4V_{ss\sigma}\cos(\vec k.\vec d_1)\cos(\vec k.\vec d_2)\,c_{SB}(\vec k)=E(\vec k)\,c_{SA}(\vec k)$$

where the following identity has been used:

$$e^{i\vec k\,.\,(\vec d_1+\vec d_2)}+e^{i\vec k\,.\,(\vec d_1-\vec d_2)}+e^{i\vec k\,.\,(-\vec d_1+\vec d_2)}+e^{i\vec k\,.\,(-\vec d_1-\vec d_2)}=4\cos(\vec k\,.\,\vec d_1)\cos(\vec k\,.\,\vec d_2)$$

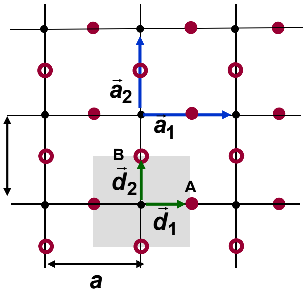
Tight Binding Solution

Step 2:

Multiply the equation with $\langle \phi_{SB}(\vec{r}-\vec{d}_2)|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors, and
- assume that the orbitals on different atoms are orthogonal

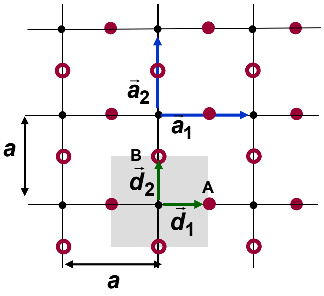
$$E_{SB}\, c_{SB}(\vec{k}) - 4V_{ss\sigma}\cos(\vec{k}.\vec{d}_1)\cos(\vec{k}.\vec{d}_2)\, c_{SA}(\vec{k}) = E(\vec{k})\, c_{SB}(\vec{k})$$

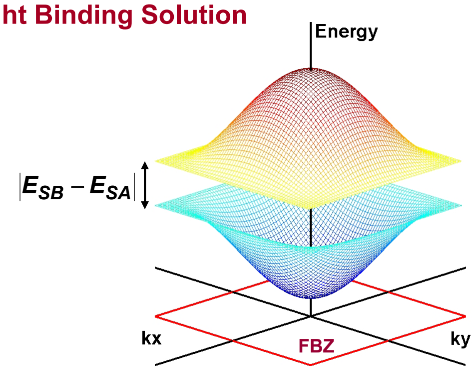


Write the equations obtained in a matrix form:

$$\begin{bmatrix} E_{SA} & -4V_{ss\sigma}\cos(\vec{k}.\vec{d}_1)\cos(\vec{k}.\vec{d}_2) \\ -4V_{ss\sigma}\cos(\vec{k}.\vec{d}_1)\cos(\vec{k}.\vec{d}_2) & E_{SB} \end{bmatrix} \begin{bmatrix} c_{SA}(\vec{k}) \\ c_{SB}(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_{SA}(\vec{k}) \\ c_{SB}(\vec{k}) \end{bmatrix}$$

Tight Binding Solution

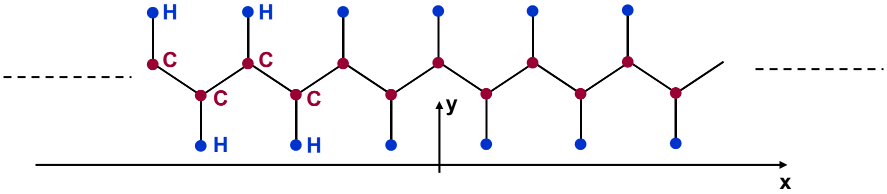




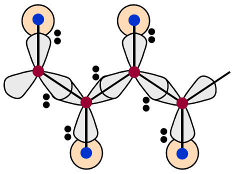
$$\begin{bmatrix} E_{SA} & -4V_{ss\sigma}\cos(\vec{k}.\vec{d}_1)\cos(\vec{k}.\vec{d}_2) \\ -4V_{ss\sigma}\cos(\vec{k}.\vec{d}_1)\cos(\vec{k}.\vec{d}_2) & E_{SB} \end{bmatrix} \begin{bmatrix} c_{SA}(\vec{k}) \\ c_{SB}(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_{SA}(\vec{k}) \\ c_{SB}(\vec{k}) \end{bmatrix}$$

Polyacetylene

Polyacetylene is a one-dimensional conducting hydrocarbon polymer



- Carbon atoms are all sp2 hybridized (one 2s orbital together with the $2p_x$ and the $2p_y$ orbitals generate three sp2 orbitals)

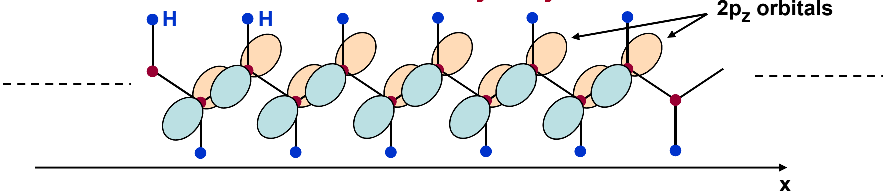


- Two sp2 orbitals form σ-bonds with the sp2 orbitals of the neigboring carbon atoms and one remaining sp2 orbital forms a σ-bond with the 1s orbital of the hydrogen atom

- The bonding orbital associated with each σ-bond is occupied by two electrons (spin-up and spin-down)

- There is one electron per carbon atom left in the $2p_z$ orbital

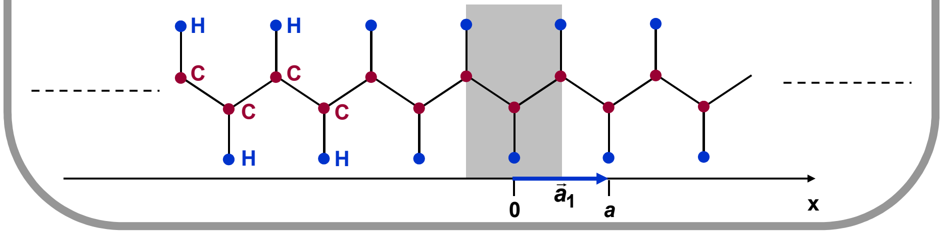
π-Bands in Polyacetylene



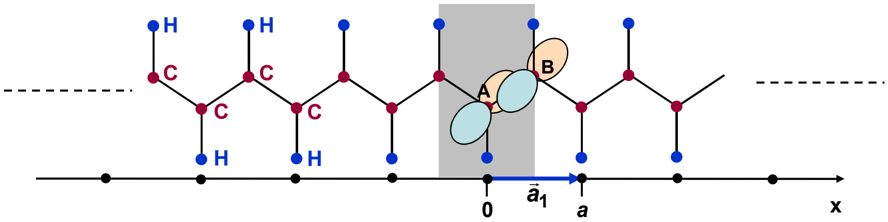
- The $2p_z$ orbital stick out of the plane of the chain and form π-bonds with neigboring $2p_z$ orbitals

- The p-bonding results in energy bands that we will study via tight binding

The primitive cell of the 1D chain is as shown below (it consists of two carbon atoms and two hydrogen atoms)



π-Bands in Polyacetylene



Two carbon atoms per primitive cell implies we have a 1D crystal with a two-atom basis with basis vectors:

$$\vec d_1 = 0 \qquad \vec d_2 = \frac{a}{2}\,\hat x$$

- Each basis atom contributes one $2p_z$-orbital that participates in bonding

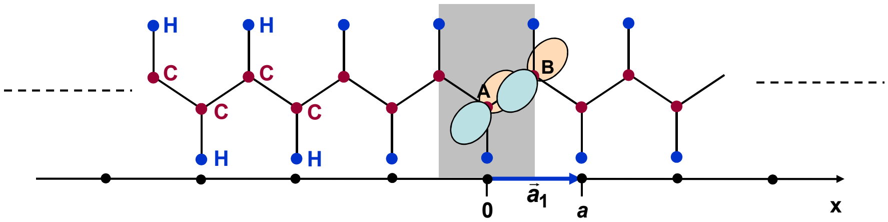
⇒ Each primitive cell contributes two $2p_z$-orbitals that participate in bonding

$$\phi_{pzA}(\vec r) \;\leftrightarrow\; E_p \qquad\qquad \phi_{pzB}(\vec r) \;\leftrightarrow\; E_p$$

One can write the trial tight-binding solution for wavevector $\vec k$ as:

$$\psi_{\vec k}(\vec r) = \sum_m \frac{e^{i\,\vec k\,.\,\vec R_m}}{\sqrt N}\left[c_{pzA}(\vec k)\,\phi_{pzA}(\vec r - \vec R_m) + c_{pzB}(\vec k)\,e^{i\vec k\,.\,\vec d_2}\,\phi_{pzB}(\vec r - \vec R_m - \vec d_2)\right]$$

π-Bands in Polyacetylene



Plug the solution into the Schrodinger equation: $\hat H\,\left|\psi_{\vec k}(\vec r)\right\rangle = E(\vec k)\left|\psi_{\vec k}(\vec r)\right\rangle$

And then, one by one, multiply by from the left by the bra's corresponding to every orbital in one primitive cell to generate as many equations as the number of orbitals per primitive cell

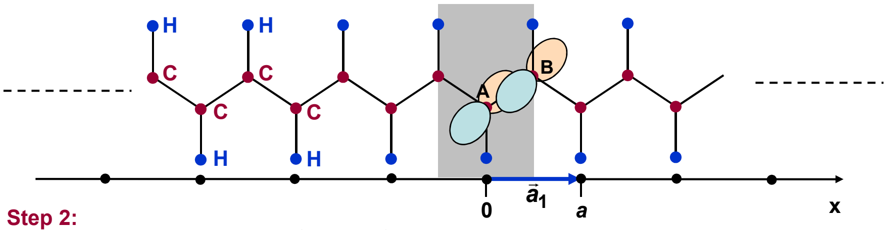
Step 1:

Multiply the equation with $\left\langle\phi_{pzA}(\vec r)\right|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors, and
- assume that the orbitals on different atoms are orthogonal

$$E_p\, c_{pzA}(\vec k) - 2V_{pp\pi}\cos(\vec k.\vec d_2)\,c_{pzB}(\vec k) = E(\vec k)\,c_{pzA}(\vec k)$$

π-Bands in Polyacetylene



Step 2:

Multiply the equation with $\langle \phi_{pzB}(\vec{r})|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors, and
- assume that the orbitals on different atoms are orthogonal

$$E_p\, c_{pzB}(\vec{k}) - 2V_{pp\pi}\cos(\vec{k}.\vec{d}_2)\, c_{pzA}(\vec{k}) = E(\vec{k})\, c_{pzB}(\vec{k})$$

Write the equations obtained in a matrix form:

$$\begin{bmatrix} E_p & -2V_{pp\pi}\cos(\vec{k}.\vec{d}_2) \\ -2V_{pp\pi}\cos(\vec{k}.\vec{d}_2) & E_p \end{bmatrix}\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix} = E(\vec{k})\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}$$

π-Bands in Polyacetylene

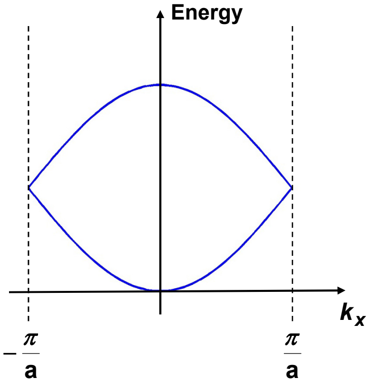
$$\begin{bmatrix} E_p & -2V_{pp\pi}\cos(\vec{k}.\vec{d}_2) \\ -2V_{pp\pi}\cos(\vec{k}.\vec{d}_2) & E_p \end{bmatrix}\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix} = E(\vec{k})\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}$$

Solutions are:

$$E(\vec{k}) = E_p \pm 2V_{pp\pi}\left|\cos(\vec{k}.\vec{d}_2)\right|$$

$$\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}_+ = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

$$\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}_- = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

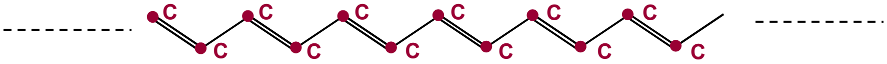


- There is no bandgap between the upper and lower bands!

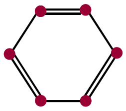
- Since each primitive cell contributes two electrons, the lower band is completely filled and the upper band is completely empty at *T*=0K

Other Conducting π-Conjugated Molecules and Polymers

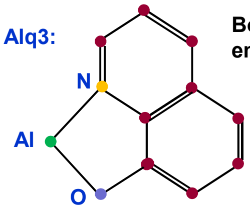
Polyacetylene:



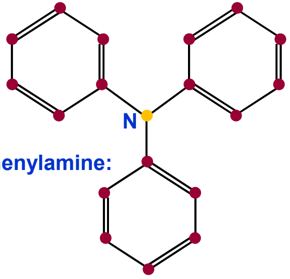
Benzene:



Alq3:

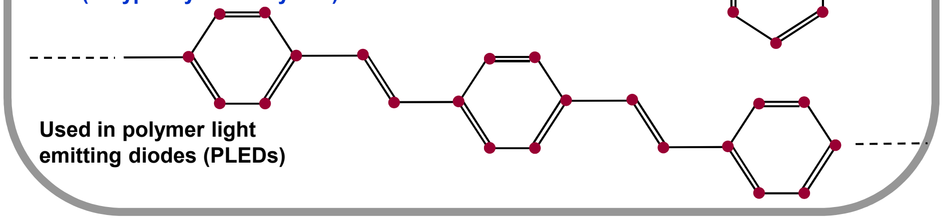


Both used in organic light emitting diodes (OLEDs)



Triphenylamine:

PPV (Polyphenylene Vinylene):



Used in polymer light emitting diodes (PLEDs)

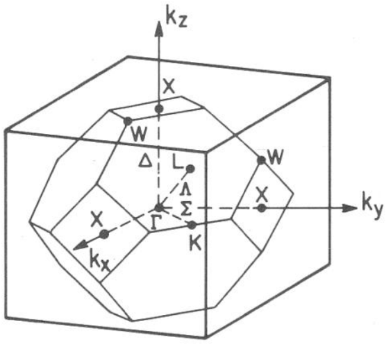
Tight Binding Bands For Germanium

Germanium:

Atomic number: 32

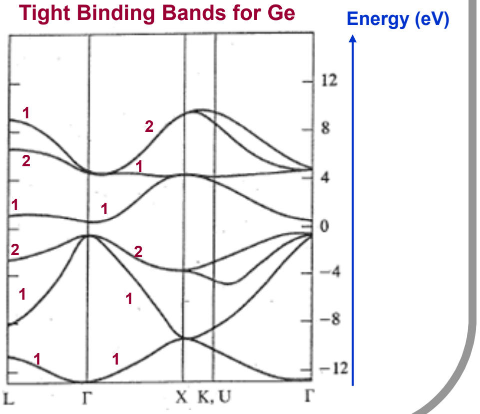
Electron Configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^2$

Number of electrons in the outermost shell: 4



FBZ (for FCC lattice)

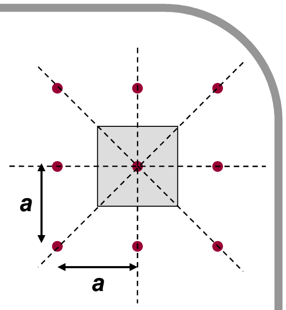
Tight Binding Bands for Ge



Symmetry and Energy Bands

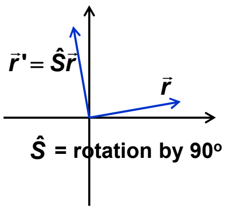
The crystal potential $V(\vec{r})$ generally has certain other symmetries in addition to the lattice translation symmetry:

$$V(\vec{r}+\vec{R}) = V(\vec{r})$$



For example, the 2D potential of a square atomic lattice, as shown, has the following symmetries:

a) Symmetry under rotations by 90, 180, and 270 degrees
b) Symmetry under reflections w.r.t. x-axis and y-axis
c) Symmetry under reflections w.r.t. the two diagonals



Let $\hat{S}$ be the operator (in matrix representation) for any one of these symmetry operations then:

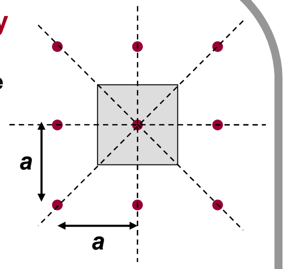
$$\vec{r}\,' = \hat{S}\vec{r}$$

$$\Rightarrow V(\hat{S}\vec{r}) = V(\vec{r})$$

Crystal Point-Group Symmetry

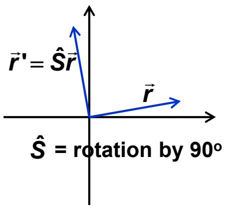
Point-Group Symmetry

The point group symmetry operation of a lattice are all those operations that leave the lattice unchanged and at least one point of the lattice remains unmoved under the operation



Point group symmetry operations can include:

i) Rotations (w.r.t. to axes of rotation)
ii) Reflections (across lines or planes)
iii) Inversions (w.r.t. to a point)



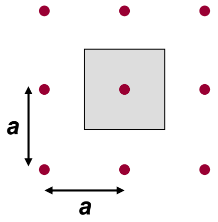
Let $\hat{S}$ be the operator for a point-group symmetry operation, such that:

$$V(\hat{S}\vec{r}) = V(\vec{r})$$

The operator $\hat{S}$ is unitary:

$$\hat{S}^T = \vec{S}^{-1} \Rightarrow \text{unitary}$$

Crystal Point-Group Symmetry and Energy Bands



Let $\hat{S}$ be the operator for a point-group symmetry operation, such that:

$$\vec{r}\,' = \hat{S}\vec{r} \qquad \left\{ \hat{S}^T = \hat{S}^{-1} \Rightarrow \text{unitary} \right.$$

$$\Rightarrow V(\hat{S}\vec{r}) = V(\vec{r})$$

Suppose one has solved the Shrodinger equation and obtained the energy and wavefunction of a Bloch State $\psi_{n,\vec{k}}(\vec{r})$

$$\left[-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r})\right]\psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\psi_{n,\vec{k}}(\vec{r})$$

Now replace $\vec{r}$ by $\hat{S}\vec{r}$ everywhere in the Schrodinger equation:

$$\left[-\frac{\hbar^2\nabla^2_{\hat{S}\vec{r}}}{2m} + V(\hat{S}\vec{r})\right]\psi_{n,\vec{k}}(\hat{S}\vec{r}) = E_n(\vec{k})\psi_{n,\vec{k}}(\hat{S}\vec{r}) \longrightarrow \left\{ \begin{array}{l} \nabla^2_{\hat{S}\vec{r}} = \nabla^2_{\vec{r}} \\ \text{Laplacian is invariant} \end{array} \right.$$

$$\Rightarrow \left[-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r})\right]\psi_{n,\vec{k}}(\hat{S}\vec{r}) = E_n(\vec{k})\psi_{n,\vec{k}}(\hat{S}\vec{r})$$

Crystal Point-Group Symmetry and Energy Bands

$$\left[-\frac{\hbar^2\nabla^2}{2m} + V(\hat{S}\vec{r})\right]\psi_{n,\vec{k}}(\hat{S}\vec{r}) = E_n(\vec{k})\psi_{n,\vec{k}}(\hat{S}\vec{r}) \Rightarrow \left[-\frac{\hbar^2\nabla^2}{2m} + V(\vec{r})\right]\psi_{n,\vec{k}}(\hat{S}\vec{r}) = E_n(\vec{k})\psi_{n,\vec{k}}(\hat{S}\vec{r})$$

The above equation says that the function $\psi_{n,\vec{k}}(\hat{S}\vec{r})$ is also a Bloch state with the same energy as $\psi_{n,\vec{k}}(\vec{r})$ (we have found a new eigenfunction!)

The question is if we really have found a new eigenfunction or not, and if so what is the wavevector of this new eigenfunction

We know that Bloch functions have the property that: $\psi_{n,\vec{k}}(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})$

So we try this on $\psi_{n,\vec{k}}(\hat{S}\vec{r})$:

$$\psi_{n,\vec{k}}\left(\hat{S}(\vec{r}+\vec{R})\right) = \psi_{n,\vec{k}}(\hat{S}\vec{r}+\hat{S}\vec{R}) \longrightarrow \left\{ \hat{S}\vec{R} \text{ is also a lattice vector} \right.$$

$$= e^{i\,\vec{k}\,.\,\hat{S}\vec{R}}\,\psi_{n,\vec{k}}(\hat{S}\vec{r}) = e^{i\left[\hat{S}^{-1}\vec{k}\right].\,\vec{R}}\,\psi_{n,\vec{k}}(\hat{S}\vec{r}) \longrightarrow \left\{ \vec{k}.(\hat{S}\vec{R}) = (\hat{S}^{-1}\vec{k}).\vec{R} \right.$$

$\Rightarrow \psi_{n,\vec{k}}(\hat{S}\vec{r})$ is a Bloch function with wavevector $\hat{S}^{-1}\vec{k}$ and energy $E_n(\vec{k})$

$$\Rightarrow \psi_{n,\vec{k}}(\hat{S}\vec{r}) = \psi_{n,\hat{S}^{-1}\vec{k}}(\vec{r})$$

Crystal Point-Group Symmetry and Energy Bands

So we finally have for the symmetry operation $\hat{S}$:

$$\Rightarrow \psi_{n,\vec{k}}\left(\hat{S}\vec{r}\right) = \psi_{n,\hat{S}^{-1}\vec{k}}\left(\vec{r}\right)$$

We also know that the eigenenergy of $\psi_{n,\hat{S}^{-1}\vec{k}}\left(\vec{r}\right)$ is $E_n\left(\vec{k}\right)$
Therefore:

$$E_n\left(\hat{S}^{-1}\vec{k}\right) = E_n\left(\vec{k}\right)$$

Or, equivalently:

$$E_n\left(\hat{S}\vec{k}\right) = E_n\left(\vec{k}\right)$$

Important Lessons:

1) If $\hat{S}$ is a symmetry of the potential such that in real-space we have:

$$V\left(\hat{S}\vec{r}\right) = V\left(\vec{r}\right)$$

then the energy bands also enjoy the symmetry of the potential such that in k-space:

$$E_n\left(\hat{S}\vec{k}\right) = E_n\left(\vec{k}\right)$$

2) Degeneracies in the energy bands can therefore arise from crystal point-group symmetries!

Time Reversal Symmetry and Energy Bands

Suppose we have solved the time dependent Schrodinger and obtained the Bloch state $\psi_{n,\vec{k}}\left(\vec{r}\right)$ with energy $E_n\left(\vec{k}\right)$:

$$\left[-\frac{\hbar^2\nabla^2}{2m} + V\left(\vec{r}\right)\right]\psi_{n,\vec{k}}\left(\vec{r},t\right) = i\hbar\frac{\partial\psi_{n,\vec{k}}\left(\vec{r},t\right)}{\partial t} \longrightarrow \psi_{n,\vec{k}}\left(\vec{r},t\right) = \psi_{n,\vec{k}}\left(\vec{r}\right)e^{-i\frac{E_n\left(\vec{k}\right)}{\hbar}t}$$

After plugging the solution in the time-dependent equation, we get:

$$\left[-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m} + V\left(\vec{r}\right)\right]\psi_{n,\vec{k}}\left(\vec{r}\right) = E_n\left(\vec{k}\right)\psi_{n,\vec{k}}\left(\vec{r}\right)$$

If we take the complex conjugate of the above equation, we get:

$$\left[-\frac{\hbar^2\nabla^2}{2m} + V\left(\vec{r}\right)\right]\psi^*_{n,\vec{k}}\left(\vec{r}\right) = E_n\left(\vec{k}\right)\psi^*_{n,\vec{k}}\left(\vec{r}\right)$$

We have found another Bloch function, i.e. $\psi^*_{n,\vec{k}}\left(\vec{r}\right)$, with the same energy as $\psi_{n,\vec{k}}\left(\vec{r}\right)$

Question: What is the physical significance of the state $\psi^*_{n,\vec{k}}\left(\vec{r}\right)$?

Time Reversal Symmetry and Energy Bands

Suppose we have solved the time dependent Schrodinger and obtained the Bloch state $\psi_{n,\vec{k}}(\vec{r})$ with energy $E_n(\vec{k})$:

$$\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi_{n,\vec{k}}(\vec{r},t)=i\hbar\frac{\partial\psi_{n,\vec{k}}(\vec{r},t)}{\partial t} \longrightarrow \psi_{n,\vec{k}}(\vec{r},t)=\psi_{n,\vec{k}}(\vec{r})\,e^{-i\frac{E_n(\vec{k})}{\hbar}t}$$

Lets see if we can find a solution under time-reversal (i.e. when *t* is replaced by –*t*):

$$\Rightarrow\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi_{n,\vec{k}}(\vec{r},-t)=-i\hbar\frac{\partial\psi_{n,\vec{k}}(\vec{r},-t)}{\partial t}$$

The above does not look like a Schrodinger equation so we complex conjugate it:

$$\Rightarrow\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi^*_{n,\vec{k}}(\vec{r},-t)=i\hbar\frac{\partial\psi^*_{n,\vec{k}}(\vec{r},-t)}{\partial t}$$

This means that $\psi^*_{n,\vec{k}}(\vec{r},-t)$ is the time-reversed state corresponding to the state $\psi_{n,\vec{k}}(\vec{r},t)$

$$\psi^*_{n,\vec{k}}(\vec{r},-t)=\psi^*_{n,\vec{k}}(\vec{r})\,e^{-i\frac{E_n(\vec{k})}{\hbar}t} \longrightarrow \left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi^*_{n,\vec{k}}(\vec{r})=E_n(\vec{k})\,\psi^*_{n,\vec{k}}(\vec{r})$$

The function $\psi^*_{n,\vec{k}}(\vec{r})$ is the time-reversed Bloch state corresponding to $\psi_{n,\vec{k}}(\vec{r})$

Time Reversal Symmetry and Energy Bands

$$\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi^*_{n,\vec{k}}(\vec{r})=E_n(\vec{k})\,\psi^*_{n,\vec{k}}(\vec{r})$$

We have found another Bloch function, i.e. $\psi^*_{n,\vec{k}}(\vec{r})$, with the same energy as $\psi_{n,\vec{k}}(\vec{r})$

The question is if we really have found a new eigenfunction or not, and if so what is the wavevector of this new eigenfunction

We know that Bloch functions have the property that: $\psi_{n,\vec{k}}(\vec{r}+\vec{R})=e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})$

So we try this on $\psi^*_{n,\vec{k}}(\vec{r})$:

$$\psi^*_{n,\vec{k}}(\vec{r}+\vec{R})=\left[\psi_{n,\vec{k}}(\vec{r}+\vec{R})\right]^*=\left[e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})\right]^*=e^{i\,[-\vec{k}]\,.\,\vec{R}}\,\psi^*_{n,\vec{k}}(\vec{r})$$

$\Rightarrow$ $\psi^*_{n,\vec{k}}(\vec{r})$ is a Bloch function with wavevector $-\vec{k}$ and energy $E_n(\vec{k})$

$\Rightarrow$ $\psi_{n,-\vec{k}}(\vec{r})=\psi^*_{n,\vec{k}}(\vec{r})$ and $E_n(-\vec{k})=E_n(\vec{k})$

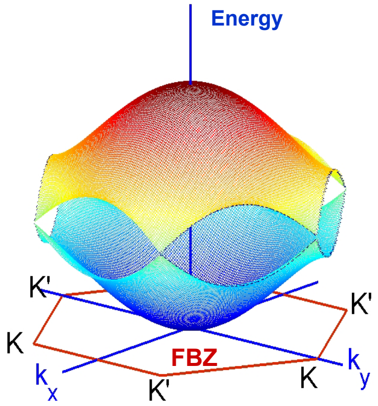
Important Lesson:
Time reversal symmetry implies that $E_n(-\vec{k})=E_n(\vec{k})$ even if the crystal lacks spatial inversion symmetry (e.g. GaAs, InP, etc)

Handout 11

Energy Bands in Graphene: Tight Binding and the Nearly Free Electron Approach

In this lecture you will learn:

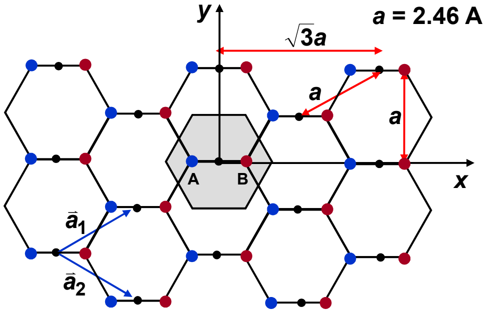
- The tight binding method (contd…)
- The π-bands in graphene



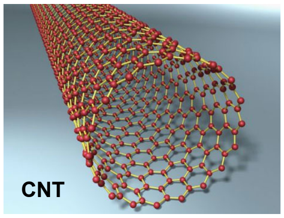
Graphene and Carbon Nanotubes: Basics

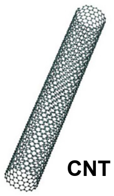
- Graphene is a two dimensional single atomic layer of carbon atoms arranged in a Honeycomb lattice (which is not a Bravais lattice)
- The underlying Bravais lattice is shown by the location of the black dots and is a hexagonal lattice
- There are two carbon atoms per primitive cell, A and B (shown in blue and red colors, respectively)
- Graphene can be rolled into tubes that are called carbon nanotubes (CNTs)

a = 2.46 A



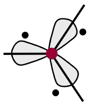
$$\vec{a}_1 = \left(\frac{\sqrt{3}}{2}\hat{x} + \frac{1}{2}\hat{y}\right)a \qquad \vec{a}_2 = \left(\frac{\sqrt{3}}{2}\hat{x} - \frac{1}{2}\hat{y}\right)a$$

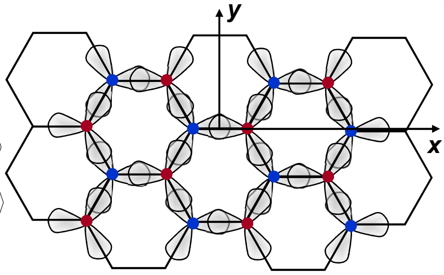

CNT


CNT

Graphene: Sp2 Hybridization

Sp2 hybridization in carbon:





$$|\varphi_1(\vec{r})\rangle = \frac{1}{\sqrt{3}}|\phi_{2s}(\vec{r})\rangle + \frac{1}{\sqrt{6}}|\phi_{2px}(\vec{r})\rangle + \frac{1}{\sqrt{2}}|\phi_{2py}(\vec{r})\rangle$$

$$|\varphi_2(\vec{r})\rangle = \frac{1}{\sqrt{3}}|\phi_{2s}(\vec{r})\rangle + \frac{1}{\sqrt{6}}|\phi_{2px}(\vec{r})\rangle - \frac{1}{\sqrt{2}}|\phi_{2py}(\vec{r})\rangle$$

$$|\varphi_3(\vec{r})\rangle = \frac{1}{\sqrt{3}}|\phi_{2s}(\vec{r})\rangle - \sqrt{\frac{2}{3}}|\phi_{2px}(\vec{r})\rangle$$

- All carbon atoms are all sp2 hybridized (one 2s orbital together with the $2p_x$ and the $2p_y$ orbitals generate three sp2 orbitals)

- All sp2 orbitals form σ-bonds with the sp2 orbitals of the neigboring carbon atoms

- The bonding orbital associated with each σ-bond is occupied by two electrons (spin-up and spin-down)

- There is one electron per carbon atom left in the $2p_z$ orbital

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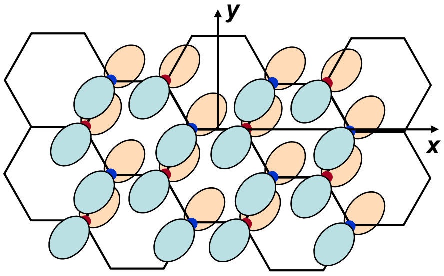
Graphene: 2pz Orbitals



π-bonding:

- Each carbon atom contributes one $2p_z$-orbital that participates in bonding

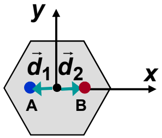
⇒ Each primitive cell contributes two $2p_z$-orbitals that participate in bonding

- The $2p_z$ orbital stick out of the plane of the chain and form π-bonds with neigboring $2p_z$ orbitals

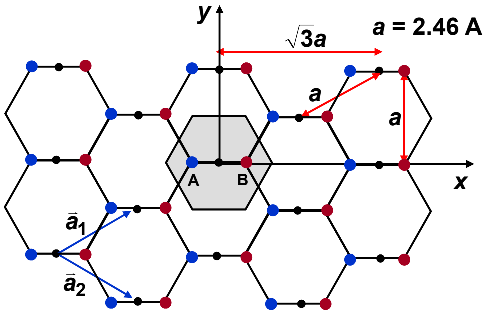
- The π-bonding results in energy bands (π-bands) that we will study via tight binding

Graphene: Some Useful Vectors

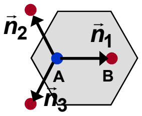
Basis vectors:



$$\vec{d}_1 = -\frac{a}{2\sqrt{3}}\hat{x} \qquad \vec{d}_2 = \frac{a}{2\sqrt{3}}\hat{x}$$



Nearest neighbor vectors:



$$\vec{n}_1 = \frac{a}{\sqrt{3}}\hat{x}$$

$$\vec{n}_2 = \frac{a}{\sqrt{3}}\left(-\frac{1}{2}\hat{x} + \frac{\sqrt{3}}{2}\hat{y}\right)$$

$$\vec{n}_3 = \frac{a}{\sqrt{3}}\left(-\frac{1}{2}\hat{x} - \frac{\sqrt{3}}{2}\hat{y}\right)$$

These will be useful for writing the final solution in a compact form

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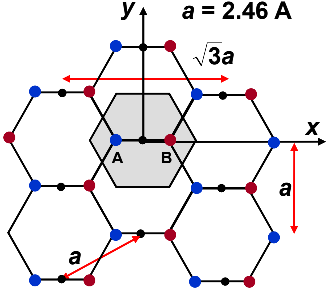
Graphene: Tight Binding Solution



- Each basis atom contributes one 2p$_z$-orbital that participates in bonding

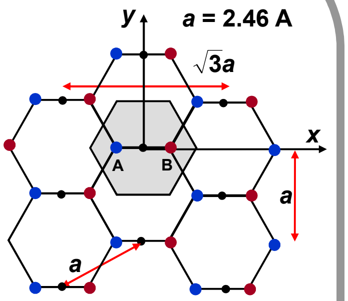
⇒ Each primitive cell contributes two 2p$_z$-orbitals that participate in bonding

$$\phi_{pzA}(\vec{r}) \leftrightarrow E_p \qquad \phi_{pzB}(\vec{r}) \leftrightarrow E_p$$

One can then write the trial tight-binding solution for wavevector $\vec{k}$ as:

$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}}\left[c_{pzA}(\vec{k})\,e^{i\vec{k}\,.\,\vec{d}_1}\phi_{pzA}(\vec{r}-\vec{R}_m-\vec{d}_1) + c_{pzB}(\vec{k})\,e^{i\vec{k}\,.\,\vec{d}_2}\phi_{pzB}(\vec{r}-\vec{R}_m-\vec{d}_2)\right]$$

Graphene: Tight Binding Solution



Plug the solution into the Schrodinger equation:

$$\hat{H}\,\left|\psi_{\vec{k}}(\vec{r})\right\rangle = E(\vec{k})\left|\psi_{\vec{k}}(\vec{r})\right\rangle$$

And then, one by one, multiply by from the left by the bra's corresponding to every orbital in one primitive cell to generate as many equations as the number of orbitals per primitive cell

Step 1:

Multiply the equation with $\left\langle\phi_{pzA}(\vec{r}-\vec{d}_1)\right|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors, and
- assume that the orbitals on different atoms are orthogonal

$$E_p\, c_{pzA}(\vec{k}) - V_{pp\pi}\left(e^{i\,\vec{k}\,.\,\vec{n}_1} + e^{i\,\vec{k}\,.\,\vec{n}_2} + e^{i\,\vec{k}\,.\,\vec{n}_3}\right)c_{pzB}(\vec{k}) = E(\vec{k})\,c_{pzA}(\vec{k})$$

Notice that the final result can be written in terms of the nearest neighbor vectors

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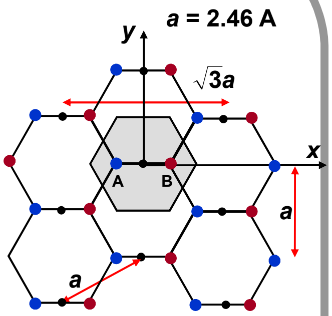
Graphene: Tight Binding Solution



Step 2:

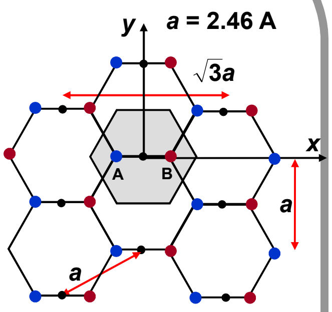
Multiply the equation with $\left\langle\phi_{pzB}(\vec{r}-\vec{d}_2)\right|$ and:

- keep the energy matrix elements for orbitals that are nearest neighbors, and
- assume that the orbitals on different atoms are orthogonal

$$E_p\, c_{pzB}(\vec{k}) - V_{pp\pi}\left(e^{-i\,\vec{k}\,.\,\vec{n}_1} + e^{-i\,\vec{k}\,.\,\vec{n}_2} + e^{-i\,\vec{k}\,.\,\vec{n}_3}\right)c_{pzA}(\vec{k}) = E(\vec{k})\,c_{pzB}(\vec{k})$$

Notice that the final result can be written in terms of the nearest neighbor vectors

Graphene: Tight Binding Solution



Write the equations obtained in a matrix form:

$$\begin{bmatrix} E_p & -V_{pp\pi}\, f(\vec{k}) \\ -V_{pp\pi}\, f^*(\vec{k}) & E_p \end{bmatrix}\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k})\end{bmatrix} = E(\vec{k})\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k})\end{bmatrix}$$

Where the function $f(\vec{k})$ is:

$$f(\vec{k}) = \left(e^{i\,\vec{k}.\vec{n}_1} + e^{i\,\vec{k}.\vec{n}_2} + e^{i\,\vec{k}.\vec{n}_3}\right)$$

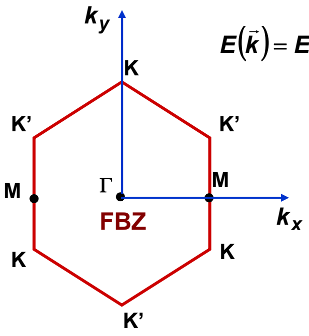
Solutions are:

$$E(\vec{k}) = E_p \pm V_{pp\pi}\,\left|f(\vec{k})\right|$$

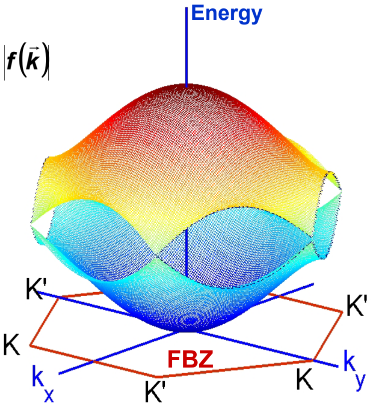
And the corresponding eigenvectors are:

$$\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k})\end{bmatrix}_+ = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -f^*(\vec{k})/\left|f(\vec{k})\right|\end{bmatrix} \qquad \begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k})\end{bmatrix}_- = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ f^*(\vec{k})/\left|f(\vec{k})\right|\end{bmatrix}$$

Graphene: π-Energy Bands



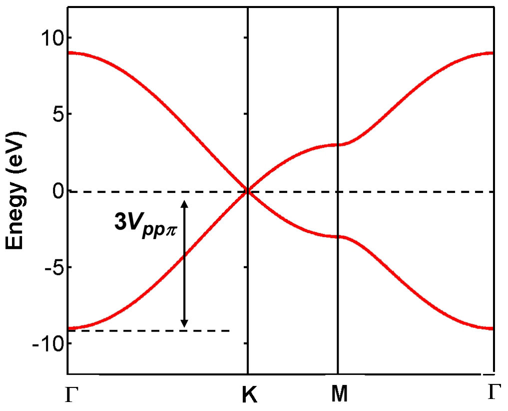
$$E(\vec{k}) = E_p \pm V_{pp\pi}\,\left|f(\vec{k})\right|$$



- Bandgaps open at the M-points between the first and the second bands
- No bandgaps open at the K-points and the K'-points

Graphene: π-Energy Bands

- Since graphene has two electrons per primitive cell contributing to π-bonding, the lower π-band will be completely filled at $T \approx 0K$
- The location of Fermi level near $T \approx 0K$ is shown by the dashed curve



In generating the plots I chose energy zero such that:

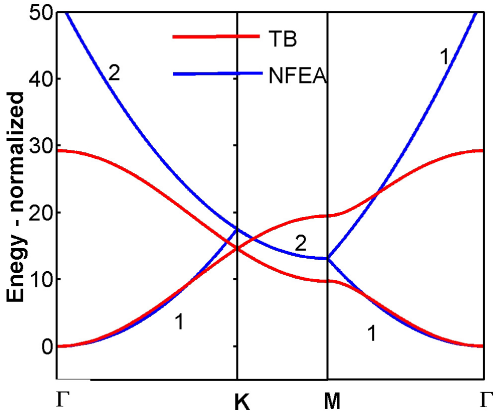
$$E_p = 0$$

And for graphene:

$$V_{pp\pi} = 3.0 \text{ eV}$$

Graphene: A Comparison of NFEA and TB

Scale normalized to: $\frac{\hbar^2}{2m}\left(\frac{1}{a}\right)^2$ and offset by V_o



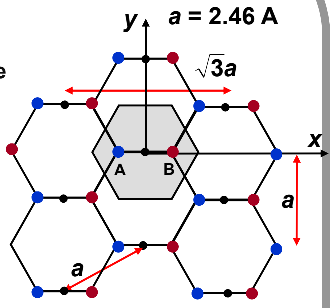
To compare the nearly-free-electron approach (NFEA) to tight-binding (TB) I assumed the DC potential in NFEA to be:

$$V_o = E_p - 3V_{pp\pi}$$

And in graphene:

$$V_{pp\pi} = 3.0 \text{ eV}$$

Why the Zero Bandgap in Graphene?



The answer from tight binding:

The two atoms in a primitive cell are identical. If they were different then there would be a non-zero bandgap:

$$\begin{bmatrix} \boxed{E_{pA}} & -V_{pp\pi}\, f(\vec{k}) \\ -V_{pp\pi}\, f^{*}(\vec{k}) & \boxed{E_{pB}} \end{bmatrix}\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix} = E(\vec{k})\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}$$

$$\Rightarrow E(\vec{k}) = \frac{E_{pA}+E_{pB}}{2} \pm \sqrt{\left(\frac{E_{pA}-E_{pB}}{2}\right)^{2} + V_{pp\pi}^{2}\,\left|f(\vec{k})\right|}$$

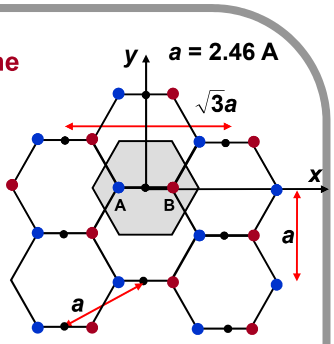
$$\Rightarrow E_g = \left|E_{pA}-E_{pB}\right| \longrightarrow \text{at the K(K')-points}$$

The answer from the nearly-free-electron approach:

As you saw in your homework, if the crystal potential lacked inversion symmetry w.r.t. the y-axis (i.e. $V(-x,y) \neq V(x,y)$) then there would be a non-zero bandgap.

Of course, if the two atoms in the primitive cell were different then the crystal would lack inversion symmetry! So both the approaches explaining the zero bandgap are consistent.

Pseudospin in Graphene



Solutions are:

$$E(\vec{k}) = E_p \pm V_{pp\pi}\left|f(\vec{k})\right|$$

$$f(\vec{k}) = \left(e^{i\,\vec{k}.\vec{n}_1} + e^{i\,\vec{k}.\vec{n}_2} + e^{i\,\vec{k}.\vec{n}_3}\right)$$

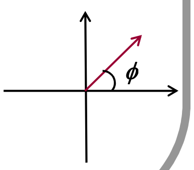
And the corresponding eigenvectors are:

$$\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}_{+} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -f^{*}(\vec{k})/\left|f(\vec{k})\right| \end{bmatrix} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ e^{i\phi(\vec{k})} \end{bmatrix}$$

$$\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}_{-} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ f^{*}(\vec{k})/\left|f(\vec{k})\right| \end{bmatrix} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -e^{i\phi(\vec{k})} \end{bmatrix} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ e^{i\phi(\vec{k})+i\pi} \end{bmatrix} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ e^{i\theta(\vec{k})} \end{bmatrix}$$

Compare with the case of 1/2 spin particles with spins in the x-y plane:

$$\left.\begin{aligned} |x\rangle_{+} &= \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix} & |x\rangle_{-} &= \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix} \\ |y\rangle_{+} &= \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ i \end{bmatrix} & |y\rangle_{-} &= \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -i \end{bmatrix} \end{aligned}\right\} \longrightarrow |\phi\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ e^{i\phi} \end{bmatrix}$$



Handout 12

Energy Bands in Group IV and III-V Semiconductors

In this lecture you will learn:

- The tight binding method (contd…)
- The energy bands in group IV and group III-V semiconductors with FCC lattice structure
- Spin-orbit coupling effects in solids

FCC Lattice: A Review

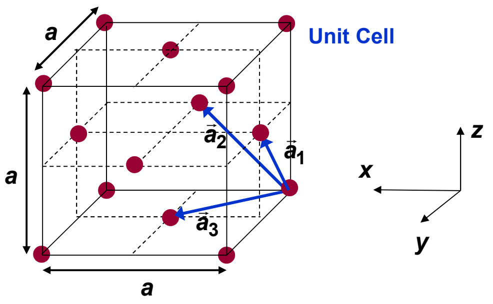
Most group VI and group III-V semiconductor, such as Si, Ge, GaAs, InP, etc have FCC lattices with a two-atom basis

Face Centered Cubic (FCC) Lattice:

$$\vec{a}_1 = \frac{a}{2}(\hat{y} + \hat{z})$$

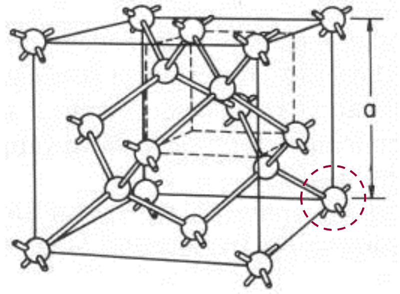
$$\vec{a}_2 = \frac{a}{2}(\hat{x} + \hat{z})$$

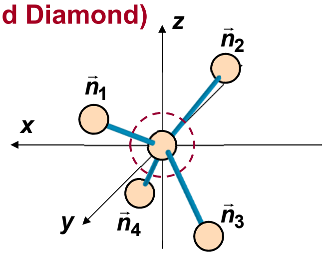
$$\vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{y})$$



Lattices of Group IV Semiconductors (Silicon, Germanium, and Diamond)

Diamond lattice (Si, Ge, and Diamond)





Nearest neighbor vectors

$$\vec{n}_1 = \frac{a}{4}(1,1,1) \qquad \vec{n}_2 = \frac{a}{4}(-1,-1,1)$$

$$\vec{n}_3 = \frac{a}{4}(-1,1,-1) \qquad \vec{n}_4 = \frac{a}{4}(1,-1,-1)$$

Basis vectors

$$\vec{d}_1 = 0 \qquad \vec{d}_2 = \frac{a}{4}(1,1,1)$$

- The underlying lattice is an FCC lattice with a two-point (or two-atom) basis.

- Each atom is covalently bonded to four other atoms (and vice versa) via sp3 bonds in a tetrahedral configuration

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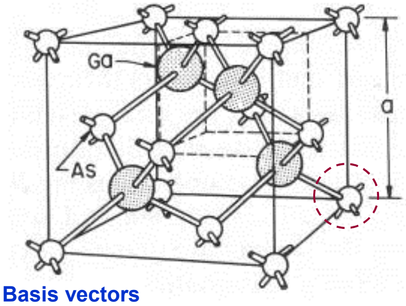
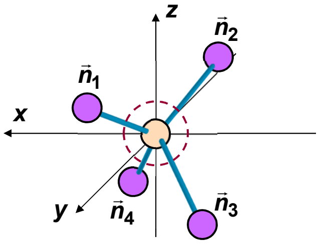
Lattices of III-V Binaries (GaAs, InP, InAs, AlAs, InSb, etc)

Zincblende lattice (GaAs, InP, InAs)





Nearest neighbor vectors

$$\vec{n}_1 = \frac{a}{4}(1,1,1) \qquad \vec{n}_2 = \frac{a}{4}(-1,-1,1)$$

$$\vec{n}_3 = \frac{a}{4}(-1,1,-1) \qquad \vec{n}_4 = \frac{a}{4}(1,-1,-1)$$

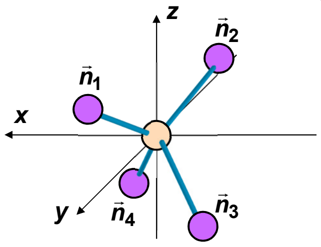
Basis vectors

$$\vec{d}_1 = 0 \qquad \vec{d}_2 = \frac{a}{4}(1,1,1)$$

- The underlying lattice is an FCC lattice with a two-point (or two-atom) basis. In contrast to the diamond lattice, the two atoms in the basis of zincblende lattice are different – one belongs to group III and one belongs to group V

- Each Group III atom is covalently bonded to four other group V atoms (and vice versa) via sp3 bonds in a tetrahedral configuration

Example: Tight Binding Solution for GaAs



- Each Ga atom contributes one 4s-orbital and three 4p-robitals

- Each As atom also contributes one 4s-orbital and three 4p-robitals

⇒ Each primitive cell contributes a total of eight orbitals that participate in bonding

1	$\phi_{SG}(\vec{r})$ ↔	E_{SG}		5	$\phi_{SA}(\vec{r})$ ↔	E_{SA}
2	$\phi_{PxG}(\vec{r})$ ↔	E_{PG}		6	$\phi_{PxA}(\vec{r})$ ↔	E_{PA}
3	$\phi_{PyG}(\vec{r})$ ↔	E_{PG}		7	$\phi_{PyA}(\vec{r})$ ↔	E_{PA}
4	$\phi_{PzG}(\vec{r})$ ↔	E_{PG}		8	$\phi_{PzA}(\vec{r})$ ↔	E_{PA}

One can write the trial tight-binding solution for wavevector $\vec{k}$ as:

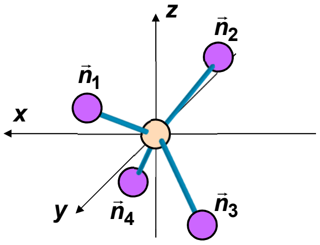
$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \left[\sum_{j=1}^{4} c_j \left|\phi_j\left(\vec{r}-\vec{R}_m\right)\right\rangle + e^{i\,\vec{k}\,.\,\vec{d}_2} \sum_{j=5}^{8} c_j \left|\phi_j\left(\vec{r}-\vec{R}_m-\vec{d}_2\right)\right\rangle \right]$$

Example: Tight Binding Solution for GaAs

$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\,\vec{k}\,.\,\vec{R}_m}}{\sqrt{N}} \left[\sum_{j=1}^{4} c_j \left|\phi_j\left(\vec{r}-\vec{R}_m\right)\right\rangle + e^{i\,\vec{k}\,.\,\vec{d}_2} \sum_{j=5}^{8} c_j \left|\phi_j\left(\vec{r}-\vec{R}_m-\vec{d}_2\right)\right\rangle \right]$$

Plug the solution above into the Schrodinger equation to get:

$$H \begin{bmatrix} c_1(\vec{k}) \\ c_2(\vec{k}) \\ c_3(\vec{k}) \\ c_4(\vec{k}) \\ c_5(\vec{k}) \\ c_6(\vec{k}) \\ c_7(\vec{k}) \\ c_8(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_1(\vec{k}) \\ c_2(\vec{k}) \\ c_3(\vec{k}) \\ c_4(\vec{k}) \\ c_5(\vec{k}) \\ c_6(\vec{k}) \\ c_7(\vec{k}) \\ c_8(\vec{k}) \end{bmatrix}$$



Tight Binding Solution for GaAs: The Matrix

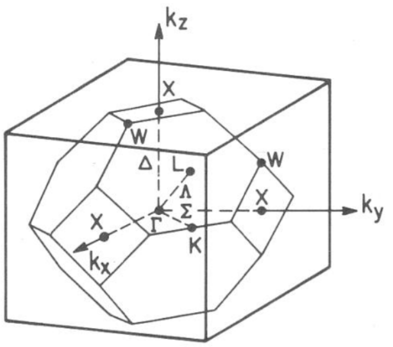
$$
H = \begin{bmatrix}
E_{SG} & 0 & 0 & 0 & -V_{ss\sigma} g_0(\vec{k}) & \frac{V_{sp\sigma}}{\sqrt{3}} g_1(\vec{k}) & \frac{V_{sp\sigma}}{\sqrt{3}} g_2(\vec{k}) & \frac{V_{sp\sigma}}{\sqrt{3}} g_3(\vec{k}) \\
0 & E_{PG} & 0 & 0 & -\frac{V_{sp\sigma}}{\sqrt{3}} g_1(\vec{k}) & V_1\, g_0(\vec{k}) & V_2\, g_3(\vec{k}) & V_2\, g_2(\vec{k}) \\
0 & 0 & E_{PG} & 0 & -\frac{V_{sp\sigma}}{\sqrt{3}} g_2(\vec{k}) & V_2\, g_3(\vec{k}) & V_1\, g_0(\vec{k}) & V_2\, g_1(\vec{k}) \\
0 & 0 & 0 & E_{PG} & -\frac{V_{sp\sigma}}{\sqrt{3}} g_3(\vec{k}) & V_2\, g_2(\vec{k}) & V_2\, g_1(\vec{k}) & V_1\, g_0(\vec{k}) \\
 & & & & E_{SA} & 0 & 0 & 0 \\
 & \text{Hermitian} & & & 0 & E_{PA} & 0 & 0 \\
 & & & & 0 & 0 & E_{PA} & 0 \\
 & & & & 0 & 0 & 0 & E_{PA}
\end{bmatrix}
$$

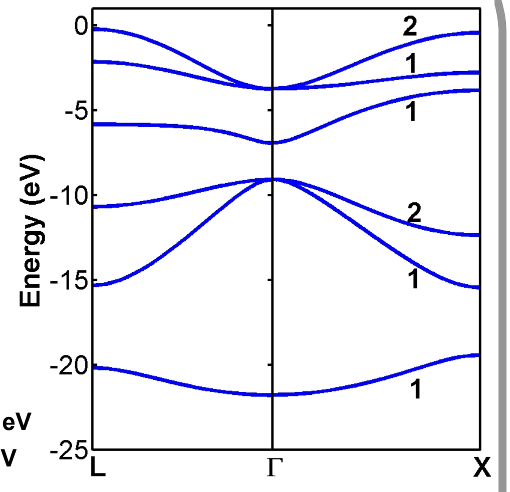
$$g_0(\vec{k}) = e^{i\vec{k}.\vec{n}_1} + e^{i\vec{k}.\vec{n}_2} + e^{i\vec{k}.\vec{n}_3} + e^{i\vec{k}.\vec{n}_4} \qquad g_2(\vec{k}) = e^{i\vec{k}.\vec{n}_1} - e^{i\vec{k}.\vec{n}_2} + e^{i\vec{k}.\vec{n}_3} - e^{i\vec{k}.\vec{n}_4}$$

$$g_1(\vec{k}) = e^{i\vec{k}.\vec{n}_1} - e^{i\vec{k}.\vec{n}_2} - e^{i\vec{k}.\vec{n}_3} + e^{i\vec{k}.\vec{n}_4} \qquad g_3(\vec{k}) = e^{i\vec{k}.\vec{n}_1} + e^{i\vec{k}.\vec{n}_2} - e^{i\vec{k}.\vec{n}_3} - e^{i\vec{k}.\vec{n}_4}$$

$$V_1 = \frac{1}{3}V_{pp\sigma} - \frac{2}{3}V_{pp\pi} \qquad V_2 = \frac{1}{3}V_{pp\sigma} + \frac{1}{3}V_{pp\pi}$$

Tight Binding Solution for GaAs





Tight Binding Solution

Parameter values for GaAs:

$E_{SG} = -11.37$ eV $\qquad E_{SA} = -17.33$ eV

$E_{PG} = -4.90$ eV $\qquad E_{PA} = -7.91$ eV

$V_{ss\sigma} = 1.70$ eV $\qquad V_{pp\sigma} = 3.44$ eV

$V_{sp\sigma} = 2.15$ eV $\qquad V_{pp\pi} = 0.89$ eV

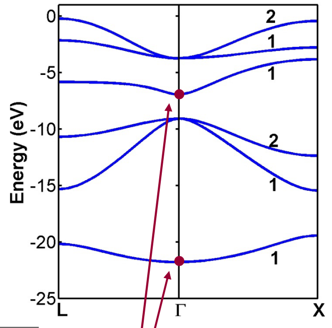
Tight Binding Solution for GaAs: States at the Γ-Point

At the Γ-point:

$$g_0(\vec{k}=0)=4$$

$$g_1(\vec{k})=g_2(\vec{k})=g_3(\vec{k})=0$$

⇒ **Energy eigenvalues can be found analytically**



Two of the eigenvalues at the Γ-point are:

$$E_{\substack{5\\1}}(\vec{k}=0)=\left(\frac{E_{SG}+E_{SA}}{2}\right)\pm\sqrt{\left(\frac{E_{SG}-E_{SGA}}{2}\right)^2+(4V_{ss\sigma})^2}$$

The Bloch function of the lowest energy band and of the conduction band at Γ-point are made up of ONLY s-orbitals from the Ga and As atoms

$$\psi_{c,\vec{k}=0}(\vec{r})=\sum_m\frac{1}{\sqrt{N}}\left[c_1\,|\phi_1(\vec{r}-\vec{R}_m)\rangle+c_5\,|\phi_5(\vec{r}-\vec{R}_m-\vec{d}_2)\rangle\right]$$

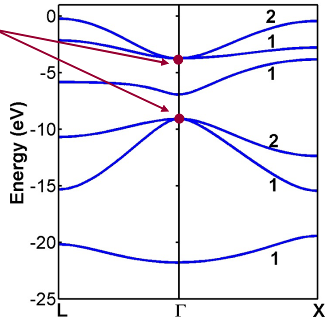
Tight Binding Solution for GaAs: States at the Γ-Point

Six remaining eigenvalues at the Γ-point are:

$$E_{\substack{678\\234}}(\vec{k}=0)=\left(\frac{E_{PG}+E_{PA}}{2}\right)\pm\sqrt{\left(\frac{E_{PG}-E_{PA}}{2}\right)^2+(4V_1)^2}$$

Each eignevalue above is triply degenerate

The Bloch function of the highest three energy bands and of the three valence bands at Γ-point are made up of ONLY p-orbitals from the Ga and As atoms



$$\psi_{v,\vec{k}=0}(\vec{r})=\sum_m\frac{1}{\sqrt{N}}\left[\begin{array}{l}\sum_{j=2}^{4}c_j\,|\phi_j(\vec{r}-\vec{R}_m)\rangle\\ \qquad+\sum_{j=6}^{8}c_j\,|\phi_j(\vec{r}-\vec{R}_m-\vec{d}_2)\rangle\end{array}\right]$$

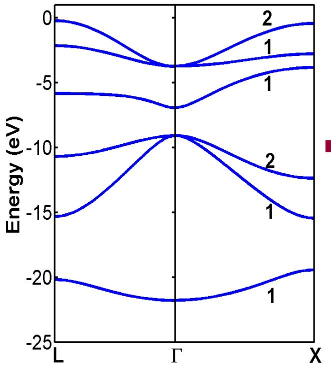
Improved Tight Binding Approaches

- Need to include the effect of spin-orbit-coupling on the valence bands

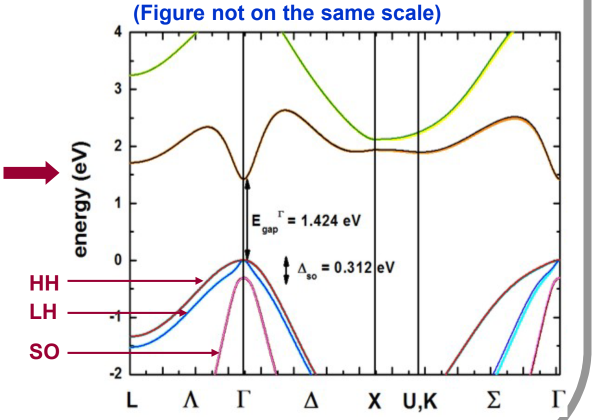
Spin orbit coupling lifts the degeneracy of the valence bands

- Need to include more orbitals (20 per primitive cell as opposed to 8 per primitive cell)
- Use better parameter values

Simplest TB Approach



Improved TB Approach with SO-Coupling (Figure not on the same scale)



Spin-Orbit Interaction in Solids

An electron moving in an electric field sees an effective magnetic field given by:

$$\vec{B}_{eff} = \frac{\vec{E} \times \vec{P}}{2mc^2} \longrightarrow$$

The additional factor of 2 is coming from Thomas precession

The electron has a magnetic moment $\vec{\mu}$ related to its spin angular momentum $\vec{S}$ by:

$$\vec{\mu} = -g\frac{\mu_B}{\hbar}\vec{S} \longrightarrow \hat{\vec{S}} = \frac{\hbar}{2}\hat{\vec{\sigma}} \qquad \mu_B = \frac{e\hbar}{2m} \qquad g \approx 2 \longrightarrow \hat{\vec{\mu}} = -\mu_B\hat{\vec{\sigma}}$$

$$\hat{\vec{\sigma}} = \hat{\sigma}_x\hat{x} + \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z} \quad \left\{ \hat{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \hat{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right.$$

The interaction between the electron spin and the effective magnetic field adds a new term to the Hamiltonian:

$$\hat{H}_{so} = -\vec{\mu}.\vec{B}_{eff} = \mu_B\hat{\vec{\sigma}}.\vec{B}_{eff} = \mu_B\hat{\vec{\sigma}}\,.\,\frac{1}{2mc^2}\left[\frac{\nabla V(\hat{\vec{r}})}{e} \times \hat{\vec{P}}\right] = \frac{\hbar}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla V(\hat{\vec{r}}) \times \hat{\vec{P}}\right]$$

Spin-Orbit Interaction in Solids: Simplified Treatment

Near an atom, where electrons spend most of their time, the potential varies mostly only in the radial direction away from the atom. Therefore:

$$\hat{H}_{so} = \frac{\hbar}{4m^2c^2}\hat{\vec{\sigma}}\cdot\left[\nabla V\left(\hat{\vec{r}}\right)\times\hat{\vec{P}}\right] = \frac{\hbar}{4m^2c^2}\frac{1}{r}\frac{\partial V(r)}{\partial r}\hat{\vec{\sigma}}\cdot\left[\hat{\vec{r}}\times\hat{\vec{P}}\right]$$

$$= \frac{\hbar}{4m^2c^2}\frac{1}{r}\frac{\partial V(r)}{\partial r}\hat{\vec{\sigma}}\cdot\hat{\vec{L}} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{\partial V(r)}{\partial r}\hat{\vec{S}}\cdot\hat{\vec{L}}$$

$\hat{\vec{L}} = \hat{\vec{r}}\times\hat{\vec{P}}$ is the orbital angular momentum of an electron near an atom

Recall from quantum mechanics that the total angular momentum $\hat{\vec{J}}$ is:

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$$

$$\Rightarrow \hat{J}^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{\vec{S}}.\hat{\vec{L}}$$

$$\Rightarrow \hat{\vec{S}}.\hat{\vec{L}} = \frac{1}{2}\left[\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right]$$

Therefore:

$$\hat{H}_{so} = \frac{1}{4m^2c^2}\frac{1}{r}\frac{\partial V(r)}{\partial r}\left[\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right]$$

Spin-Orbit Interaction in Solids: Simplified Treatment

For an electron in a p-orbital:

$$\left\langle \phi_p(\vec{r})\right|\hat{L}^2\left|\phi_p(\vec{r})\right\rangle = \hbar^2\ell(\ell+1) = 2\hbar$$

For an electron in a s-orbital:

$$\left\langle \phi_s(\vec{r})\right|\hat{L}^2\left|\phi_s(\vec{r})\right\rangle = \hbar^2\ell(\ell+1) = 0$$

And we always have for an electron:

$$\left\langle \hat{S}^2\right\rangle = \hbar^2 s(s+1) = \frac{3}{4}\hbar^2$$

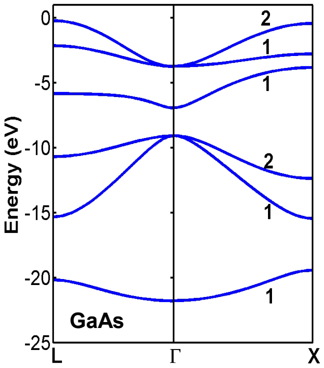
If the electron is in s-orbital then: $\left\langle \hat{J}^2 - \hat{L}^2 - \hat{S}^2\right\rangle = 0 \quad\Rightarrow\quad \left\langle \hat{H}_{so}\right\rangle = 0$

If the electron is in p-orbital then: $\left\langle \hat{J}^2 - \hat{L}^2 - \hat{S}^2\right\rangle \neq 0 \quad\Rightarrow\quad \left\langle \hat{H}_{so}\right\rangle \neq 0$

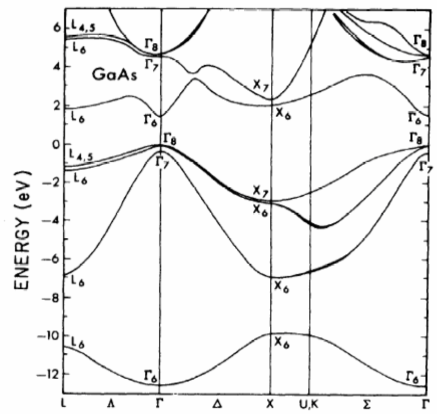
⇒ The energies of the Bloch states made up of p-orbitals (like in the case of the three degenerate valence bands at the Γ point in GaAs) will be most affected by spin-orbit coupling

Tight Binding Vs Pseudopotential Technique

Simplest TB Approach

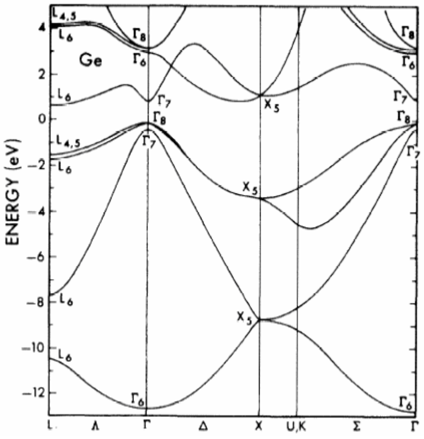


A Little More Sophisticated Approach
Nonlocal Pseudopotential Method

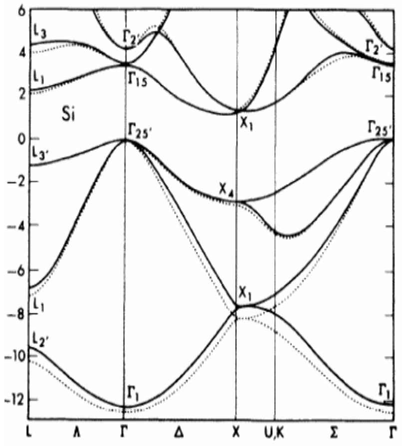


GaAs Energy Bands
(Chelikowski and Cohen, 1976)

Energy Bands of Silicon and Germanium



Germanium Energy Bands
(Chelikowski and Cohen, 1976)



Silicon Energy Bands
(Chelikowski and Cohen, 1976)

Appendix: Spin-Orbit Interaction and Bloch Functions

In the absence of spin-orbit interaction we had:

$$\hat{H}_o \psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\, \psi_{n,\vec{k}}(\vec{r})$$

$$\left[-\frac{\hbar^2 \nabla_{\vec{r}}^2}{2m} + V(\vec{r})\right] \psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\, \psi_{n,\vec{k}}(\vec{r})$$

Electron states with spin-up and spin-down were degenerate $\left\{ E_{n,\uparrow}(\vec{k}) = E_{n,\downarrow}(\vec{k}) \right.$

In the presence of spin-orbit coupling the Hamiltonian becomes:

$$\hat{H} = \hat{H}_o + \hat{H}_{so}$$

$$\hat{H}_{so} = \frac{\hbar}{4m^2c^2}\, \hat{\vec{\sigma}} \,.\, \left[\nabla_{\vec{r}} V(\hat{\vec{r}}) \times \hat{\vec{P}}\right] = -i\, \frac{\hbar^2}{4m^2c^2}\, \hat{\vec{\sigma}} \,.\, \left[\nabla_{\vec{r}} V(\hat{\vec{r}}) \times \vec{\nabla}_{\vec{r}}\right]$$

Since the Hamiltonian is now spin-dependent, pure spin-up or pure spin-down states are no longer the eigenstates of the Hamiltonian

The eigenstates can be written most generally as a superposition of up and down spin states, or:

$$\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = \alpha_{n,\vec{k}}(\vec{r})\left|\uparrow\right\rangle + \beta_{n,\vec{k}}(\vec{r})\left|\downarrow\right\rangle$$

χ **=Quantum number for the two spin degrees of freedom, usually taken to be +1 or -1**

Appendix: Spin-Orbit Interaction and Bloch Functions

$$\hat{H} \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = E_{n,\chi}(\vec{k}) \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

$$\left\{-\frac{\hbar^2 \nabla_{\vec{r}}^2}{2m} + V(\vec{r}) - i\, \frac{\hbar^2}{4m^2c^2}\, \hat{\vec{\sigma}} \,.\, \left[\nabla_{\vec{r}} V(\hat{\vec{r}}) \times \vec{\nabla}_{\vec{r}}\right]\right\} \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = E_{n,\chi}(\vec{k}) \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

For each wavevector in the FBZ, and for each band index, one will obtain two solutions of the above equation

We label one as χ = +1 and the other with χ = -1 and in general $E_{n,-\chi}(\vec{k}) \neq E_{n,\chi}(\vec{k})$

These two solutions will correspond to spins pointing in two different directions (usually collinear and opposite directions). Let these directions be specified by $\hat{n}$ at the location $\vec{r}$:

$$\hat{\vec{\sigma}}.\hat{n}\, \psi_{n,\vec{k},\chi}(\vec{r}) = +1\, \psi_{n,\vec{k},\chi}(\vec{r})$$

$$\hat{\vec{\sigma}}.\hat{n}\, \psi_{n,\vec{k},-\chi}(\vec{r}) = -1\, \psi_{n,\vec{k},-\chi}(\vec{r})$$

Appendix: Spin-Orbit Interaction and Lattice Symmetries

In the presence of spin-orbit interaction we have the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\,.\left[\nabla_{\vec r}V(\hat{\vec r})\times\vec\nabla_{\vec r}\right]\right\}\begin{bmatrix}\alpha_{n,\vec k}(\vec r)\\ \beta_{n,\vec k}(\vec r)\end{bmatrix}=E_{n,\chi}(\vec k)\begin{bmatrix}\alpha_{n,\vec k}(\vec r)\\ \beta_{n,\vec k}(\vec r)\end{bmatrix}$$

Lattice Translation Symmetry:

$$\psi_{n,\vec k,\chi}(\vec r+\vec R)=\begin{bmatrix}\alpha_{n,\vec k}(\vec r+\vec R)\\ \beta_{n,\vec k}(\vec r+\vec R)\end{bmatrix}=\begin{bmatrix}e^{i\vec k.\vec R}\alpha_{n,\vec k}(\vec r)\\ e^{i\vec k.\vec R}\beta_{n,\vec k}(\vec r)\end{bmatrix}=e^{i\vec k.\vec R}\psi_{n,\vec k,\chi}(\vec r)$$

Rotation Symmetry:

Let $\hat S$ be an operator belonging to the rotation subgroup of the crystal point-group, such that:

$$V(\hat S\vec r)=V(\vec r) \qquad \left\{\hat S^T=\vec S^{-1}\Rightarrow \text{unitary}\right.$$

(The case of inversion symmetry will be treated separately)

Appendix: Spin-Orbit Interaction and Rotation Symmetry

Suppose we have found the solution to the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\,.\left[\nabla_{\vec r}V(\hat{\vec r})\times\vec\nabla_{\vec r}\right]\right\}\begin{bmatrix}\alpha_{n,\vec k}(\vec r)\\ \beta_{n,\vec k}(\vec r)\end{bmatrix}=E_{n,\chi}(\vec k)\begin{bmatrix}\alpha_{n,\vec k}(\vec r)\\ \beta_{n,\vec k}(\vec r)\end{bmatrix}$$

And the solution is:

$$\psi_{n,\vec k,\chi}(\vec r)=\begin{bmatrix}\alpha_{n,\vec k}(\vec r)\\ \beta_{n,\vec k}(\vec r)\end{bmatrix}\quad\Leftrightarrow\quad E_{n,\chi}(\vec k)$$

We replace $\vec r$ by $\hat S\vec r$ everywhere in the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\hat S\vec r}^2}{2m}+V(\hat S\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\,.\left[\nabla_{\hat S\vec r}V(\hat S\hat{\vec r})\times\vec\nabla_{\hat S\vec r}\right]\right\}\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}=E_{n,\chi}(\vec k)\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}$$

$$\Rightarrow\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\,.\,\hat S\left[\nabla_{\vec r}V(\hat{\vec r})\times\vec\nabla_{\vec r}\right]\right\}\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}=E_{n,\chi}(\vec k)\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}$$

Appendix: Spin-Orbit Interaction and Rotation Symmetry

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\,\hat{S}\left[\nabla_{\vec{r}}V\left(\hat{\vec{r}}\right)\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}=E_{n,\chi}\left(\vec{k}\right)\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}$$

The above equation does not look like the Schrodinger equation!

We define a unitary spin rotation operator $\hat{R}_{\hat{S}}$ that operates in the Hilbert space of spins and rotates spin states in the sense of the operator $\hat{S}$

Consider a spin vector pointing in the $\hat{n}$ direction:

$$\hat{\vec{\sigma}}.\hat{n}\begin{bmatrix}a\\ b\end{bmatrix}=+1\begin{bmatrix}a\\ b\end{bmatrix}$$

$$\Rightarrow\hat{\vec{\sigma}}.\hat{n}\hat{R}_{\hat{S}}^{-1}\hat{R}_{\hat{S}}\begin{bmatrix}a\\ b\end{bmatrix}=+1\begin{bmatrix}a\\ b\end{bmatrix}$$

$$\Rightarrow\hat{R}_{\hat{S}}\hat{\vec{\sigma}}.\hat{n}\hat{R}_{\hat{S}}^{-1}\hat{R}_{\hat{S}}\begin{bmatrix}a\\ b\end{bmatrix}=+1\,\hat{R}_{\hat{S}}\begin{bmatrix}a\\ b\end{bmatrix}$$

$$\Rightarrow\left(\hat{\vec{\sigma}}.\hat{S}\hat{n}\right)\hat{R}_{\hat{S}}\begin{bmatrix}a\\ b\end{bmatrix}=+1\hat{R}_{\hat{S}}\begin{bmatrix}a\\ b\end{bmatrix}$$

The spin rotation operators have the property: $\hat{R}_{\hat{S}}\left(\hat{\vec{\sigma}}.\hat{n}\right)\hat{R}_{\hat{S}}^{-1}=\hat{\vec{\sigma}}.\hat{S}\hat{n}$

Appendix: Spin-Orbit Interaction and Point-Group Symmetry

Start from:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\,\hat{S}\left[\nabla_{\vec{r}}V\left(\hat{\vec{r}}\right)\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}=E_{n,\chi}\left(\vec{k}\right)\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}$$

Introduce spin rotation operator $\hat{R}_{\hat{S}}$ corresponding to the rotation generated by the matrix $\hat{S}$:

$$\hat{R}_{\hat{S}}^{-1}\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\,\hat{S}\left[\nabla_{\vec{r}}V\left(\hat{\vec{r}}\right)\times\vec{\nabla}_{\vec{r}}\right]\right\}\hat{R}_{\hat{S}}\hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}=E_{n,\chi}\left(\vec{k}\right)\hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}$$

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V\left(\hat{\vec{r}}\right)\times\vec{\nabla}_{\vec{r}}\right]\right\}\hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}=E_{n,\chi}\left(\vec{k}\right)\hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}$$

The above equation shows that the new state:

$$\hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}$$

satisfies the Schrodinger equation and has the same energy as the state: $\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$

Appendix: Spin-Orbit Interaction and Point-Group Symmetry

Since:

$$\hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}(\vec{r}+\vec{R})\right)\\ \beta_{n,\vec{k}}\left(\hat{S}(\vec{r}+\vec{R})\right)\end{bmatrix}=e^{i\vec{k}.\hat{S}\vec{R}}\,\hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}=e^{i\hat{S}^{-1}\vec{k}.\vec{R}}\,\hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}$$

The new state is a Bloch state with wavevector $\hat{S}^{-1}\vec{k}$

Summary:

If $\hat{S}$ is an operator for a point-group symmetry operation then the two states given by:

$$\psi_{n,\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

$$\psi_{n,\hat{S}^{-1}\vec{k},\chi'}(\vec{r})=\hat{R}_{\hat{S}}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}$$

This represents a rotated (in space) version of the original Bloch state. Even the spin is rotated appropriately by the spin rotation operator.

have the same energy:

$$E_{n,\chi'}\left(\hat{S}^{-1}\vec{k}\right)=E_{n,\chi}\left(\vec{k}\right)$$

Appendix: Spin-Orbit Interaction and Inversion Symmetry

Suppose the crystal potential has inversion symmetry:

$$V(-\vec{r})=V(\vec{r})$$

Suppose we have found the solution to the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V\left(\hat{\vec{r}}\right)\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}=E_{n,\chi}\left(\vec{k}\right)\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

And the solution is:

$$\psi_{n,\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}\qquad\Leftrightarrow\qquad E_{n,\chi}\left(\vec{k}\right)$$

We replace $\vec{r}$ by $-\vec{r}$ everywhere in the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{-\vec{r}}^2}{2m}+V(-\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{-\vec{r}}V\left(-\hat{\vec{r}}\right)\times\vec{\nabla}_{-\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}=E_{n,\chi}\left(\vec{k}\right)\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

$$\Rightarrow\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V\left(\hat{\vec{r}}\right)\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}=E_{n,\chi}\left(\vec{k}\right)\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

Appendix: Spin-Orbit Interaction and Inversion Symmetry

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\,.\left[\nabla_{\vec r}V(\hat{\vec r})\times\vec\nabla_{\vec r}\right]\right\}\begin{bmatrix}\alpha_{n,\vec k}(-\vec r)\\ \beta_{n,\vec k}(-\vec r)\end{bmatrix}=E_{n,\chi}(\vec k)\begin{bmatrix}\alpha_{n,\vec k}(-\vec r)\\ \beta_{n,\vec k}(-\vec r)\end{bmatrix}$$

The above equation shows that the new state: $\begin{bmatrix}\alpha_{n,\vec k}(-\vec r)\\ \beta_{n,\vec k}(-\vec r)\end{bmatrix}$

satisfies the Schrodinger equation and has the same energy as the state: $\begin{bmatrix}\alpha_{n,\vec k}(\vec r)\\ \beta_{n,\vec k}(\vec r)\end{bmatrix}$

Since:

$$\begin{bmatrix}\alpha_{n,\vec k}\left(-\left(\vec r+\vec R\right)\right)\\ \beta_{n,\vec k}\left(-\left(\vec r+\vec R\right)\right)\end{bmatrix}=e^{i\left(-\vec k\right).\vec R}\begin{bmatrix}\alpha_{n,\vec k}(-\vec r)\\ \beta_{n,\vec k}(-\vec r)\end{bmatrix}$$

the new state is a Bloch state with wavevector $-\vec k$

In most cases, the new state: $\begin{bmatrix}\alpha_{n,\vec k}(-\vec r)\\ \beta_{n,\vec k}(-\vec r)\end{bmatrix}$

has the same spin direction as the state: $\begin{bmatrix}\alpha_{n,\vec k}(\vec r)\\ \beta_{n,\vec k}(\vec r)\end{bmatrix}$

So we can write: $\psi_{n,-\vec k,\chi}(\vec r)=\begin{bmatrix}\alpha_{n,\vec k}(-\vec r)\\ \beta_{n,\vec k}(-\vec r)\end{bmatrix}$

Appendix: Spin-Orbit Interaction and Inversion Symmetry

Summary:

If the crystal potential has inversion symmetry then the two states given by:

$$\psi_{n,\vec k,\chi}(\vec r)=\begin{bmatrix}\alpha_{n,\vec k}(\vec r)\\ \beta_{n,\vec k}(\vec r)\end{bmatrix}\qquad\qquad \psi_{n,-\vec k,\chi}(\vec r)=\begin{bmatrix}\alpha_{n,\vec k}(-\vec r)\\ \beta_{n,\vec k}(-\vec r)\end{bmatrix}$$

have the same energy:

$$E_{n,\chi}\left(-\vec k\right)=E_{n,\chi}\left(\vec k\right)$$

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

Consider the Bloch function:

$$\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = \alpha_{n,\vec{k}}(\vec{r})|\uparrow\rangle + \beta_{n,\vec{k}}(\vec{r})|\downarrow\rangle$$

Suppose the Bloch function corresponds to the spin pointing in the direction of the unit vector $\hat{n}$ at the location $\vec{r}$:

$$\hat{\vec{\sigma}}.\hat{n}\,\psi_{n,\vec{k},\chi}(\vec{r}) = \hat{\vec{\sigma}}.\hat{n}\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = +1\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = +1\,\psi_{n,\vec{k},\chi}(\vec{r})$$

What if we want the state with the opposite spin at the same location?

The answer is:

$$-i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix} -\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

Proof:

$$\hat{\vec{\sigma}}.\hat{n}\left[-i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r})\right] = -i\left[-\hat{\vec{\sigma}}^*.\hat{n}\,\hat{\sigma}_y\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^*$$
$$= -i\left[-\hat{\sigma}_y\hat{\sigma}_y\hat{\vec{\sigma}}^*.\hat{n}\,\hat{\sigma}_y\hat{\sigma}_y\hat{\sigma}_y\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^* = -i\left[\hat{\sigma}_y\hat{\vec{\sigma}}.\hat{n}\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^*$$
$$= -i\left[\hat{\sigma}_y\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^* = -1\left[-i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r})\right]$$

$$\left\{\hat{\vec{\sigma}} = \hat{\sigma}_x\hat{x} + \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z} \quad \Rightarrow \quad \hat{\vec{\sigma}}^* = \hat{\sigma}_x\hat{x} - \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z} \neq \hat{\vec{\sigma}}\right\}$$

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

In the presence of spin-orbit interaction we have the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}.\left[\nabla V(\hat{\vec{r}}) \times \vec{\nabla}\right]\right\}\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = E_{n,\chi}(\vec{k})\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

Suppose we have solved it and found the solution: $\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} \Leftrightarrow E_{n,\chi}(\vec{k})$

We complex conjugate it:

$$\left\{-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r}) + i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^*.\left[\nabla V(\hat{\vec{r}}) \times \vec{\nabla}\right]\right\}\begin{bmatrix} \alpha^*_{n,\vec{k}}(\vec{r}) \\ \beta^*_{n,\vec{k}}(\vec{r}) \end{bmatrix} = E_{n,\chi}(\vec{k})\begin{bmatrix} \alpha^*_{n,\vec{k}}(\vec{r}) \\ \beta^*_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

It does not look like the original Schrodinger equation!

Note that:

$$\hat{\vec{\sigma}} = \hat{\sigma}_x\hat{x} + \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z}$$

$$\Rightarrow \hat{\vec{\sigma}}^* = \hat{\sigma}_x\hat{x} - \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z} \neq \hat{\vec{\sigma}}$$

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

Given an eigenvalue matrix equation:

$$Av = \lambda v$$

One can always perform a unitary transformation with matrix T and obtain:

$$\begin{aligned} TAT^{-1}Tv &= \lambda Tv \\ \Rightarrow Bu &= \lambda u \end{aligned} \qquad \left\{ \begin{aligned} B &= TAT^{-1} \\ u &= Tv \end{aligned} \right.$$

So try a transformation with the unitary matrix $-i\hat{\sigma}_y$ with the equation:

$$(-i\hat{\sigma}_y)\left\{-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r}) + i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^* . \left[\nabla V(\hat{\vec{r}}) \times \vec{\nabla}\right]\right\}(+i\hat{\sigma}_y)(-i\hat{\sigma}_y)\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r}) \\ \beta^*_{n,\vec{k}}(\vec{r})\end{bmatrix} = E_{n,\chi}(\vec{k})(-i\hat{\sigma}_y)\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r}) \\ \beta^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

$$\Rightarrow \left\{-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}} . \left[\nabla V(\hat{\vec{r}}) \times \vec{\nabla}\right]\right\}\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix} = E_{n,\chi}(\vec{k})\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

We have found a new solution: $\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$

with the same energy $E_{n,\chi}(\vec{k})$ as the original solution: $\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$

Question: What is the physical significance of the new solution?

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

Under lattice translation we get for the new solution:

$$\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}+\vec{R}) \\ \alpha^*_{n,\vec{k}}(\vec{r}+\vec{R})\end{bmatrix} = e^{-i\vec{k}.\vec{R}}\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

So the new solution is a Bloch state with wavevector $-\vec{k}$

$$\psi_{n,-\vec{k},?}(\vec{r}) = \begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

Note that the new solution found can also be written as:

$$-i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

But as shown earlier, the above state has spin opposite to the state $\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$

Therefore, the new solution is a Bloch state $\psi_{n,-\vec{k},-\chi}(\vec{r})$, i.e.:

$$\psi_{n,-\vec{k},-\chi}(\vec{r}) = -i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

And we have also found that its energy is the same as that of the state $\psi_{n,\vec{k},\chi}(\vec{r})$:

$$E_{n,-\chi}(-\vec{k}) = E_{n,\chi}(\vec{k})$$

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

In the presence of spin-orbit interaction we have the time-dependent Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},t)\\ \beta_{n,\vec{k}}(\vec{r},t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},t)\\ \beta_{n,\vec{k}}(\vec{r},t)\end{bmatrix}$$

Solution is:

$$\psi_{n,\vec{k},\chi}(\vec{r},t)=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},t)\\ \beta_{n,\vec{k}}(\vec{r},t)\end{bmatrix}=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\\ \beta_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\end{bmatrix}=\psi_{n,\vec{k},\chi}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}$$

Lets see if we can find a solution under time-reversal (i.e. when *t* is replaced by –*t*):

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},-t)\\ \beta_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=-i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},-t)\\ \beta_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}$$

The above does not look like a Schrodinger equation so we complex conjugate it:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})+i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^*\,.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}$$

And it still does not look like the original Schrodinger equation!

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

Given an eigenvalue matrix equation:

$$Av=\lambda v$$

One can always perform a unitary transformation with matrix *T* and obtain:

$$\begin{aligned}&TAT^{-1}Tv=\lambda Tv\\ &\Rightarrow Bu=\lambda u\end{aligned}\qquad\left\{\begin{aligned}&B=TAT^{-1}\\ &u=Tv\end{aligned}\right.$$

So try a transformation with the unitary matrix $-i\hat{\sigma}_y$ with the equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})+i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^*\,.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}$$

$$\left(-i\hat{\sigma}_y\right)\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})+i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^*\,.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\left(+i\hat{\sigma}_y\right)\left(-i\hat{\sigma}_y\right)\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\left(-i\hat{\sigma}_y\right)\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}$$

$$\Rightarrow\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r},-t)\\ \alpha^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r},-t)\\ \alpha^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}$$

The above equation now looks like the time-dependent Schrodinger equation

Appendix: Spin-Orbit Interaction and Time Reversal Symmetry

Summary:

Corresponding to the Bloch state:

$$\psi_{n,\vec{k},\chi}(\vec{r},t)=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},t)\\ \beta_{n,\vec{k}}(\vec{r},t)\end{bmatrix}=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\\ \beta_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\end{bmatrix}=\psi_{n,\vec{k},\chi}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}$$

with energy:

$$E_{n,\chi}(\vec{k})$$

the time-reversed Bloch state is:

$$\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r},-t)\\ \alpha^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\\ \alpha^*_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\end{bmatrix}=\psi_{n,-\vec{k},-\chi}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}$$

and the time-reversed state has the same energy as the original state:

$$E_{n,-\chi}(-\vec{k})=E_{n,\chi}(\vec{k})$$

Appendix: Crystal Inversion Symmetry and Time Reversal Symmetry

Time reversal symmetry implies:

$$E_{n,-\chi}(-\vec{k})=E_{n,\chi}(\vec{k})$$

Inversion symmetry implies:

$$E_{n,\chi}(-\vec{k})=E_{n,\chi}(\vec{k})$$

In crystals which have inversion and time reversal symmetries the above two imply:

$$E_{n,-\chi}(\vec{k})=E_{n,\chi}(\vec{k}) \longrightarrow$$

There is spin degeneracy!

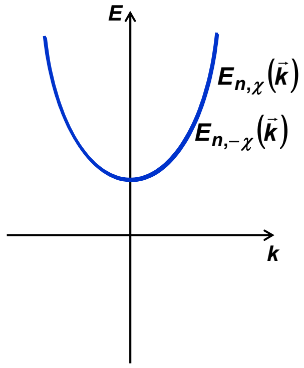
In crystals which do not have inversion symmetry the above two do not guarantee spin degeneracy. In general:

$$E_{n,-\chi}(\vec{k})\neq E_{n,\chi}(\vec{k}) \longrightarrow$$

Bands with different spins can have different energy dispersion relations

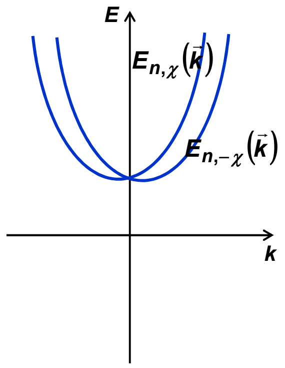
Appendix: Crystal Inversion Symmetry and Time Reversal Symmetry

Cartoon (and much exaggerated) sketches of the conduction bands of Ge and GaAs are shown below:



Ge

$$E_{n,-\chi}(\vec{k}) = E_{n,\chi}(\vec{k})$$



GaAs

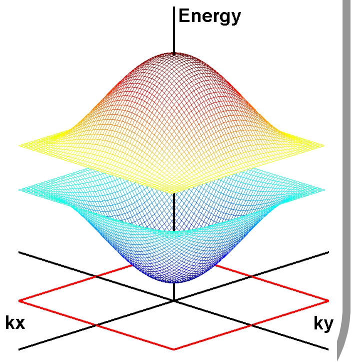
$$E_{n,-\chi}(\vec{k}) \neq E_{n,\chi}(\vec{k})$$

Handout on

Crystal Symmetries and Energy Bands

In this lecture you will learn:

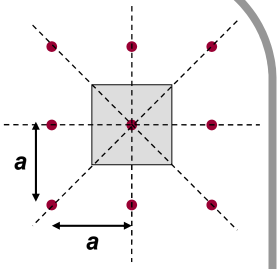
- The relationship between symmetries and energy bands in the absence of spin-orbit coupling
- The relationship between symmetries and energy bands in the presence of spin-orbit coupling



Symmetry and Energy Bands

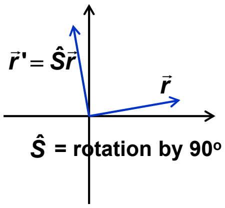
The crystal potential $V(\vec{r})$ generally has certain other symmetries in addition to the lattice translation symmetry:

$$V(\vec{r}+\vec{R})=V(\vec{r})$$



For example, the 2D potential of a square atomic lattice, as shown, has the following symmetries:

a) Symmetry under rotations by 90, 180, and 270 degrees
b) Symmetry under reflections w.r.t. x-axis and y-axis
c) Symmetry under reflections w.r.t. the two diagonals

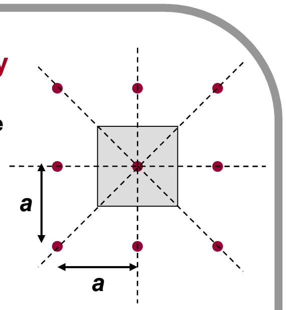


Let $\hat{S}$ be the operator (in matrix representation) for any one of these symmetry operations then:

$$\vec{r}\,'=\hat{S}\vec{r}$$

$$\Rightarrow V(\hat{S}\vec{r})=V(\vec{r})$$

Crystal Point-Group Symmetry

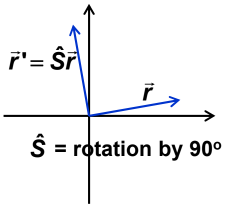


Point-Group Symmetry

The point group symmetry operation of a lattice are all those operations that leave the lattice unchanged and at least one point of the lattice remains unmoved under the operation

Point group symmetry operations can include:

i) Rotations (w.r.t. to axes of rotation)
ii) Reflections (across lines or planes)
iii) Inversions (w.r.t. to a point)



$\hat{S}$ = rotation by 90°

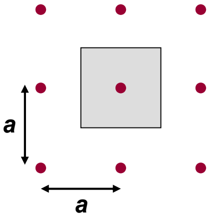
Let $\hat{S}$ be the operator for a point-group symmetry operation, such that:

$$V\left(\hat{S}\vec{r}\right) = V(\vec{r})$$

The operator $\hat{S}$ is unitary:

$$\hat{S}^T = \hat{S}^{-1} \Rightarrow \text{unitary}$$

Crystal Point-Group Symmetry and Energy Bands



Let $\hat{S}$ be the operator for a point-group symmetry operation, such that:

$$\vec{r}\,' = \hat{S}\vec{r} \qquad \left\{\hat{S}^T = \hat{S}^{-1} \Rightarrow \text{unitary}\right.$$

$$\Rightarrow V\left(\hat{S}\vec{r}\right) = V(\vec{r})$$

Suppose one has solved the Shrodinger equation and obtained the energy and wavefunction of a Bloch State $\psi_{n,\vec{k}}(\vec{r})$

$$\left[-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r})\right]\psi_{n,\vec{k}}(\vec{r}) = E_n\left(\vec{k}\right)\psi_{n,\vec{k}}(\vec{r})$$

Now replace $\vec{r}$ by $\hat{S}\vec{r}$ everywhere in the Schrodinger equation:

$$\left[-\frac{\hbar^2\nabla^2_{\hat{S}\vec{r}}}{2m} + V\left(\hat{S}\vec{r}\right)\right]\psi_{n,\vec{k}}\left(\hat{S}\vec{r}\right) = E_n\left(\vec{k}\right)\psi_{n,\vec{k}}\left(\hat{S}\vec{r}\right) \longrightarrow \left\{\begin{array}{l}\nabla^2_{\hat{S}\vec{r}} = \nabla^2_{\vec{r}} \\ \text{Laplacian is invariant}\end{array}\right.$$

$$\Rightarrow \left[-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r})\right]\psi_{n,\vec{k}}\left(\hat{S}\vec{r}\right) = E_n\left(\vec{k}\right)\psi_{n,\vec{k}}\left(\hat{S}\vec{r}\right)$$

Crystal Point-Group Symmetry and Energy Bands

$$\left[-\frac{\hbar^2\nabla^2}{2m}+V(\hat{S}\vec{r})\right]\psi_{n,\vec{k}}(\hat{S}\vec{r})=E_n(\vec{k})\psi_{n,\vec{k}}(\hat{S}\vec{r})\Rightarrow\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi_{n,\vec{k}}(\hat{S}\vec{r})=E_n(\vec{k})\psi_{n,\vec{k}}(\hat{S}\vec{r})$$

The above equation says that the function $\psi_{n,\vec{k}}(\hat{S}\vec{r})$ is also a Bloch state with the same energy as $\psi_{n,\vec{k}}(\vec{r})$ (we have found a new eigenfunction!)

The question is if we really have found a new eigenfunction or not, and if so what is the wavevector of this new eigenfunction

We know that Bloch functions have the property that: $\psi_{n,\vec{k}}(\vec{r}+\vec{R})=e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})$

So we try this on $\psi_{n,\vec{k}}(\hat{S}\vec{r})$:

$$\psi_{n,\vec{k}}(\hat{S}(\vec{r}+\vec{R}))=\psi_{n,\vec{k}}(\hat{S}\vec{r}+\hat{S}\vec{R}) \longrightarrow \left\{\ \hat{S}\vec{R}\ \text{is also a lattice vector}\right.$$

$$=e^{i\,\vec{k}\,.\,\hat{S}\vec{R}}\,\psi_{n,\vec{k}}(\hat{S}\vec{r})=e^{i\left[\hat{S}^{-1}\vec{k}\right].\vec{R}}\,\psi_{n,\vec{k}}(\hat{S}\vec{r}) \longrightarrow \left\{\ \vec{k}.(\hat{S}\vec{R})=(\hat{S}^{-1}\vec{k}).\vec{R}\right.$$

$\Rightarrow$ $\psi_{n,\vec{k}}(\hat{S}\vec{r})$ **is a Bloch function with wavevector** $\hat{S}^{-1}\vec{k}$ **and energy** $E_n(\vec{k})$

$$\Rightarrow\psi_{n,\vec{k}}(\hat{S}\vec{r})=\psi_{n,\hat{S}^{-1}\vec{k}}(\vec{r})$$

Crystal Point-Group Symmetry and Energy Bands

So we finally have for the symmetry operation $\hat{S}$:

$$\Rightarrow\psi_{n,\vec{k}}(\hat{S}\vec{r})=\psi_{n,\hat{S}^{-1}\vec{k}}(\vec{r})$$

We also know that the eigenenergy of $\psi_{n,\hat{S}^{-1}\vec{k}}(\vec{r})$ is $E_n(\vec{k})$
Therefore:

$$E_n(\hat{S}^{-1}\vec{k})=E_n(\vec{k})$$

Or, equivalently:

$$E_n(\hat{S}\vec{k})=E_n(\vec{k})$$

Important Lessons:

1) If $\hat{S}$ is a symmetry of the potential such that in real-space we have:

$$V(\hat{S}\vec{r})=V(\vec{r})$$

then the energy bands also enjoy the symmetry of the potential such that in k-space:

$$E_n(\hat{S}\vec{k})=E_n(\vec{k})$$

2) Degeneracies in the energy bands can therefore arise from crystal point-group symmetries!

Time Reversal Symmetry and Energy Bands

Suppose we have solved the time dependent Schrodinger and obtained the Bloch state $\psi_{n,\vec{k}}(\vec{r})$ with energy $E_n(\vec{k})$:

$$\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi_{n,\vec{k}}(\vec{r},t)=i\hbar\frac{\partial\psi_{n,\vec{k}}(\vec{r},t)}{\partial t}\quad\longrightarrow\quad\psi_{n,\vec{k}}(\vec{r},t)=\psi_{n,\vec{k}}(\vec{r})\,e^{-i\frac{E_n(\vec{k})}{\hbar}t}$$

After plugging the solution in the time-dependent equation, we get:

$$\left[-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})\right]\psi_{n,\vec{k}}(\vec{r})=E_n(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})$$

If we take the complex conjugate of the above equation, we get:

$$\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi^*_{n,\vec{k}}(\vec{r})=E_n(\vec{k})\,\psi^*_{n,\vec{k}}(\vec{r})$$

We have found another Bloch function, i.e. $\psi^*_{n,\vec{k}}(\vec{r})$, with the same energy as $\psi_{n,\vec{k}}(\vec{r})$

Question: What is the physical significance of the state $\psi^*_{n,\vec{k}}(\vec{r})$?

Time Reversal Symmetry and Energy Bands

Suppose we have solved the time dependent Schrodinger and obtained the Bloch state $\psi_{n,\vec{k}}(\vec{r})$ with energy $E_n(\vec{k})$:

$$\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi_{n,\vec{k}}(\vec{r},t)=i\hbar\frac{\partial\psi_{n,\vec{k}}(\vec{r},t)}{\partial t}\quad\longrightarrow\quad\psi_{n,\vec{k}}(\vec{r},t)=\psi_{n,\vec{k}}(\vec{r})\,e^{-i\frac{E_n(\vec{k})}{\hbar}t}$$

Lets see if we can find a solution under time-reversal (i.e. when *t* is replaced by *–t*):

$$\Rightarrow\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi_{n,\vec{k}}(\vec{r},-t)=-i\hbar\frac{\partial\psi_{n,\vec{k}}(\vec{r},-t)}{\partial t}$$

The above does not look like a Schrodinger equation so we complex conjugate it:

$$\Rightarrow\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi^*_{n,\vec{k}}(\vec{r},-t)=i\hbar\frac{\partial\psi^*_{n,\vec{k}}(\vec{r},-t)}{\partial t}$$

This means that $\psi^*_{n,\vec{k}}(\vec{r},-t)$ is the time-reversed state corresponding to the state $\psi_{n,\vec{k}}(\vec{r},t)$

$$\psi^*_{n,\vec{k}}(\vec{r},-t)=\psi^*_{n,\vec{k}}(\vec{r})\,e^{-i\frac{E_n(\vec{k})}{\hbar}t}\quad\longrightarrow\quad\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi^*_{n,\vec{k}}(\vec{r})=E_n(\vec{k})\,\psi^*_{n,\vec{k}}(\vec{r})$$

The function $\psi^*_{n,\vec{k}}(\vec{r})$ is the time-reversed Bloch state corresponding to $\psi_{n,\vec{k}}(\vec{r})$

Time Reversal Symmetry and Energy Bands

$$\left[-\frac{\hbar^2\nabla^2}{2m}+V(\vec{r})\right]\psi^*_{n,\vec{k}}(\vec{r})=E_n(\vec{k})\psi^*_{n,\vec{k}}(\vec{r})$$

We have found another Bloch function, i.e. $\psi^*_{n,\vec{k}}(\vec{r})$, with the same energy as $\psi_{n,\vec{k}}(\vec{r})$

The question is if we really have found a new eigenfunction or not, and if so what is the wavevector of this new eigenfunction

We know that Bloch functions have the property that: $\psi_{n,\vec{k}}(\vec{r}+\vec{R})=e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})$

So we try this on $\psi^*_{n,\vec{k}}(\vec{r})$:

$$\psi^*_{n,\vec{k}}(\vec{r}+\vec{R})=\left[\psi_{n,\vec{k}}(\vec{r}+\vec{R})\right]^*=\left[e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})\right]^*=e^{i\,[-\vec{k}]\,.\,\vec{R}}\,\psi^*_{n,\vec{k}}(\vec{r})$$

$\Rightarrow$ $\psi^*_{n,\vec{k}}(\vec{r})$ is a Bloch function with wavevector $-\vec{k}$ and energy $E_n(\vec{k})$

$\Rightarrow$ $\psi_{n,-\vec{k}}(\vec{r})=\psi^*_{n,\vec{k}}(\vec{r})$ and $E_n(-\vec{k})=E_n(\vec{k})$

Important Lesson:
Time reversal symmetry implies that $E_n(-\vec{k})=E_n(\vec{k})$ even if the crystal lacks spatial inversion symmetry (e.g. GaAs, InP, etc)

Spin-Orbit Interaction in Solids

An electron moving in an electric field sees an effective magnetic field given by:

$$\vec{B}_{eff}=\frac{\vec{E}\times\vec{P}}{2mc^2}\longrightarrow$$

The additional factor of 2 is coming from Thomas precession

The electron has a magnetic moment $\vec{\mu}$ related to its spin angular momentum $\vec{S}$ by:

$$\vec{\mu}=-g\frac{\mu_B}{\hbar}\vec{S}\longrightarrow\quad\hat{\vec{S}}=\frac{\hbar}{2}\hat{\vec{\sigma}}\qquad\mu_B=\frac{e\hbar}{2m}\qquad g\approx 2\longrightarrow\quad\hat{\vec{\mu}}=-\mu_B\hat{\vec{\sigma}}$$

$$\hat{\vec{\sigma}}=\hat{\sigma}_x\hat{x}+\hat{\sigma}_y\hat{y}+\hat{\sigma}_z\hat{z}\quad\left\{\quad\hat{\sigma}_x=\begin{bmatrix}0&1\\1&0\end{bmatrix}\qquad\hat{\sigma}_y=\begin{bmatrix}0&-i\\i&0\end{bmatrix}\qquad\hat{\sigma}_z=\begin{bmatrix}1&0\\0&-1\end{bmatrix}\right.$$

The interaction between the electron spin and the effective magnetic field adds a new term to the Hamiltonian:

$$\hat{H}_{so}=-\vec{\mu}.\vec{B}_{eff}=\mu_B\hat{\vec{\sigma}}.\vec{B}_{eff}=\mu_B\hat{\vec{\sigma}}\,.\,\frac{1}{2mc^2}\left[\frac{\nabla V(\hat{\vec{r}})}{e}\times\hat{\vec{P}}\right]=\frac{\hbar}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla V(\hat{\vec{r}})\times\hat{\vec{P}}\right]$$

Spin-Orbit Interaction and Bloch Functions

In the absence of spin-orbit interaction we had:

$$\hat{H}_o \psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})$$

$$\left[-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m} + V(\vec{r})\right]\psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})$$

Electron states with spin-up and spin-down were degenerate $\left\{ E_{n,\uparrow}(\vec{k}) = E_{n,\downarrow}(\vec{k}) \right.$

In the presence of spin-orbit coupling the Hamiltonian becomes:

$$\hat{H} = \hat{H}_o + \hat{H}_{so}$$

$$\hat{H}_{so} = \frac{\hbar}{4m^2c^2}\,\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\hat{\vec{P}}\right] = -i\,\frac{\hbar^2}{4m^2c^2}\,\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\vec{\nabla}_{\vec{r}}\right]$$

Since the Hamiltonian is now spin-dependent, pure spin-up or pure spin-down states are no longer the eigenstates of the Hamiltonian

The eigenstates can be written most generally as a superposition of up and down spin states, or:

$$\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix} = \alpha_{n,\vec{k}}(\vec{r})\left|\uparrow\right\rangle + \beta_{n,\vec{k}}(\vec{r})\left|\downarrow\right\rangle$$

χ =Quantum number for the two spin degrees of freedom, usually taken to be +1 or -1

Spin-Orbit Interaction and Bloch Functions

$$\hat{H}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix} = E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m} + V(\vec{r}) - i\,\frac{\hbar^2}{4m^2c^2}\,\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix} = E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

For each wavevector in the FBZ, and for each band index, one will obtain two solutions of the above equation

We label one as χ = +1 and the other with χ = -1 and in general $E_{n,-\chi}(\vec{k}) \neq E_{n,\chi}(\vec{k})$

These two solutions will correspond to spins pointing in two different directions (usually collinear and opposite directions). Let these directions be specified by $\hat{n}$ at the location $\vec{r}$:

$$\hat{\vec{\sigma}}.\hat{n}\,\psi_{n,\vec{k},\chi}(\vec{r}) = +1\,\psi_{n,\vec{k},\chi}(\vec{r})$$

$$\hat{\vec{\sigma}}.\hat{n}\,\psi_{n,\vec{k},-\chi}(\vec{r}) = -1\,\psi_{n,\vec{k},-\chi}(\vec{r})$$

Spin-Orbit Interaction and Lattice Symmetries

In the presence of spin-orbit interaction we have the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}=E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

Lattice Translation Symmetry:

$$\psi_{n,\vec{k},\chi}(\vec{r}+\vec{R})=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r}+\vec{R})\\ \beta_{n,\vec{k}}(\vec{r}+\vec{R})\end{bmatrix}=\begin{bmatrix}e^{i\vec{k}.\vec{R}}\alpha_{n,\vec{k}}(\vec{r})\\ e^{i\vec{k}.\vec{R}}\beta_{n,\vec{k}}(\vec{r})\end{bmatrix}=e^{i\vec{k}.\vec{R}}\psi_{n,\vec{k},\chi}(\vec{r})$$

Rotation Symmetry:

Let $\hat{S}$ be an operator belonging to the rotation subgroup of the crystal point-group, such that:

$$V(\hat{S}\vec{r})=V(\vec{r}) \qquad \left\{\hat{S}^T=\vec{S}^{-1}\Rightarrow \text{unitary}\right.$$

(The case of inversion symmetry will be treated separately)

Spin-Orbit Interaction and Rotation Symmetry

Suppose we have found the solution to the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}=E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

And the solution is:

$$\psi_{n,\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix} \qquad \Leftrightarrow \qquad E_{n,\chi}(\vec{k})$$

We replace $\vec{r}$ by $\hat{S}\vec{r}$ everywhere in the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\hat{S}\vec{r}}^2}{2m}+V(\hat{S}\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{\hat{S}\vec{r}}V(\hat{S}\vec{r})\times\vec{\nabla}_{\hat{S}\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\hat{S}\vec{r})\\ \beta_{n,\vec{k}}(\hat{S}\vec{r})\end{bmatrix}=E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(\hat{S}\vec{r})\\ \beta_{n,\vec{k}}(\hat{S}\vec{r})\end{bmatrix}$$

$$\Rightarrow\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\,\hat{S}\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\hat{S}\vec{r})\\ \beta_{n,\vec{k}}(\hat{S}\vec{r})\end{bmatrix}=E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(\hat{S}\vec{r})\\ \beta_{n,\vec{k}}(\hat{S}\vec{r})\end{bmatrix}$$

Spin-Orbit Interaction and Rotation Symmetry

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\,.\,\hat S\left[\nabla_{\vec r}V(\hat{\vec r})\times\vec\nabla_{\vec r}\right]\right\}\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}=E_{n,\chi}(\vec k)\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}$$

The above equation does not look like the Schrodinger equation!

We define a unitary spin rotation operator $\hat R_{\hat S}$ that operates in the Hilbert space of spins and rotates spin states in the sense of the operator $\hat S$

Consider a spin vector pointing in the $\hat n$ direction:

$$\hat{\vec\sigma}.\hat n\begin{bmatrix}a\\ b\end{bmatrix}=+1\begin{bmatrix}a\\ b\end{bmatrix}$$

$$\Rightarrow\hat{\vec\sigma}.\hat n\hat R_{\hat S}^{-1}\hat R_{\hat S}\begin{bmatrix}a\\ b\end{bmatrix}=+1\begin{bmatrix}a\\ b\end{bmatrix}$$

$$\Rightarrow\hat R_{\hat S}\hat{\vec\sigma}.\hat n\hat R_{\hat S}^{-1}\hat R_{\hat S}\begin{bmatrix}a\\ b\end{bmatrix}=+1\,\hat R_{\hat S}\begin{bmatrix}a\\ b\end{bmatrix}$$

$$\Rightarrow\left(\hat{\vec\sigma}.\hat S\hat n\right)\hat R_{\hat S}\begin{bmatrix}a\\ b\end{bmatrix}=+1\hat R_{\hat S}\begin{bmatrix}a\\ b\end{bmatrix}$$

The spin rotation operators have the property: $\hat R_{\hat S}\left(\hat{\vec\sigma}.\hat n\right)\hat R_{\hat S}^{-1}=\hat{\vec\sigma}.\hat S\hat n$

Spin-Orbit Interaction and Point-Group Symmetry

Start from:

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\,.\,\hat S\left[\nabla_{\vec r}V(\hat{\vec r})\times\vec\nabla_{\vec r}\right]\right\}\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}=E_{n,\chi}(\vec k)\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}$$

Introduce spin rotation operator $\hat R_{\hat S}$ corresponding to the rotation generated by the matrix $\hat S$:

$$\hat R_{\hat S}^{-1}\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\,.\,\hat S\left[\nabla_{\vec r}V(\hat{\vec r})\times\vec\nabla_{\vec r}\right]\right\}\hat R_{\hat S}\hat R_{\hat S}^{-1}\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}=E_{n,\chi}(\vec k)\hat R_{\hat S}^{-1}\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}$$

$$\left\{-\frac{\hbar^2\nabla_{\vec r}^2}{2m}+V(\vec r)-i\frac{\hbar^2}{4m^2c^2}\hat{\vec\sigma}\,.\left[\nabla_{\vec r}V(\hat{\vec r})\times\vec\nabla_{\vec r}\right]\right\}\hat R_{\hat S}^{-1}\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}=E_{n,\chi}(\vec k)\hat R_{\hat S}^{-1}\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}$$

The above equation shows that the new state:

$$\hat R_{\hat S}^{-1}\begin{bmatrix}\alpha_{n,\vec k}(\hat S\vec r)\\ \beta_{n,\vec k}(\hat S\vec r)\end{bmatrix}$$

satisfies the Schrodinger equation and has the same energy as the state: $\begin{bmatrix}\alpha_{n,\vec k}(\vec r)\\ \beta_{n,\vec k}(\vec r)\end{bmatrix}$

Spin-Orbit Interaction and Point-Group Symmetry

Since:

$$\hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\left(\vec{r}+\vec{R}\right)\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\left(\vec{r}+\vec{R}\right)\right)\end{bmatrix}=e^{i\vec{k}.\hat{S}\vec{R}}\ \hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}=e^{i\hat{S}^{-1}\vec{k}.\vec{R}}\ \hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix}$$

The new state is a Bloch state with wavevector $\hat{S}^{-1}\vec{k}$

Summary:

If $\hat{S}$ is an operator for a point-group symmetry operation then the two states given by:

$$\psi_{n,\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

$$\psi_{n,\hat{S}^{-1}\vec{k},\chi'}(\vec{r})=\hat{R}_{\hat{S}}^{-1}\begin{bmatrix}\alpha_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\\ \beta_{n,\vec{k}}\left(\hat{S}\vec{r}\right)\end{bmatrix} \rightarrow$$

This represents a rotated (in space) version of the original Bloch state. Even the spin is rotated appropriately by the spin rotation operator.

have the same energy:

$$E_{n,\chi'}\left(\hat{S}^{-1}\vec{k}\right)=E_{n,\chi}\left(\vec{k}\right)$$

Spin-Orbit Interaction and Inversion Symmetry

Suppose the crystal potential has inversion symmetry:

$$V(-\vec{r})=V(\vec{r})$$

Suppose we have found the solution to the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V\left(\hat{\vec{r}}\right)\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}=E_{n,\chi}\left(\vec{k}\right)\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

And the solution is:

$$\psi_{n,\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}\qquad\Leftrightarrow\qquad E_{n,\chi}\left(\vec{k}\right)$$

We replace $\vec{r}$ by $-\vec{r}$ everywhere in the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{-\vec{r}}^2}{2m}+V(-\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{-\vec{r}}V\left(-\hat{\vec{r}}\right)\times\vec{\nabla}_{-\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}=E_{n,\chi}\left(\vec{k}\right)\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

$$\Rightarrow\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V\left(\hat{\vec{r}}\right)\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}=E_{n,\chi}\left(\vec{k}\right)\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

Spin-Orbit Interaction and Inversion Symmetry

$$\left\{-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\,.\left[\nabla_{\vec{r}}V(\hat{\vec{r}})\times\vec{\nabla}_{\vec{r}}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}=E_{n,\chi}(\vec{k})\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

The above equation shows that the new state: $\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$

satisfies the Schrodinger equation and has the same energy as the state: $\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$

Since:

$$\begin{bmatrix}\alpha_{n,\vec{k}}(-(\vec{r}+\vec{R}))\\ \beta_{n,\vec{k}}(-(\vec{r}+\vec{R}))\end{bmatrix}=e^{i(-\vec{k}).\vec{R}}\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

the new state is a Bloch state with wavevector $-\vec{k}$

In most cases, the new state: $\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$

has the same spin direction as the state: $\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$

So we can write: $\psi_{n,-\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$

Spin-Orbit Interaction and Inversion Symmetry

Summary:

If the crystal potential has inversion symmetry then the two states given by:

$$\psi_{n,\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})\\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}\qquad \psi_{n,-\vec{k},\chi}(\vec{r})=\begin{bmatrix}\alpha_{n,\vec{k}}(-\vec{r})\\ \beta_{n,\vec{k}}(-\vec{r})\end{bmatrix}$$

have the same energy:

$$E_{n,\chi}(-\vec{k})=E_{n,\chi}(\vec{k})$$

Spin-Orbit Interaction and Time Reversal Symmetry

Consider the Bloch function:

$$\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = \alpha_{n,\vec{k}}(\vec{r})|\uparrow\rangle + \beta_{n,\vec{k}}(\vec{r})|\downarrow\rangle$$

Suppose the Bloch function corresponds to the spin pointing in the direction of the unit vector $\hat{n}$ at the location $\vec{r}$:

$$\hat{\vec{\sigma}}.\hat{n}\,\psi_{n,\vec{k},\chi}(\vec{r}) = \hat{\vec{\sigma}}.\hat{n}\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = +1\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = +1\,\psi_{n,\vec{k},\chi}(\vec{r})$$

What if we want the state with the opposite spin at the same location?

The answer is:

$$-i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix} -\beta^*_{n,\vec{k}}(\vec{r}) \\ \alpha^*_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

Proof:

$$\begin{aligned} \hat{\vec{\sigma}}.\hat{n}\left[-i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r})\right] &= -i\left[-\hat{\vec{\sigma}}^*.\hat{n}\,\hat{\sigma}_y\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^* \\ &= -i\left[-\hat{\sigma}_y\hat{\sigma}_y\hat{\vec{\sigma}}^*.\hat{n}\,\hat{\sigma}_y\hat{\sigma}_y\hat{\sigma}_y\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^* = -i\left[\hat{\sigma}_y\hat{\vec{\sigma}}.\hat{n}\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^* \\ &= -i\left[\hat{\sigma}_y\,\psi_{n,\vec{k},\chi}(\vec{r})\right]^* = -1\left[-i\hat{\sigma}_y\,\psi^*_{n,\vec{k},\chi}(\vec{r})\right] \end{aligned}$$

$$\left\{\hat{\vec{\sigma}} = \hat{\sigma}_x\hat{x} + \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z} \quad \Rightarrow \quad \hat{\vec{\sigma}}^* = \hat{\sigma}_x\hat{x} - \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z} \neq \hat{\vec{\sigma}}\right\}$$

Spin-Orbit Interaction and Time Reversal Symmetry

In the presence of spin-orbit interaction we have the Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} = E_{n,\chi}(\vec{k})\begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

Suppose we have solved it and found the solution: $\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix} \alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r}) \end{bmatrix} \Leftrightarrow E_{n,\chi}(\vec{k})$

We complex conjugate it:

$$\left\{-\frac{\hbar^2\nabla^2_{\vec{r}}}{2m} + V(\vec{r}) + i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^*.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix} \alpha^*_{n,\vec{k}}(\vec{r}) \\ \beta^*_{n,\vec{k}}(\vec{r}) \end{bmatrix} = E_{n,\chi}(\vec{k})\begin{bmatrix} \alpha^*_{n,\vec{k}}(\vec{r}) \\ \beta^*_{n,\vec{k}}(\vec{r}) \end{bmatrix}$$

It does not look like the original Schrodinger equation!

Note that:

$$\hat{\vec{\sigma}} = \hat{\sigma}_x\hat{x} + \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z}$$

$$\Rightarrow \hat{\vec{\sigma}}^* = \hat{\sigma}_x\hat{x} - \hat{\sigma}_y\hat{y} + \hat{\sigma}_z\hat{z} \neq \hat{\vec{\sigma}}$$

Spin-Orbit Interaction and Time Reversal Symmetry

Given an eigenvalue matrix equation:

$$Av = \lambda v$$

One can always perform a unitary transformation with matrix T and obtain:

$$\begin{aligned} &TAT^{-1}Tv = \lambda Tv \\ &\Rightarrow Bu = \lambda u \end{aligned} \qquad \left\{ \begin{aligned} &B = TAT^{-1} \\ &u = Tv \end{aligned} \right.$$

So try a transformation with the unitary matrix $-i\hat{\sigma}_y$ with the equation:

$$\left(-i\hat{\sigma}_y\right)\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m} + V(\vec{r}) + i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^{*}.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\left(+i\hat{\sigma}_y\right)\left(-i\hat{\sigma}_y\right)\begin{bmatrix}\alpha^{*}_{n,\vec{k}}(\vec{r}) \\ \beta^{*}_{n,\vec{k}}(\vec{r})\end{bmatrix} = E_{n,\chi}(\vec{k})\left(-i\hat{\sigma}_y\right)\begin{bmatrix}\alpha^{*}_{n,\vec{k}}(\vec{r}) \\ \beta^{*}_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

$$\Rightarrow \left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m} + V(\vec{r}) - i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}.\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix}-\beta^{*}_{n,\vec{k}}(\vec{r}) \\ \alpha^{*}_{n,\vec{k}}(\vec{r})\end{bmatrix} = E_{n,\chi}(\vec{k})\begin{bmatrix}-\beta^{*}_{n,\vec{k}}(\vec{r}) \\ \alpha^{*}_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

We have found a new solution: $\begin{bmatrix}-\beta^{*}_{n,\vec{k}}(\vec{r}) \\ \alpha^{*}_{n,\vec{k}}(\vec{r})\end{bmatrix}$

with the same energy $E_{n,\chi}(\vec{k})$ as the original solution: $\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$

Question: What is the physical significance of the new solution?

Spin-Orbit Interaction and Time Reversal Symmetry

Under lattice translation we get for the new solution:

$$\begin{bmatrix}-\beta^{*}_{n,\vec{k}}(\vec{r}+\vec{R}) \\ \alpha^{*}_{n,\vec{k}}(\vec{r}+\vec{R})\end{bmatrix} = e^{-i\vec{k}.\vec{R}}\begin{bmatrix}-\beta^{*}_{n,\vec{k}}(\vec{r}) \\ \alpha^{*}_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

So the new solution is a Bloch state with wavevector $-\vec{k}$

$$\psi_{n,-\vec{k},?}(\vec{r}) = \begin{bmatrix}-\beta^{*}_{n,\vec{k}}(\vec{r}) \\ \alpha^{*}_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

Note that the new solution found can also be written as:

$$-i\hat{\sigma}_y\,\psi^{*}_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}-\beta^{*}_{n,\vec{k}}(\vec{r}) \\ \alpha^{*}_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

But as shown earlier, the above state has spin opposite to the state $\psi_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r}) \\ \beta_{n,\vec{k}}(\vec{r})\end{bmatrix}$

Therefore, the new solution is a Bloch state $\psi_{n,-\vec{k},-\chi}(\vec{r})$, i.e.:

$$\psi_{n,-\vec{k},-\chi}(\vec{r}) = -i\hat{\sigma}_y\,\psi^{*}_{n,\vec{k},\chi}(\vec{r}) = \begin{bmatrix}-\beta^{*}_{n,\vec{k}}(\vec{r}) \\ \alpha^{*}_{n,\vec{k}}(\vec{r})\end{bmatrix}$$

And we have also found that its energy is the same as that of the state $\psi_{n,\vec{k},\chi}(\vec{r})$:

$$E_{n,-\chi}(-\vec{k}) = E_{n,\chi}(\vec{k})$$

Spin-Orbit Interaction and Time Reversal Symmetry

In the presence of spin-orbit interaction we have the time-dependent Schrodinger equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\cdot\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},t)\\ \beta_{n,\vec{k}}(\vec{r},t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},t)\\ \beta_{n,\vec{k}}(\vec{r},t)\end{bmatrix}$$

Solution is:

$$\psi_{n,\vec{k},\chi}(\vec{r},t)=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},t)\\ \beta_{n,\vec{k}}(\vec{r},t)\end{bmatrix}=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\\ \beta_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\end{bmatrix}=\psi_{n,\vec{k},\chi}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}$$

Lets see if we can find a solution under time-reversal (i.e. when *t* is replaced by −*t*):

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\cdot\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},-t)\\ \beta_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=-i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},-t)\\ \beta_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}$$

The above does not look like a Schrodinger equation so we complex conjugate it:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})+i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^*\cdot\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}$$

And it still does not look like the original Schrodinger equation!

Spin-Orbit Interaction and Time Reversal Symmetry

Given an eigenvalue matrix equation:

$$Av=\lambda v$$

One can always perform a unitary transformation with matrix *T* and obtain:

$$\begin{aligned}&TAT^{-1}Tv=\lambda Tv\\ &\Rightarrow Bu=\lambda u\end{aligned}\qquad\left\{\begin{aligned}&B=TAT^{-1}\\ &u=Tv\end{aligned}\right.$$

So try a transformation with the unitary matrix $-i\hat{\sigma}_y$ with the equation:

$$\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})+i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^*\cdot\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}$$

$$\left(-i\hat{\sigma}_y\right)\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})+i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}^*\cdot\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\left(+i\hat{\sigma}_y\right)\left(-i\hat{\sigma}_y\right)\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\left(-i\hat{\sigma}_y\right)\begin{bmatrix}\alpha^*_{n,\vec{k}}(\vec{r},-t)\\ \beta^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}$$

$$\Rightarrow\left\{-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m}+V(\vec{r})-i\frac{\hbar^2}{4m^2c^2}\hat{\vec{\sigma}}\cdot\left[\nabla V(\hat{\vec{r}})\times\vec{\nabla}\right]\right\}\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r},-t)\\ \alpha^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=i\hbar\frac{\partial}{\partial t}\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r},-t)\\ \alpha^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}$$

The above equation now looks like the time-dependent Schrodinger equation

Spin-Orbit Interaction and Time Reversal Symmetry

Summary:

Corresponding to the Bloch state:

$$\psi_{n,\vec{k},\chi}(\vec{r},t)=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r},t)\\ \beta_{n,\vec{k}}(\vec{r},t)\end{bmatrix}=\begin{bmatrix}\alpha_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\\ \beta_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\end{bmatrix}=\psi_{n,\vec{k},\chi}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}$$

with energy:

$$E_{n,\chi}(\vec{k})$$

the time-reversed Bloch state is:

$$\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r},-t)\\ \alpha^*_{n,\vec{k}}(\vec{r},-t)\end{bmatrix}=\begin{bmatrix}-\beta^*_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\\ \alpha^*_{n,\vec{k}}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}\end{bmatrix}=\psi_{n,-\vec{k},-\chi}(\vec{r})e^{-iE_{n,\chi}(\vec{k})t}$$

and the time-reversed state has the same energy as the original state:

$$E_{n,-\chi}(-\vec{k})=E_{n,\chi}(\vec{k})$$

Crystal Inversion Symmetry and Time Reversal Symmetry

Time reversal symmetry implies:

$$E_{n,-\chi}(-\vec{k})=E_{n,\chi}(\vec{k})$$

Inversion symmetry implies:

$$E_{n,\chi}(-\vec{k})=E_{n,\chi}(\vec{k})$$

In crystals which have inversion and time reversal symmetries the above two imply:

$$E_{n,-\chi}(\vec{k})=E_{n,\chi}(\vec{k}) \longrightarrow \text{There is spin degeneracy!}$$

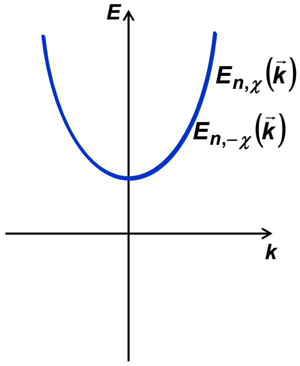
In crystals which do not have inversion symmetry the above two do not guarantee spin degeneracy. In general:

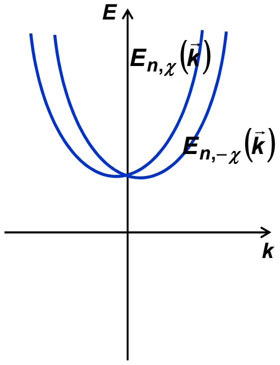
$$E_{n,-\chi}(\vec{k})\neq E_{n,\chi}(\vec{k}) \longrightarrow$$

Bands with different spins can have different energy dispersion relations

Crystal Inversion Symmetry and Time Reversal Symmetry

Cartoon (and much exaggerated) sketches of the conduction bands of Ge and GaAs are shown below:





Ge

GaAs

$$E_{n,-\chi}(\vec{k}) = E_{n,\chi}(\vec{k})$$

$$E_{n,-\chi}(\vec{k}) \neq E_{n,\chi}(\vec{k})$$

Handout 13

Properties of Electrons in Energy Bands

In this lecture you will learn:

- Properties of Bloch functions
- Average momentum and velocity of electrons in energy bands
- Energy band dispersion near band extrema
- Effective mass tensor
- Crystal momentum

Bloch Functions: A Review

1) The quantum states of an electron in a crystal are given by Bloch functions that obey the Schrodinger equation:

$$\hat{H}\,\psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})$$

where the wavevector $\vec{k}$ is confined to the FBZ and "*n*" is the band index

2) Under a lattice translation, Bloch functions obey the relation:

$$\psi_{n,\vec{k}}(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})$$

3) Bloch functions can be written as the product of a plane wave times a lattice periodic function:

$$\psi_{n,\vec{k}}(\vec{r}) = \frac{e^{i\,\vec{k}\,.\,\vec{r}}}{\sqrt{V}}\,u_{n,\vec{k}}(\vec{r})$$

4) Bloch function of wavevector $\vec{k}$ can be written as a superposition of plane waves with wavevectors that differ from $\vec{k}$ by reciprocal lattice vectors:

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_j c_{n,\vec{k}}(\vec{G}_j)\sqrt{\frac{1}{V}}\,e^{i\left(\vec{k}+\vec{G}_j\right).\,\vec{r}}$$

Bloch Functions: Orthogonality and Completeness

Orthogonality:

Bloch functions are eigenstates of a Hermitian operator and therefore must be orthogonal. In "*d*" dimensions:

$$\left.\begin{aligned}\int d^d\vec{r}\ \ \psi^*_{n,\vec{k}}(\vec{r})\,\psi_{m,\vec{k}'}(\vec{r}) &= \delta_{\vec{k},\vec{k}'}\ \ \delta_{n,m}\\ &= \frac{(2\pi)^d}{V}\,\delta^d\!\left(\vec{k}-\vec{k}'\right)\ \delta_{n,m}\end{aligned}\right\}$$

Both expression valid depending upon context

Completeness:

Bloch functions for ALL wavevectors in the FBZ and for ALL energy band satisfy the following completeness relation in "*d*" dimensions:

$$\sum_{n}\ \sum_{\vec{k}\ \text{in FBZ}} \psi_{n,\vec{k}}(\vec{r})\,\psi^*_{n,\vec{k}}(\vec{r}\,') = \sum_{n} V \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d}\ \psi_{n,\vec{k}}(\vec{r})\,\psi^*_{n,\vec{k}}(\vec{r}\,') = \delta^d(\vec{r}-\vec{r}\,')$$

Another Schrodinger-like Equation for Bloch Functions

The periodic part of a Bloch function satisfies a Schrodinger-like equation:

$$\hat{H}\,\psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})$$

$$\Rightarrow \left(\frac{\hat{\vec{P}}^2}{2m} + V(\hat{\vec{r}})\right)\psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})$$

$$\Rightarrow\ e^{i\vec{k}\cdot\vec{r}}\left(\frac{\left(\hat{\vec{P}}+\hbar\vec{k}\right)^2}{2m} + V(\hat{\vec{r}})\right)u_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\ e^{i\vec{k}\cdot\vec{r}}u_{n,\vec{k}}(\vec{r})$$

$$\Rightarrow \left(\frac{\left(\hat{\vec{P}}+\hbar\vec{k}\right)^2}{2m} + V(\hat{\vec{r}})\right)u_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,u_{n,\vec{k}}(\vec{r})$$

Result:

$$\Rightarrow \left(\frac{\hat{\vec{P}}^2}{2m} + \frac{\hat{\vec{P}}}{m}\cdot\hbar\vec{k} + \frac{\hbar^2k^2}{2m} + V(\hat{\vec{r}})\right)u_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,u_{n,\vec{k}}(\vec{r})$$

Where the following two relations have been used:

$$\hat{\vec{P}}\ e^{i\vec{k}\cdot\vec{r}}\ f(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\left(\hat{\vec{P}}+\hbar\vec{k}\right)f(\vec{r})$$

$$\hat{\vec{P}}^2\ e^{i\vec{k}\cdot\vec{r}}\ f(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\left(\hat{\vec{P}}+\hbar\vec{k}\right)^2 f(\vec{r})$$

Bloch Functions and Electron Momentum

- For an electron with wavefunction given by a plane wave:

$$\phi_{\vec{k}}(\vec{r}) = \sqrt{\frac{1}{V}}\, e^{i\,\vec{k}\,.\,\vec{r}}$$

the quantity $\hbar\vec{k}$ is the momentum of the electron

- A plane wave is an eigenfunction of the momentum operator with eigenvalue $\hbar\vec{k}$:

$$\hat{\vec{P}}\,\phi_{\vec{k}}(\vec{r}) = \frac{\hbar}{i}\nabla\,\phi_{\vec{k}}(\vec{r}) = \hbar\vec{k}\,\phi_{\vec{k}}(\vec{r})$$

- A Bloch function is a superposition of plane waves of different wavevectors:

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_{j} c_{n,\vec{k}}\left(\vec{G}_j\right)\sqrt{\frac{1}{V}}\, e^{i\left(\vec{k}+\vec{G}_j\right).\vec{r}}$$

So clearly it is not an eigenfunction of the momentum operator (i.e. it has no well defined momentum). So what exactly is the significance of the wavevector $\vec{k}$ that labels a Bloch function?

- As you will see, even the average momentum of an electron in a Bloch state is NOT given by $\hbar\vec{k}$:

$$\left\langle \psi_{n,\vec{k}}\middle|\hat{\vec{P}}\middle|\psi_{n,\vec{k}}\right\rangle = \int d^{d}\vec{r}\;\; \psi^{*}{}_{n,\vec{k}}(\vec{r})\,\frac{\hbar}{i}\nabla\,\psi_{n,\vec{k}}(\vec{r}) \neq \hbar\vec{k}$$

Average Momentum and Velocity of Bloch States

We need to find the average momentum and average velocity of an electron in a Bloch state:

$$\left\langle \psi_{n,\vec{k}}\middle|\hat{\vec{P}}\middle|\psi_{n,\vec{k}}\right\rangle = ? \qquad\qquad \vec{v}_n\left(\vec{k}\right) = \left\langle \psi_{n,\vec{k}}\middle|\frac{\hat{\vec{P}}}{m}\middle|\psi_{n,\vec{k}}\right\rangle = ?$$

Start from a very different point:

Suppose we have solved the Schrodinger-like equation for a particular wavevector $\vec{k}$:

$$\left(\frac{\hat{\vec{P}}^2}{2m} + \frac{\hat{\vec{P}}}{m}.\hbar\vec{k} + \frac{\hbar^2 k^2}{2m} + V\left(\hat{\vec{r}}\right)\right) u_{n,\vec{k}}(\vec{r}) = E_n\left(\vec{k}\right) u_{n,\vec{k}}(\vec{r})$$

The “Hamiltonian” is:

$$\hat{H}_{\vec{k}} = \frac{\hat{\vec{P}}^2}{2m} + \frac{\hat{\vec{P}}}{m}.\hbar\vec{k} + \frac{\hbar^2 k^2}{2m} + V\left(\hat{\vec{r}}\right)$$

Suppose now we want to solve it again for a neighboring wavevector $\vec{k} + \Delta\vec{k}$:

$$\left(\frac{\hat{\vec{P}}^2}{2m} + \frac{\hat{\vec{P}}}{m}.\hbar\left(\vec{k}+\Delta\vec{k}\right) + \frac{\hbar^2\left(\vec{k}+\Delta\vec{k}\right)^2}{2m} + V\left(\hat{\vec{r}}\right)\right) u_{n,\vec{k}+\Delta\vec{k}}(\vec{r}) = E_n\left(\vec{k}+\Delta\vec{k}\right) u_{n,\vec{k}+\Delta\vec{k}}(\vec{r})$$

Average Momentum and Velocity of Bloch States

The new "Hamiltonian" is:

$$\hat{H}_{\vec{k}+\Delta\vec{k}} = \frac{\hat{\vec{P}}^2}{2m} + \frac{\hat{\vec{P}}}{m}\cdot\hbar\left(\vec{k}+\Delta\vec{k}\right) + \frac{\hbar^2\left(\vec{k}+\Delta\vec{k}\right)^2}{2m} + V\left(\hat{\vec{r}}\right)$$

$$= \hat{H}_{\vec{k}} + \underbrace{\frac{\hat{\vec{P}}}{m}\cdot\hbar\Delta\vec{k} + \frac{\hbar^2\left(2\vec{k}\cdot\Delta\vec{k}+\Delta k^2\right)}{2m}} = \hat{H}_{\vec{k}} + \Delta\hat{H}_{\vec{k}}$$

Treat this part as a perturbation to the old "Hamiltonian"

Using concepts from time-independent perturbation theory, the first order correction to the energy eigenvalue would be:

$$E_n\left(\vec{k}+\Delta\vec{k}\right) - E_n\left(\vec{k}\right) \approx \left\langle u_{n,\vec{k}}\right|\Delta\hat{H}_{\vec{k}}\left|u_{n,\vec{k}}\right\rangle$$

As written, the above expression is approximate but becomes exact in the limit $\Delta\vec{k}\to 0$

$$\lim \Delta\vec{k}\to 0: \quad E_n\left(\vec{k}+\Delta\vec{k}\right) - E_n\left(\vec{k}\right) = \left\langle u_{n,\vec{k}}\right|\Delta\hat{H}_{\vec{k}}\left|u_{n,\vec{k}}\right\rangle$$

$$\Rightarrow \quad \Delta\vec{k}\cdot\nabla_{\vec{k}}\, E_n\left(\vec{k}\right) = \left\langle u_{n,\vec{k}}\right|\frac{\hat{\vec{P}}}{m}\cdot\hbar\Delta\vec{k} + \frac{\hbar\vec{k}}{m}\cdot\hbar\Delta\vec{k}\left|u_{n,\vec{k}}\right\rangle$$

$$\Rightarrow \quad \frac{1}{\hbar}\nabla_{\vec{k}}\, E_n\left(\vec{k}\right) = \left\langle u_{n,\vec{k}}\right|\frac{\left(\hat{\vec{P}}+\hbar\vec{k}\right)}{m}\left|u_{n,\vec{k}}\right\rangle$$

Average Momentum and Velocity of Bloch States

(Contd…)

$$\frac{1}{\hbar}\nabla_{\vec{k}}\, E_n\left(\vec{k}\right) = \left\langle u_{n,\vec{k}}\right|\frac{\left(\hat{\vec{P}}+\hbar\vec{k}\right)}{m}\left|u_{n,\vec{k}}\right\rangle = \int d^d\vec{r}\;\; u^*_{n,\vec{k}}(\vec{r})\,\frac{\left(\hat{\vec{P}}+\hbar\vec{k}\right)}{m}\,u_{n,\vec{k}}(\vec{r})$$

$$\Rightarrow \frac{1}{\hbar}\nabla_{\vec{k}}\, E_n\left(\vec{k}\right) = \int d^d\vec{r}\quad e^{-i\vec{k}\cdot\vec{r}}e^{i\vec{k}\cdot\vec{r}}\;\; u^*_{n,\vec{k}}(\vec{r})\,\frac{\left(\hat{\vec{P}}+\hbar\vec{k}\right)}{m}\,u_{n,\vec{k}}(\vec{r})$$

$$\Rightarrow \frac{1}{\hbar}\nabla_{\vec{k}}\, E_n\left(\vec{k}\right) = \int d^d\vec{r}\quad e^{-i\vec{k}\cdot\vec{r}}\; u^*_{n,\vec{k}}(\vec{r})\,\frac{\hat{\vec{P}}}{m}\,e^{i\vec{k}\cdot\vec{r}}\;\; u_{n,\vec{k}}(\vec{r})$$

$$\Rightarrow \frac{1}{\hbar}\nabla_{\vec{k}}\, E_n\left(\vec{k}\right) = \int d^d\vec{r}\quad \psi^*_{n,\vec{k}}(\vec{r})\,\frac{\hat{\vec{P}}}{m}\;\;\psi_{n,\vec{k}}(\vec{r})$$

$$\Rightarrow \frac{1}{\hbar}\nabla_{\vec{k}}\, E_n\left(\vec{k}\right) = \left\langle \psi_{n,\vec{k}}\right|\frac{\hat{\vec{P}}}{m}\left|\psi_{n,\vec{k}}\right\rangle$$

⇒ The average momentum of an electron in a Bloch state is:

$$\left\langle \psi_{n,\vec{k}}\right|\hat{\vec{P}}\left|\psi_{n,\vec{k}}\right\rangle = \frac{m}{\hbar}\nabla_{\vec{k}}\, E_n\left(\vec{k}\right)$$

⇒ The average velocity of an electron in a Bloch state is:

$$\vec{v}_n\left(\vec{k}\right) = \left\langle \psi_{n,\vec{k}}\right|\frac{\hat{\vec{P}}}{m}\left|\psi_{n,\vec{k}}\right\rangle = \frac{1}{\hbar}\nabla_{\vec{k}}\, E_n\left(\vec{k}\right)$$

Average Momentum and Velocity of Bloch States: 1D Example

The average velocity of an electron in a Bloch state is given by:

$$\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}}\, E_n(\vec{k})$$

Recall from E&M theory (ECE303) that the group velocity of a electric field wavepacket made of plane waves:

$$\vec{E}(\vec{r},t) = \hat{x}\int_{k_o-\Delta k}^{k_o+\Delta k} \frac{dk}{2\pi}\, A(k)\, e^{i\,k\,x}\; e^{-i\,\omega(k)\,t}$$

is given by:

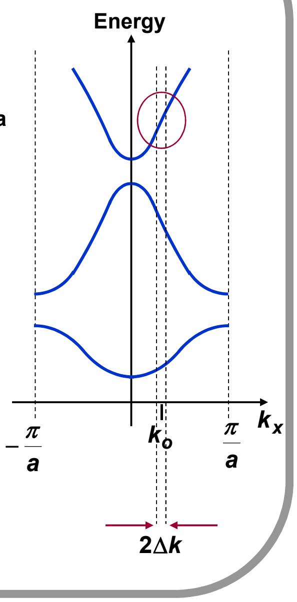
$$v_g(k_o) = \left.\frac{d\omega(k)}{dk}\right|_{k=k_o}$$

Similarly, the "group velocity" of an electron wavepacket made up of Bloch states from the *n*-th band:

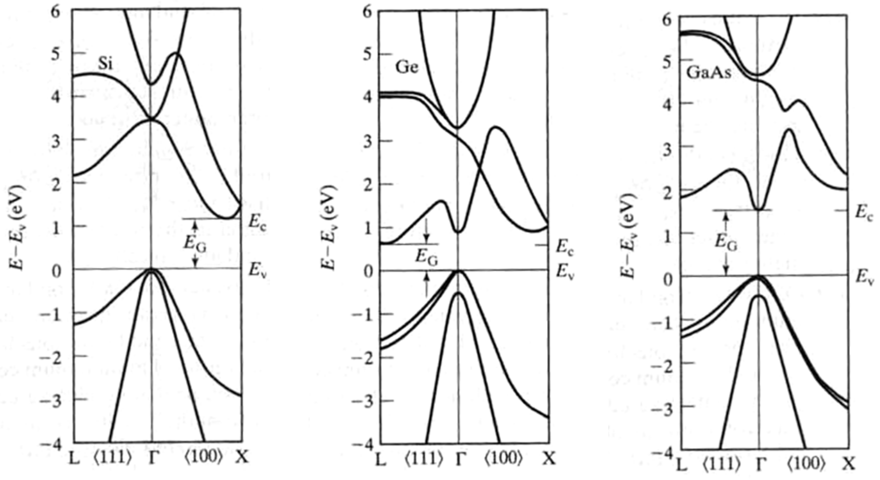
$$\psi(x,t) = \int_{k_o-\Delta k}^{k_o+\Delta k} \frac{dk}{2\pi}\, A(k)\quad \psi_{n,k}(x)\, e^{-i\frac{E_n(k)}{\hbar}t}$$

would be given by:

$$v_n(k_o) = \left.\frac{1}{\hbar}\frac{dE_n(k)}{dk}\right|_{k=k_o}$$



Energy Bands of Si, Ge, and GaAs for Reference



Energy Band Dispersion Near Band Extrema

Most of the times, it is useful to approximate the energy band dispersion near the band extrema (e.g. at bottom of the conduction band or at the top of the valence band)

Suppose the *n*-th band has an extrema at $\vec{k} = \vec{k}_o$. Therefore:

$$\nabla_{\vec{k}} E_n(\vec{k})\Big|_{\vec{k}=\vec{k}_o} = 0$$

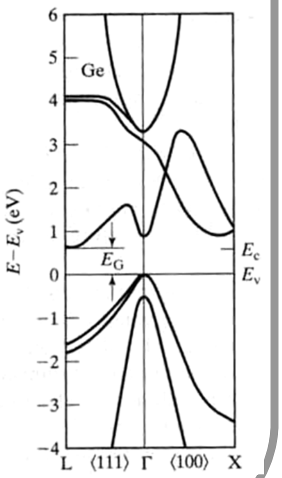
$$\Rightarrow \frac{dE_n(\vec{k})}{dk_x}\bigg|_{\vec{k}=\vec{k}_o} = \frac{dE_n(\vec{k})}{dk_y}\bigg|_{\vec{k}=\vec{k}_o} = \frac{dE_n(\vec{k})}{dk_z}\bigg|_{\vec{k}=\vec{k}_o} = 0$$

Now for $\vec{k}$ near $\vec{k}_o$ one can Taylor expand the energy dispersion relation:

$$E_n(\vec{k}) = E_n(\vec{k}_o) + \sum_{j=x,y,z} \cancelto{0}{(\vec{k}-\vec{k}_o)_j \frac{dE_n(\vec{k})}{dk_j}}$$

$$+\frac{1}{2}\sum_{\substack{r=x,y,z\\ j=x,y,z}} (\vec{k}-\vec{k}_o)_r \frac{d^2E_n(\vec{k})}{dk_r dk_j} (\vec{k}-\vec{k}_o)_j + \ldots\ldots.$$

$$E_n(\vec{k}) = E_n(\vec{k}_o) + \frac{1}{2}\sum_{\substack{r=x,y,z\\ j=x,y,z}} (\vec{k}-\vec{k}_o)_r \frac{d^2E_n(\vec{k})}{dk_r dk_j} (\vec{k}-\vec{k}_o)_j + \ldots\ldots.$$



Effective Mass Tensor

$$E_n(\vec{k}) = E_n(\vec{k}_o) + \frac{1}{2}\sum_{\substack{r=x,y,z\\ j=x,y,z}} (\vec{k}-\vec{k}_o)_r \frac{d^2E_n(\vec{k})}{dk_r dk_j}\bigg|_{\vec{k}=\vec{k}_o} (\vec{k}-\vec{k}_o)_j + \ldots\ldots.$$

$$E_n(\vec{k}) = E_n(\vec{k}_o) + \frac{\hbar^2}{2}\sum_{\substack{r=x,y,z\\ j=x,y,z}} (\vec{k}-\vec{k}_o)_r M^{-1}_{rj} (\vec{k}-\vec{k}_o)_j + \ldots\ldots$$

Parabolic approximation

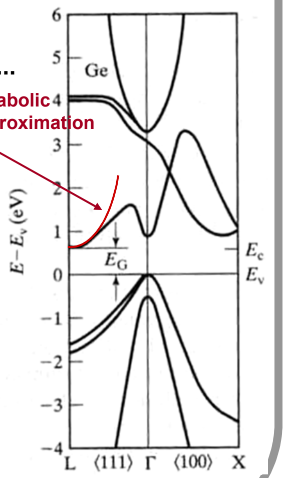
Where the elements of the matrix M^{-1} are defined as:

$$M^{-1}_{rj} = \frac{1}{\hbar^2}\frac{d^2E_n(\vec{k})}{dk_r dk_j}\bigg|_{\vec{k}=\vec{k}_o}$$

M **is called the "effective mass" tensor. M^{-1} is the "inverse effective mass" tensor**

Note that M^{-1} is symmetric: $M^{-1}_{rj} = M^{-1}_{jr}$

And so *M* is also symmetric: $M_{rj} = M_{jr}$



Effective Mass Tensor and Electron Average Velocity

The energy band dispersion near a band extremum (e.g. at bottom of the conduction band or at the top of the valence band) can be written as:

$$E_n(\vec{k}) = E_n(\vec{k}_o) + \frac{\hbar^2}{2} \sum_{\substack{r=x,y,z \\ j=x,y,z}} (\vec{k}-\vec{k}_o)_r \, M^{-1}_{r\,j} \, (\vec{k}-\vec{k}_o)_j + \ldots\ldots$$

Or:

$$E_n(\vec{k}) = E_n(\vec{k}_o) + \frac{\hbar^2}{2} \begin{bmatrix} k_x - k_{ox} & k_y - k_{oy} & k_z - k_{oz} \end{bmatrix} M^{-1} \begin{bmatrix} k_x - k_{ox} \\ k_y - k_{oy} \\ k_z - k_{oz} \end{bmatrix}$$

Or:

$$E_n(\vec{k}) = E_n(\vec{k}_o) + \frac{\hbar^2}{2} (\vec{k}-\vec{k}_o)^T \, . \, M^{-1} \, . \, (\vec{k}-\vec{k}_o)$$

Equivalent ways of writing the same thing

Since the average velocity of an electron in a Bloch state is given by:

$$\vec{v}_n(\vec{k}) = \frac{1}{\hbar} \nabla_{\vec{k}} \, E_n(\vec{k})$$

Near a band extremum, we have:

$$\vec{v}_n(\vec{k}) = M^{-1} \, . \, \hbar \, (\vec{k}-\vec{k}_o) \qquad \text{Or :} \quad \vec{v}_n(\vec{k}) = M^{-1} \begin{bmatrix} \hbar\,(k_x - k_{ox}) \\ \hbar\,(k_y - k_{oy}) \\ \hbar\,(k_z - k_{oz}) \end{bmatrix}$$

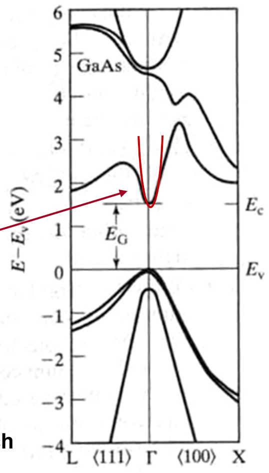
Example: Conduction Band of GaAs

Consider the conduction band of GaAs near the band bottom at the Γ-point:

$$\vec{k}_o = 0 \qquad E_c(\vec{k}_o = 0) = E_c$$

$$M^{-1} = \begin{bmatrix} 1/m_e & 0 & 0 \\ 0 & 1/m_e & 0 \\ 0 & 0 & 1/m_e \end{bmatrix}$$

Isotropic!



Parabolic approximation

This implies the energy dispersion relation is:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2\,m_e} = E_c + \frac{\hbar^2 k^2}{2\,m_e}$$

The dispersion looks like that of a free-electron with a mass equal to "m_e" instead of m. In GaAs, m_e = .067 m

The average momentum and velocity of an electron in a Bloch state near the conduction band bottom is given by:

$$\langle \psi_{c,\vec{k}} | \hat{\vec{P}} | \psi_{c,\vec{k}} \rangle = \frac{m}{\hbar} \nabla_{\vec{k}} \, E_c(\vec{k}) = \left(\frac{m}{m_e}\right) \hbar \vec{k} \qquad \vec{v}_c(\vec{k}) = \frac{1}{\hbar} \nabla_{\vec{k}} \, E_c(\vec{k}) = \frac{\hbar \, \vec{k}}{m_e}$$

Example: Valence Band of GaAs – Heavy Hole Band

Consider the top most valence band (hh-band) of GaAs near the band maximum at the Γ-point:

$$\vec{k}_o = 0 \qquad E_{hh}\left(\vec{k}_o = 0\right) = E_v$$

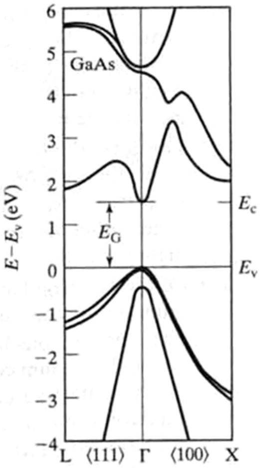
$$M^{-1} = \begin{bmatrix} -1/m_{hh} & 0 & 0 \\ 0 & -1/m_{hh} & 0 \\ 0 & 0 & -1/m_{hh} \end{bmatrix}$$

Isotropic!

This implies:

$$E_{hh}\left(\vec{k}\right) = E_v - \frac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2\,m_{hh}} = E_v - \frac{\hbar^2 k^2}{2\,m_{hh}}$$

The dispersion looks like that of a free-electron with a mass equal to "$-m_{hh}$" instead of m. In GaAs, $m_{hh} = .5\,m$



The average velocity of an electron in a Bloch state near the valence band maximum is given by:

$$\vec{v}_{hh}\left(\vec{k}\right) = \frac{1}{\hbar}\nabla_{\vec{k}}\, E_{hh}\left(\vec{k}\right) = -\frac{\hbar\,\vec{k}}{m_{hh}}$$

Example: Valence Band of GaAs – Light Hole Band

Now consider the top most valence band (ℓh-band) of GaAs near the band maximum at the Γ-point:

$$\vec{k}_o = 0 \qquad E_{\ell h}\left(\vec{k}_o = 0\right) = E_v$$

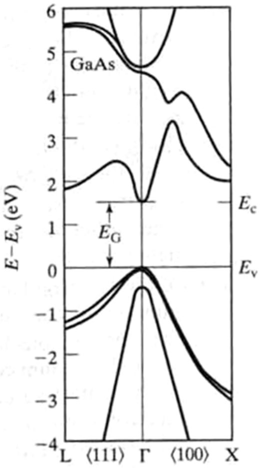
$$M^{-1} = \begin{bmatrix} -1/m_{\ell h} & 0 & 0 \\ 0 & -1/m_{\ell h} & 0 \\ 0 & 0 & -1/m_{\ell h} \end{bmatrix}$$

Isotropic!

This implies:

$$E_{hh}\left(\vec{k}\right) = E_v - \frac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2\,m_{\ell h}} = E_v - \frac{\hbar^2 k^2}{2\,m_{\ell h}}$$

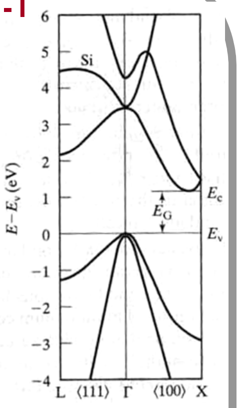
The dispersion looks like that of a free-electron with a mass equal to "$-m_{\ell h}$" instead of m. In GaAs, $m_{\ell h} = .076\,m$



The average velocity of an electron in a Bloch state near the valence band maximum is given by:

$$\vec{v}_{\ell h}\left(\vec{k}\right) = \frac{1}{\hbar}\nabla_{\vec{k}}\, E_{\ell h}\left(\vec{k}\right) = -\frac{\hbar\,\vec{k}}{m_{\ell h}}$$

Example: Conduction Band of Silicon - I



In Silicon there are six conduction band minima that occur along the six Γ-X directions. For the one that occurs along the Γ-X(2π/a,0,0) direction:

$$\vec{k}_o = 0.85\left(\frac{2\pi}{a},0,0\right) \qquad E_c(\vec{k}_o) = E_c$$

$$M^{-1} = \begin{bmatrix} 1/m_\ell & 0 & 0 \\ 0 & 1/m_t & 0 \\ 0 & 0 & 1/m_t \end{bmatrix}$$

Not isotropic!

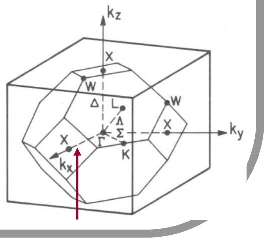
$m_\ell = 0.92\, m$
$m_t = 0.19\, m$

This implies:

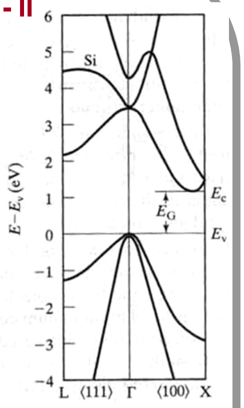
$$E_c(\vec{k}) = E_c + \frac{\hbar^2(k_x-k_{ox})^2}{2m_\ell} + \frac{\hbar^2(k_y-k_{oy})^2}{2m_t} + \frac{\hbar^2(k_z-k_{oz})^2}{2m_t}$$

The average velocity of an electron in a Bloch state near the conduction band bottom is given by:

$$\vec{v}_c(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}}\, E_c(\vec{k}) = \frac{\hbar\,(k_x-k_{ox})}{m_\ell} + \frac{\hbar\,(k_y-k_{oy})}{m_t} + \frac{\hbar\,(k_z-k_{oz})}{m_t}$$



Example: Conduction Band of Silicon - II



Now we look at the conduction band minimum that occurs along the Γ-X(0,2π/a,0) direction:

$$\vec{k}_o = 0.85\left(0,\frac{2\pi}{a},0\right) \qquad E_c(\vec{k}_o) = E_c$$

$$M^{-1} = \begin{bmatrix} 1/m_t & 0 & 0 \\ 0 & 1/m_\ell & 0 \\ 0 & 0 & 1/m_t \end{bmatrix}$$

Not isotropic!

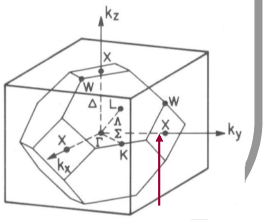
$m_\ell = 0.92\, m$
$m_t = 0.19\, m$

This implies:

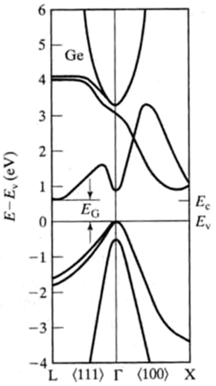
$$E_c(\vec{k}) = E_c + \frac{\hbar^2(k_x-k_{ox})^2}{2m_t} + \frac{\hbar^2(k_y-k_{oy})^2}{2m_\ell} + \frac{\hbar^2(k_z-k_{oz})^2}{2m_t}$$

The average velocity of an electron in a Bloch state near the conduction band bottom is given by:

$$\vec{v}_c(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}}\, E_c(\vec{k}) = \frac{\hbar\,(k_x-k_{ox})}{m_t} + \frac{\hbar\,(k_y-k_{oy})}{m_\ell} + \frac{\hbar\,(k_z-k_{oz})}{m_t}$$



Example: Conduction Band of Germanium - I



In germanium there are eight conduction band minima that occur at the L-points. For the one that occurs at the L(π/a, π/a, π/a) point:

$$\vec{k}_o = \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right) \qquad E_c\left(\vec{k}_o\right) = E_c$$

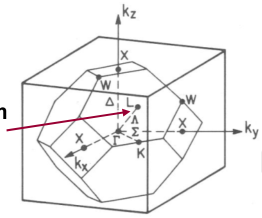
$$M^{-1} = \begin{bmatrix} 1/3m_\ell + 2/3m_t & 1/3m_\ell - 1/3m_t & 1/3m_\ell - 1/3m_t \\ 1/3m_\ell - 1/3m_t & 1/3m_\ell + 2/3m_t & 1/3m_\ell - 1/3m_t \\ 1/3m_\ell - 1/3m_t & 1/3m_\ell - 1/3m_t & 1/3m_\ell + 2/3m_t \end{bmatrix}$$

Not isotropic! Not even diagonal!

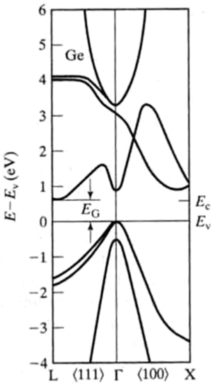
$m_\ell = 1.6\ m$

$m_t = 0.08\ m$

Since the inverse effective mass tensor is symmetric (it always is) one can rotate the co-ordinate system such that the inverse effective mass tensor is diagonal in the new co-ordinate system (Recall from linear algebra that a symmetric matrix can always be diagonalized by a rotation of the basis)



Example: Conduction Band of Germanium - II



Define a new rotated co-ordinate system, call it the primed co-ordinate system, in which the x'-axis points in the $(1,1,1)/\sqrt{3}$ direction. Co-ordinate rotation is accomplished by a rotation matrix *R*:

$$E_c\left(\vec{k}\right) = E_c + \frac{\hbar^2}{2}\left(\vec{k} - \vec{k}_o\right)^T . M^{-1} . \left(\vec{k} - \vec{k}_o\right)$$

$$\Rightarrow E_c\left(\vec{k}\right) = E_c + \frac{\hbar^2}{2}\left(\vec{k} - \vec{k}_o\right)^T . R^{-1} R\, M^{-1} R^{-1} R . \left(\vec{k} - \vec{k}_o\right)$$

$$\Rightarrow E_c\left(\vec{k}\right) = E_c + \frac{\hbar^2}{2}\left[R . \left(\vec{k} - \vec{k}_o\right)\right]^T . R\, M^{-1} R^{-1} . \left[R . \left(\vec{k} - \vec{k}_o\right)\right]$$

$$\Rightarrow E_c\left(\vec{k}'\right) = E_c + \frac{\hbar^2}{2}\left(\vec{k}' - \vec{k}'_o\right)^T . M'^{-1} . \left(\vec{k}' - \vec{k}'_o\right)$$

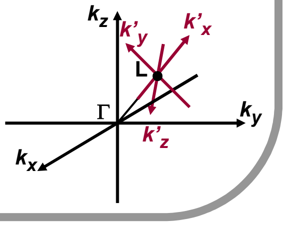
$$M'^{-1} = \begin{bmatrix} 1/m_\ell & 0 & 0 \\ 0 & 1/m_t & 0 \\ 0 & 0 & 1/m_t \end{bmatrix}$$

In Ge:

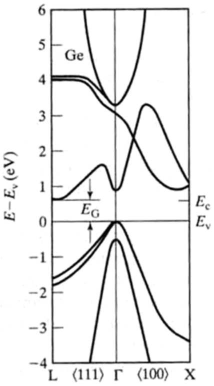
$m_\ell = 1.6\ m$

$m_t = 0.08\ m$

Effective mass along the Γ-L direction is m_ℓ and in the two directions perpendicular to this direction it is m_t



Example: Conduction Band of Germanium - III



In the primed (rotated) co-ordinate system, we have at the L-point:

$$E_c(\vec{k}') = E_c + \frac{\hbar^2}{2}\left(\vec{k}' - \vec{k}'_o\right)^T . M'^{-1} . \left(\vec{k}' - \vec{k}'_o\right)$$

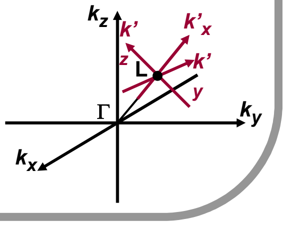
$$\Rightarrow E_c(\vec{k}') = E_c + \frac{\hbar^2 (k'_x - k'_{ox})^2}{2 m_\ell} + \frac{\hbar^2 (k'_y - k'_{oy})^2}{2 m_t} + \frac{\hbar^2 (k'_z - k'_{oz})^2}{2 m_t}$$

The average velocity of an electron in a Bloch state near the conduction band bottom is then given by:

$$\vec{v}_c(\vec{k}') = \frac{1}{\hbar}\nabla_{\vec{k}'} E_c(\vec{k}')$$

$$= \frac{\hbar\,(k'_x - k'_{ox})}{m_\ell} + \frac{\hbar\,(k'_y - k'_{oy})}{m_t} + \frac{\hbar\,(k'_z - k'_{oz})}{m_t}$$

Same procedure can be applied to the conduction band minima at the other L-points



Average Momentum and Crystal Momentum

The wavevector $\vec{k}$ associated with a Bloch state $\psi_{n,\vec{k}}(\vec{r})$ is not the momentum of the electron and it is not even the average momentum of the electron in the Bloch state

The average momentum of an electron in a Bloch state is given as:

$$\left\langle \psi_{n,\vec{k}} \middle| \hat{\vec{P}} \middle| \psi_{n,\vec{k}} \right\rangle = \frac{m}{\hbar}\nabla_{\vec{k}} E_n(\vec{k})$$

Near a band extrema, assuming:

$$E_n(\vec{k}) = E_n(\vec{k}_o) + \frac{\hbar^2}{2}\left(\vec{k} - \vec{k}_o\right)^T . M^{-1} . \left(\vec{k} - \vec{k}_o\right)$$

We have for the average momentum:

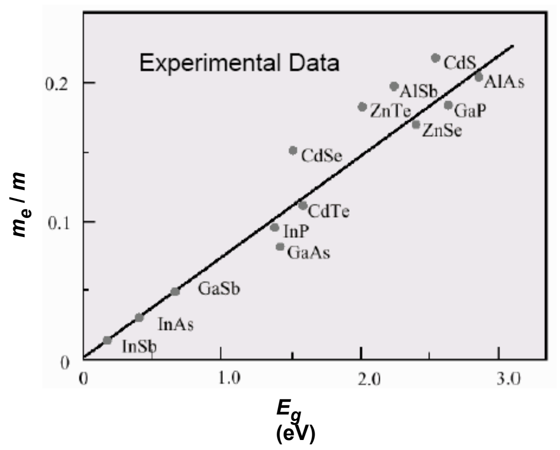
$$\left\langle \psi_{n,\vec{k}} \middle| \hat{\vec{P}} \middle| \psi_{n,\vec{k}} \right\rangle = m\, M^{-1} . \hbar\left(\vec{k} - \vec{k}_o\right)$$

Example: For GaAs conduction band, the average momentum of an electron near the band bottom equals:

$$\left\langle \psi_{n,\vec{k}} \middle| \hat{\vec{P}} \middle| \psi_{n,\vec{k}} \right\rangle = \left(\frac{m}{m_e}\right)\hbar\,\vec{k}$$

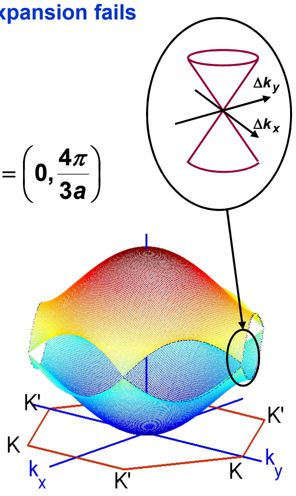
The quantity $\hbar\,\vec{k}$ is called the crystal momentum of an electron in an energy band. As we will see, it satisfies several conservation rules just like the actual momentum does for a free-electron.

Effective Mass vs Bandgap



Energy Band Dispersion Near Band Extrema: When Taylor Expansion Fails

Graphene is a classical example of the case when Taylor expansion fails
So a different strategy is needed near band extrema



$$\begin{bmatrix} E_p & -V_{pp\pi}\, f(\vec{k}) \\ -V_{pp\pi}\, f^*(\vec{k}) & E_p \end{bmatrix}\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix} = E(\vec{k})\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}$$

Suppose one is interested in band dispersion near $\vec{k}_o = \vec{\mathrm{K}} = \left(0, \dfrac{4\pi}{3a}\right)$

Expand the function $f(\vec{k})$ near $\vec{\mathrm{K}}$ as follows:

$$\vec{k} = \vec{\mathrm{K}} + \Delta\vec{k}$$

$$f(\vec{k} = \vec{\mathrm{K}} + \Delta\vec{k}) = \left[e^{i\,\vec{k}.\vec{n}_1} + e^{i\,\vec{k}.\vec{n}_2} + e^{i\,\vec{k}.\vec{n}_3} \right]_{\vec{k} = \vec{\mathrm{K}} + \Delta\vec{k}}$$

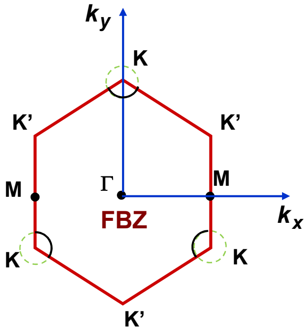
$$\approx i\frac{\sqrt{3}}{2}a\left[\Delta k_x + i\Delta k_y\right]$$

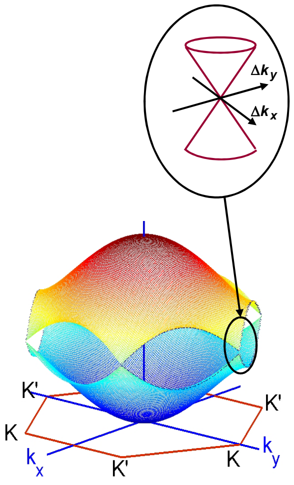
$$E(\vec{k} = \vec{\mathrm{K}} + \Delta\vec{k}) = E_p \pm V_{pp\pi}\left| f(\vec{k} = \vec{\mathrm{K}} + \Delta\vec{k}) \right|$$

$$\approx E_p \pm \frac{\sqrt{3}}{2} a V_{pp\pi}\sqrt{\Delta k_x^2 + \Delta k_y^2}$$

$$E(\vec{k} = \vec{\mathrm{K}} + \Delta\vec{k}) \approx E_p \pm \hbar v\sqrt{\Delta k_x^2 + \Delta k_y^2} \qquad \left\{ v = \frac{\sqrt{3}}{2}\frac{aV_{pp\pi}}{\hbar} \approx 10^6 \text{ m/s} \right.$$

Energy Band Dispersion Near Band Extrema





- There are 6 one-third cones sitting inside the FBZ

⇒ There are 2 full cones sitting inside the FBZ: one at the K-point and one at the K’-point

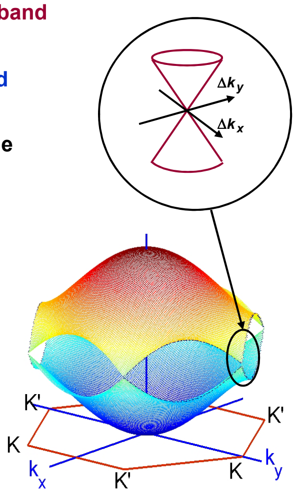
Energy Band Dispersion in Graphene: Massless Dirac Fermions

$$E_c\left(\vec{k}=\mathbf{K}+\Delta\vec{k}\right)\approx E_p+\hbar v\sqrt{\Delta k_x^2+\Delta k_y^2}$$

Conduction band dispersion

$$E_v\left(\vec{k}=\mathbf{K}+\Delta\vec{k}\right)\approx E_p-\hbar v\sqrt{\Delta k_x^2+\Delta k_y^2}$$

Valence band dispersion



The average velocity of an electron in a Bloch state near the conduction band bottom is then given by:

$$\vec{v}_c\left(\vec{k}\right)=\frac{1}{\hbar}\nabla_{\vec{k}}\,E_c\left(\vec{k}\right)=v\,\frac{\Delta k_x\hat{x}+\Delta k_y\hat{y}}{\sqrt{\Delta k_x^2+\Delta k_y^2}}$$

Similarly,

$$\vec{v}_v\left(\vec{k}\right)=\frac{1}{\hbar}\nabla_{\vec{k}}\,E_v\left(\vec{k}\right)=-v\,\frac{\Delta k_x\hat{x}+\Delta k_y\hat{y}}{\sqrt{\Delta k_x^2+\Delta k_y^2}}$$

Note that: $\left|\vec{v}_c\left(\vec{k}\right)\right|=\left|\vec{v}_v\left(\vec{k}\right)\right|=v\approx 10^6$ m/s

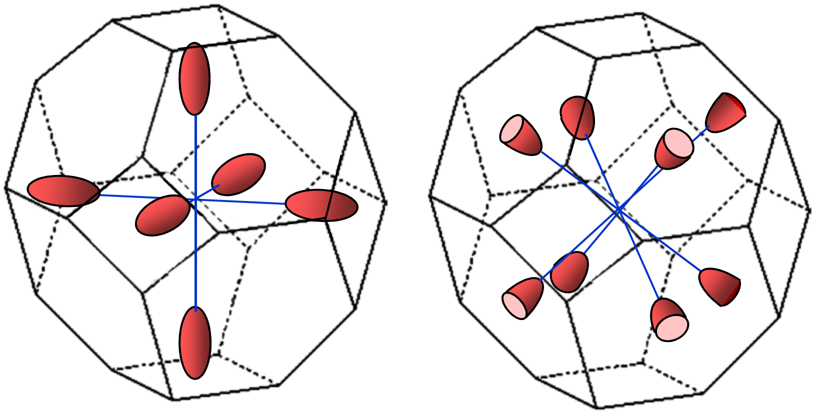
All electrons in the conduction band (and in the valence band as well) move with the same speed (i.e. magnitude of the velocity) !!

This is similar to how massless particles, such as photons, behave

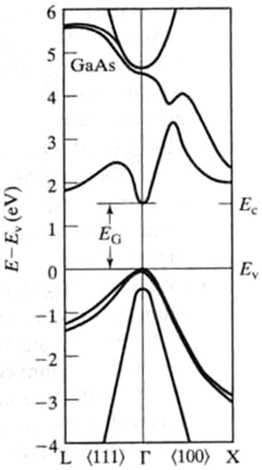
Handout 14

Statistics of Electrons in Energy Bands

In this lecture you will learn:



Example: Electron Statistics in GaAs - Conduction Band



Consider the conduction band of GaAs near the band bottom at the Γ-point:

$$M^{-1} = \begin{bmatrix} 1/m_e & 0 & 0 \\ 0 & 1/m_e & 0 \\ 0 & 0 & 1/m_e \end{bmatrix}$$

This implies the energy dispersion relation near the band bottom is:

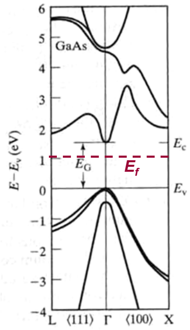
$$E_c(\vec{k}) = E_c + \frac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2\,m_e} = E_c + \frac{\hbar^2 k^2}{2\,m_e}$$

Suppose we want to find the total number of electrons in the conduction band:

We can write the following summation:

$$N = 2 \times \sum_{\vec{k}\ \text{in FBZ}} f_c(\vec{k})$$

Example: Electron Statistics in GaAs - Conduction Band



$$N = 2 \times \sum_{\vec{k} \text{ in FBZ}} f_c(\vec{k})$$

Where the Fermi-Dirac distribution function is:

$$f_c(\vec{k}) = \frac{1}{1+\exp\left(\frac{E_c(\vec{k})-E_f}{KT}\right)} \quad \left\{ = f\left(E_c(\vec{k}) - E_f\right) \right.$$

Another way of writing it

We convert the summation into an integral:

$$N = 2 \times \sum_{\vec{k} \text{ in FBZ}} f_c(\vec{k}) = 2 \times V \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3} \frac{1}{1+\exp\left(\frac{E_c(\vec{k})-E_f}{KT}\right)}$$

Then we convert the k-space integral into an integral over energy:

$$N = 2 \times V \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3} \frac{1}{1+\exp\left(\frac{E_c(\vec{k})-E_f}{KT}\right)} = \int_{?}^{?} dE \;\; g_c(E) f(E - E_f)$$

We need to find the density of states function $g_c(E)$ for the conduction band and need to find the limits of integration

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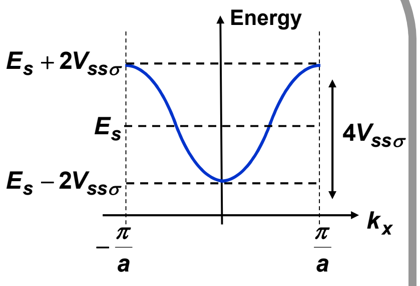
Density of States in Energy Bands

Consider the 1D energy band that results from tight binding:



$$E(k_x) = E_s - 2V_{ss\sigma} \cos(k_x\, a)$$

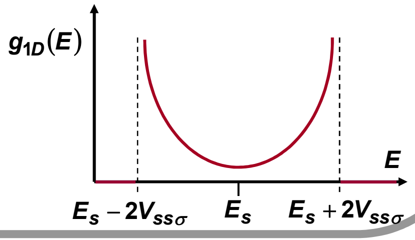
$$\Rightarrow \frac{dE}{dk_x} = 2aV_{ss\sigma} \sin(k_x\, a)$$

We need to find the density of states function $g_{1D}(E)$:

$$2 \times \sum_{k_x \text{ in FBZ}} \rightarrow 2 \times L \int_{-\pi/a}^{\pi/a} \frac{dk_x}{2\pi} \rightarrow 4 \times L \int_{0}^{\pi/a} \frac{dk_x}{2\pi} \rightarrow \frac{2}{\pi} \times L \int_{E_s - 2V_{ss\sigma}}^{E_s + 2V_{ss\sigma}} \left|\frac{dk_x}{dE}\right| dE$$

$$\rightarrow L \int_{E_s - 2V_{ss\sigma}}^{E_s + 2V_{ss\sigma}} g_{1D}(E)\, dE$$

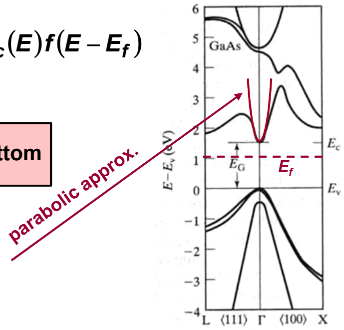
$$\Rightarrow g_{1D}(E) = \frac{2}{\pi a} \frac{1}{\sqrt{(2V_{ss\sigma})^2 - (E - E_s)^2}}$$



Example: Electron Statistics in GaAs - Conduction Band

$$N = 2\times V \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3}\,\frac{1}{1+\exp\left(\dfrac{E_c(\vec{k})-E_f}{KT}\right)} = \int_{?}^{?} dE\;\; g_c(E)\,f(E-E_f)$$

Electrons will only be present near the band bottom

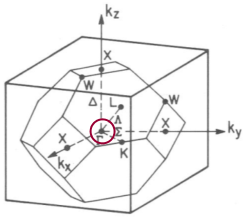


Energy dispersion near the band bottom is:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2\left(k_x^2+k_y^2+k_z^2\right)}{2m_e} = E_c + \frac{\hbar^2k^2}{2m_e}$$

(parabolic and isotropic)

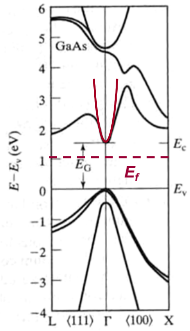
Since the electrons are likely present near the band bottom, we can limit the integral over the entire FBZ to an integral in a spherical region right close to the Γ-point:



$$N = 2\times V \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3}\,f_c(\vec{k}) = \;2\times V \int_{\Gamma-\text{point}} \frac{4\pi k^2}{8\pi^3}\,dk\;\; f(E_c(k)-E_f)$$

Example: Electron Statistics in GaAs - Conduction Band

$$N = 2\times V \int_{\Gamma-\text{point}} \frac{4\pi k^2}{8\pi^3}\,dk\;\; f(E_c(k)-E_f)$$



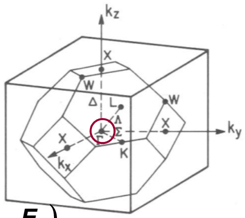
Since the Fermi-Dirac distribution will be non-zero only for small values of *k*, one can safely extend the upper limit of the integration to infinity:

$$N = 2\times V \int_0^{\infty} \frac{4\pi k^2}{8\pi^3}\,dk\;\; f(E_c(k)-E_f)$$

We know that:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2\left(k_x^2+k_y^2+k_z^2\right)}{2m_e} = E_c + \frac{\hbar^2k^2}{2m_e}$$

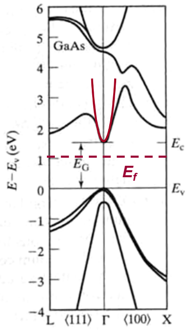
$$\Rightarrow k = \sqrt{\frac{2m_e}{\hbar^2}(E-E_c)} \qquad \text{and} \qquad \frac{dE}{dk} = \frac{\hbar^2 k\,dk}{m_e}$$



We have finally:

$$N = \;2\times V \int_0^{\infty} \frac{4\pi k^2}{8\pi^3}\,dk\;\; f(E_c(k)-E_f) = V\int_{E_c}^{\infty} dE\;\; g_c(E)\;\; f(E-E_f)$$

Example: Electron Statistics in GaAs - Conduction Band

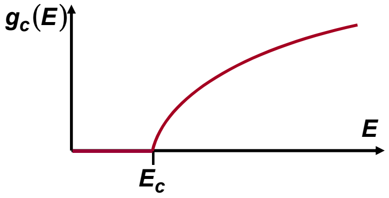


We have finally:

$$N = 2 \times V \int_0^{\infty} \frac{4\pi k^2}{8\pi^3} dk \;\; f(E_c(k) - E_f) = V \int_{E_c}^{\infty} dE \;\; g_c(E) \;\; f(E - E_f)$$

Where the conduction band density of states function is:

$$g_c(E) = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \sqrt{E - E_c}$$



The density of states function looks like that of a 3D free electron gas except that the mass is the effective mass m_e and the density of states go to zero at the band edge energy E_c

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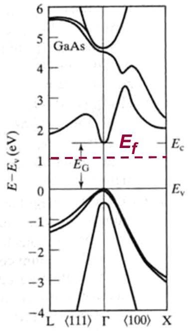
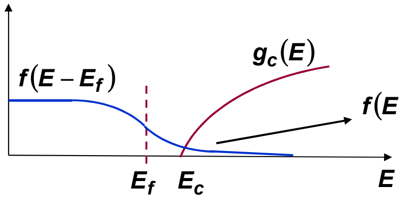
Example: Electron Statistics in GaAs - Conduction Band



$$n = \int_{E_c}^{\infty} dE \;\; g_c(E) \;\; f(E - E_f) \qquad g_c(E) = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \sqrt{E - E_c}$$



$$f(E - E_f) \approx e^{-\frac{(E - E_f)}{KT}}$$

If $E_c - E_f >> KT$ then one may approximate the Fermi-Dirac function as an exponential:

$$f(E - E_f) = \frac{1}{1 + \exp\left(\frac{E - E_f}{KT} \right)} \approx \exp\left(-\frac{(E - E_f)}{KT} \right) \longrightarrow$$

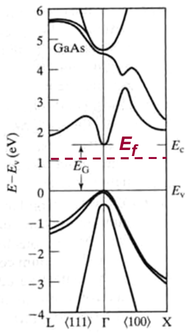
Maxwell-Boltzman approximation

$$n = \int_{E_c}^{\infty} dE \;\; g_c(E) \;\; f(E - E_f) = N_c \exp\left(-\frac{(E_c - E_f)}{KT} \right)$$

Where: $$N_c = 2 \left[\frac{m_e \, KT}{2\pi \, \hbar^2} \right]^{3/2} \longrightarrow$$

Effective density of states (units: #/cm³)

Example: Electron Statistics in GaAs - Valence Band and Holes



- At zero temperature, the valence band is completely filled and the conduction band is completely empty

- At any finite temperature, some electrons near the top of the valence band will get thermally excited from the valence band and occupy the conduction band and their density will be given by:

$$n = N_c \exp\left(-\frac{(E_c - E_f)}{KT}\right)$$

- The question we ask here is how many empty states are left in the valence band as a result of the electrons being thermally excited. The answer is (assuming the heavy-hole valence band):

$$2 \times \sum_{\vec{k} \text{ in FBZ}} \left[1 - f\left(E_{hh}(\vec{k}) - E_f\right)\right]$$

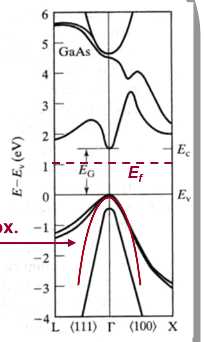
- We call this the number of "holes" left behind in the valence band and the number of these holes is *P*:

$$P = 2 \times \sum_{\vec{k} \text{ in FBZ}} 1 - f\left(E_{hh}(\vec{k}) - E_f\right) = 2 \times V \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3} \left[\, 1 - f\left(E_{hh}(\vec{k}) - E_f\right)\right]$$

Example: Electron Statistics in GaAs - Valence Band and Holes

$$P = 2 \times V \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3} \left[\, 1 - f\left(E_{hh}(\vec{k}) - E_f\right)\right]$$

Holes will only be present near the top of the valence band

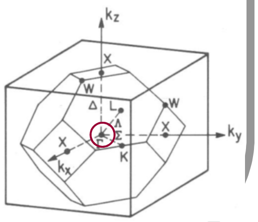


Energy dispersion near the top of the valence band is:

$$E_{hh}(\vec{k}) = Ev - \frac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2\,m_{hh}} = E_v - \frac{\hbar^2 k^2}{2\,m_{hh}}$$

parabolic approx.

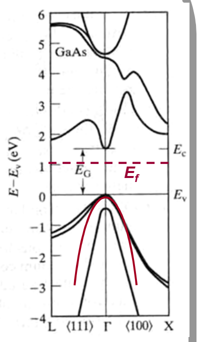
Since the holes are likely present near the band maximum, we can limit the integral over the entire FBZ to an integral in a spherical region right close to the Γ-point:



$$P = \; 2 \times V \int_{\Gamma-\text{point}} \frac{4\pi\, k^2}{8\pi^3}\, dk\; \left[1 - f\left(E_{hh}(k) - E_f\right)\right]$$

Example: Electron Statistics in GaAs - Valence Band and Holes

$$P = 2\times V \int_{\Gamma-\text{point}} \frac{4\pi k^2}{8\pi^3}\, dk\ \left[1 - f\left(E_{hh}(k) - E_f\right)\right]$$



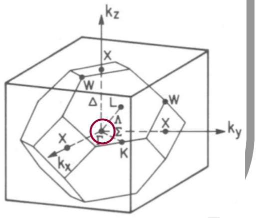
Since the Fermi-Dirac distribution will be non-zero only for small values of *k*, one can safely extend the upper limit of the integration to infinity:

$$P = 2\times V \int_0^\infty \frac{4\pi k^2}{8\pi^3}\, dk\ \left[1 - f\left(E_{hh}(k) - E_f\right)\right]$$

We know that:

$$E_{hh}(\vec{k}) = Ev - \frac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2\, m_{hh}} = E_v - \frac{\hbar^2 k^2}{2\, m_{hh}}$$

$$\Rightarrow k = \sqrt{\frac{2m_{hh}}{\hbar^2}\left(E_v - E\right)} \qquad \text{and} \qquad \frac{dE}{dk} = \frac{\hbar^2 k\, dk}{m_{hh}}$$



We have finally:

$$P = 2\times V \int_0^\infty \frac{4\pi k^2}{8\pi^3}\, dk\ \left[1 - f\left(E_{hh}(k) - E_f\right)\right]$$

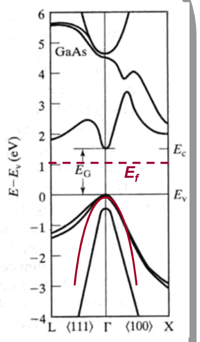
$$= V \int_{-\infty}^{E_v} dE\ \ g_{hh}(E)\ \left[1 - f\left(E - E_f\right)\right]$$

Example: Electron Statistics in GaAs - Valence Band and Holes

We have finally:

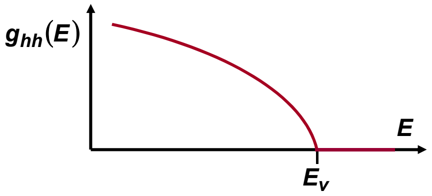
$$P = 2\times V \int_0^\infty \frac{4\pi k^2}{8\pi^3}\, dk\ \left[1 - f\left(E_{hh}(k) - E_f\right)\right]$$

$$= V \int_{-\infty}^{E_v} dE\ \ g_{hh}(E)\ \left[1 - f\left(E - E_f\right)\right]$$



Where the heavy hole band density of states function is:

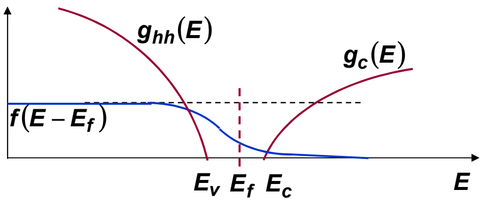
$$g_{hh}(E) = \frac{1}{2\pi^2}\left(\frac{2m_{hh}}{\hbar^2}\right)^{3/2}\sqrt{E_v - E}$$

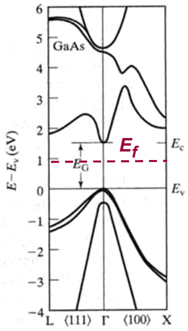


Note that the mass that comes in the density of states is the heavy hole effective mass m_{hh} and the density of states go to zero at the band edge energy E_v, and the density of states increase for smaller energies

Example: Electron Statistics in GaAs - Valence Band and Holes

$$p=\int_{-\infty}^{E_v} dE\;\; g_{hh}(E)\;\left[1-f(E-E_f)\right] \qquad g_{hh}(E)=\frac{1}{2\pi^2}\left(\frac{2m_{hh}}{\hbar^2}\right)^{3/2}\sqrt{E_v-E}$$





If $E_f - E_v >> KT$ then one may approximate the Fermi-Dirac function as an exponential:

$$1-f(E-E_f)=\frac{1}{1+\exp\left(\frac{E_f-E}{KT}\right)}\approx\exp\left(-\frac{(E_f-E)}{KT}\right)$$

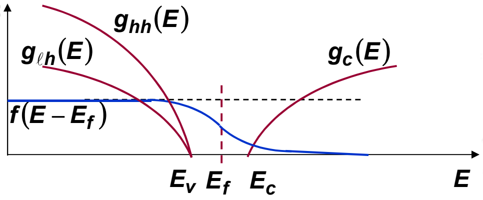
Maxwell-Boltzman approximation for holes

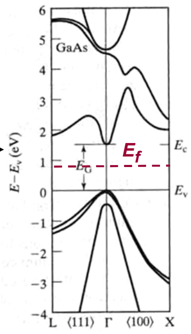
$$p=\int_{-\infty}^{E_v} dE\;\; g_{hh}(E)\;\left[1-f(E-E_f)\right]=N_{hh}\exp\left(-\frac{(E_f-E_v)}{KT}\right)$$

Where: $$N_{hh}=2\left[\frac{m_{hh}\,KT}{2\pi\,\hbar^2}\right]^{3/2}$$ → Effective density of states (units: #/cm^3)

Example: Electron Statistics in GaAs - Valence Band and Holes

In most semiconductors, the light-hole band is degenerate with the heavy hole band at the Γ-point. So one always needs to include the holes in the light-hole valence band as well:





$$p=\int_{-\infty}^{E_v} dE\;\; g_{hh}(E)\;\left[1-f(E-E_f)\right]+\int_{-\infty}^{E_v} dE\;\; g_{\ell h}(E)\;\left[1-f(E-E_f)\right]$$

$$=\int_{-\infty}^{E_v} dE\;\left[g_{hh}(E)+g_{\ell h}(E)\right]\;\left[1-f(E-E_f)\right]$$

$$=\int_{-\infty}^{E_v} dE\;\; g_v(E)\;\left[1-f(E-E_f)\right]$$

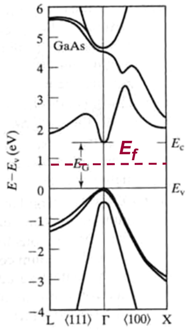
$$\left\{\begin{aligned} g_v(E)&=g_{\ell h}(E)+g_{hh}(E)\\ &=\frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2}\sqrt{E_v-E}\end{aligned}\right.$$

$$p=N_v\exp\left(-\frac{(E_f-E_v)}{KT}\right)$$

Where: $$N_v=2\left[\frac{m_h\,KT}{2\pi\,\hbar^2}\right]^{3/2}$$ and $$m_h=\left(m_{hh}^{3/2}+m_{\ell h}^{3/2}\right)^{2/3}$$ → Density of states effective mass

Example: Electron Statistics in GaAs – Electrons and Holes

At any temperature, the total number of electrons and holes (including both heavy and light holes) must be equal:



$$\Rightarrow p = n$$

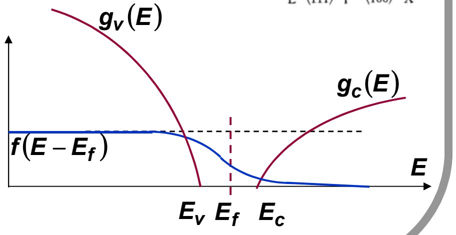
$$\Rightarrow N_v \exp\left(-\frac{(E_f - E_v)}{KT}\right) = N_c \exp\left(-\frac{(E_c - E_f)}{KT}\right)$$

$$\Rightarrow \frac{N_v}{N_c} = \exp\left(\frac{2E_f - E_c - E_v}{KT}\right)$$

$$\Rightarrow E_f = \frac{E_c + E_v}{2} + \frac{KT}{2}\log\left(\frac{N_v}{N_c}\right)$$

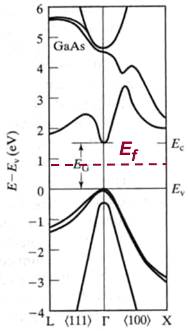
Because the effective density of states for electrons and holes are not the same (i.e. $N_v \neq N_c$), the Fermi level at any finite temperature is not right in the middle of the bandgap.

But at zero temperature, the Fermi-level is exactly in the middle of the bandgap



Example: Electron Statistics in GaAs – Electrons and Holes

At any temperature, the total number of electrons and holes (including both heavy and light holes) must be equal:



$$\Rightarrow p = n = n_i$$

where n_i is called the intrinsic electron (or hole) density

$$\Rightarrow p = n = n_i$$

$$\Rightarrow p\,n = n_i^2$$

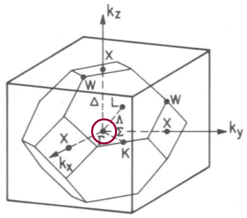
$$\Rightarrow N_v \exp\left(-\frac{(E_f - E_v)}{KT}\right) N_c \exp\left(-\frac{(E_c - E_f)}{KT}\right) = n_i^2$$

$$\Rightarrow N_v N_c \exp\left(-\frac{(E_c - E_v)}{KT}\right) = n_i^2$$

$$\Rightarrow n_i = \sqrt{N_v N_c}\exp\left(-\frac{E_g}{2KT}\right)$$

Note that the smaller the bandgap the larger than intrinsic electron (or hole) density

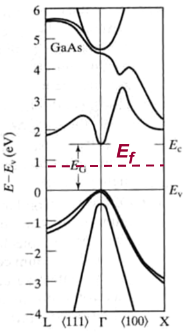
Electron and Hole Pockets in GaAs

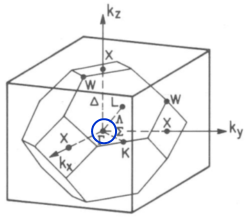


Electron pocket

- At any non-zero temperature, electrons occupy states in k-space that are located in a spherically symmetric distribution around the Γ-point

- This distrbution is referred to as the "**electron pocket**" at the Γ-point



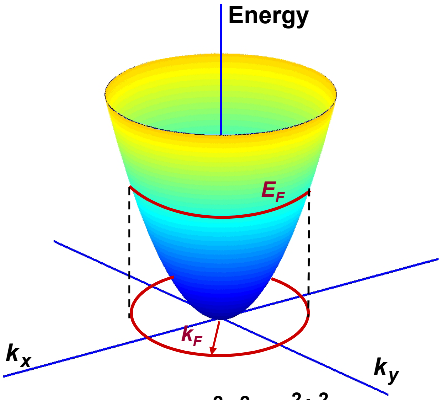


Hole pocket

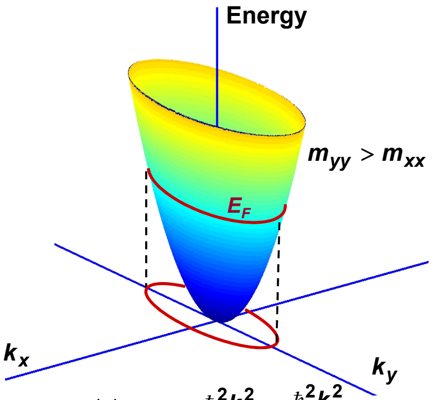
- At any non-zero temperature, the holes (heavy and light) also occupy states in k-space that are located in a spherically symmetric distribution around the Γ-point

- This distribution is referred to as the "**hole pocket**" at the Γ-point

Shape of Fermi Surface/Contour and Mass Tensor: 2D Example



$$E_c(\vec{k}) = E_c + \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m}$$



$$E_c(\vec{k}) = E_c + \frac{\hbar^2 k_x^2}{2m_{xx}} + \frac{\hbar^2 k_y^2}{2m_{yy}}$$

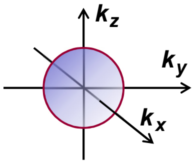
When the energy dispersion relation is anisotropic, the distribution of carriers in k-space, and the Fermi surface/contour, are not spherical/circular but become ellipsoidal/elliptical

Constant Energy Surfaces

Constant energy surfaces are in the reciprocal space and are such that the energy of every point on the surface is the same.

For example, the conduction band energy dispersion:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_e}$$



All points in k-space that are equidistant from the origin (Γ-point) have the same energy.
⇒ Constant energy surfaces in 3D are spherical shells, and in 2D are circles, with the origin as their center.

Equation of a Constant Energy Surface with Energy E_o:

$$E_c + \frac{\hbar^2 k^2}{2m_e} = E_o \quad \Rightarrow \quad \underbrace{k_x^2 + k_y^2 + k_z^2 = \frac{2m}{\hbar^2}(E_o - E_c)}$$

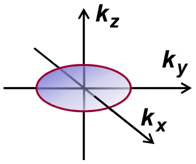
Equation of a sphere in k-space of radius = $\sqrt{\frac{2m}{\hbar^2}(E_o - E_c)}$

Constant Energy Surfaces

Now consider the energy band dispersion: $E_c(\vec{k}) = E_c + \frac{\hbar^2 k_x^2}{2m_{xx}} + \frac{\hbar^2 k_y^2}{2m_{yy}} + \frac{\hbar^2 k_z^2}{2m_{zz}}$

Now the equation of a constant energy surface with energy E_o is:

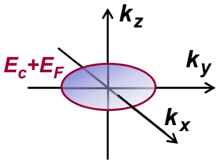
$$E_c + \frac{\hbar^2 k_x^2}{2m_{xx}} + \frac{\hbar^2 k_y^2}{2m_{yy}} + \frac{\hbar^2 k_z^2}{2m_{zz}} = E_o \quad \Rightarrow \quad \underbrace{\frac{k_x^2}{m_{xx}} + \frac{k_y^2}{m_{yy}} + \frac{k_z^2}{m_{zz}} = \frac{2}{\hbar^2}(E_o - E_c)}$$



Equation of an ellipsoid in k-space with semi-major axes given by:

$$\sqrt{\frac{2m_{xx}}{\hbar^2}(E_o - E_c)} \quad \sqrt{\frac{2m_{yy}}{\hbar^2}(E_o - E_c)} \quad \sqrt{\frac{2m_{zz}}{\hbar^2}(E_o - E_c)}$$

Fermi-Surfaces are Examples of Constant Energy Surfaces:



$$E_c + \frac{\hbar^2 k_x^2}{2m_{xx}} + \frac{\hbar^2 k_y^2}{2m_{yy}} + \frac{\hbar^2 k_z^2}{2m_{zz}} = E_c + E_F$$

Silicon: Electrons in the Conduction Band

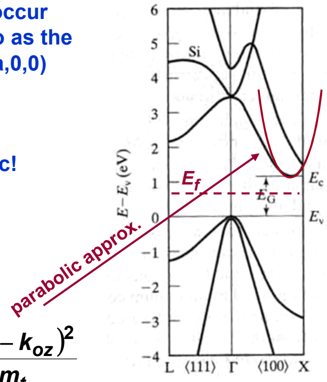
In Silicon there are six conduction band minima that occur along the six Γ-X directions. These are also referred to as the six valleys. For the one that occurs along the Γ-X(2π/a,0,0) direction:

$$\vec{k}_o = 0.85\left(\frac{2\pi}{a},0,0\right) \qquad E_c\left(\vec{k}_o\right) = E_c$$

$$M^{-1} = \begin{bmatrix} 1/m_\ell & 0 & 0 \\ 0 & 1/m_t & 0 \\ 0 & 0 & 1/m_t \end{bmatrix}$$

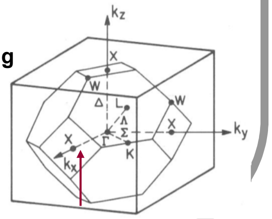
Not isotropic!

$m_\ell = 0.92\ m$
$m_t = 0.19\ m$



This implies:

$$E_c\left(\vec{k}\right) = E_c + \frac{\hbar^2\left(k_x - k_{ox}\right)^2}{2\,m_\ell} + \frac{\hbar^2\left(k_y - k_{oy}\right)^2}{2\,m_t} + \frac{\hbar^2\left(k_z - k_{oz}\right)^2}{2\,m_t}$$



Expression for the electron density in the valley located at along the Γ-X(2π/a,0,0) direction can be written as:

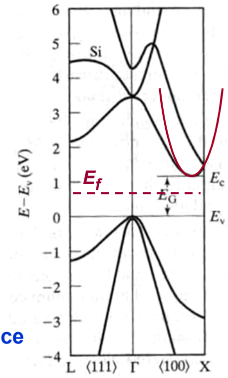
$$2 \int_{\vec{k}\text{ near }\vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3}\, f\left(E_c\left(\vec{k}\right) - E_f\right)$$

Silicon: Electrons in the Conduction Band

Define:

$$q_x = \sqrt{\frac{m}{m_\ell}}\left(k_x - k_{ox}\right) \qquad q_y = \sqrt{\frac{m}{m_t}}\left(k_y - k_{oy}\right)$$

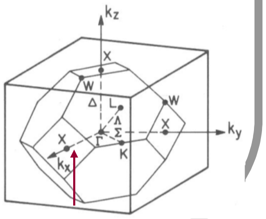
$$q_z = \sqrt{\frac{m}{m_t}}\left(k_z - k_{oz}\right)$$



This implies:

$$E_c\left(\vec{k}\right) = E_c + \frac{\hbar^2\left(k_x - k_{ox}\right)^2}{2\,m_\ell} + \frac{\hbar^2\left(k_y - k_{oy}\right)^2}{2\,m_t} + \frac{\hbar^2\left(k_z - k_{oz}\right)^2}{2\,m_t}$$

$$E_c(\vec{q}) = E_c + \frac{\hbar^2 q^2}{2\,m} \longrightarrow$$ Dispersion is isotropic in q-space



Therefore, expression for the electron density in the valley located at along the Γ-X(2π/a,0,0) direction can be written as:

$$2 \int_{\vec{k}\text{ near }\vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3}\, f\left(E_c\left(\vec{k}\right) - E_f\right)$$

$$= \sqrt{\frac{m_\ell m_t m_t}{m^3}}\; 2 \int_{\vec{q}\text{ near }0} \frac{d^3\vec{q}}{(2\pi)^3}\, f\left(E_c(\vec{q}) - E_f\right)$$

Silicon: Electrons in the Conduction Band

$$\sqrt{\frac{m_\ell m_t m_t}{m^3}}\;\; 2\int_{\vec{q}\text{ near }0}\frac{d^3\vec{q}}{(2\pi)^3}\, f\big(E_c(\vec{q})-E_f\big)$$

$$\approx \sqrt{\frac{m_\ell m_t m_t}{m^3}}\;\; 2\int_0^\infty\frac{4\pi q^2}{8\pi^3}\,dq\;\; f\big(E_c(q)-E_f\big)$$

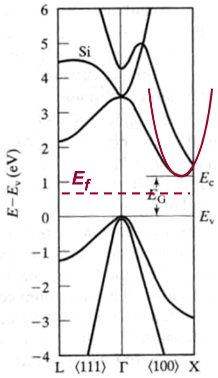
Total electron density in the conduction band consists of contributions from electron density sitting in all the six valleys:

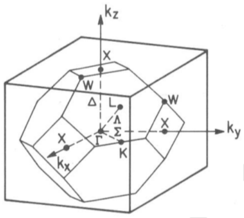
$$n = 6\times\sqrt{\frac{m_\ell m_t m_t}{m^3}}\;\; 2\int_0^\infty\frac{4\pi q^2}{8\pi^3}\,dq\;\; f\big(E_c(q)-E_f\big)$$

$$\Rightarrow n = \int_{E_c}^{\infty} dE\;\; g_c(E)\;\; f(E-E_f)$$

Where: $$g_c(E) = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\sqrt{E-E_c}$$

and: $m_e = 6^{2/3}(m_\ell m_t m_t)^{1/3}$ $\longrightarrow$ **Density of states effective mass**





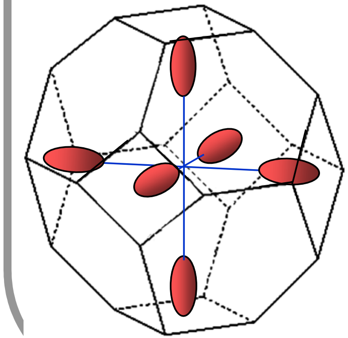
Silicon: Electrons in the Conduction Band

$$n = \int_{E_c}^{\infty} dE\;\; g_c(E)\;\; f(E-E_f) = N_c \exp\left(-\frac{(E_c-E_f)}{KT}\right)$$

Where: $$N_c = 2\left[\frac{m_e\,KT}{2\pi\,\hbar^2}\right]^{3/2}$$

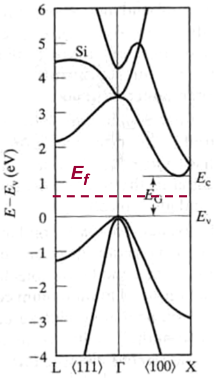
And: $$m_e = 6^{2/3}(m_\ell m_t m_t)^{1/3}$$

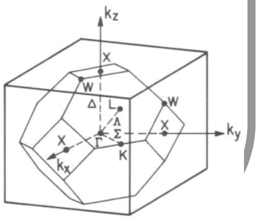
Six electron pockets in FBZ:



There are six electron pockets in Silicon - one at each of the valleys (conduction band minima)

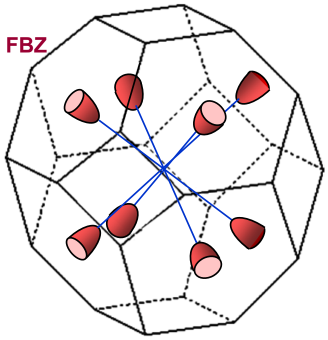
The electron distribution in k-space in each pocket is not spherical but ellipsoidal since the electron masses in different directions are not the same





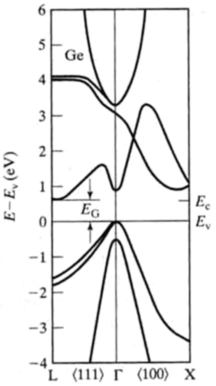
Germanium: Electrons in the Conduction Band

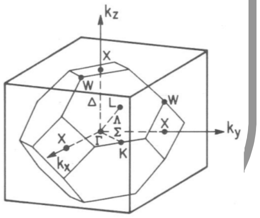
In germanium there are eight conduction band minima that occur at the L-points



The L-point is at the edge of the FBZ, so one-half of each electron pocket is not in the FBZ and therefore one-half of the electron distribution in each L-valley should not be counted in the sum for calculating the number of electrons:

$$N = 2\times \sum_{\vec{k}\ \text{in FBZ}} f\left(E_c\left(\vec{k}\right) - E_f\right)$$





The other way to look at the problem is to realize that the other-half of each pocket is also located in the FBZ on the opposite side – so in reality there are four complete pockets of electrons in the FBZ

Handout 15

Dynamics of Electrons in Energy Bands

In this lecture you will learn:

- The behavior of electrons in energy bands subjected to uniform electric fields
- The dynamical equation for the crystal momentum
- The effective mass tensor and inertia of electrons in energy bands
- Examples
- Magnetic fields
- Appendix: Electron dynamics using gauge invariance arguments, Berry's phase, and Berry's curvature

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Electron Dynamics in Energy Bands

1) The quantum states of an electron in a crystal are given by Bloch functions that obey the Schrodinger equation:

$$\hat{H}\,\psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})$$

where the wavevector $\vec{k}$ is confined to the FBZ and "*n*" is the band index

2) Under a lattice translation, Bloch functions obey the relation:

$$\psi_{n,\vec{k}}(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})$$

Now we ask the following question: if an external potential is added to the crystal Hamiltonian,

$$\hat{H} + \hat{U}(\vec{r},t)$$

then what happens? How do the electrons behave? How do we find the new energies and eigenstates?

The external potential could represent, for example, an applied E-field or an applied B-field, or an electromagnetic wave (like light)

Periodicity of Energy Bands

Recall from homework that the energy bands are lattice-periodic in the reciprocal space,

$$E_n(\vec{k}+\vec{G})=E_n(\vec{k})$$

When a function in real space is lattice-periodic, we can expand it in a Fourier series,

$$V(\vec{r}+\vec{R})=V(\vec{r}) \quad \Rightarrow \quad V(\vec{r})=\sum_j V(\vec{G}_j)\,e^{i\,\vec{G}_j\cdot\vec{r}}$$

⇒ When a function is lattice-periodic in reciprocal space, we can also expand it in a Fourier series of the form,

$$E_n(\vec{k}+\vec{G})=E_n(\vec{k}) \quad \Rightarrow \quad \underbrace{E_n(\vec{k})=\sum_j E_n(\vec{R}_j)\,e^{i\,\vec{R}_j\cdot\vec{k}}}_{\text{Fourier representation of energy bands}}$$

A New Operator - I

Consider the following mathematical identity (Taylor expansion):

$$f(x+a)=f(x)+f'(x)\,a+\frac{1}{2}f''(x)\,a^2+\ldots\ldots\ldots\ldots$$

$$=e^{a\frac{d}{dx}}\,f(x)$$

Generalize to 3 dimensions:

$$f(\vec{r}+\vec{a})=e^{\vec{a}\cdot\nabla}\,f(\vec{r})$$

Now go back to the relation:

$$E_n(\vec{k}+\vec{G})=E_n(\vec{k}) \quad \Rightarrow \quad E_n(\vec{k})=\sum_j E_n(\vec{R}_j)\,e^{i\,\vec{R}_j\cdot\vec{k}}$$

and consider the operator:

$$\hat{E}_n(-i\nabla)=\sum_j E_n(\vec{R}_j)\,e^{\vec{R}_j\cdot\nabla}$$

We apply this operator to a Bloch function from the same band (i.e. the *n*-th band) and see what happens:

$$\hat{E}_n(-i\nabla)\,\psi_{n,\vec{k}}(\vec{r})=\sum_j E_n(\vec{R}_j)\,e^{\vec{R}_j\cdot\nabla}\,\psi_{n,\vec{k}}(\vec{r})=\,?$$

A New Operator - II

$$\begin{aligned}
\hat{E}_n(-i\nabla)\,\psi_{n,\vec{k}}(\vec{r}) &= \sum_j E_n(\vec{R}_j)\,e^{\vec{R}_j\cdot\nabla}\,\psi_{n,\vec{k}}(\vec{r}) \\
&= \sum_j E_n(\vec{R}_j)\,\psi_{n,\vec{k}}(\vec{r}+\vec{R}_j) \\
&= \sum_j E_n(\vec{R}_j)\,e^{i\,\vec{k}\,.\,\vec{R}_j}\,\psi_{n,\vec{k}}(\vec{r}) \\
&= E_n(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})
\end{aligned}$$

The result above implies that the action of the operator $\hat{E}_n(-i\nabla)$ on a Bloch function belonging to the same band (i.e. *n*-th band) is that of the Hamiltonian!

$$\hat{E}_n(-i\nabla)\,\psi_{n,\vec{k}}(\vec{r}) = \hat{H}\,\psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})$$

This also implies that if we have a superposition of Bloch functions from a single band then:

$$\begin{aligned}
\hat{H}\sum_{\vec{k}\ \text{in FBZ}} c(\vec{k})\,\psi_{n,\vec{k}}(\vec{r}) &= \hat{E}_n(-i\nabla)\sum_{\vec{k}\ \text{in FBZ}} c(\vec{k})\,\psi_{n,\vec{k}}(\vec{r}) \\
&= \sum_{\vec{k}\ \text{in FBZ}} c(\vec{k})\,E_n(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})
\end{aligned}$$

The Case of Uniform Electric Field

Statement of problem: Need to solve,

$$\left[\hat{H} + e\,\vec{E}\,.\,\hat{\vec{r}}\,\right]\psi(\vec{r},t) = i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}$$

given that at time $t = 0$ the state of the electron is a Bloch function with wavevector $\vec{k}$,

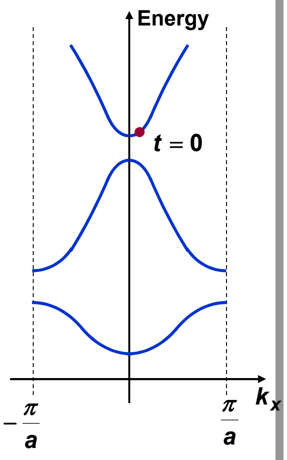
$$\psi(\vec{r},t=0) = \psi_{n,\vec{k}}(\vec{r})$$

Assumption: Assume that the state at any later time is going to be a Bloch function or a linear combination of Bloch functions belonging to the same band (valid for weak E-fields)

Then one can replace the Hamiltonian with $\hat{E}_n(-i\nabla)$,

$$\left[\hat{H} + e\,\vec{E}\,.\,\hat{\vec{r}}\,\right]\psi(\vec{r},t) = i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}$$

$$\Rightarrow\ \left[E_n(-i\nabla) + e\,\vec{E}\,.\,\hat{\vec{r}}\,\right]\psi(\vec{r},t) = i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}$$



The Case of Uniform Electric Field

$$\left[E_n(-i\nabla)+e\vec{E}\,.\,\hat{\vec{r}}\,\right]\psi(\vec{r},t)=i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}$$

Try the following time-dependent solution with a time-dependent energy:

$$\psi(\vec{r},t)=\psi_{n,\vec{k}}(\vec{r})\,\exp\left[-\frac{i}{\hbar}\int_{0}^{t}\left(E(t')+e\vec{E}\,.\,\vec{r}\right)dt'\right]$$

First see how the assumed solution behaves under a lattice translation:

$$\psi\left(\vec{r}+\vec{R},t\right)=\psi_{n,\vec{k}}\left(\vec{r}+\vec{R}\right)\exp\left[-\frac{i}{\hbar}\int_{0}^{t}\left(E(t')+e\vec{E}\,.\left(\vec{r}+\vec{R}\right)\right)dt'\right]$$

$$=e^{i\left(\vec{k}-\frac{e\vec{E}\,t}{\hbar}\right).\vec{R}}\,\psi(\vec{r},t)$$

So the assumed solution looks like a Bloch function with a time dependent k-vector:

$$\vec{k}(t)=\vec{k}-\frac{e\,\vec{E}\,t}{\hbar}$$

But we still don't know what is the time-dependent energy *E*(*t*)

The Case of Uniform Electric Field

Take the trial solution and plug it into the equation:

$$\left[E_n(-i\nabla)+e\vec{E}\,.\,\hat{\vec{r}}\,\right]\psi(\vec{r},t)=i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}$$

LHS (first term):

$$E_n(-i\nabla)\,\psi(\vec{r},t)=\sum_j E_n\left(\vec{R}_j\right)e^{\vec{R}_j\,.\,\nabla}\psi(\vec{r},t)$$

$$=\sum_j E_n\left(\vec{R}_j\right)\psi\left(\vec{r}+\vec{R}_j,t\right)$$

$$=\sum_j E_n\left(\vec{R}_j\right)e^{i\left(\vec{k}-\frac{e\vec{E}}{\hbar}t\right).\vec{R}_j}\psi(\vec{r},t)$$

$$=E_n\left(\vec{k}-\frac{e\vec{E}}{\hbar}t\right)\psi(\vec{r},t)$$

RHS:

$$i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}=\left[E(t)+e\vec{E}\,.\,\vec{r}\,\right]\psi(\vec{r},t)$$

The Case of Uniform Electric Field

Putting it together:

$$\left[E_n(-i\nabla) + e\,\vec{E}\,.\,\hat{\vec{r}}\,\right]\psi(\vec{r},t) = i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}$$

$$\Rightarrow \left[\,E_n\!\left(\vec{k}-\frac{e\,\vec{E}\,t}{\hbar}\right)+e\,\vec{E}\,.\,\hat{\vec{r}}\,\right]\psi(\vec{r},t) = \left[E(t)+e\,\vec{E}\,.\,\hat{\vec{r}}\,\right]\psi(\vec{r},t)$$

$$\Rightarrow E(t) = E_n\!\left(\vec{k}-\frac{e\,\vec{E}\,t}{\hbar}\right)$$

The time-dependent energy is consistent with our solution being a Bloch function with a time-dependent k-vector,

$$\vec{k}(t) = \vec{k} - \frac{e\,\vec{E}\,t}{\hbar}$$

So the solution for the initial condition:

$$\psi(\vec{r},t=0) = \psi_{n,\vec{k}}(\vec{r})$$

is approximately a Bloch function with a time-dependent k-vector:

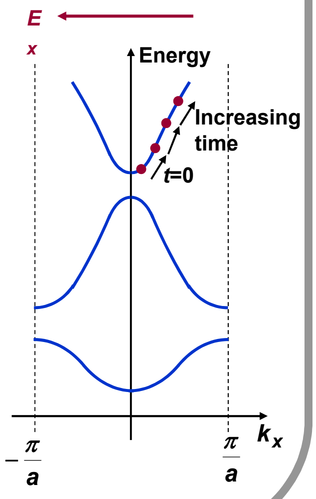
$$\psi(\vec{r},t) = \psi_{n,\vec{k}(t)}(\vec{r})\,\exp\!\left[-\frac{i}{\hbar}\int_0^t E_n(k(t'))\,dt'\right]$$

The Case of Uniform Electric Field

Final result: In the presence of a uniform electric field the electrons in energy bands have a time-dependent crystal momentum that satisfies the dynamical equation:

$$\boxed{\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}}$$

⇒ The rate of change of the crystal momentum is equal to the force on the electron



Note that (perhaps) the more intuitive result that the rate of change of the average electron momentum equals the applied force DOES NOT hold,

$$\frac{d\,\langle\psi(\vec{r},t)|\hat{P}|\psi(\vec{r},t)\rangle}{dt} \neq -e\,\vec{E}$$

The dynamical equation is instead given in terms of the crystal momentum

What Happened to Ehrenfest's Theorem of QM?

In quantum mechanics, Ehrenfest's theorem is the closest to Newton's second law.

Ehrenfest's theorem: For a time dependent quantum state, the rate of change of the average momentum equals the average force:

$$\frac{d\,\langle\psi(\vec{r},t)|\hat{P}|\psi(\vec{r},t)\rangle}{dt} = \langle\psi(\vec{r},t)|\hat{F}(\vec{r})|\psi(\vec{r},t)\rangle$$

We saw that for electrons in solids, in the presence of a uniform applied E-field, the following equation does not hold:

$$\frac{d\,\langle\psi(\vec{r},t)|\hat{P}|\psi(\vec{r},t)\rangle}{dt} \neq \langle\psi(\vec{r},t)|-e\,\vec{E}|\psi(\vec{r},t)\rangle = -e\,\vec{E}$$

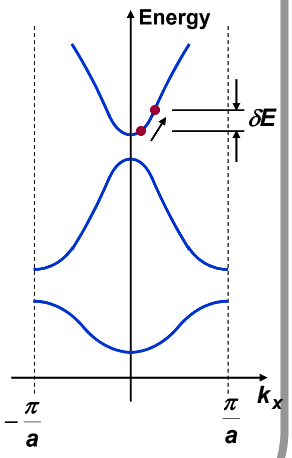
The reason is that in solids, in the presence of an applied E-field, the electrons not only feel the force from the applied E-field but they also feel the force from the periodic atomic potential. If all forces are correctly taken into account then, of course, Ehrenfest's theorem would hold. But it is more useful and simpler to use the dynamical equation involving the crystal momentum:

$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}$$

Another Look at the Dynamical Equation: Energy Conservation

One can also derive the dynamical equation: $\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}$

from arguments involving energy conservation



Consider an electron with an initial Bloch state with wavevector $\vec{k}$. Suppose in the presence of an E-field the wavevector is time-dependent - but we don't know what is the time dependence:

$$\frac{d\,\vec{k}(t)}{dt} = ?$$

In time δt the electron energy will increase by:

$$\delta E = \nabla E_n(\vec{k}) \,.\, \frac{d\,\vec{k}(t)}{dt}\,\delta t \qquad \text{——— (1)}$$

The increase in electron energy also equals the work done by the E-field on the electron in time δt:

$$\delta E = \vec{v}_n(\vec{k})\,.\,\left(-e\vec{E}\right)\,\delta t \qquad \text{——— (2)}$$

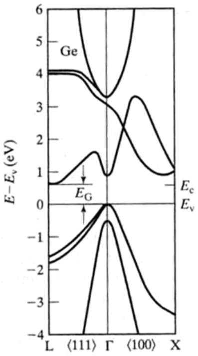
Equating (1) and (2) gives:

$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}$$

Effective Mass Tensor and Acceleration

Consider a solid in which the energy dispersion near a band extremum is given by:

$$E_n(\vec{k}) = E_n(\vec{k}_o) + \frac{\hbar^2}{2}(\vec{k}-\vec{k}_o)^T \,.\, M^{-1} \,.\, (\vec{k}-\vec{k}_o)$$



The average velocity is:

$$\vec{v}_n(\vec{k}) = M^{-1} \,.\, \hbar\,(\vec{k}-\vec{k}_o)$$

Consequently, the rate of change of the velocity satisfies:

$$\frac{d\,\vec{v}_n(\vec{k}(t))}{dt} = M^{-1} \,.\, \frac{d\,\hbar\,\vec{k}(t)}{dt}$$

In the presence of an E-field the crystal momentum changes as:

$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}$$

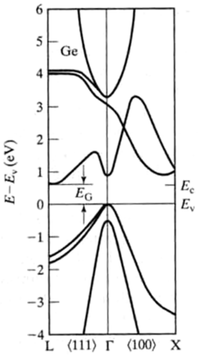
Therefore:

$$\frac{d\,\vec{v}_n(\vec{k}(t))}{dt} = M^{-1} \,.\, \frac{d\,\hbar\,\vec{k}(t)}{dt} = M^{-1} \,.\, -e\vec{E}$$

$$\Rightarrow \frac{d\,\vec{v}_n(t)}{dt} = -e\,M^{-1} \,.\, \vec{E}$$

Effective Mass Tensor and Acceleration

$$\frac{d\,\vec{v}_n(t)}{dt} = -e\,M^{-1} \,.\, \vec{E} \qquad \text{Or :} \qquad M \,.\, \frac{d\,\vec{v}_n(t)}{dt} = -e\,\vec{E}$$



The acceleration of electrons in energy bands in response to an applied force is governed by the effective mass tensor.

The above relation shows that the effective mass tensor, which up to this point just represented coefficients for Taylor expansion of the energy dispersion relation, is also a measure of the inertia of electrons in energy bands just like ordinary mass is a measure of the inertia of free electrons.

Written out in component form we have:

$$\frac{d}{dt}\begin{bmatrix} v_{x,n}(t) \\ v_{y,n}(t) \\ v_{z,n}(t) \end{bmatrix} = -e \begin{bmatrix} 1/m_{xx} & 1/m_{xy} & 1/m_{xz} \\ 1/m_{yx} & 1/m_{yy} & 1/m_{yz} \\ 1/m_{zx} & 1/m_{zy} & 1/m_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

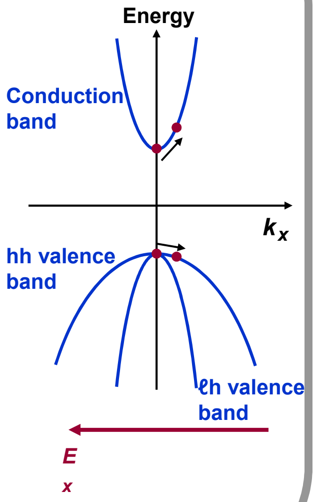
In general, the electrons are accelerated in a direction different from the direction of the force due to the applied E-field !

Example: Conduction and Heavy-Hole Valence Bands of GaAs

Consider the conduction band of GaAs near the band bottom at the Γ-point:

$$M^{-1} = \begin{bmatrix} 1/m_e & 0 & 0 \\ 0 & 1/m_e & 0 \\ 0 & 0 & 1/m_e \end{bmatrix}$$

$$\frac{d\,\vec{v}_c(t)}{dt} = -e\,M^{-1}\,.\,\vec{E} = -\frac{e}{m_e}\,\vec{E}$$



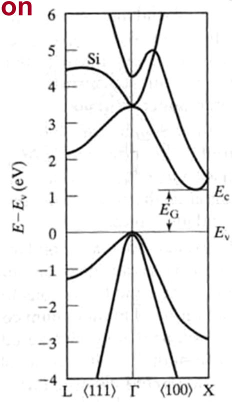
Now consider the heavy-hole valence band of GaAs near the band maximum at the Γ-point:

$$M^{-1} = \begin{bmatrix} -1/m_{hh} & 0 & 0 \\ 0 & -1/m_{hh} & 0 \\ 0 & 0 & -1/m_{hh} \end{bmatrix}$$

$$\frac{d\,\vec{v}_{hh}(t)}{dt} = -e\,M^{-1}\,.\,\vec{E} = \frac{e}{m_{hh}}\,\vec{E}$$

Electrons in the valence band are accelerated in the direction opposite to the force acting upon them due to the applied E-field

Example: Conduction Band of Silicon



In Silicon there are six conduction band minima (valleys) that occur along the six Γ-X directions. For the one that occurs along the Γ-X(2π/a,0,0) direction:

$$\vec{k}_o = 0.85\left(\frac{2\pi}{a},0,0\right)$$

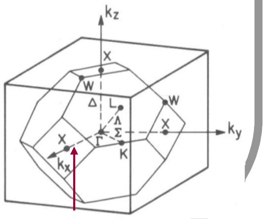
$$M^{-1} = \begin{bmatrix} 1/m_\ell & 0 & 0 \\ 0 & 1/m_t & 0 \\ 0 & 0 & 1/m_t \end{bmatrix}$$

Not isotropic!

$m_\ell = 0.92\ m$
$m_t = 0.19\ m$

This implies:

$$\frac{d}{dt}\begin{bmatrix} v_{x,c}(t) \\ v_{y,c}(t) \\ v_{z,c}(t) \end{bmatrix} = -e\begin{bmatrix} 1/m_\ell & 0 & 0 \\ 0 & 1/m_t & 0 \\ 0 & 0 & 1/m_t \end{bmatrix}\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$



Electrons in this valley have larger inertia (i.e. larger mass) for E-field applied in the x-direction (i.e. the longitudinal direction) and smaller inertia (i.e. smaller mass) for E-field applied in the y- or z-directions (i.e. the transverse directions)

Generalization to Include Applied Magnetic Fields

We had for only electric fields:

$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}$$

(assuming parabolic energy band dispersion)

$$M\,.\frac{d\,\vec{v}_n\left(\vec{k}(t)\right)}{dt} = -e\,\vec{E}$$

Magnetic fields can also be included as follows:

$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E} - e\,\vec{v}_n\left(\vec{k}(t)\right)\times\vec{B}$$

(assuming parabolic energy band dispersion)

$$M\,.\frac{d\,\vec{v}_n\left(\vec{k}(t)\right)}{dt} = -e\,\vec{E} - e\,\vec{v}_n\left(\vec{k}(t)\right)\times\vec{B}$$

Note: If the energy band dispersion is not parabolic (as in graphene) then the equations on the right hand side have no meaning

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Appendix: Electron Dynamics from Gauge Invariance

Consider the Schrodinger equation for an electron in a solid:

$$\left[\frac{\hat{\vec{P}}^2}{2m} + V\left(\hat{\vec{r}}\right)\right]\psi(\vec{r},t) = i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}$$

We have seen that the stationary solutions are the Bloch states:

$$\left[\frac{\hat{\vec{P}}^2}{2m} + V\left(\hat{\vec{r}}\right)\right]\psi_{n,\vec{k}}(\vec{r}) = E_n\left(\vec{k}\right)\psi_{n,\vec{k}}(\vec{r})$$

Or since: $\psi_{n,\vec{k}}(\vec{r}) = \frac{e^{i\vec{k}.\vec{r}}}{\sqrt{V}}\,u_{n,\vec{k}}(\vec{r})$

$$\Rightarrow \left[\frac{\left(\hat{\vec{P}} + \hbar\vec{k}\right)^2}{2m} + V\left(\hat{\vec{r}}\right)\right]u_{n,\vec{k}}(\vec{r}) = E_n\left(\vec{k}\right)u_{n.\vec{k}}(\vec{r})$$

In the presence of electromagnetic vector and scalar potentials the time-dependent Schrodinger equation becomes:

$$\left[\frac{\left(\hat{\vec{P}} + e\vec{A}\left(\hat{\vec{r}},t\right)\right)^2}{2m} + V\left(\hat{\vec{r}}\right) - e\phi\left(\hat{\vec{r}},t\right)\right]\psi(\vec{r},t) = i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}$$

Appendix: Electron Dynamics from Gauge Invariance

$$\left[\frac{\left(\hat{\vec{P}}+e\vec{A}(\hat{\vec{r}},t)\right)^2}{2m}+V(\hat{\vec{r}})-e\phi(\hat{\vec{r}},t)\right]\psi(\vec{r},t)=i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}$$

The Schrodinger equation is invariant (i.e. does not change) under the following gauge transformation:

$$\vec{A}(\hat{\vec{r}},t)\to\vec{A}(\hat{\vec{r}},t)+\nabla f(\hat{\vec{r}},t)$$

$$\phi(\hat{\vec{r}},t)\to\phi(\hat{\vec{r}},t)-\frac{\partial f(\hat{\vec{r}},t)}{\partial t}$$

$$\psi(\vec{r},t)\to e^{-i\frac{e}{\hbar}f(\vec{r},t)}\psi(\vec{r},t)$$

Now get back to the problem of an electron in an applied electric field. The Schrodinger equation is:

$$\left[\frac{\hat{\vec{P}}^2}{2m}+V(\hat{\vec{r}})+e\vec{E}.\hat{\vec{r}}\right]\psi(\vec{r},t)=i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}$$

Perform the following gauge transformation to eliminate the scalar potential in favor of the vector potential:

$$f(\vec{r},t)=-\vec{E}.\vec{r}\,t$$

Appendix: Electron Dynamics from Gauge Invariance

We get:

$$\left[\frac{\left(\hat{\vec{P}}-e\vec{E}t\right)^2}{2m}+V(\hat{\vec{r}})\right]e^{i\frac{e}{\hbar}\vec{E}.\vec{r}t}\psi(\vec{r},t)=i\hbar\frac{\partial}{\partial t}e^{i\frac{e}{\hbar}\vec{E}.\vec{r}t}\psi(\vec{r},t)$$

Let:

$$\phi(\vec{r},t)=e^{i\frac{e}{\hbar}\vec{E}.\vec{r}t}\psi(\vec{r},t)$$

$$\Rightarrow\left[\frac{\left(\hat{\vec{P}}-e\vec{E}t\right)^2}{2m}+V(\hat{\vec{r}})\right]\phi(\vec{r},t)=i\hbar\frac{\partial\phi(\vec{r},t)}{\partial t}$$

Now we have to solve a time-dependent equation BUT the Hamiltonian is now lattice periodic! Assume, in the spirit of Bloch's analysis, solution of the form:

$$\phi(\vec{r},t)=\frac{e^{i\vec{k}.\vec{r}}}{\sqrt{V}}u(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E(t')dt'}$$

And plug the assumed form in the above equation to get:

Appendix: Electron Dynamics from Gauge Invariance

$$\left[\frac{\left(\hat{\vec{P}}+\hbar\vec{k}-e\vec{E}t\right)^2}{2m}+V\left(\hat{\vec{r}}\right)\right]u(\vec{r})=E(t)u(\vec{r})$$

If one now defines a time-dependent wavevector as follows:

$$\hbar\vec{k}(t)=\hbar\vec{k}-e\vec{E}t$$

Then the above equation is just the familiar equation for the periodic part of a Bloch function whose wavevector is time dependent:

$$\left[\frac{\left(\hat{\vec{P}}+\hbar\vec{k}(t)\right)^2}{2m}+V\left(\hat{\vec{r}}\right)\right]u_{n,\vec{k}(t)}(\vec{r})=E_n\left(\vec{k}(t)\right)u_{n,\vec{k}(t)}(\vec{r})$$

So the answer is:

$$\phi(\vec{r},t)=\frac{e^{i\vec{k}.\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n\left(\vec{k}(t')\right)dt'}$$

And finally the solution of the original problem is (as expected):

$$\psi(\vec{r},t)=e^{-i\frac{e}{\hbar}\vec{E}.\vec{r}t}\phi(\vec{r},t)=\frac{e^{i\vec{k}(t).\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n\left(\vec{k}(t')\right)dt'}=\psi_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n\left(\vec{k}(t')\right)dt'}$$

Appendix: Electron Dynamics and Berry's Phase

Note that the solution:

$$\phi(\vec{r},t)=\frac{e^{i\vec{k}.\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n\left(\vec{k}(t')\right)dt'} \qquad \left\{\ \hbar\vec{k}(t)=\hbar\vec{k}-e\vec{E}t\right.$$

is not an exact solution of the equation:

$$\left[\frac{\left(\hat{\vec{P}}-e\vec{E}t\right)^2}{2m}+V\left(\hat{\vec{r}}\right)\right]\phi(\vec{r},t)=i\hbar\frac{\partial\phi(\vec{r},t)}{\partial t}$$

It misses a very important phase factor even if the time dependence is not fast enough to cause transitions between states. To capture this we try:

$$\phi(\vec{r},t)=\frac{e^{i\vec{k}.\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n\left(\vec{k}(t')\right)dt'+i\gamma_{n,\vec{k}}(t)}$$

Plugging it in, multiplying both sides by $u^*_{n,\vec{k}(t)}(\vec{r})$, integrating, and using the fact that:

$$\left[\frac{\left(\hat{\vec{P}}+\hbar\vec{k}(t)\right)^2}{2m}+V\left(\hat{\vec{r}}\right)\right]u_{n,\vec{k}(t)}(\vec{r})=E_n\left(\vec{k}(t)\right)u_{n,\vec{k}(t)}(\vec{r})$$

We get (PTO):

Appendix: Electron Dynamics and Berry's Phase

$$\frac{\partial \gamma_{n,\vec{k}}(t)}{\partial t} = i\int d^d\vec{r}\; u^*_{n,\vec{k}(t)}(\vec{r})\frac{\partial}{\partial t}u_{n,\vec{k}(t)}(\vec{r}) = i\left\langle u_{n,\vec{k}(t)}\middle|\frac{\partial}{\partial t}\middle|u_{n,\vec{k}(t)}\right\rangle$$

$$\Rightarrow \gamma_{n,\vec{k}}(t) = i\int_{t=0}^{t} dt'\left\langle u_{n,\vec{k}(t')}\middle|\frac{\partial}{\partial t'}\middle|u_{n,\vec{k}(t')}\right\rangle = i\int_{\vec{q}=\vec{k}(t=0)=\vec{k}}^{\vec{q}=\vec{k}(t)}\left\langle u_{n,\vec{q}}\middle|\nabla_{\vec{q}}\middle|u_{n,\vec{q}}\right\rangle.d\vec{q}$$

$$= \int_{\vec{q}=\vec{k}(t=0)=\vec{k}}^{\vec{q}=\vec{k}(t)}\vec{A}_{n,q}.d\vec{q} \qquad \left\{\; \vec{A}_{\vec{q}} = i\left\langle u_{n,\vec{q}}\middle|\nabla_{\vec{q}}\middle|u_{n,\vec{q}}\right\rangle \right.$$

The final complete solution is then:

$$\psi(\vec{r},t) = e^{-i\frac{e}{\hbar}\vec{E}.\vec{r}t}\phi(\vec{r},t) = \frac{e^{i\vec{k}(t).\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n(\vec{k}(t'))dt' + i\gamma_{n,\vec{k}}(t)}$$

$$= \psi_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n(\vec{k}(t'))dt'}\underbrace{e^{i\gamma_{n,\vec{k}}(t)}}_{\text{Berry's phase}}$$

The extra phase factor is called the Berry's phase and appears in many places in physics (and in optics)

It is appropriate to write the Berry's phase as, $\gamma_{n,\vec{k}}(t) = \gamma_n(\vec{k}(t))$, since it depends on the trajectory of the time-dependent wavevector in reciprocal space

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Appendix: Bloch Velocity and Berry's Phase

The velocity of an electron packet in the presence of an E-field is not the same as in the absence of it

Consider an electron packet:

$$\theta(\vec{r},t) = \int\frac{d^d\vec{k}}{(2\pi)^2}f(\vec{k})\psi_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n(\vec{k}(t'))dt' + i\gamma_n(\vec{k}(t))}$$

$$= \int\frac{d^d\vec{k}}{(2\pi)^2}f(\vec{k})\frac{e^{i\vec{k}(t).\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n(\vec{k}(t'))dt' + i\gamma_n(\vec{k}(t))}$$

and assume that the function $f(\vec{k})$ peaks when $\vec{k} = \vec{k}_o$

In the absence of Berry's phase the group velocity of the packet can be found from the usual stationary phase argument:

$$v_g(\vec{k}_o).(\vec{k}-\vec{k}_o) = \frac{1}{\hbar}\frac{d}{dt}\int_{t'=0}^{t'=t}dt'\left(E_n(\vec{k}-e\vec{E}t/\hbar) - -E_n(\vec{k}_o - e\vec{E}t/\hbar)\right)$$

$$\Rightarrow v_g(\vec{k}_o) = \frac{1}{\hbar}\nabla_{\vec{k}}E_n(\vec{k})\Big|_{\vec{k}_o}$$

Appendix: Bloch Velocity and Berry's Phase

In the presence of Berry's phase the group velocity of the packet from the stationary phase argument gives an extra term:

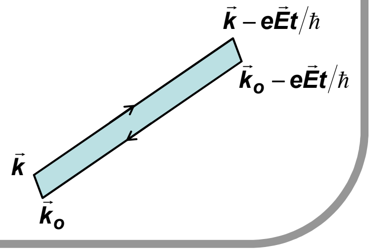
$$v_g(\vec{k}_o).(\vec{k}-\vec{k}_o)=\frac{1}{\hbar}\nabla_{\vec{k}}E_n(\vec{k})\Big|_{\vec{k}_o}.(\vec{k}-\vec{k}_o)-\frac{d}{dt}\left[\gamma_n\left(\vec{k}-e\vec{E}t/\hbar\right)-\gamma_n\left(\vec{k}_o-e\vec{E}t/\hbar\right)\right]$$

$$v_g(\vec{k}_o).(\vec{k}-\vec{k}_o)=\frac{1}{\hbar}\nabla_{\vec{k}}E_n(\vec{k})\Big|_{\vec{k}_o}.(\vec{k}-\vec{k}_o)-\frac{d}{dt}\left[\int_{\vec{q}=\vec{k}}^{\vec{q}=\vec{k}-e\vec{E}t/\hbar}\vec{A}_{n,q}.d\vec{q}-\int_{\vec{q}=\vec{k}_o}^{\vec{q}=\vec{k}_o-e\vec{E}t/\hbar}\vec{A}_{n,q}.d\vec{q}\right]$$

The second term in brackets represents the rate of change of the (oriented) area of the figure below and equals:

$$-\frac{d}{dt}\left[\int_{\vec{q}=\vec{k}}^{\vec{q}=\vec{k}-e\vec{E}t/\hbar}\vec{A}_{n,q}.d\vec{q}-\int_{\vec{q}=\vec{k}_o}^{\vec{q}=\vec{k}_o-e\vec{E}t/\hbar}\vec{A}_{n,q}.d\vec{q}\right]=-\nabla_{\vec{q}}\times\vec{A}_{n,\vec{q}}\Big|_{\vec{q}=\vec{k}_o}.\left[\frac{e}{\hbar}\vec{E}\times(\vec{k}-\vec{k}_o)\right]$$

$$=\left(\frac{e}{\hbar}\vec{E}\times\nabla_{\vec{q}}\times\vec{A}_{n,\vec{q}}\Big|_{\vec{q}=\vec{k}_o}\right).(\vec{k}-\vec{k}_o)$$



The packet group velocity is then:

$$v_g(\vec{k}_o)=\frac{1}{\hbar}\nabla_{\vec{k}}E_n(\vec{k})\Big|_{\vec{k}_o}+\frac{e}{\hbar}\vec{E}\times\left(\nabla_{\vec{q}}\times\vec{A}_{n,\vec{q}}\Big|_{\vec{q}=\vec{k}_o}\right)$$

Appendix: Berry's Phase and Berry's Curvature

So, more generally, one can write the velocity of Bloch electrons (in the presence of a field as):

$$\vec{v}_n(\vec{k})=\frac{1}{\hbar}\nabla_{\vec{k}}E_n(\vec{k})-\frac{d\vec{k}}{dt}\times\left(\nabla_{\vec{k}}\times\vec{A}_{n,\vec{k}}\right)$$

The quantity:

$$\vec{\Omega}_n(\vec{k})=\nabla_{\vec{k}}\times\vec{A}_{n,\vec{k}}$$

is called Berry's curvature and plays an important role in many different places in solid state physics (spin Hall effect for example)

If a solid possesses time reversal symmetry (all materials in the absence of an external magnetic field):

$$\vec{\Omega}_n(-\vec{k})=-\vec{\Omega}_n(\vec{k})$$

If a solid possesses inversion symmetry (like Si, Ge):

$$\vec{\Omega}_n(-\vec{k})=\vec{\Omega}_n(\vec{k})$$

It follows that if a solid possesses both time reversal symmetry and inversion symmetry (like Si, Ge):

$$\vec{\Omega}_n(\vec{k})=0$$

Dynamics of Electrons in Energy Bands from Gauge Invariance
Berry's Phase and Berry's Curvature

In this lecture you will learn:

- Electron dynamics using gauge invariance arguments
- Berry's phase and Berry's curvature in solid state physics

Electron Dynamics from Gauge Invariance

Consider the Schrodinger equation for an electron in a solid:

$$\left[\frac{\hat{\vec{P}}^2}{2m}+V\left(\hat{\vec{r}}\right)\right]\psi(\vec{r},t)=i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}$$

We have seen that the stationary solutions are the Bloch states:

$$\left[\frac{\hat{\vec{P}}^2}{2m}+V\left(\hat{\vec{r}}\right)\right]\psi_{n,\vec{k}}(\vec{r})=E_n\left(\vec{k}\right)\psi_{n,\vec{k}}(\vec{r})$$

Or since: $\psi_{n,\vec{k}}(\vec{r})=\frac{e^{i\vec{k}.\vec{r}}}{\sqrt{V}}u_{n,\vec{k}}(\vec{r})$

$$\Rightarrow\left[\frac{\left(\hat{\vec{P}}+\hbar\vec{k}\right)^2}{2m}+V\left(\hat{\vec{r}}\right)\right]u_{n,\vec{k}}(\vec{r})=E_n\left(\vec{k}\right)u_{n.\vec{k}}(\vec{r})$$

In the presence of electromagnetic vector and scalar potentials the time-dependent Schrodinger equation becomes:

$$\left[\frac{\left(\hat{\vec{P}}+e\vec{A}\left(\hat{\vec{r}},t\right)\right)^2}{2m}+V\left(\hat{\vec{r}}\right)-e\phi\left(\hat{\vec{r}},t\right)\right]\psi(\vec{r},t)=i\hbar\,\frac{\partial\psi(\vec{r},t)}{\partial t}$$

Electron Dynamics from Gauge Invariance

$$\left[\frac{\left(\hat{\vec{P}}+e\vec{A}(\hat{\vec{r}},t)\right)^2}{2m}+V(\hat{\vec{r}})-e\phi(\hat{\vec{r}},t)\right]\psi(\vec{r},t)=i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}$$

The Schrodinger equation is invariant (i.e. does not change) under the following gauge transformation:

$$\vec{A}(\hat{\vec{r}},t)\rightarrow\vec{A}(\hat{\vec{r}},t)+\nabla f(\hat{\vec{r}},t)$$

$$\phi(\hat{\vec{r}},t)\rightarrow\phi(\hat{\vec{r}},t)-\frac{\partial f(\hat{\vec{r}},t)}{\partial t}$$

$$\psi(\vec{r},t)\rightarrow e^{-i\frac{e}{\hbar}f(\vec{r},t)}\psi(\vec{r},t)$$

Now get back to the problem of an electron in an applied electric field. The Schrodinger equation is:

$$\left[\frac{\hat{\vec{P}}^2}{2m}+V(\hat{\vec{r}})+e\vec{E}.\hat{\vec{r}}\right]\psi(\vec{r},t)=i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}$$

Perform the following gauge transformation to eliminate the scalar potential in favor of the vector potential:

$$f(\vec{r},t)=-\vec{E}.\vec{r}\,t$$

Electron Dynamics from Gauge Invariance

We get:

$$\left[\frac{\left(\hat{\vec{P}}-e\vec{E}t\right)^2}{2m}+V(\hat{\vec{r}})\right]e^{i\frac{e}{\hbar}\vec{E}.\vec{r}t}\psi(\vec{r},t)=i\hbar\frac{\partial}{\partial t}e^{i\frac{e}{\hbar}\vec{E}.\vec{r}t}\psi(\vec{r},t)$$

Let:

$$\phi(\vec{r},t)=e^{i\frac{e}{\hbar}\vec{E}.\vec{r}t}\psi(\vec{r},t)$$

$$\Rightarrow\left[\frac{\left(\hat{\vec{P}}-e\vec{E}t\right)^2}{2m}+V(\hat{\vec{r}})\right]\phi(\vec{r},t)=i\hbar\frac{\partial\phi(\vec{r},t)}{\partial t}$$

Now we have to solve a time-dependent equation BUT the Hamiltonian is now lattice periodic! Assume, in the spirit of Bloch's analysis, solution of the form:

$$\phi(\vec{r},t)=\frac{e^{i\vec{k}.\vec{r}}}{\sqrt{V}}u(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E(t')dt'}$$

And plug the assumed form in the above equation to get:

Electron Dynamics from Gauge Invariance

$$\left[\frac{\left(\hat{\vec{P}}+\hbar\vec{k}-e\vec{E}t\right)^2}{2m}+V\left(\hat{\vec{r}}\right)\right]u(\vec{r})=E(t)u(\vec{r})$$

If one now defines a time-dependent wavevector as follows:

$$\hbar\vec{k}(t)=\hbar\vec{k}-e\vec{E}t$$

Then the above equation is just the familiar equation for the periodic part of a Bloch function whose wavevector is time dependent:

$$\left[\frac{\left(\hat{\vec{P}}+\hbar\vec{k}(t)\right)^2}{2m}+V\left(\hat{\vec{r}}\right)\right]u_{n,\vec{k}(t)}(\vec{r})=E_n\left(\vec{k}(t)\right)u_{n,\vec{k}(t)}(\vec{r})$$

So the answer is:

$$\phi(\vec{r},t)=\frac{e^{i\vec{k}.\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n\left(\vec{k}(t')\right)dt'}$$

And finally the solution of the original problem is (as expected):

$$\psi(\vec{r},t)=e^{-i\frac{e}{\hbar}\vec{E}.\vec{r}t}\phi(\vec{r},t)=\frac{e^{i\vec{k}(t).\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n\left(\vec{k}(t')\right)dt'}=\psi_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n\left(\vec{k}(t')\right)dt'}$$

Electron Dynamics and Berry's Phase

Note that the solution:

$$\phi(\vec{r},t)=\frac{e^{i\vec{k}.\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n\left(\vec{k}(t')\right)dt'}\qquad\left\{\;\hbar\vec{k}(t)=\hbar\vec{k}-e\vec{E}t\right.$$

is not an exact solution of the equation:

$$\left[\frac{\left(\hat{\vec{P}}-e\vec{E}t\right)^2}{2m}+V\left(\hat{\vec{r}}\right)\right]\phi(\vec{r},t)=i\hbar\frac{\partial\phi(\vec{r},t)}{\partial t}$$

It misses a very important phase factor even if the time dependence is not fast enough to cause transitions between states. To capture this we try:

$$\phi(\vec{r},t)=\frac{e^{i\vec{k}.\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n\left(\vec{k}(t')\right)dt'+\underbrace{i\gamma_{n,\vec{k}}(t)}_{\text{Added phase}}}$$

Plugging it in, multiplying both sides by $u^*_{n,\vec{k}(t)}(\vec{r})$, integrating, and using the fact that:

$$\left[\frac{\left(\hat{\vec{P}}+\hbar\vec{k}(t)\right)^2}{2m}+V\left(\hat{\vec{r}}\right)\right]u_{n,\vec{k}(t)}(\vec{r})=E_n\left(\vec{k}(t)\right)u_{n,\vec{k}(t)}(\vec{r})$$

We get (PTO):

Electron Dynamics and Berry's Phase

$$\frac{\partial \gamma_{n,\vec{k}}(t)}{\partial t} = i\int d^d\vec{r}\; u^*_{n,\vec{k}(t)}(\vec{r})\frac{\partial}{\partial t}u_{n,\vec{k}(t)}(\vec{r}) = i\left\langle u_{n,\vec{k}(t)}\right|\frac{\partial}{\partial t}\left|u_{n,\vec{k}(t)}\right\rangle$$

$$\Rightarrow \gamma_{n,\vec{k}}(t) = i\int_{t=0}^{t} dt'\left\langle u_{n,\vec{k}(t')}\right|\frac{\partial}{\partial t'}\left|u_{n,\vec{k}(t')}\right\rangle = i\int_{\vec{q}=\vec{k}(t=0)}^{\vec{q}=\vec{k}(t)}\left\langle u_{n,\vec{q}}\right|\nabla_{\vec{q}}\left|u_{n,\vec{q}}\right\rangle.d\vec{q}$$

$$= \int_{\vec{q}=\vec{k}(t=0)}^{\vec{q}=\vec{k}(t)} \vec{A}_{n,q}.d\vec{q} \qquad \left\{ \; \vec{A}_{\vec{q}} = i\left\langle u_{n,\vec{q}}\right|\nabla_{\vec{q}}\left|u_{n,\vec{q}}\right\rangle \right.$$

The final complete solution is then:

$$\psi(\vec{r},t) = e^{-i\frac{e}{\hbar}\vec{E}.\vec{r}t}\phi(\vec{r},t) = \frac{e^{i\vec{k}(t).\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n(\vec{k}(t'))dt' + i\gamma_{n,\vec{k}}(t)}$$

$$= \psi_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n(\vec{k}(t'))dt'}\; e^{\underbrace{i\gamma_{n,\vec{k}}(t)}_{\text{Berry's phase}}}$$

The extra phase factor is called the Berry's phase and appears in many places in physics (and in optics)

It is appropriate to write the Berry's phase as, $\gamma_{n,\vec{k}}(t) = \gamma_n(\vec{k}(t))$, since it depends on the trajectory of the time-dependent wavevector in reciprocal space

Bloch Velocity and Berry's Phase

The velocity of an electron packet in the presence of an E-field is not the same as in the absence of it

Consider an electron packet made up of the time-dependent Bloch functions:

$$\theta(\vec{r},t) = \int\frac{d^d\vec{k}}{(2\pi)^2}f(\vec{k})\psi_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n(\vec{k}(t'))dt' + i\gamma_n(\vec{k}(t))}$$

$$= \int\frac{d^d\vec{k}}{(2\pi)^2}f(\vec{k})\frac{e^{i\vec{k}(t).\vec{r}}}{\sqrt{V}}u_{n,\vec{k}(t)}(\vec{r})e^{-\frac{i}{\hbar}\int_0^t E_n(\vec{k}(t'))dt' + i\gamma_n(\vec{k}(t))}$$

Assume that the function $f(\vec{k})$ peaks when $\vec{k} = \vec{k}_o$

In the absence of Berry's phase, the group velocity of the packet can be found from the usual stationary phase argument:

$$v_g(\vec{k}_o).(\vec{k}-\vec{k}_o) = \frac{1}{\hbar}\frac{d}{dt}\int_{t'=0}^{t'=t} dt'\left(E_n(\vec{k}-e\vec{E}t/\hbar) - -E_n(\vec{k}_o - e\vec{E}t/\hbar)\right)$$

$$\Rightarrow v_g(\vec{k}_o) = \frac{1}{\hbar}\nabla_{\vec{k}}E_n(\vec{k})\Big|_{\vec{k}_o}$$

Bloch Velocity and Berry's Phase

In the presence of Berry's phase the group velocity of the packet from the stationary phase argument gives an extra term:

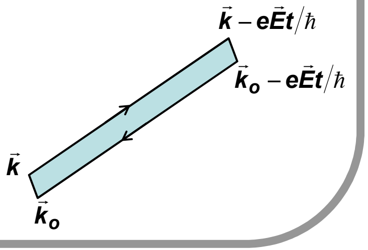
$$v_g(\vec{k}_o).(\vec{k}-\vec{k}_o) = \frac{1}{\hbar}\nabla_{\vec{k}} E_n(\vec{k})\Big|_{\vec{k}_o}.(\vec{k}-\vec{k}_o) - \frac{d}{dt}\left[\gamma_n\left(\vec{k}-e\vec{E}t/\hbar\right) - \gamma_n\left(\vec{k}_o-e\vec{E}t/\hbar\right)\right]$$

$$v_g(\vec{k}_o).(\vec{k}-\vec{k}_o) = \frac{1}{\hbar}\nabla_{\vec{k}} E_n(\vec{k})\Big|_{\vec{k}_o}.(\vec{k}-\vec{k}_o) - \frac{d}{dt}\left[\int_{\vec{q}=\vec{k}}^{\vec{q}=\vec{k}-e\vec{E}t/\hbar} \vec{A}_{n,q}.d\vec{q} - \int_{\vec{q}=\vec{k}_o}^{\vec{q}=\vec{k}_o-e\vec{E}t/\hbar} \vec{A}_{n,q}.d\vec{q}\right]$$

The second term in brackets represents the rate of change of the (oriented) area of the figure below and equals:

$$-\frac{d}{dt}\left[\int_{\vec{q}=\vec{k}}^{\vec{q}=\vec{k}-e\vec{E}t/\hbar} \vec{A}_{n,q}.d\vec{q} - \int_{\vec{q}=\vec{k}_o}^{\vec{q}=\vec{k}_o-e\vec{E}t/\hbar} \vec{A}_{n,q}.d\vec{q}\right] = -\nabla_{\vec{q}}\times\vec{A}_{n,\vec{q}}\Big|_{\vec{q}=\vec{k}_o}.\left[\frac{e}{\hbar}\vec{E}\times\left(\vec{k}-\vec{k}_o\right)\right]$$

$$= \left(\frac{e}{\hbar}\vec{E}\times\nabla_{\vec{q}}\times\vec{A}_{n,\vec{q}}\Big|_{\vec{q}=\vec{k}_o}\right).\left(\vec{k}-\vec{k}_o\right)$$



The packet group velocity is then:

$$v_g(\vec{k}_o) = \frac{1}{\hbar}\nabla_{\vec{k}} E_n(\vec{k})\Big|_{\vec{k}_o} + \frac{e}{\hbar}\vec{E}\times\left(\nabla_{\vec{q}}\times\vec{A}_{n,\vec{q}}\Big|_{\vec{q}=\vec{k}_o}\right)$$

Berry's Phase and Berry's Curvature

So, more generally, one can write the velocity of Bloch electrons (in the presence of a field as):

$$\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}} E_n(\vec{k}) - \frac{d\vec{k}}{dt}\times\left(\nabla_{\vec{k}}\times\vec{A}_{n,\vec{k}}\right)$$

The quantity:

$$\vec{\Omega}_n(\vec{k}) = \nabla_{\vec{k}}\times\vec{A}_{n,\vec{k}}$$

is called Berry's curvature and plays an important role in many different places in solid state physics (spin Hall effect for example)

If a solid possesses time reversal symmetry (e.g. all materials in the absence of magnetic fields):

$$\vec{\Omega}_n(-\vec{k}) = -\vec{\Omega}_n(\vec{k})$$

If a solid possesses inversion symmetry (e.g. Si, Ge):

$$\vec{\Omega}_n(-\vec{k}) = \vec{\Omega}_n(\vec{k})$$

It follows that if a solid possesses both time reversal symmetry and inversion symmetry (e.g. Si, Ge):

$$\vec{\Omega}_n(\vec{k}) = 0$$

Handout 16

Electrical Conduction in Energy Bands

In this lecture you will learn:

- The conductivity of electrons in energy bands
- The electron-hole transformation
- The conductivity tensor
- Examples
- Bloch oscillations

Inversion Symmetry of Energy Bands

Recall that because of time reversal symmetry:

$$\boxed{\psi^{*}_{n,-\vec{k}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r}) \qquad E_n(-\vec{k}) = E_n(\vec{k})}$$

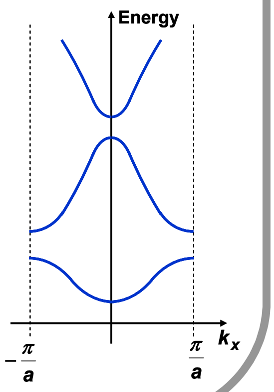
We know that:

$$\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}} E_n(\vec{k})$$

Now let $\vec{k}$ go to $-\vec{k}$ in the above equation:

$$\begin{aligned}\vec{v}_n(-\vec{k}) &= \frac{1}{\hbar}\nabla_{-\vec{k}} E_n(-\vec{k}) \\ &= -\frac{1}{\hbar}\nabla_{\vec{k}} E_n(-\vec{k}) \\ &= -\frac{1}{\hbar}\nabla_{\vec{k}} E_n(\vec{k}) \\ &= -\vec{v}_n(\vec{k})\end{aligned}$$

$$\boxed{\Rightarrow \vec{v}_n(-\vec{k}) = -\vec{v}_n(\vec{k})}$$



Current Density for Energy Bands

In **Drude model**, the electron current density was given as:

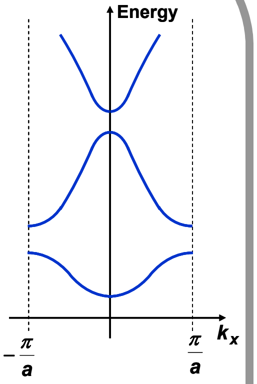
$$\vec{J} = n\,(-e)\,\vec{v}$$

For a **free electron gas** the current density was given as:

$$\vec{J} = (-e)\frac{2}{V}\times\sum_{\text{all }\vec{k}} f(\vec{k})\,\vec{v}(\vec{k}) = -2\,e\times\int\frac{d^3\vec{k}}{(2\pi)^3}\,f(\vec{k})\,\vec{v}(\vec{k})$$

Now we want to find the current density due to electrons in energy bands

The current density due to electrons in the *n*-th band can be written in a manner similar to the free-electron case:



$$\vec{J}_n = (-e)\frac{2}{V}\times\sum_{\vec{k}\text{ in FBZ}} f_n(\vec{k})\,\vec{v}_n(\vec{k})$$

$$= -2\,e\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\,f_n(\vec{k})\,\vec{v}_n(\vec{k})$$

Current Density for a Completely Filled or Empty Bands

Consider a **completely filled band** for which $f_n(\vec{k}) = 1$ for all $\vec{k}$ in FBZ

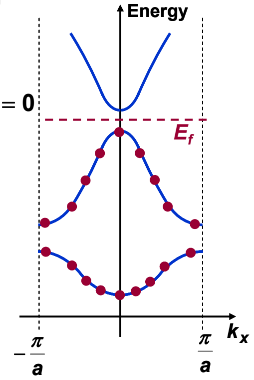
Application of an external field will not change anything!

$$\vec{J}_n = -2\,e\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\,f_n(\vec{k})\,\vec{v}_n(\vec{k}) = -2\,e\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\,\vec{v}_n(\vec{k}) = 0$$

where I have used the fact:

$$\vec{v}_n(-\vec{k}) = -\vec{v}_n(\vec{k})$$

⇒ Completely filled bands do not contribute to electrical current or to electrical conductivity



Of course, if $f_n(\vec{k}) = 0$ for all $\vec{k}$ in FBZ:

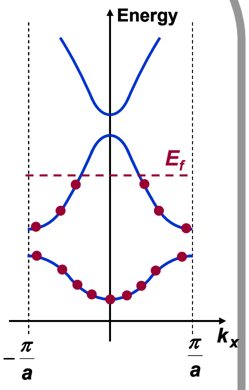
$$\vec{J}_n = -2\,e\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\,f_n(\vec{k})\,\vec{v}_n(\vec{k}) = 0$$

⇒ Completely empty bands do not contribute to electrical current or to electrical conductivity

Only partially filled bands contribute to electrical current and to electrical conductivity

Current Density and Electron-Hole Transformation

Consider the expression for the current density for a partially filled band:



$$\vec{J}_n = 2\,(-e)\times \int_{FBZ} \frac{d^3\vec{k}}{(2\pi)^3}\, f_n(\vec{k})\,\vec{v}_n(\vec{k}) \longrightarrow (1)$$

$$= 2\,(e)\times \int_{FBZ} \frac{d^3\vec{k}}{(2\pi)^3}\left[1-f_n(\vec{k})-1\right]\vec{v}_n(\vec{k})$$

$$= \cancelto{0}{-2\,e\times \int_{FBZ} \frac{d^3\vec{k}}{(2\pi)^3}\,\vec{v}_n(\vec{k})} + 2\,e\times \int_{FBZ} \frac{d^3\vec{k}}{(2\pi)^3}\left[1-f_n(\vec{k})\right]\vec{v}_n(\vec{k})$$

$$= 2\,(+e)\times \int_{FBZ} \frac{d^3\vec{k}}{(2\pi)^3}\left[1-f_n(\vec{k})\right]\vec{v}_n(\vec{k}) \longrightarrow (2)$$

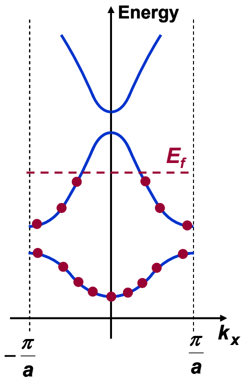
The final result implies that since the current density of a filled band is zero, the current density for any band can always be expressed in two equivalent ways:

a) As an integral over all the occupied states assuming negatively charged particles (as in (1) above)

a) As an integral over all the unoccupied states assuming positively charged particles (as in (2) above)

Current Density and Electron-Hole Transformation

One has two choices when calculating current from a partially filled band:



The Electron Choice:

The current density is given by:

$$\vec{J}_n = 2\,(-e)\times \int_{FBZ} \frac{d^3\vec{k}}{(2\pi)^3}\, f_n(\vec{k})\,\vec{v}_n(\vec{k})$$

- Current is understood to be due to negatively charged electrons
- This choice is better when the electron number is smaller than the hole number

The Hole Choice:

The current density is given by:

$$\vec{J}_n = 2\,(+e)\times \int_{FBZ} \frac{d^3\vec{k}}{(2\pi)^3}\left[1-f_n(\vec{k})\right]\vec{v}_n(\vec{k})$$

- Current is understood to be due to positively charged fictitious particles called “holes”
- This choice is better when the hole number is smaller than the electron number

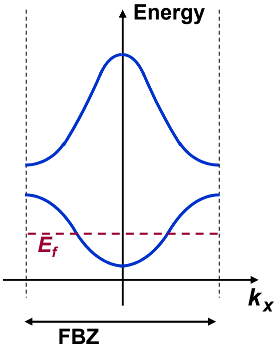
Metals, Semiconductors, and Insulators

Materials can be classified into three main categories w.r.t. their electrical properties:

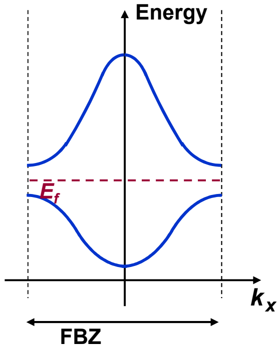
Metals: In metals, the highest filled band is partially filled (usually half-filled)

Semiconductors: In semiconductors, the highest filled band is completely filled (at least at zero temperature)

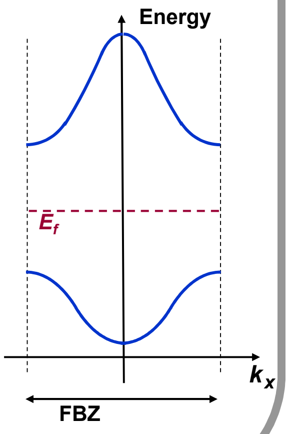
Insulators: Insulators are like semiconductors but usually have a much larger bandgap



Metal



Semiconductor



Insulator

Inclusion of Scattering in the Dynamical Equation

In the presence of a uniform electric field the crystal momentum satisfies the dynamical equation:

$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}$$

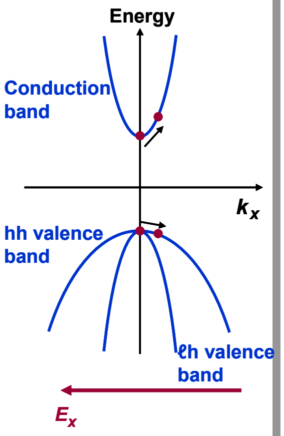
Now we need to add the effect of electron scattering. As in the free-electron case, we assume that scattering adds damping:

$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E} - \frac{\hbar\left[\vec{k}(t)-\vec{k}\right]}{\tau}$$

The boundary condition is that: $\vec{k}(t=0)=\vec{k}$

Note: the damping term ensures that when the field is turned off, the crystal momentum of the electron goes back to its original value

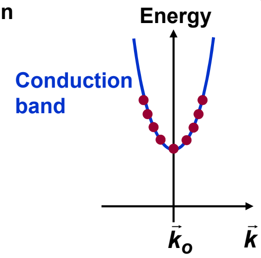
Steady State Solution: $\vec{k}(t=\infty)=\vec{k}-\frac{e\,\tau}{\hbar}\vec{E}$



In the presence of an electric field, the crystal momentum of every electron is shifted by an equal amount that is determined by the scattering time and the field strength

Electrical Conductivity: Conduction Band

Consider a solid in which the energy dispersion for conduction band near a band minimum is given by:



$$E_c(\vec{k}) = E_c(\vec{k}_o) + \frac{\hbar^2}{2}(\vec{k}-\vec{k}_o)^T \, . \, M^{-1} \, . \, (\vec{k}-\vec{k}_o)$$

The velocity of electrons is:

$$\vec{v}_c(\vec{k}) = M^{-1} \, . \, \hbar \, (\vec{k}-\vec{k}_o)$$

The current density is:

$$\vec{J}_c = -2\,e \times \int_{\text{near } \vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3} f_c(\vec{k}) \vec{v}_c(\vec{k})$$

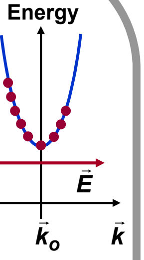
In equilibrium, for every state with crystal momentum $(\vec{k}-\vec{k}_o)$ that is occupied, the state $-(\vec{k}-\vec{k}_o)$ is also occupied and these two states have opposite velocities.

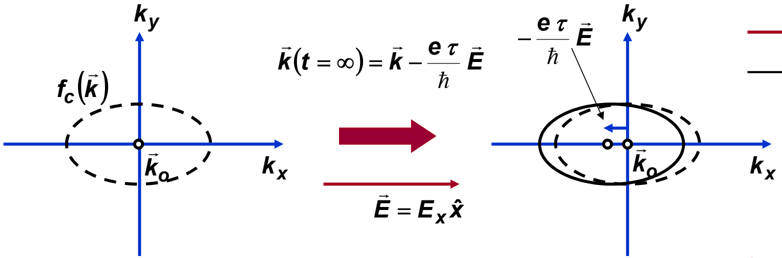
Therefore in equilibrium:

$$\vec{J}_c = -2\,e \times \int_{\text{near } \vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3} f_c(\vec{k}) \vec{v}_c(\vec{k}) = 0$$

Electrical Conductivity: Conduction Band

Now assume that an electric field is present that shifts the crystal momentum of all electrons:





$$\vec{k}(t=\infty) = \vec{k} - \frac{e\,\tau}{\hbar}\vec{E}$$

$$\vec{E} = E_x \hat{x}$$

Electron distribution in k-space when E-field is zero

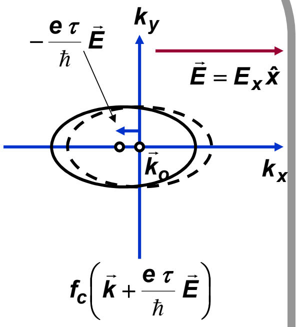
Distribution function: $f_c(\vec{k})$

Electron distribution is shifted in k-space when E-field is not zero

Distribution function: $f_c\left(\vec{k} + \frac{e\,\tau}{\hbar}\vec{E}\right)$

Since the wavevector of each electron is shifted by the same amount in the presence of the E-field, the net effect in k-space is that the entire electron distribution is shifted as shown

Electrical Conductivity: Conduction Band



Current Density:

$$\vec{J}_c = -2\,e \times \int_{\text{near } \vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3}\, f_c\left(\vec{k} + \frac{e\tau}{\hbar}\vec{E}\right)\vec{v}_c\left(\vec{k}\right)$$

Do a shift in the integration variable:

$$\vec{J}_c = -2\,e \times \int_{\text{near } \vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3}\, f_c\left(\vec{k}\right)\vec{v}_c\left(\vec{k} - \frac{e\,\tau}{\hbar}\vec{E}\right)$$

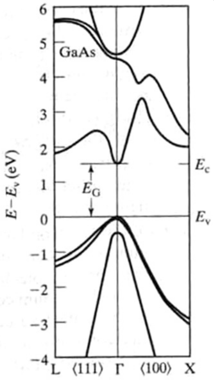
$$\vec{J}_c = -2\,e \times \int_{\text{near } \vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3}\, f_c\left(\vec{k}\right) M^{-1} . \hbar\left(\vec{k} - \vec{k}_o - \frac{e\,\tau}{\hbar}\vec{E}\right)$$

$$\vec{J}_c = e^2\tau\left[2 \times \int_{\text{near } \vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3}\, f_c\left(\vec{k}\right)\right] M^{-1} . \vec{E}$$

$$\vec{J}_c = n\,e^2\tau\, M^{-1} . \vec{E}$$
$$= \overline{\overline{\sigma}} . \vec{E}$$

Where the conductivity is now a tensor given by: $\overline{\overline{\sigma}} = n\,e^2\tau\, M^{-1}$

Electrical Conductivity Example: Conduction Band of GaAs



Consider the conduction band of GaAs near the Γ-point:

$$M^{-1} = \begin{bmatrix} 1/m_e & 0 & 0 \\ 0 & 1/m_e & 0 \\ 0 & 0 & 1/m_e \end{bmatrix}$$

Isotropic!

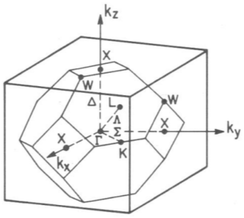
This implies:

$$\vec{J}_c = n\,e^2\tau\, M^{-1} . \vec{E}$$

$$\begin{bmatrix} J_{x,c} \\ J_{y,c} \\ J_{z,c} \end{bmatrix} = n\,e^2\tau \begin{bmatrix} 1/m_e & 0 & 0 \\ 0 & 1/m_e & 0 \\ 0 & 0 & 1/m_e \end{bmatrix}\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

$$= \frac{n\,e^2\tau}{m_e}\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \sigma\,\vec{E}$$

$$\Rightarrow \sigma = \frac{n\,e^2\tau}{m_e}$$



Electrical Conductivity Example: Conduction Band of Silicon

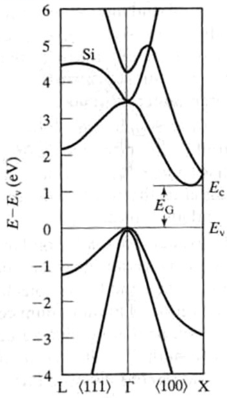
In Silicon there are six conduction band minima (valleys) that occur along the six Γ-X directions. For the one that occurs along the Γ-X(2π/a,0,0) direction:

$$\Rightarrow \quad \vec{k}_o = 0.85\left(\frac{2\pi}{a},0,0\right)$$

$$M^{-1} = \begin{bmatrix} 1/m_\ell & 0 & 0 \\ 0 & 1/m_t & 0 \\ 0 & 0 & 1/m_t \end{bmatrix}$$

Not isotropic!

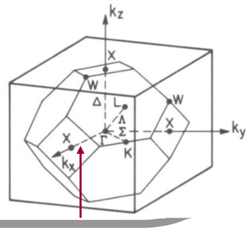
$m_\ell = 0.92\, m$
$m_t = 0.19\, m$



This implies that for this valley:

$$\vec{J}_c = \frac{n}{6} e^2 \tau\, M^{-1} . \vec{E}$$

$$\begin{bmatrix} J_{x,c} \\ J_{y,c} \\ J_{z,c} \end{bmatrix} = \frac{n}{6} e^2 \tau \begin{bmatrix} 1/m_\ell & 0 & 0 \\ 0 & 1/m_t & 0 \\ 0 & 0 & 1/m_t \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$



The factor of 6 is there because only 1/6th of the total conduction electron density in Silicon is in one valley

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Electrical Conductivity Example: Conduction Band of Silicon

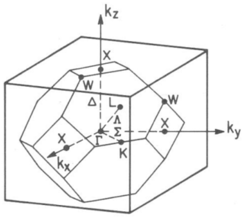
To find the conductivity tensor for Silicon one needs to sum over the current density contributions from all six valleys:

$$\begin{bmatrix} J_{x,c} \\ J_{y,c} \\ J_{z,c} \end{bmatrix} = \frac{n}{6} e^2 \tau \begin{bmatrix} 2/m_\ell + 4/m_t & 0 & 0 \\ 0 & 2/m_\ell + 4/m_t & 0 \\ 0 & 0 & 2/m_\ell + 4/m_t \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

Isotropic!

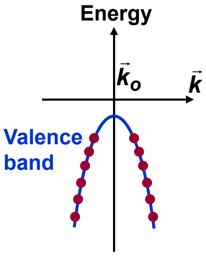
$$= \frac{n\, e^2 \tau}{m_e} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \sigma\, \vec{E}$$

$$\frac{1}{m_e} = \frac{1}{3}\left(\frac{1}{m_\ell} + \frac{2}{m_t}\right) =$$ Conductivity effective mass



After adding the current density contributions from all six valleys, the resulting conductivity tensor in Silicon is isotropic and described by a conductivity effective mass

Electrical Conductivity: Valence Band



Consider a solid in which the energy dispersion for valence band near a band maximum is given by:

$$E_v(\vec{k}) = E_v(\vec{k}_o) + \frac{\hbar^2}{2}(\vec{k}-\vec{k}_o)^T \,.\, M^{-1} \,.\, (\vec{k}-\vec{k}_o)$$

The velocity of electrons is:

$$\vec{v}_v(\vec{k}) = M^{-1} \,.\, \hbar\,(\vec{k}-\vec{k}_o)$$

The current density is (using the electron-hole transformation):

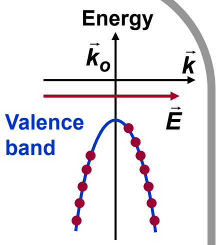
$$\vec{J}_v = -2\,e \times \int_{\text{near } \vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3} f_v(\vec{k})\,\vec{v}_v(\vec{k}) = 2\,e \times \int_{\text{near } \vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3} \left[1 - f_v(\vec{k})\right]\vec{v}_v(\vec{k})$$

In equilibrium, for every state with crystal momentum $(\vec{k}-\vec{k}_o)$ that is unoccupied, the state $-(\vec{k}-\vec{k}_o)$ is also unoccupied and these two states have opposite velocities.

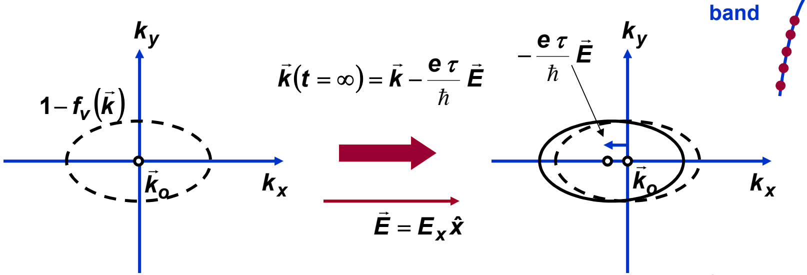
Therefore in equilibrium:

$$\vec{J}_v = 2\,e \times \int_{\text{near } \vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3} \left[1 - f_v(\vec{k})\right]\vec{v}_v(\vec{k}) = 0$$

Electrical Conductivity: Valence Band



Now assume that an electric field is present that shifts the crystal momentum of all electrons in the valence band:



$$\vec{k}(t=\infty) = \vec{k} - \frac{e\,\tau}{\hbar}\vec{E}$$

Hole distribution in k-space when E-field is zero

Distribution function: $1 - f_v(\vec{k})$

Hole distribution is shifted in k-space when E-field is not zero

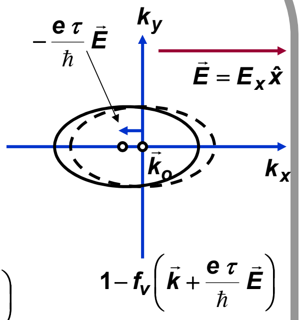
Distribution function: $1 - f_v\left(\vec{k} + \frac{e\,\tau}{\hbar}\vec{E}\right)$

Since the wavevector of each electron is shifted by the same amount in the presence of the E-field, the net effect in k-space is that the entire electron distribution (and hole distribution) is shifted as shown

Electrical Conductivity: Valence Band

Current Density:

$$\vec{J}_v = 2\,e \times \int_{\text{near }\vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3}\left[1 - f_v\!\left(\vec{k} + \frac{e\tau}{\hbar}\vec{E}\right)\right]\vec{v}_v\!\left(\vec{k}\right)$$



Do a shift in the integration variable:

$$\vec{J}_v = 2\,e \times \int_{\text{near }\vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3}\left[1 - f_v\!\left(\vec{k}\right)\right]\vec{v}_v\!\left(\vec{k} - \frac{e\,\tau}{\hbar}\vec{E}\right)$$

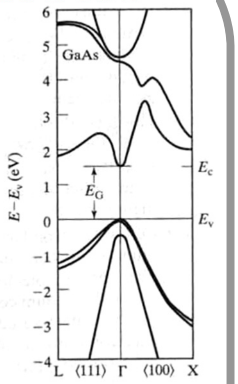
$$\vec{J}_v = 2\,e \times \int_{\text{near }\vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3}\left[1 - f_v\!\left(\vec{k}\right)\right]M^{-1}\,.\,\hbar\left(\vec{k} - \vec{k}_o - \frac{e\,\tau}{\hbar}\vec{E}\right)$$

$$\vec{J}_v = -e^2\tau\left[2 \times \int_{\text{near }\vec{k}_o} \frac{d^3\vec{k}}{(2\pi)^3}\left[1 - f_v\!\left(\vec{k}\right)\right]\right]M^{-1}\,.\,\vec{E}$$

$$\vec{J}_v = -p\,e^2\tau\,M^{-1}\,.\,\vec{E}$$
$$= \overline{\overline{\sigma}}\,.\,\vec{E}$$

Where the conductivity is now a tensor given by: $\overline{\overline{\sigma}} = -p\,e^2\tau\,M^{-1}$

Electrical Conductivity Example: Heavy-Hole Band of GaAs



Consider the heavy-hole band of GaAs near the Γ-point:

$$M^{-1} = \begin{bmatrix} -1/m_{hh} & 0 & 0 \\ 0 & -1/m_{hh} & 0 \\ 0 & 0 & -1/m_{hh} \end{bmatrix}$$

Isotropic!

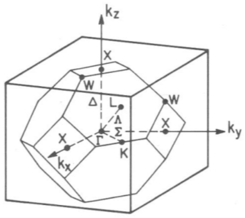
This implies:

$$\vec{J}_{hh} = -p_{hh}\,e^2\tau\,M^{-1}\,.\,\vec{E}$$

$$\begin{bmatrix} J_{x,hh} \\ J_{y,hh} \\ J_{z,hh} \end{bmatrix} = -p_{hh}\,e^2\tau\begin{bmatrix} -1/m_{hh} & 0 & 0 \\ 0 & -1/m_{hh} & 0 \\ 0 & 0 & -1/m_{hh} \end{bmatrix}\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

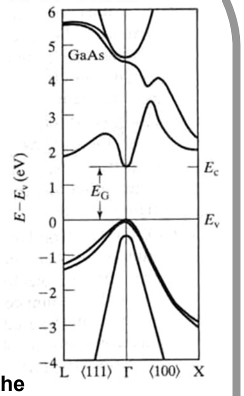
$$= \frac{p_{hh}\,e^2\tau}{m_{hh}}\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \sigma\,\vec{E}$$

$$\Rightarrow \sigma = \frac{p_{hh}\,e^2\tau}{m_{hh}}$$



Electrical Conductivity Example: Light-Hole Band of GaAs

Consider the light-hole band of GaAs near the Γ-point:



$$M^{-1}=\begin{bmatrix}-1/m_{\ell h} & 0 & 0\\ 0 & -1/m_{\ell h} & 0\\ 0 & 0 & -1/m_{\ell h}\end{bmatrix}$$

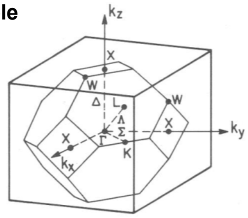
Isotropic!

This implies:

$$\vec{J}_{\ell h}=-p_{\ell h}\,e^{2}\tau\,M^{-1}.\vec{E}=\sigma\,\vec{E}$$

$$\Rightarrow\sigma=\frac{p_{\ell h}\,e^{2}\tau}{m_{\ell h}}$$

The total valence band conductivity of GaAs can be written as the sum of the contributions from the heavy-hole and the light-hole bands:



$$\sigma=\frac{p_{hh}\,e^{2}\tau}{m_{hh}}+\frac{p_{\ell h}\,e^{2}\tau}{m_{\ell h}}$$

The Phenomenology Of Transport

The presence of external fields, and scattering, the following relations work for electrons in any energy band near the band edge (assuming parabolic bands):

$$\frac{d\;\hbar\vec{k}(t)}{dt}=-e\,\vec{E}-\frac{\hbar\left[\vec{k}(t)-\vec{k}\right]}{\tau}$$

$$\vec{v}_n\left(\vec{k}(t)\right)=M^{-1}.\hbar\left(\vec{k}(t)-\vec{k}_o\right)$$

$$\vec{J}_n(t)=-2\,e\times\int_{\text{FBZ}}\frac{d^{3}\vec{k}}{(2\pi)^{3}}\,f_n\left(\vec{k}\right)\vec{v}_n\left(\vec{k}(t)\right)=+2\,e\times\int_{\text{FBZ}}\frac{d^{3}\vec{k}}{(2\pi)^{3}}\left[1-f_n\left(\vec{k}\right)\right]\vec{v}_n\left(\vec{k}(t)\right)$$

The first two can also be written as:

$$M.\frac{d\left[\vec{v}_n\left(\vec{k}(t)\right)-\vec{v}_n\left(\vec{k}\right)\right]}{dt}=-e\,\vec{E}-\frac{M.\left[\vec{v}_n\left(\vec{k}(t)\right)-\vec{v}_n\left(\vec{k}\right)\right]}{\tau}$$

Problem: One needs simple models for current transport so that non-specialists, like circuit designers, can understand devices and circuits without having to understand energy bands

Drift Velocity and Mobility for Electrons

We define the **drift velocity** for the electrons in the conduction band (for parabolic bands) as:

$$\vec{v}_e(t)=\vec{v}_c\left(\vec{k}(t)\right)-\vec{v}_c\left(\vec{k}\right)$$

The **drift velocity is independent of wavevector for parabolic bands** and satisfies:

$$M\,.\,\frac{d\,\vec{v}_e(t)}{dt}=-e\,\vec{E}-\frac{M\,.\,\vec{v}_e(t)}{\tau}\quad\longrightarrow\quad(1)$$

In steady state:

$$\vec{v}_e(t\rightarrow\infty)=\vec{v}_c\left(\vec{k}(t\rightarrow\infty)\right)-\vec{v}_c\left(\vec{k}\right)=-e\tau\,M^{-1}\,.\,\vec{E}=-\overline{\overline{\mu}}_e\,.\,\vec{E}\qquad\Big\{\ \overline{\overline{\mu}}_e=\text{mobility tensor}$$

Once the drift velocity is calculated, the electron current density is:

$$\vec{J}_e(t)=-2\,e\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\,f_c\left(\vec{k}\right)\vec{v}_c\left(\vec{k}(t)\right)=-2\,e\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\,f_c\left(\vec{k}\right)\left[\vec{v}_c\left(\vec{k}(t)\right)-\vec{v}_c\left(\vec{k}\right)+\cancelto{0}{\vec{v}_c\left(\vec{k}\right)}\right]$$

$$=-2\,e\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\,f_c\left(\vec{k}\right)\left[v_e(t)\right]=n\,(-e)\,v_e(t)\quad\longrightarrow\quad(2)$$

Electrons in the conduction band are to be thought of as **negatively charged particles**. In case of multiple electron pockets, current density contributions are calculated separately for each and added in the end.

Drift Velocity and Mobility for Holes

We define the **drift velocity** for the "holes" in the valence band (assuming parabolic bands) as:

$$\vec{v}_h(t)=\vec{v}_v\left(\vec{k}(t)\right)-\vec{v}_v\left(\vec{k}\right)$$

The **drift velocity is independent of wavevector** and satisfies the equation:

$$(-M)\,.\,\frac{d\ \vec{v}_h(t)}{dt}=+e\,\vec{E}-\frac{(-M)\,.\,\vec{v}_h(t)}{\tau}\quad\longrightarrow\quad(1)$$

Where realizing that the inverse effective mass tensor will have negative diagonal terms for valence band, I have multiplied throughout by a negative sign, with the result that the charge "-e" becomes "+e"

In steady state: $\vec{v}_h(t\rightarrow\infty)=-e\tau\,M^{-1}\,.\,\vec{E}=\overline{\overline{\mu}}_h\,.\,\vec{E}$ $\Big\{\ \overline{\overline{\mu}}_h=$ mobility tensor

Once the drift velocity is calculated, the hole current density is:

$$\vec{J}_h(t)=+2\,e\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\left[1-f_v\left(\vec{k}\right)\right]\vec{v}_v\left(\vec{k}(t)\right)=p\,(+e)\,v_h(t)\quad\longrightarrow\quad(2)$$

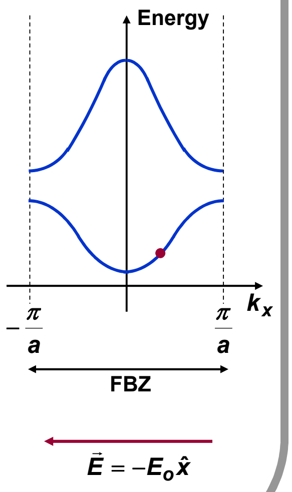
Holes in the valence band are to be thought of as **positively charged particles**. In case of degenerate valence band maxima, the heavy and light hole current density contributions are calculated separately and added in the end.

The Case of No Scattering: Bloch Oscillations

Consider an electron in a 1D crystal subjected to a uniform electric field. The energy band dispersion and velocity are:

$$E_n(k_x) = E_s - 2\,V_{ss\sigma}\cos(k_x a)$$

$$v_n(k_x) = \frac{1}{\hbar}\frac{dE_n(k_x)}{dk_x} = 2a\,V_{ss\sigma}\sin(k_x a)$$



In the absence of scattering, the crystal momentum satisfies the dynamical equation:

$$\frac{d\,\hbar k_x(t)}{dt} = eE_o$$

$$\Rightarrow k_x(t) = \frac{eE_o}{\hbar}t + k_x(t=0)$$

The time-dependent velocity of the electron is:

$$v_n(t) = 2a\,V_{ss\sigma}\sin(k_x(t)a)$$
$$= 2a\,V_{ss\sigma}\sin\left(\frac{e\,a\,E_o}{\hbar}t + k_x(t=0)a\right)$$

Periodic!

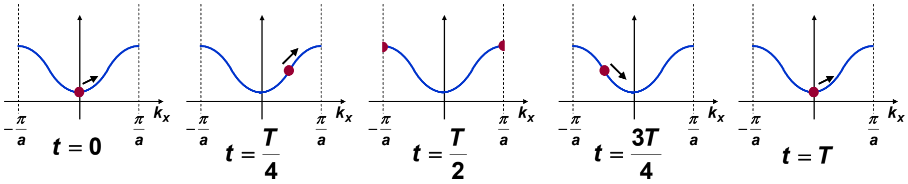
The Case of No Scattering: Bloch Oscillations

A periodic velocity means that the electron motion in real space is also periodic:

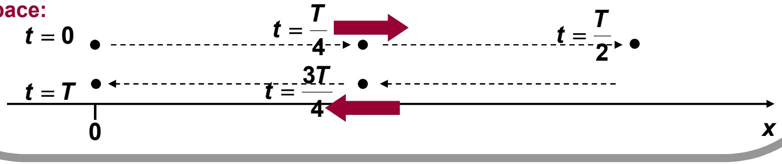
$$\frac{dx(t)}{dt} = v_n(t) = 2a\,V_{ss\sigma}\sin\left(\frac{e\,a\,E_o}{\hbar}t + k_x(t=0)a\right)$$

$$\Rightarrow \int_o^T \frac{dx(t)}{dt}dt = x(t=T) - x(t=0) = 0$$ **where the period T is:** $$T = \frac{2\pi\,\hbar}{e\,a\,E_o}$$

Reciprocal space:



Real space:



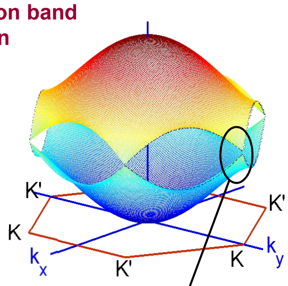
Conductivity of Electrons in Graphene

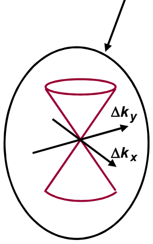
$\vec{k}_o = \mathrm{K}$

$$E_c(\vec{k}) \approx E_p + \hbar v\sqrt{(k_x-k_{ox})^2+(k_y-k_{oy})^2}\;\Big\}\;\text{Conduction band dispersion}$$

$$\vec{v}_c(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}}\,E_c(\vec{k}) = v\,\frac{(k_x-k_{ox})\hat{x}+(k_y-k_{oy})\hat{y}}{\sqrt{(k_x-k_{ox})^2+(k_y-k_{oy})^2}}$$

$$= v\,\frac{\vec{k}-\vec{k}_o}{\left|\vec{k}-\vec{k}_o\right|} = v\,\frac{\Delta\vec{k}}{\left|\Delta\vec{k}\right|}$$

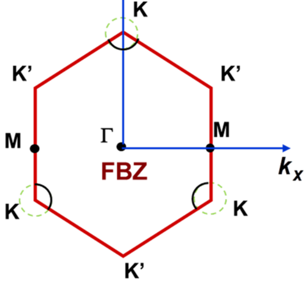




The dynamical equation for the crystal momentum still works:

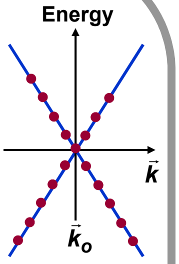
$$\frac{d\;\hbar\vec{k}(t)}{dt} = -e\,\vec{E} - \frac{\hbar\left[\vec{k}(t)-\vec{k}\right]}{\tau}$$

$$\Rightarrow \vec{k}(t=\infty) = \vec{k} - \frac{e\,\tau}{\hbar}\,\vec{E}$$

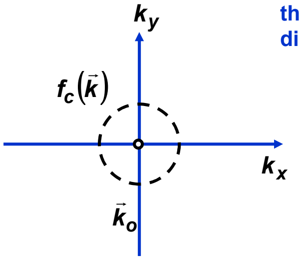


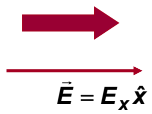
Conductivity of Electrons in Graphene

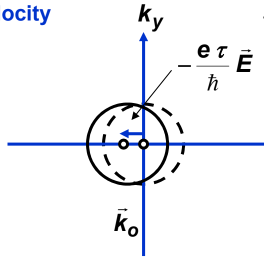
$$\vec{k}(t=\infty) = \vec{k} - \frac{e\,\tau}{\hbar}\,\vec{E} \;\Rightarrow\; \vec{v}_c(\vec{k}(t)) = v\,\frac{\vec{k}-e\tau\vec{E}/\hbar-\vec{k}_o}{\left|\vec{k}-e\tau\vec{E}/\hbar-\vec{k}_o\right|}$$



Velocity magnitude remains the same but the velocity direction changes







Electron distribution in k-space when E-field is zero

Distribution function: $f_c(\vec{k})$

Electron distribution is shifted in k-space when E-field is not zero

Distribution function: $f_c\left(\vec{k}+\frac{e\,\tau}{\hbar}\vec{E}\right)$

Current density can be obtained by the familiar expression:

$$\vec{J} = -e\times\overset{\text{2 pockets or valleys}}{2}\times\overset{\text{2 spins}}{2}\times\int_{\text{near }\vec{k}_o}\frac{d^2\vec{k}}{(2\pi)^2}\;f\left(\vec{k}+\frac{e\tau\,\vec{E}}{\hbar}\right)\vec{v}(\vec{k})$$

Handout 17

Lattice Waves (Phonons) in 1D Crystals: Monoatomic Basis and Diatomic Basis

In this lecture you will learn:

- Equilibrium bond lengths
- Atomic motion in lattices
- Lattice waves (phonons) in a 1D crystal with a monoatomic basis
- Lattice waves (phonons) in a 1D crystal with a diatomic basis
- Dispersion of lattice waves
- Acoustic and optical phonons

The Hydrogen Molecule: Equilibrium Bond Length

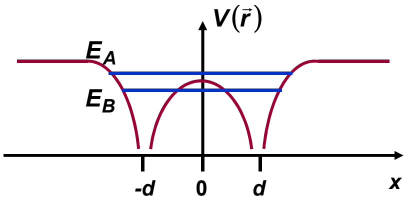
The equilibrium distance between the two hydrogen atoms in a hydrogen molecule is set by the balance among several different competing factors:

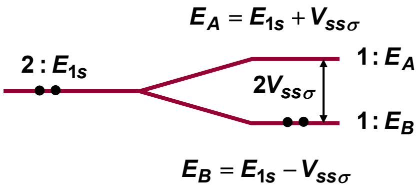
- The reduction in electronic energy due to co-valent bonding is $2V_{ss\sigma}$. If the atoms are too far apart, $V_{ss\sigma}$ becomes to small

$$\langle \phi_{1s}(\vec{r}-d\hat{x}) | \hat{H} | \phi_{1s}(\vec{r}+d\hat{x}) \rangle \approx -V_{ss\sigma}$$

- If the atoms are too close, the positively charged nuclei (protons) will repel each other and this leads to an increase in the system energy

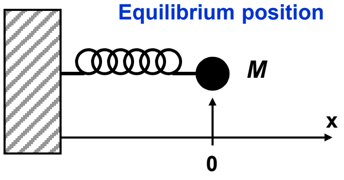
- Electron-electron repulsion also plays a role



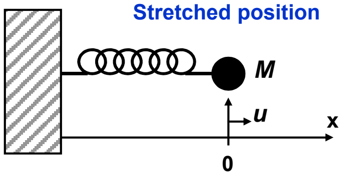


A Mass Attached to a Spring: A Simple Harmonic Oscillator

Equilibrium position



Stretched position



Potential Energy:

$$PE = V(u) = \frac{1}{2} k\, u^2$$

spring constant = k
(units: Newton/meter)

PE varies quadratically with the displacement "u" of the mass from the equilibrium position

Kinetic Energy:

$$KE = \frac{M}{2}\left(\frac{du}{dt}\right)^2$$

Dynamical Equation (Newton's Second Law):

$$M\frac{d^2u}{dt^2} = -\frac{dV}{du} = -k\,u \longrightarrow$$

Restoring force varies linearly with the displacement "u" of the mass from its equilibrium position

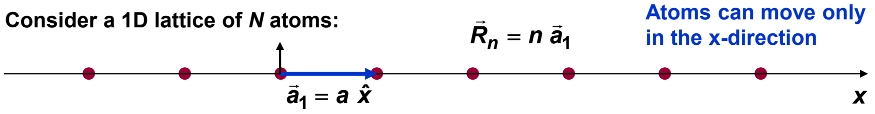
Solution:

$$u(t) = A\cos(\omega_o t) + B\sin(\omega_o t) \qquad \text{where:} \qquad \omega_o = \sqrt{\frac{k}{M}}$$

A 1D Crystal: Potential Energy

Consider a 1D lattice of *N* atoms:

Atoms can move only in the x-direction



- The potential energy of the entire crystal can be expressed in terms of the positions of the atoms. The potential energy will be minimum when all the atoms are at their equilibrium positions.

- Let the displacement of the atom at the lattice site given by $\vec{R}_n$ from its equilibrium position be $u(\vec{R}_n)$

- One can Taylor expand the potential energy of the entire crystal around its minimum equilibrium value:

$$V\left[u(\vec{R}_1), u(\vec{R}_2), u(\vec{R}_3) \ldots\ldots\ldots\, u(\vec{R}_N)\right] = V_{EQ} + \sum_j \cancelto{0}{\left.\frac{\partial V}{\partial u(\vec{R}_j)}\right|_{EQ}} u(\vec{R}_j)$$

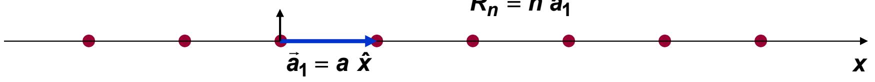
$$+ \frac{1}{2}\sum_k \sum_j \left.\frac{\partial^2 V}{\partial u(\vec{R}_j)\,\partial u(\vec{R}_k)}\right|_{EQ} u(\vec{R}_j)\,u(\vec{R}_k)$$

Potential energy varies quadratically with the displacements of the atoms from their equilibrium positions

A 1D Crystal: Potential and Kinetic Energies

A1D lattice of *N* atoms:

$$\vec{R}_n = n\,\vec{a}_1$$



Potential Energy:

$$V = V_{EQ} + \frac{1}{2}\sum_k\sum_j \left.\frac{\partial^2 V}{\partial u(\vec{R}_j)\partial u(\vec{R}_k)}\right|_{EQ} u(\vec{R}_j,t)\,u(\vec{R}_k,t)$$

$$= V_{EQ} + \frac{1}{2}\sum_k\sum_j K(\vec{R}_j\,,\vec{R}_k)\,u(\vec{R}_j,t)\,u(\vec{R}_k,t) \qquad \left\{ K(\vec{R}_j\,,\vec{R}_k) = \left.\frac{\partial^2 V}{\partial u(\vec{R}_j)\partial u(\vec{R}_k)}\right|_{EQ} \right.$$

Kinetic Energy:

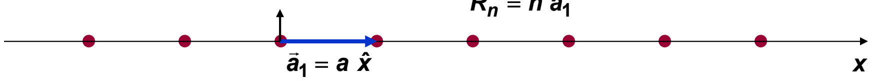
$$KE = \sum_j \frac{M}{2}\left(\frac{du(\vec{R}_j,t)}{dt}\right)^2$$

- The kinetic energy of all the atoms is the sum of their individual kinetic energies

A 1D Crystal: Dynamical Equation

A1D lattice of *N* atoms:

$$\vec{R}_n = n\,\vec{a}_1$$



Write Newtons law for the atom sitting at the site $\vec{R}_n$:

$$M\frac{d^2u(\vec{R}_n,t)}{dt^2} = -\frac{\partial V}{\partial u(\vec{R}_n)} = -\sum_j K(\vec{R}_n\,,\vec{R}_j)\,u(\vec{R}_j,t)$$

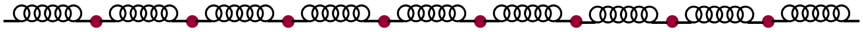
Remember that:

$$K(\vec{R}_j\,,\vec{R}_k) = \left.\frac{\partial^2 V}{\partial u(\vec{R}_j)\partial u(\vec{R}_k)}\right|_{EQ}$$

The restoring forces on the atoms vary linearly with the displacement of the atoms from their equilibrium positions

Dynamical Equation for Nearest-Neighbor Interactions

A1D lattice of *N* atoms:



$$M\frac{d^2u(\vec{R}_n,t)}{dt^2} = -\frac{\partial V}{\partial u(\vec{R}_n)} = -\sum_j K(\vec{R}_n\,,\vec{R}_j)\,u(\vec{R}_j,t)$$

Assume nearest-neighbor interactions:

$$K(\vec{R}_n\,,\vec{R}_j) = -\alpha\,\delta_{j,n+1} - \alpha\,\delta_{j,n-1} + 2\alpha\,\delta_{j,n}$$

This gives:

$$M\frac{d^2u(\vec{R}_n,t)}{dt^2} = -\alpha\left[u(\vec{R}_n,t) - u(\vec{R}_{n-1},t)\right] - \alpha\left[u(\vec{R}_n,t) - u(\vec{R}_{n+1},t)\right]$$

The constants "α" provide restoring forces as if the atoms were connected together with springs of spring constant "α"

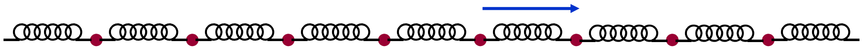
The constant α is called "force constant" (not spring constant) in solid state physics

We have *N* linear coupled differential equations for *N* unknowns

$$u(\vec{R}_n,t) \quad \{\, n = 0,1,2.......(N-1)$$

Solution of the Dynamical Equation: Lattice Waves (Phonons)

A1D lattice of *N* atoms: $\vec{a}_1 = a\,\hat{x}$ $\quad$ $\vec{R}_n = n\,\vec{a}_1$



$$M\frac{d^2u(\vec{R}_n,t)}{dt^2} = -\alpha\left[u(\vec{R}_n,t) - u(\vec{R}_{n-1},t)\right] - \alpha\left[u(\vec{R}_n,t) - u(\vec{R}_{n+1},t)\right]$$

Assume a solution of the form:

$$u(\vec{R}_n,t) = \mathrm{Re}\left[u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega\,t}\right] \longrightarrow$$

Represents a wave with wavevector $\vec{q}$, frequency ω, and amplitude $u(\vec{q})$

Or: $u(\vec{R}_n,t) = u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega\,t}$ $\longrightarrow$ **Slight abuse of notation**

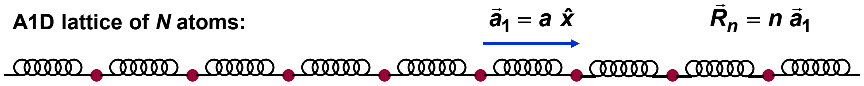
Note that:

$$u(\vec{R}_{n+1},t) = u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_{n+1}}\,e^{-i\,\omega\,t} = u(\vec{q})\,e^{i\,\vec{q}\,.\,(\vec{R}_n+\vec{a}_1)}\,e^{-i\,\omega\,t}$$
$$= e^{i\,\vec{q}\,.\,\vec{a}_1}u(\vec{q})\;e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega\,t}$$

$$u(\vec{R}_{n-1},t) = u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_{n-1}}\,e^{-i\,\omega\,t} = u(\vec{q})\,e^{i\,\vec{q}\,.\,(\vec{R}_n-\vec{a}_1)}\,e^{-i\,\omega\,t}$$
$$= e^{-i\,\vec{q}\,.\,\vec{a}_1}u(\vec{q})\;e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega\,t}$$

Solution of the Dynamical Equation: Lattice Waves (Phonons)

A1D lattice of *N* atoms: $\vec{a}_1 = a\,\hat{x}$ $\vec{R}_n = n\,\vec{a}_1$



$$M\frac{d^2u(\vec{R}_n,t)}{dt^2} = -\alpha\left[u(\vec{R}_n,t)-u(\vec{R}_{n-1},t)\right]-\alpha\left[u(\vec{R}_n,t)-u(\vec{R}_{n+1},t)\right]$$

Plug in the assumed solution: $u(\vec{R}_n,t) = u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_n}\;e^{-i\,\omega\,t}$

$\left\{ q = q_x\,\hat{x} \right.$

To get:

$$-\omega^2\,M\,u(\vec{q}) = -\alpha\left[u(\vec{q})-e^{-i\,\vec{q}\,.\,\vec{a}_1}\,u(\vec{q})\right]-\alpha\left[u(\vec{q})-e^{+i\,\vec{q}\,.\,\vec{a}_1}\,u(\vec{q})\right]$$

Which simplifies to:

$$\omega^2 = \frac{2\alpha}{M}\left[1-\cos(\vec{q}\,.\,\vec{a}_1)\right]$$

$$= \frac{4\alpha}{M}\sin^2\left(\frac{\vec{q}\,.\,\vec{a}_1}{2}\right)$$

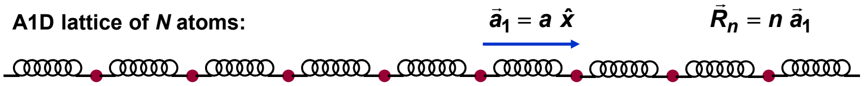
Or:

$$\omega = \pm\sqrt{\frac{4\alpha}{M}}\sin\left(\frac{\vec{q}\,.\,\vec{a}_1}{2}\right) \longrightarrow$$

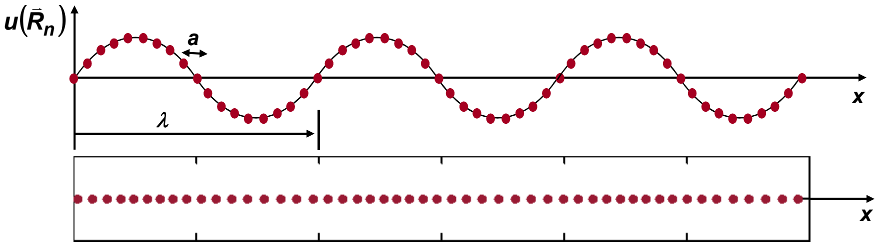
Since ω is always positive, the negative sign is chosen when the sine term is negative

Solution of the Dynamical Equation: Lattice Waves (Phonons)

A1D lattice of *N* atoms: $\vec{a}_1 = a\,\hat{x}$ $\vec{R}_n = n\,\vec{a}_1$



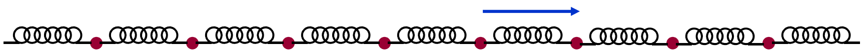
Solution is: $u(\vec{R}_n,t) = u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_n}\;e^{-i\,\omega\,t}$ and $\omega = \sqrt{\frac{4\alpha}{M}}\sin\left(\frac{\vec{q}\,.\,\vec{a}_1}{2}\right)$



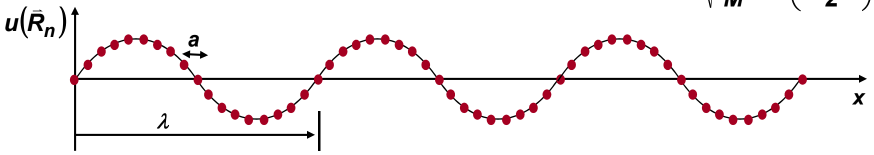
- The lattice waves are like the compressional sound waves in the air

Solution of the Dynamical Equation: Lattice Waves (Phonons)

A1D lattice of N atoms: $\vec{a}_1 = a\,\hat{x}$ $\vec{R}_n = n\,\vec{a}_1$



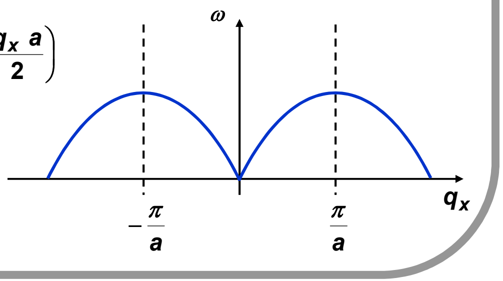
Solution is: $u(\vec{R}_n,t) = u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega\,t}$ and $\omega = \sqrt{\frac{4\alpha}{M}}\sin\left(\frac{\vec{q}\,.\,\vec{a}_1}{2}\right)$



The relation:

$$\omega = \pm\sqrt{\frac{4\alpha}{M}}\sin\left(\frac{\vec{q}\,.\,\vec{a}_1}{2}\right) = \pm\sqrt{\frac{4\alpha}{M}}\sin\left(\frac{q_x\,a}{2}\right)$$

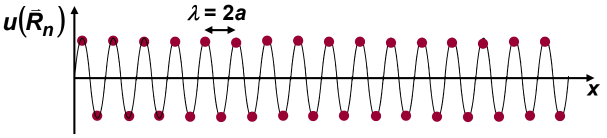
represents the dispersion of the lattice waves or phonons



Lattice Waves and the First BZ

Solution is: $u(\vec{R}_n,t) = u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega\,t}$ and $\omega = \sqrt{\frac{4\alpha}{M}}\sin\left(\frac{\vec{q}\,.\,\vec{a}_1}{2}\right)$

Question: What is the shortest wavelength (or the largest wavevector) the lattice waves can have?



⇒For the shortest wavelength:

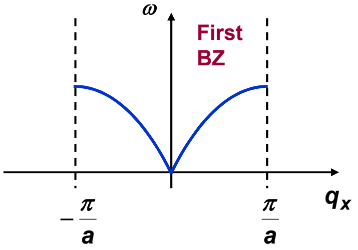
$$\lambda = 2a$$

⇒The largest wavevector is then:

$$|q_x| = \frac{2\pi}{\lambda} = \frac{\pi}{a}$$

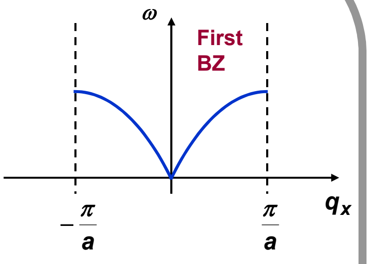
⇒The wavevector values can be restricted to the First BZ

- No new solutions are found for values of the wavevector outside the first BZ



Phase and Group Velocities

$$\omega = \pm\sqrt{\frac{4\alpha}{M}}\,\sin\left(\frac{q_x a}{2}\right)$$



Phase velocity and group velocity of lattice waves are defined as:

$$\vec{v}_p(\vec{q}) = \frac{\omega(\vec{q})}{|\vec{q}|}\hat{q} \xrightarrow{1D} \frac{\omega}{q_x}\hat{x}$$

$$\vec{v}_g(\vec{q}) = \nabla_{\vec{q}}\,\omega(\vec{q}) \xrightarrow{1D} \frac{d\omega}{dq_x}\hat{x}$$

Case I: For $q_x \approx 0$ (i.e. $q_x a << \pi$):

$$\omega \approx \sqrt{\frac{\alpha}{M}}\,q_x a \longrightarrow$$ Linear dispersion $$\Rightarrow v_p = \sqrt{\frac{\alpha}{M}}\,a = v_g$$

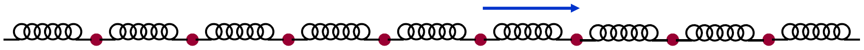
Case II: For $q_x a = \pi$:

$$\omega = \sqrt{\frac{4\alpha}{M}} \qquad \Rightarrow v_p = \sqrt{\frac{4\alpha}{M}}\,\frac{a}{\pi}$$

$$\Rightarrow v_g = 0$$

Periodic Boundary Conditions

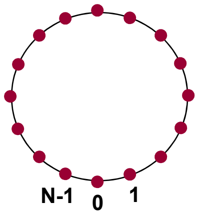
A1D lattice of *N* atoms: $\vec{a}_1 = a\,\hat{x}$ $\qquad \vec{R}_n = n\,\vec{a}_1$



In the solution:

$$u(\vec{R}_n,t) = u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega\,t}$$

allowed values of the wavevector depend on the boundary conditions



Periodic Boundary Condition:

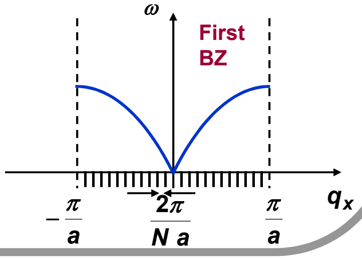
The *N*-th atom is the same as the 0-th atom
This implies:

$$u(\vec{R}_N,t) = u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_N}\,e^{-i\,\omega\,t} = u(\vec{R}_0,t) = u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_0}\,e^{-i\,\omega\,t}$$

$$\Rightarrow e^{i\,\vec{q}\,.\,(\vec{R}_N - \vec{R}_0)} = 1$$

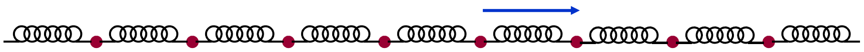
$$\Rightarrow e^{i\,q_x N\,a} = 1$$

$$\Rightarrow q_x = \frac{m}{N}\frac{2\pi}{a} \qquad \begin{cases} m = \text{integer} \\ -\frac{N}{2} < m \le \frac{N}{2} \end{cases}$$



Counting and Conserving Degrees of Freedom

A1D lattice of *N* atoms: $\vec{a}_1 = a\,\hat{x}$ $\vec{R}_n = n\,\vec{a}_1$

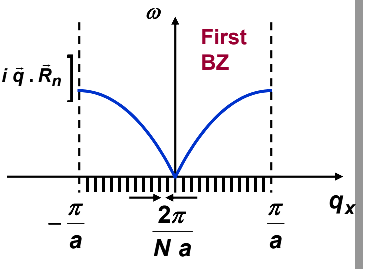


- We started with *N* degrees of freedom which were related to the motion in 1D of *N* different atoms
- The dynamical variables were the amplitudes of the displacements of *N* different atoms

$$u\left(\vec{R}_n,t\right) \quad \left\{ n = 0,1,2.......(N-1)\right.$$

We then ended up with lattice waves:

$$u\left(\vec{R}_n,t\right) = \mathrm{Re}\left[u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega(\vec{q})\,t}\right] = \mathrm{Re}\left[u(\vec{q},t)\,e^{i\,\vec{q}\,.\,\vec{R}_n}\right]$$



- There are *N* different lattice wave modes corresponding to the *N* different possible wavevector values in the first BZ
- The dynamical variables are the amplitudes of the *N* different lattice wave modes

$$u(\vec{q},t) \quad \left\{ q_x = \frac{m}{N}\frac{2\pi}{a} \quad \text{and} \quad -\frac{N}{2} < m \le \frac{N}{2}\right.$$

The number of degrees of freedom are the same before and after – as they should be!

Counting and Conserving Degrees of Freedom

The atomic displacements,

$$u\left(\vec{R}_n,t\right) \quad \left\{ n = 0,1,2.......(N-1)\right.$$

taken together provide a complete description of the motion of all the atoms in the crystal

In general, one can expand the atomic displacements in terms of all the lattice wave modes (resembles a Fourier series expansion):

$$u\left(\vec{R}_n,t\right) = \sum_{\vec{q}\text{ in FBZ}} \mathrm{Re}\left[u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega(\vec{q})\,t}\right]$$

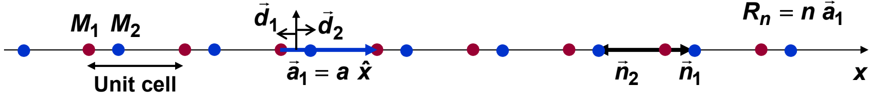
$$= \sum_{\vec{q}\text{ in FBZ}} \frac{u(\vec{q})}{2}\,e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega(\vec{q})\,t} + \frac{u^*(\vec{q})}{2}\,e^{-i\,\vec{q}\,.\,\vec{R}_n}\,e^{i\,\omega(\vec{q})\,t}$$

$$= \sum_{\vec{q}\text{ in FBZ}} \frac{u(\vec{q},t)}{2}\,e^{i\,\vec{q}\,.\,\vec{R}_n} + \frac{u^*(\vec{q},t)}{2}\,e^{-i\,\vec{q}\,.\,\vec{R}_n}$$

Therefore, the lattice wave amplitudes also provide a complete description of the motion of all the atoms in the crystal

Lattice Waves (Phonons) in a 1D crystal: Diatomic Basis

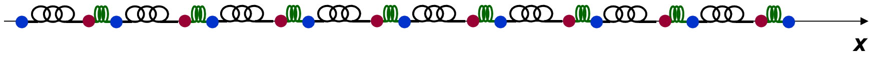
A1D lattice of *N* red atoms and *N* blue atoms and *N* primitive cells:



The basis vectors are: $\vec{d}_1 \quad \vec{d}_2$

The nearest neighbor vectors are: $\vec{n}_1 \quad \vec{n}_2$

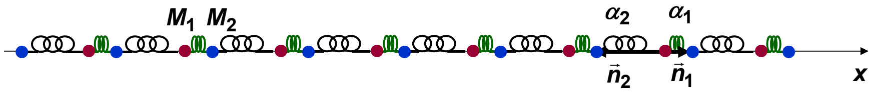
The spring model for nearest neighbor interactions:



Let the displacement of the red atom in the *n*-th cell be: $u_1(\vec{R}_n + \vec{d}_1, t)$

Let the displacement of the blue atom in the *n*-th cell be: $u_2(\vec{R}_n + \vec{d}_2, t)$

Lattice Waves (Phonons) in a 1D crystal: Diatomic Basis



Write the dynamical equations for both the atoms assuming nearest neighbor interactions

$$M_1 \frac{d^2 u_1(\vec{R}_n + \vec{d}_1, t)}{dt^2} = -\alpha_2\left[u_1(\vec{R}_n + \vec{d}_1, t) - u_2(\vec{R}_{n-1} + \vec{d}_2, t)\right] - \alpha_1\left[u_1(\vec{R}_n + \vec{d}_1, t) - u_2(\vec{R}_n + \vec{d}_2, t)\right]$$

$$M_2 \frac{d^2 u_2(\vec{R}_n + \vec{d}_2, t)}{dt^2} = -\alpha_1\left[u_2(\vec{R}_n + \vec{d}_2, t) - u_1(\vec{R}_n + \vec{d}_1, t)\right] - \alpha_2\left[u_2(\vec{R}_n + \vec{d}_2, t) - u_1(\vec{R}_{n+1} + \vec{d}_1, t)\right]$$

The constants α_1 and α_2 are called "force constants" (not spring constants) in solid state physics

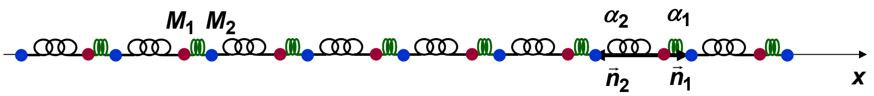
Assume a solution of the form:

$$\left.\begin{aligned} u_1(\vec{R}_n + \vec{d}_1, t) &= u_1(\vec{q})\, e^{i\,\vec{q}\,\cdot\,(\vec{R}_n + \vec{d}_1)}\, e^{-i\,\omega\,t} \\ u_2(\vec{R}_n + \vec{d}_2, t) &= u_2(\vec{q})\, e^{i\,\vec{q}\,\cdot\,(\vec{R}_n + \vec{d}_2)}\, e^{-i\,\omega\,t} \end{aligned}\right\}$$

This is again a wave-like solution with a wavevector $\vec{q}$ and frequency ω and different amplitudes for the two atoms

Notice the phases

Lattice Waves (Phonons) in a 1D crystal: Diatomic Basis



Plug the solutions in the dynamical equations to get:

$$-\omega^2 M_1 u_1(\vec{q}) = -\alpha_2\left[u_1(\vec{q}) - e^{i\,\vec{q}\,.\,\vec{n}_2}u_2(\vec{q})\right] - \alpha_1\left[u_1(\vec{q}) - e^{i\,\vec{q}\,.\,\vec{n}_1}u_2(\vec{q})\right]$$

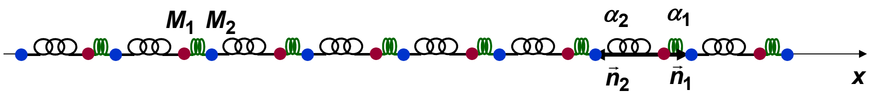
$$-\omega^2 M_2\, u_2(\vec{q}) = -\alpha_1\left[u_2(\vec{q}) - e^{-i\,\vec{q}\,.\,\vec{n}_1}u_1(\vec{q})\right] - \alpha_2\left[u_2(\vec{q}) - e^{-i\,\vec{q}\,.\,\vec{n}_2}u_1(\vec{q})\right]$$

Write the equations in a matrix form:

$$\begin{bmatrix} \alpha_1+\alpha_2 & -\left(\alpha_1\, e^{i\,\vec{q}\,.\,\vec{n}_1} + \alpha_2\, e^{i\,\vec{q}\,.\,\vec{n}_2}\right) \\ -\left(\alpha_1\, e^{-i\,\vec{q}\,.\,\vec{n}_1} + \alpha_2\, e^{-i\,\vec{q}\,.\,\vec{n}_2}\right) & \alpha_1+\alpha_2 \end{bmatrix} \begin{bmatrix} u_1(\vec{q}) \\ u_2(\vec{q}) \end{bmatrix} = \omega^2 \begin{bmatrix} M_1 & 0 \\ 0 & M_2 \end{bmatrix} \begin{bmatrix} u_1(\vec{q}) \\ u_2(\vec{q}) \end{bmatrix}$$

This is a 2x2 matrix eigenvalue equation that needs to be solved for each value of the wavevector to get the dispersion of the lattice waves

The Dynamical Matrix



$$\begin{bmatrix} \alpha_1+\alpha_2 & -\left(\alpha_1\, e^{i\,\vec{q}\,.\,\vec{n}_1} + \alpha_2\, e^{i\,\vec{q}\,.\,\vec{n}_2}\right) \\ -\left(\alpha_1\, e^{-i\,\vec{q}\,.\,\vec{n}_1} + \alpha_2\, e^{-i\,\vec{q}\,.\,\vec{n}_2}\right) & \alpha_1+\alpha_2 \end{bmatrix} \begin{bmatrix} u_1(\vec{q}) \\ u_2(\vec{q}) \end{bmatrix} = \omega^2 \begin{bmatrix} M_1 & 0 \\ 0 & M_2 \end{bmatrix} \begin{bmatrix} u_1(\vec{q}) \\ u_2(\vec{q}) \end{bmatrix}$$

Or:

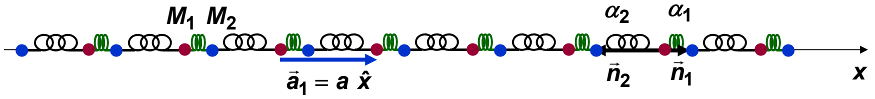
$$\overline{\overline{D}}(\vec{q}) \begin{bmatrix} u_1(\vec{q}) \\ u_2(\vec{q}) \end{bmatrix} = \omega^2\, \overline{\overline{M}} \begin{bmatrix} u_1(\vec{q}) \\ u_2(\vec{q}) \end{bmatrix}$$

Or:

$$\overline{\overline{M}}^{-1}\, \overline{\overline{D}}(\vec{q}) \begin{bmatrix} u_1(\vec{q}) \\ u_2(\vec{q}) \end{bmatrix} = \omega^2 \begin{bmatrix} u_1(\vec{q}) \\ u_2(\vec{q}) \end{bmatrix}$$

- **The matrix $\overline{\overline{D}}(\vec{q})$ is called the dynamical matrix of the medium**
- **For any medium, in any dimension, the dispersion relations for the lattice waves (phonons) are obtained by solving a similar matrix eigenvalue equation**

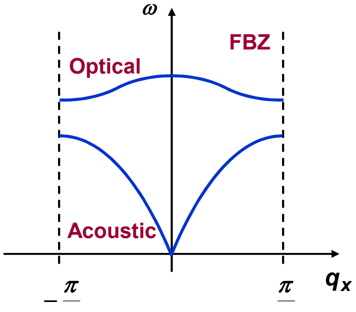
Optical and Acoustic Phonons



The frequency eigenvalues are:

$$\omega^2(\vec q) = \frac{(\alpha_1+\alpha_2)}{2M_r} \pm \frac{1}{2}\sqrt{\frac{(\alpha_1+\alpha_2)^2}{M_r^2} - 16\,\frac{\alpha_1\alpha_2}{M_1M_2}\sin^2\!\left(\frac{\vec q\cdot\vec a_1}{2}\right)}$$

$$\left\{\ \frac{1}{M_r} = \frac{1}{M_1} + \frac{1}{M_2}\right.$$



- The two frequency eigenvalues for each wavevector value in the FBZ give two phonon bands
- The higher frequency band is called the optical phonon band
- The lower frequency band is called the acoustic phonon band

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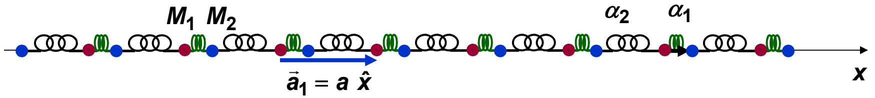
Optical and Acoustic Phonons: Special Cases



Case I: $\vec q \approx 0$

Acoustic band:

$$\omega(\vec q \approx 0) \approx \sqrt{\frac{\alpha_1\alpha_2}{(\alpha_1+\alpha_2)(M_1+M_2)}}\,q_x a \qquad \begin{bmatrix} u_1(\vec q \approx 0) \\ u_2(\vec q \approx 0)\end{bmatrix} \approx A\begin{bmatrix}1\\1\end{bmatrix}$$

$$u_1\left(\vec R_n + \vec d_1, t\right) = A\,e^{i\,\vec q\,.\left(\vec R_n+\vec d_1\right)}\,e^{-i\,\omega\,t}$$

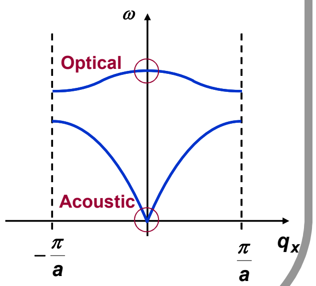
$$u_2\left(\vec R_n + \vec d_2, t\right) = A\,e^{i\,\vec q\,.\left(\vec R_n+\vec d_2\right)}\,e^{-i\,\omega\,t}$$

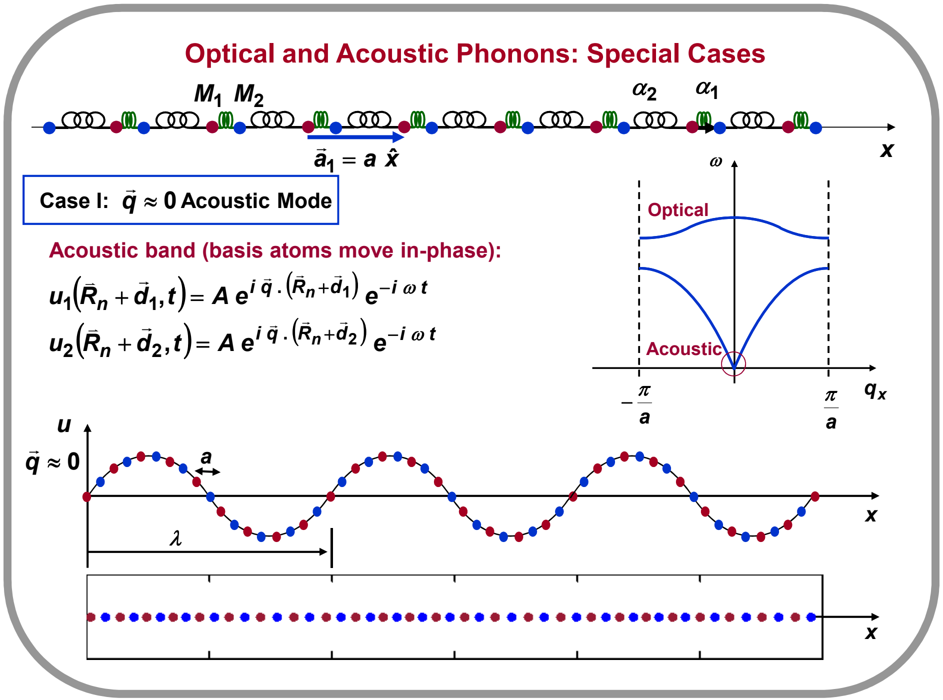
Optical band:

$$\omega(\vec q \approx 0) \approx \sqrt{\frac{(\alpha_1+\alpha_2)}{M_r}} \qquad \begin{bmatrix} u_1(\vec q \approx 0) \\ u_2(\vec q \approx 0)\end{bmatrix} \approx A\begin{bmatrix}1\\ -M_1/M_2\end{bmatrix}$$

$$u_1\left(\vec R_n + \vec d_1, t\right) = A\,e^{i\,\vec q\,.\left(\vec R_n+\vec d_1\right)}\,e^{-i\,\omega\,t}$$

$$u_2\left(\vec R_n + \vec d_2, t\right) = -A\,\frac{M_1}{M_2}\,e^{i\,\vec q\,.\left(\vec R_n+\vec d_2\right)}\,e^{-i\,\omega\,t}$$





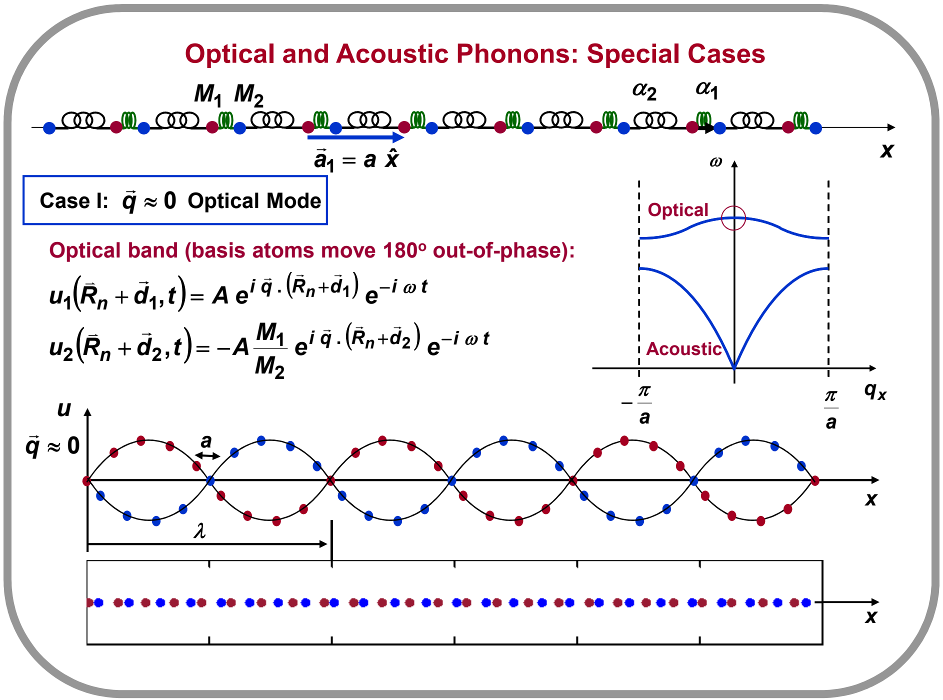
Optical and Acoustic Phonons: Special Cases

Case I: $\vec{q} \approx 0$ Acoustic Mode

Acoustic band (basis atoms move in-phase):

$$u_1\left(\vec{R}_n + \vec{d}_1, t\right) = A\, e^{i\,\vec{q}\,.\left(\vec{R}_n + \vec{d}_1\right)}\, e^{-i\,\omega\,t}$$

$$u_2\left(\vec{R}_n + \vec{d}_2, t\right) = A\, e^{i\,\vec{q}\,.\left(\vec{R}_n + \vec{d}_2\right)}\, e^{-i\,\omega\,t}$$



Optical and Acoustic Phonons: Special Cases

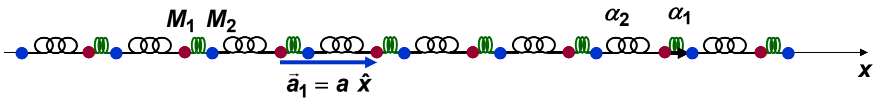
Case I: $\vec{q} \approx 0$ Optical Mode

Optical band (basis atoms move 180° out-of-phase):

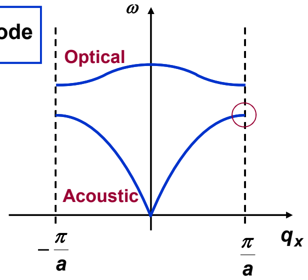
$$u_1\left(\vec{R}_n + \vec{d}_1, t\right) = A\, e^{i\,\vec{q}\,.\left(\vec{R}_n + \vec{d}_1\right)}\, e^{-i\,\omega\,t}$$

$$u_2\left(\vec{R}_n + \vec{d}_2, t\right) = -A\,\frac{M_1}{M_2}\, e^{i\,\vec{q}\,.\left(\vec{R}_n + \vec{d}_2\right)}\, e^{-i\,\omega\,t}$$

Optical and Acoustic Phonons: Special Cases



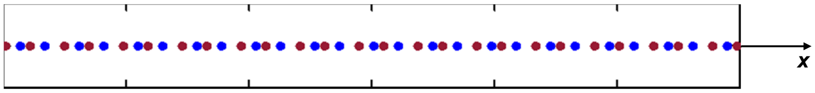
Case II: $\vec{q} = \frac{\pi}{a}\hat{x}\ ,\ M_1 = M_2 = M\ ,\ \alpha_1 > \alpha_2$ Acoustic Mode



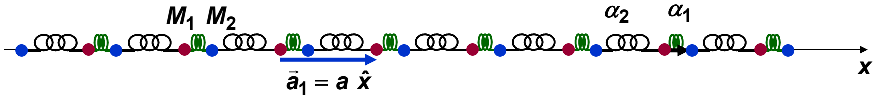
$$\omega\left(\frac{\pi}{a}\hat{x}\right) = \sqrt{\frac{2\alpha_2}{M}} \qquad \begin{bmatrix} u_1\left(\frac{\pi}{a}\hat{x}\right) \\ u_2\left(\frac{\pi}{a}\hat{x}\right) \end{bmatrix} = A\begin{bmatrix} 1 \\ e^{-i\,\vec{q}\,.\,\vec{n}_1} \end{bmatrix}$$

$$u_1\left(\vec{R}_n + \vec{d}_1, t\right) = A\,e^{i\,\vec{q}\,.\left(\vec{R}_n + \vec{d}_1\right)}\,e^{-i\,\omega\,t}$$

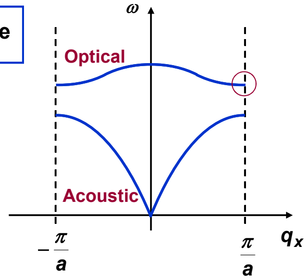
$$u_2\left(\vec{R}_n + \vec{d}_2, t\right) = A\,e^{-i\,\vec{q}\,.\,\vec{n}_1} e^{i\,\vec{q}\,.\left(\vec{R}_n + \vec{d}_2\right)}\,e^{-i\,\omega\,t}$$
$$= A\,e^{i\,\vec{q}\,.\left(\vec{R}_n + \vec{d}_1\right)}\,e^{-i\,\omega\,t}$$



Optical and Acoustic Phonons: Special Cases



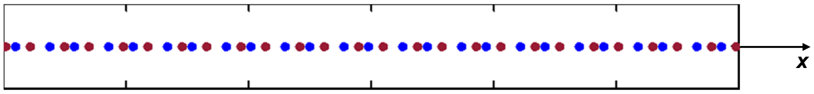
Case II: $\vec{q} = \frac{\pi}{a}\hat{x}\ ,\ M_1 = M_2 = M\ ,\ \alpha_1 > \alpha_2$ Optical Mode



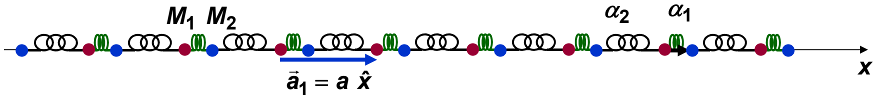
$$\omega\left(\frac{\pi}{a}\hat{x}\right) = \sqrt{\frac{2\alpha_1}{M}} \qquad \begin{bmatrix} u_1\left(\frac{\pi}{a}\hat{x}\right) \\ u_2\left(\frac{\pi}{a}\hat{x}\right) \end{bmatrix} = A\begin{bmatrix} 1 \\ -\,e^{-i\,\vec{q}\,.\,\vec{n}_1} \end{bmatrix}$$

$$u_1\left(\vec{R}_n + \vec{d}_1, t\right) = A\,e^{i\,\vec{q}\,.\left(\vec{R}_n + \vec{d}_1\right)}\,e^{-i\,\omega\,t}$$

$$u_2\left(\vec{R}_n + \vec{d}_2, t\right) = -A\,e^{-i\,\vec{q}\,.\,\vec{n}_1} e^{i\,\vec{q}\,.\left(\vec{R}_n + \vec{d}_2\right)}\,e^{-i\,\omega\,t}$$
$$= -A\,e^{i\,\vec{q}\,.\left(\vec{R}_n + \vec{d}_1\right)}\,e^{-i\,\omega\,t}$$



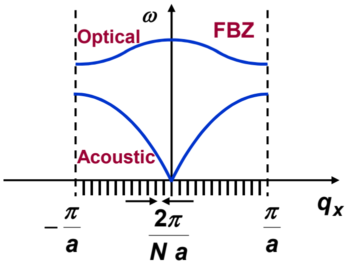
Counting and Conserving Degrees of Freedom



- We started with 2*N* degrees of freedom which were related to the motion in 1D of 2*N* different atoms
- The dynamical variables were the amplitudes of the displacements of 2*N* different atoms

$$u_1\left(\vec{R}_n+\vec{d}_1,t\right) \quad u_2\left(\vec{R}_n+\vec{d}_2,t\right) \quad \{\, n=0,1,2.......(N-1)$$

We then ended up with lattice waves:



- There are *N* different modes per phonon band corresponding to the *N* different possible wavevector values in the first BZ
- There are 2 phonon bands and therefore a total of 2*N* different phonon modes
- The dynamical variables are the amplitudes of the 2*N* different phonon modes

The number of degrees of freedom are the same before and after – as they should be!

Counting and Conserving Degrees of Freedom

The atomic displacements,

$$u_1\left(\vec{R}_n+\vec{d}_1,t\right) \quad u_2\left(\vec{R}_n+\vec{d}_2,t\right) \quad \{\, n=0,1,2.......(N-1)$$

taken together provide a complete description of the motion of all the 2*N* atoms in the crystal

In general, one can expand the atomic displacements in terms of all the lattice wave modes – all wavevectors and all bands:

$$\begin{bmatrix} u_1\left(\vec{R}_n+\vec{d}_1,t\right) \\ u_2\left(\vec{R}_n+\vec{d}_2,t\right) \end{bmatrix} = \sum_{\eta=A,O}\ \sum_{\vec{q}\text{ in FBZ}} \text{Re}\left[\begin{bmatrix} u_{1\eta}(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{d}_1} \\ u_{2\mu}(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{d}_2} \end{bmatrix} e^{i\,\vec{q}\,.\,\vec{R}_n}\ e^{-i\,\omega_\eta(\vec{q})\,t} \right]$$

$$= \sum_{\eta=A,O}\ \sum_{\vec{q}\text{ in FBZ}} \frac{1}{2} \begin{bmatrix} u_{1\eta}(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{d}_1} \\ u_{2\eta}(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{d}_2} \end{bmatrix} e^{i\,\vec{q}\,.\,\vec{R}_n}\ e^{-i\,\omega_\eta(\vec{q})\,t} + \frac{1}{2} \begin{bmatrix} u^*_{1\eta}(\vec{q})\,e^{-i\,\vec{q}\,.\,\vec{d}_1} \\ u^*_{2\eta}(\vec{q})\,e^{-i\,\vec{q}\,.\,\vec{d}_2} \end{bmatrix} e^{-i\,\vec{q}\,.\,\vec{R}_n}\ e^{i\,\omega_\eta(\vec{q})\,t}$$

$$= \sum_{\eta=A,O}\ \sum_{\vec{q}\text{ in FBZ}} \frac{1}{2} \begin{bmatrix} u_{1\eta}(\vec{q},t)\,e^{i\,\vec{q}\,.\,\vec{d}_1} \\ u_{2\eta}(\vec{q},t)\,e^{i\,\vec{q}\,.\,\vec{d}_2} \end{bmatrix} e^{i\,\vec{q}\,.\,\vec{R}_n} + \frac{1}{2} \begin{bmatrix} u^*_{1\eta}(\vec{q},t)\,e^{-i\,\vec{q}\,.\,\vec{d}_1} \\ u^*_{2\eta}(\vec{q},t)\,e^{-i\,\vec{q}\,.\,\vec{d}_2} \end{bmatrix} e^{-i\,\vec{q}\,.\,\vec{R}_n}$$

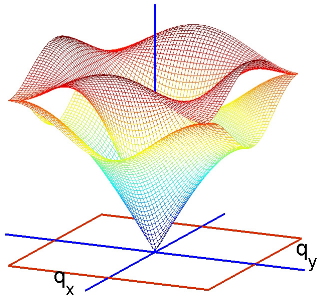
Therefore, the lattice wave amplitudes also provide a complete description of the motion of all the atoms in the crystal

Handout 18

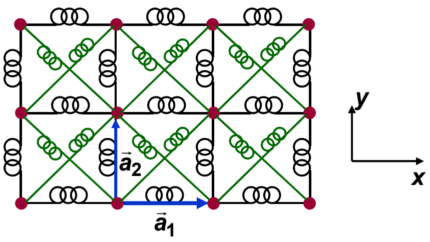
Phonons in 2D Crystals: Monoatomic Basis and Diatomic Basis

In this lecture you will learn:

- Phonons in a 2D crystal with a monoatomic basis
- Phonons in a 2D crystal with a diatomic basis
- Dispersion of phonons
- LA and TA acoustic phonons
- LO and TO optical phonons



Phonons in a 2D Crystal with a Monoatomic Basis



General lattice vector:

$$\vec{R}_{nm} = n\,\vec{a}_1 + m\vec{a}_2$$

Nearest-neighbor vectors:

$$\vec{n}_1 = a\hat{x} \qquad \vec{n}_2 = a\hat{y}$$
$$\vec{n}_3 = -a\hat{x} \qquad \vec{n}_4 = -a\hat{y}$$

Next nearest-neighbor vectors:

$$\vec{p}_1 = a\hat{x} + a\hat{y} \qquad \vec{p}_2 = -a\hat{x} + a\hat{y}$$
$$\vec{p}_3 = -a\hat{x} - a\hat{y} \qquad \vec{p}_4 = a\hat{x} - a\hat{y}$$

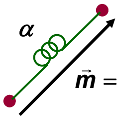
Atomic displacement vectors:

Atoms, can move in 2D therefore atomic displacements are given by a vector:

$$\vec{u}(\vec{R}_{nm},t) = \begin{bmatrix} u_x(\vec{R}_{nm},t) \\ u_y(\vec{R}_{nm},t) \end{bmatrix}$$

Vector Dynamical Equations

$$\vec{u}(\vec{R}_2,t)=\vec{u}(\vec{R}_1+\vec{m},t)$$



$$\vec{m}=\vec{R}_2-\vec{R}_1$$

$$\vec{u}(\vec{R}_1,t) \qquad \hat{m}=\frac{\vec{m}}{|\vec{m}|}$$

If the nearest-neighbor vectors are known then the dynamical equations can be written easily.

Vector dynamical equation:

$$M\frac{d^2\vec{u}(\vec{R}_1,t)}{dt^2}=\alpha\left[\left[\vec{u}(\vec{R}_2,t)-\vec{u}(\vec{R}_1,t)\right].\,\hat{m}\right]\hat{m}=\alpha\left[\left[\vec{u}(\vec{R}_1+\vec{m},t)-\vec{u}(\vec{R}_1,t)\right].\,\hat{m}\right]\hat{m}$$

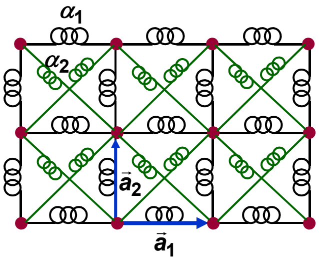
Component dynamical equation:

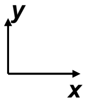
To find the equations for the x and y-components of the atomic displacement, take the dot-products of the above equation on both sides with $\hat{x}$ and $\hat{y}$, respectively:

$$M\frac{d^2u_x(\vec{R}_1,t)}{dt^2}=\alpha\left[\left[\vec{u}(\vec{R}_1+\vec{m},t)-\vec{u}(\vec{R}_1,t)\right].\,\hat{m}\right](\hat{m}.\hat{x})$$

$$M\frac{d^2u_y(\vec{R}_1,t)}{dt^2}=\alpha\left[\left[\vec{u}(\vec{R}_1+\vec{m},t)-\vec{u}(\vec{R}_1,t)\right].\,\hat{m}\right](\hat{m}.\hat{y})$$

Vector Dynamical Equations for a 2D Crystal





General lattice vector:

$$\vec{R}_{nm}=n\,\vec{a}_1+m\vec{a}_2$$

Nearest-neighbor vectors:

$$\vec{n}_1=a\hat{x} \qquad \vec{n}_2=a\hat{y}$$

$$\vec{n}_3=-a\hat{x} \qquad \vec{n}_4=-a\hat{y}$$

Next nearest-neighbor vectors:

$$\vec{p}_1=a\hat{x}+a\hat{y} \qquad \vec{p}_2=-a\hat{x}+a\hat{y}$$

$$\vec{p}_3=-a\hat{x}-a\hat{y} \qquad \vec{p}_4=a\hat{x}-a\hat{y}$$

$$M\frac{d^2\vec{u}(\vec{R}_{nm},t)}{dt^2}=\alpha_1\sum_{j=1,2,3,4}\left[\left[\vec{u}(\vec{R}_{nm}+\vec{n}_j,t)-\vec{u}(\vec{R}_{nm},t)\right].\,\hat{n}_j\right]\hat{n}_j \longrightarrow \text{summation over 4 nn}$$

$$+\alpha_2\sum_{j=1,2,3,4}\left[\left[\vec{u}(\vec{R}_{nm}+\vec{p}_j,t)-\vec{u}(\vec{R}_{nm},t)\right].\,\hat{p}_j\right]\hat{p}_j \longrightarrow \text{summation over 4 next nn}$$

Dynamical Equations

$$M\,\frac{d^2\vec{u}\left(\vec{R}_{nm},t\right)}{dt^2}=\alpha_1\sum_{j=1,2,3,4}\left[\left[\vec{u}\left(\vec{R}_{nm}+\vec{n}_j,t\right)-\vec{u}\left(\vec{R}_{nm},t\right)\right].\,\hat{n}_j\right]\hat{n}_j$$
$$+\alpha_2\sum_{j=1,2,3,4}\left[\left[\vec{u}\left(\vec{R}_{nm}+\vec{p}_j,t\right)-\vec{u}\left(\vec{R}_{nm},t\right)\right].\,\hat{p}_j\right]\hat{p}_j$$

If we take the dot-product of the above equation with $\hat{x}$ we get:

$$\begin{aligned}M\,\frac{d^2u_x\left(\vec{R}_{nm},t\right)}{dt^2}=&-\alpha_1\left[u_x\left(\vec{R}_{nm},t\right)-u_x\left(\vec{R}_{nm}+\vec{n}_1,t\right)\right]-\alpha_1\left[u_x\left(\vec{R}_{nm},t\right)-u_x\left(\vec{R}_{nm}+\vec{n}_3,t\right)\right]\\&-\frac{\alpha_2}{2}\left[u_x\left(\vec{R}_{nm},t\right)-u_x\left(\vec{R}_{nm}+\vec{p}_1,t\right)\right]-\frac{\alpha_2}{2}\left[u_y\left(\vec{R}_{nm},t\right)-u_y\left(\vec{R}_{nm}+\vec{p}_1,t\right)\right]\\&-\frac{\alpha_2}{2}\left[u_x\left(\vec{R}_{nm},t\right)-u_x\left(\vec{R}_{nm}+\vec{p}_2,t\right)\right]+\frac{\alpha_2}{2}\left[u_y\left(\vec{R}_{nm},t\right)-u_y\left(\vec{R}_{nm}+\vec{p}_2,t\right)\right]\\&-\frac{\alpha_2}{2}\left[u_x\left(\vec{R}_{nm},t\right)-u_x\left(\vec{R}_{nm}+\vec{p}_3,t\right)\right]-\frac{\alpha_2}{2}\left[u_y\left(\vec{R}_{nm},t\right)-u_y\left(\vec{R}_{nm}+\vec{p}_3,t\right)\right]\\&-\frac{\alpha_2}{2}\left[u_x\left(\vec{R}_{nm},t\right)-u_x\left(\vec{R}_{nm}+\vec{p}_4,t\right)\right]+\frac{\alpha_2}{2}\left[u_y\left(\vec{R}_{nm},t\right)-u_y\left(\vec{R}_{nm}+\vec{p}_4,t\right)\right]\end{aligned}$$

Dynamical Equations

$$M\,\frac{d^2\vec{u}\left(\vec{R}_{nm},t\right)}{dt^2}=\alpha_1\sum_{j=1,2,3,4}\left[\left[\vec{u}\left(\vec{R}_{nm}+\vec{n}_j,t\right)-\vec{u}\left(\vec{R}_{nm},t\right)\right].\,\hat{n}_j\right]\hat{n}_j$$
$$+\alpha_2\sum_{j=1,2,3,4}\left[\left[\vec{u}\left(\vec{R}_{nm}+\vec{p}_j,t\right)-\vec{u}\left(\vec{R}_{nm},t\right)\right].\,\hat{p}_j\right]\hat{p}_j$$

If we take the dot-product of the above equation with $\hat{y}$ we get:

$$\begin{aligned}M\,\frac{d^2u_y\left(\vec{R}_{nm},t\right)}{dt^2}=&-\alpha_1\left[u_y\left(\vec{R}_{nm},t\right)-u_y\left(\vec{R}_{nm}+\vec{n}_2,t\right)\right]-\alpha_1\left[u_y\left(\vec{R}_{nm},t\right)-u_y\left(\vec{R}_{nm}+\vec{n}_4,t\right)\right]\\&-\frac{\alpha_2}{2}\left[u_y\left(\vec{R}_{nm},t\right)-u_y\left(\vec{R}_{nm}+\vec{p}_1,t\right)\right]-\frac{\alpha_2}{2}\left[u_x\left(\vec{R}_{nm},t\right)-u_x\left(\vec{R}_{nm}+\vec{p}_1,t\right)\right]\\&-\frac{\alpha_2}{2}\left[u_y\left(\vec{R}_{nm},t\right)-u_y\left(\vec{R}_{nm}+\vec{p}_2,t\right)\right]+\frac{\alpha_2}{2}\left[u_x\left(\vec{R}_{nm},t\right)-u_x\left(\vec{R}_{nm}+\vec{p}_2,t\right)\right]\\&-\frac{\alpha_2}{2}\left[u_y\left(\vec{R}_{nm},t\right)-u_y\left(\vec{R}_{nm}+\vec{p}_3,t\right)\right]-\frac{\alpha_2}{2}\left[u_x\left(\vec{R}_{nm},t\right)-u_x\left(\vec{R}_{nm}+\vec{p}_3,t\right)\right]\\&-\frac{\alpha_2}{2}\left[u_y\left(\vec{R}_{nm},t\right)-u_y\left(\vec{R}_{nm}+\vec{p}_4,t\right)\right]+\frac{\alpha_2}{2}\left[u_x\left(\vec{R}_{nm},t\right)-u_x\left(\vec{R}_{nm}+\vec{p}_4,t\right)\right]\end{aligned}$$

Solution of the Dynamical Equations

Assume a wave-like solution of the form:

$$\vec{u}\left(\vec{R}_{nm},t\right)=\begin{bmatrix} u_x\left(\vec{R}_{nm},t\right) \\ u_y\left(\vec{R}_{nm},t\right) \end{bmatrix}=\begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix} e^{i\,\vec{q}\,.\,\vec{R}_{nm}}\; e^{-i\,\omega\,t}$$

Then:

$$\vec{u}\left(\vec{R}_{nm}+\vec{n}_j,t\right)=\begin{bmatrix} u_x\left(\vec{R}_{nm}+\vec{n}_j,t\right) \\ u_y\left(\vec{R}_{nm}+\vec{n}_j,t\right) \end{bmatrix}=\begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix} e^{i\,\vec{q}\,.\,\left(\vec{R}_{nm}+\vec{n}_j\right)}\; e^{-i\,\omega\,t}$$

$$= e^{i\,\vec{q}\,.\,\vec{n}_j}\begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix} e^{i\,\vec{q}\,.\,\vec{R}_{nm}}\; e^{-i\,\omega\,t}$$

$$= e^{i\,\vec{q}\,.\,\vec{n}_j}\; \vec{u}\left(\vec{R}_{nm},t\right)$$

We take the above solution form and plug it into the dynamical equations

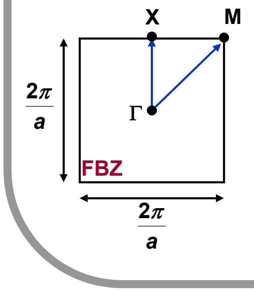
Dynamical Matrix and Phonon Bands

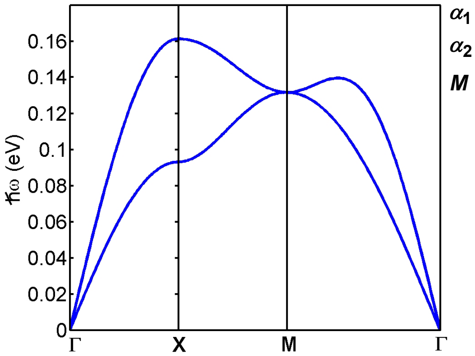
$$\begin{bmatrix} 4\alpha_1\sin^2\left(\frac{q_x a}{2}\right)+2\alpha_2\left[1-\cos(q_x a)\cos(q_y a)\right] & 2\alpha_2\sin(q_x a)\sin(q_y a) \\ 2\alpha_2\sin(q_x a)\sin(q_y a) & 4\alpha_1\sin^2\left(\frac{q_y a}{2}\right)+2\alpha_2\left[1-\cos(q_x a)\cos(q_y a)\right] \end{bmatrix}\begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix}=\omega^2 M\begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix}$$

Compare with the standard form:

$$\overline{\overline{D}}(\vec{q})\begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix}=\omega^2\begin{bmatrix} M & 0 \\ 0 & M \end{bmatrix}\begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix}$$

Solutions:





$\alpha_1 = 200$ N/m

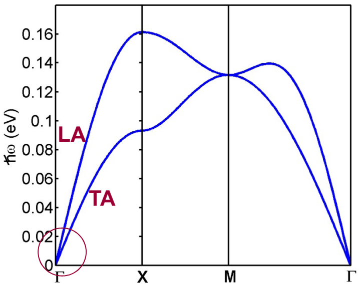
$\alpha_2 = 100$ N/m

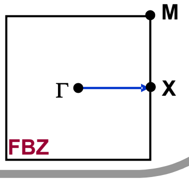
$M = 2\text{x}10^{-26}$ kg

Transverse (TA) and Longitudinal (LA) Acoustic Phonons

$$\begin{bmatrix} 4\alpha_1\left(\frac{q_x a}{2}\right)^2 + \alpha_2\left[(q_x a)^2 + (q_y a)^2\right] & 2\alpha_2(q_x a)(q_y a) \\ 2\alpha_2(q_x a)(q_y a) & 4\alpha_1\left(\frac{q_y a}{2}\right)^2 + \alpha_2\left[(q_x a)^2 + (q_y a)^2\right] \end{bmatrix} \begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix} = \omega^2 M \begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix}$$

Case I: $q_x \approx 0 \,,\, q_y = 0$





$$\omega_{LA}(q_x) = \sqrt{\frac{\alpha_1 + \alpha_2}{M}}\, q_x a \qquad \begin{bmatrix} u_x(q_x) \\ u_y(q_x) \end{bmatrix} = A \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

Longitudinal acoustic phonons: atomic motion in the direction of wave propagation

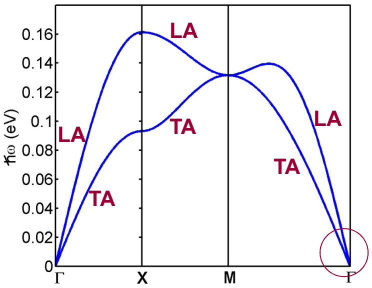
$$\omega_{TA}(q_x) = \sqrt{\frac{\alpha_2}{M}}\, q_x a \qquad \begin{bmatrix} u_x(q_x) \\ u_y(q_x) \end{bmatrix} = A \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

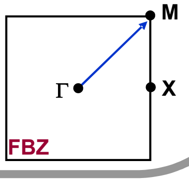
Transverse acoustic phonons: atomic motion in the direction perpendicular to wave propagation

Transverse (TA) and Longitudinal (LA) Acoustic Phonons

$$\begin{bmatrix} 4\alpha_1\left(\frac{q_x a}{2}\right)^2 + \alpha_2\left[(q_x a)^2 + (q_y a)^2\right] & 2\alpha_2(q_x a)(q_y a) \\ 2\alpha_2(q_x a)(q_y a) & 4\alpha_1\left(\frac{q_y a}{2}\right)^2 + \alpha_2\left[(q_x a)^2 + (q_y a)^2\right] \end{bmatrix} \begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix} = \omega^2 M \begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix}$$

Case II: $q_x \approx 0 \,,\, q_y \approx 0 \qquad q_x = q_y = q$





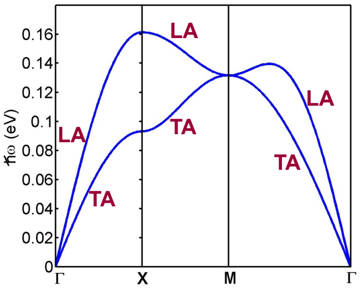
$$\omega_{LA}(q) = \sqrt{\frac{\alpha_1 + 4\alpha_2}{M}}\, q\, a \qquad \begin{bmatrix} u_x(q) \\ u_y(q) \end{bmatrix} = A \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

Longitudinal acoustic phonons: atomic motion in the direction of wave propagation

$$\omega_{TA}(q) = \sqrt{\frac{\alpha_1}{M}}\, q\, a \qquad \begin{bmatrix} u_x(q) \\ u_y(q) \end{bmatrix} = A \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

Transverse acoustic phonons: atomic motion in the direction perpendicular to wave propagation

Transverse (TA) and Longitudinal (LA) Acoustic Phonons



In general for longitudinal acoustic phonons near the zone center:

$$\begin{bmatrix} u_x(q) \\ u_y(q) \end{bmatrix} = \frac{A}{|\vec{q}|} \begin{bmatrix} q_x \\ q_y \end{bmatrix}$$

And for transverse acoustic phonons near the zone center:

$$\begin{bmatrix} u_x(q) \\ u_y(q) \end{bmatrix} = \frac{A}{|\vec{q}|} \begin{bmatrix} -q_y \\ q_x \end{bmatrix}$$

In general, away from the zone center, the LA phonons are not entirely longitudinal and neither the TA phonons are entirely transverse

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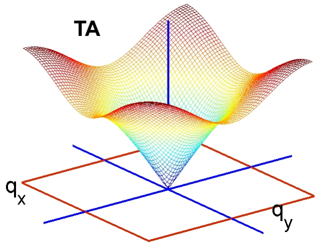
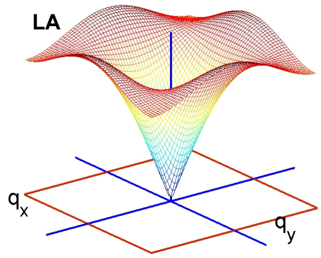
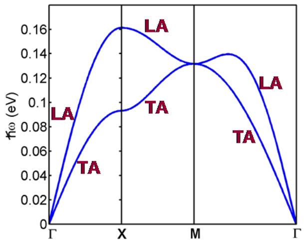
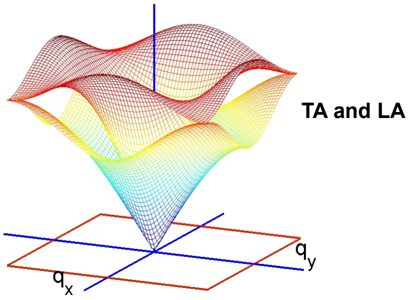
Transverse (TA) and Longitudinal (LA) Acoustic Phonons









Periodic Boundary Conditions in 2D

General lattice vector:

$$\vec{R}_{nm} = n\,\vec{a}_1 + m\vec{a}_2$$

General reciprocal lattice vector inside FBZ:

$$\vec{q} = \alpha_1\,\vec{b}_1 + \alpha_2\,\vec{b}_2 \qquad \{ \quad -1/2 \le \alpha_1\,,\,\alpha_2 \le 1/2$$

Our solution was:

$$\vec{u}(\vec{R}_{nm},t) = \begin{bmatrix} u_x(\vec{R}_{nm},t) \\ u_y(\vec{R}_{nm},t) \end{bmatrix} = \begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix} e^{i\,\vec{q}\,.\,\vec{R}_{nm}}\; e^{-i\,\omega\,t}$$

Periodic boundary conditions for a lattice of N_1xN_2 primitive cells imply:

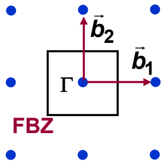
$$\vec{u}(\vec{R}_{nm} + N_1\vec{a}_1,t) = \begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix} e^{i\,\vec{q}\,.\,(\vec{R}_{nm}+N_1\vec{a}_1)}\; e^{-i\,\omega\,t} = \vec{u}(\vec{R}_{nm},t) = \begin{bmatrix} u_x(\vec{q}) \\ u_y(\vec{q}) \end{bmatrix} e^{i\,\vec{q}\,.\,\vec{R}_{nm}}\; e^{-i\,\omega\,t}$$

$$\Rightarrow e^{i\,\vec{q}\,.\,N_1\vec{a}_1} = 1$$

$$\Rightarrow \vec{q}\,.\,N_1\vec{a}_1 = m_1\,2\pi \qquad \{\text{where } m_1 \text{ is an integer}$$

$$\Rightarrow 2\pi\,\alpha_1\,N_1 = m_1\,2\pi \qquad \left\{\text{where } -\frac{1}{2} < \alpha_1 \le \frac{1}{2}\right.$$

$$\Rightarrow \alpha_1 = \frac{m_1}{N_1} \qquad \left\{\text{where } -\frac{N_1}{2} < m \le \frac{N_1}{2}\right.$$



Similarly:

$$\alpha_2 = \frac{m_2}{N_2} \qquad \left\{\text{where } -\frac{N_2}{2} < m_2 \le \frac{N_2}{2}\right.$$

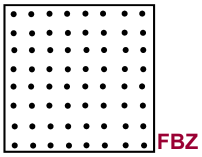
Counting Degrees of Freedom

In the solution the values of the phonon wavevector are dictated by the periodic boundary conditions:

$$\vec{q} = \alpha_1\,\vec{b}_1 + \alpha_2\,\vec{b}_2$$

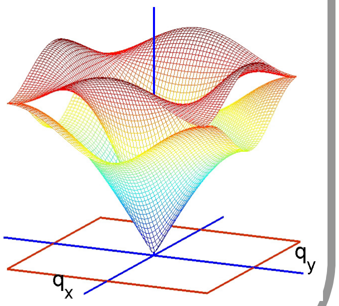
$$\alpha_1 = \frac{m_1}{N_1} \qquad \left\{\text{where } -\frac{N_1}{2} < m \le \frac{N_1}{2}\right.$$

$$\alpha_2 = \frac{m_2}{N_2} \qquad \left\{\text{where } -\frac{N_2}{2} < m_2 \le \frac{N_2}{2}\right.$$



$\Rightarrow$There are N_1N_2 allowed wavevectors in the FBZ
(There are also N_1N_2 primitive cells in the crystals)

$\Rightarrow$There are N_1N_2 phonon modes per phonon band



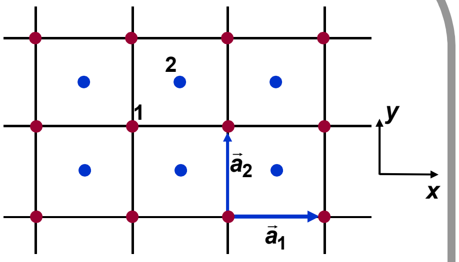
Counting degrees of freedom:

- There are $2N_1N_2$ degrees of freedom corresponding to the motion in 2D of N_1N_2 atoms

- The total number of different phonon modes in the two bands is also $2N_1N_2$

Phonons in a 2D Crystal with a Diatomic Basis

$$\vec{R}_{nm} = n\,\vec{a}_1 + m\vec{a}_2$$



Atomic displacement vectors:

The two atoms in a primitive cell can move in 2D therefore atomic displacements are given by a four-component column vector:

$$\begin{bmatrix} \vec{u}_1(\vec{R}_{nm}+\vec{d}_1,t) \\ \vec{u}_2(\vec{R}_{nm}+\vec{d}_2,t) \end{bmatrix} = \begin{bmatrix} u_{1x}(\vec{R}_{nm}+\vec{d}_1,t) \\ u_{1y}(\vec{R}_{nm}+\vec{d}_1,t) \\ u_{2x}(\vec{R}_{nm}+\vec{d}_2,t) \\ u_{2y}(\vec{R}_{nm}+\vec{d}_2,t) \end{bmatrix}$$

1^{st} nearest-neighbor vectors (red to blue):

$$\vec{h}_1 = \frac{a\hat{x}+a\hat{y}}{2} \qquad \vec{h}_2 = \frac{-a\hat{x}+a\hat{y}}{2}$$

$$\vec{h}_3 = \frac{-a\hat{x}-a\hat{y}}{2} \qquad \vec{h}_4 = \frac{a\hat{x}-a\hat{y}}{2}$$

2^{nd} nearest-neighbor vectors (red to red):

$$\vec{n}_1 = a\hat{x} \qquad \vec{n}_2 = a\hat{y}$$

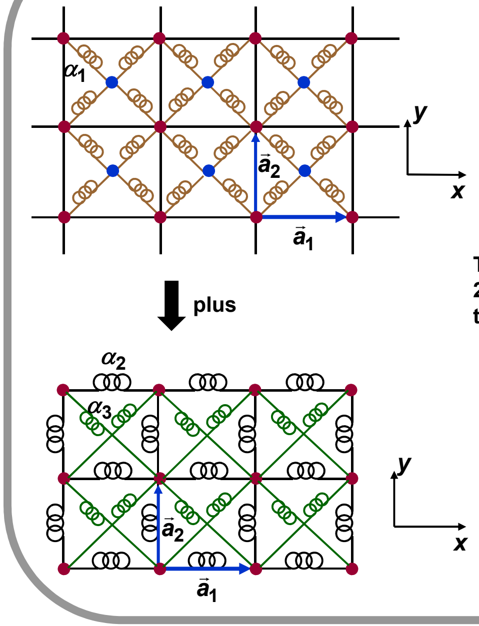
$$\vec{n}_3 = -a\hat{x} \qquad \vec{n}_4 = -a\hat{y}$$

3^{rd} nearest-neighbor vectors (red to red):

$$\vec{p}_1 = a\hat{x}+a\hat{y} \qquad \vec{p}_2 = -a\hat{x}+a\hat{y}$$

$$\vec{p}_3 = -a\hat{x}-a\hat{y} \qquad \vec{p}_4 = a\hat{x}-a\hat{y}$$

Diatomic Basis: Force Constants



The force constants between the 1^{st} 2^{nd} and 3^{rd} nearest-neighbors need to be included (at least)

Diatomic Basis: Dynamical Equations

Dynamical equation for the red(1) atom:

$$\begin{aligned}
M_1 \frac{d^2\vec{u}_1(\vec{R}_{nm}+\vec{d}_1,t)}{dt^2} = &+\alpha_1 \sum_{j=1,2,3,4} \left[\left[\vec{u}_2(\vec{R}_{nm}+\vec{d}_1+\vec{h}_j,t)-\vec{u}_1(\vec{R}_{nm}+\vec{d}_1,t)\right].\,\hat{h}_j\right]\hat{h}_j \longrightarrow \text{summation over 4 1}^{\text{st}}\text{ nn} \\
&+\alpha_2 \sum_{j=1,2,3,4} \left[\left[\vec{u}_1(\vec{R}_{nm}+\vec{d}_1+\vec{n}_j,t)-\vec{u}_1(\vec{R}_{nm}+\vec{d}_1,t)\right].\,\hat{n}_j\right]\hat{n}_j \longrightarrow \text{summation over 4 2}^{\text{nd}}\text{ nn} \\
&+\alpha_3 \sum_{j=1,2,3,4} \left[\left[\vec{u}_1(\vec{R}_{nm}+\vec{d}_1+\vec{p}_j,t)-\vec{u}_1(\vec{R}_{nm}+\vec{d}_1,t)\right].\,\hat{p}_j\right]\hat{p}_j \longrightarrow \text{summation over 4 3}^{\text{rd}}\text{ nn}
\end{aligned}$$

Dynamical equation for the blue(2) atom:

$$\begin{aligned}
M_2 \frac{d^2\vec{u}_2(\vec{R}_{nm}+\vec{d}_2,t)}{dt^2} = &+\alpha_1 \sum_{j=1,2,3,4} \left[\left[\vec{u}_2(\vec{R}_{nm}+\vec{d}_2+\vec{h}_j,t)-\vec{u}_2(\vec{R}_{nm}+\vec{d}_2,t)\right].\,\hat{h}_j\right]\hat{h}_j \longrightarrow \text{summation over 4 1}^{\text{st}}\text{ nn} \\
&+\alpha_2 \sum_{j=1,2,3,4} \left[\left[\vec{u}_2(\vec{R}_{nm}+\vec{d}_2+\vec{n}_j,t)-\vec{u}_2(\vec{R}_{nm}+\vec{d}_2,t)\right].\,\hat{n}_j\right]\hat{n}_j \longrightarrow \text{summation over 4 2}^{\text{nd}}\text{ nn} \\
&+\alpha_3 \sum_{j=1,2,3,4} \left[\left[\vec{u}_2(\vec{R}_{nm}+\vec{d}_2+\vec{p}_j,t)-\vec{u}_2(\vec{R}_{nm}+\vec{d}_2,t)\right].\,\hat{p}_j\right]\hat{p}_j \longrightarrow \text{summation over 4 3}^{\text{rd}}\text{ nn}
\end{aligned}$$

Diatomic Basis: Dynamical Equations

Assume a solution of the form:

$$\begin{bmatrix} \vec{u}_1(\vec{R}_{nm}+\vec{d}_1,t) \\ \vec{u}_2(\vec{R}_{nm}+\vec{d}_2,t) \end{bmatrix} = \begin{bmatrix} u_{1x}(\vec{R}_{nm}+\vec{d}_1,t) \\ u_{1y}(\vec{R}_{nm}+\vec{d}_1,t) \\ u_{2x}(\vec{R}_{nm}+\vec{d}_2,t) \\ u_{2y}(\vec{R}_{nm}+\vec{d}_2,t) \end{bmatrix} = \begin{bmatrix} u_{1x}(\vec{q})\, e^{i\,\vec{q}\,.\,\vec{d}_1} \\ u_{1y}(\vec{q})e^{i\,\vec{q}\,.\,\vec{d}_1} \\ u_{2x}(\vec{q})e^{i\,\vec{q}\,.\,\vec{d}_2} \\ u_{2y}(\vec{q})e^{i\,\vec{q}\,.\,\vec{d}_2} \end{bmatrix} e^{i\,\vec{q}\,.\,\vec{R}_{nm}}\ e^{-i\,\omega\,t}$$

To get a matrix equation of the form:

$$\overline{\overline{D}}(\vec{q}) \begin{bmatrix} u_{1x}(\vec{q}) \\ u_{1y}(\vec{q}) \\ u_{2x}(\vec{q}) \\ u_{2y}(\vec{q}) \end{bmatrix} = \omega^2 \begin{bmatrix} M_1 & 0 & 0 & 0 \\ 0 & M_1 & 0 & 0 \\ 0 & 0 & M_2 & 0 \\ 0 & 0 & 0 & M_2 \end{bmatrix} \begin{bmatrix} u_{1x}(\vec{q}) \\ u_{1y}(\vec{q}) \\ u_{2x}(\vec{q}) \\ u_{2y}(\vec{q}) \end{bmatrix}$$

The Dynamical Matrix

$$\overline{\overline{D}}(\vec{q})\begin{bmatrix} u_{1x}(\vec{q}) \\ u_{1y}(\vec{q}) \\ u_{2x}(\vec{q}) \\ u_{2y}(\vec{q}) \end{bmatrix} = \omega^2 \begin{bmatrix} M_1 & 0 & 0 & 0 \\ 0 & M_1 & 0 & 0 \\ 0 & 0 & M_2 & 0 \\ 0 & 0 & 0 & M_2 \end{bmatrix}\begin{bmatrix} u_{1x}(\vec{q}) \\ u_{1y}(\vec{q}) \\ u_{2x}(\vec{q}) \\ u_{2y}(\vec{q}) \end{bmatrix}$$

The matrix $\overline{\overline{D}}(\vec{q})$ is:

$2\alpha_1 + 4\alpha_2 \sin^2\left(\frac{q_x a}{2}\right) +$ $2\alpha_3\left[1-\cos(q_x a)\cos(q_y a)\right]$	$2\alpha_3 \sin(q_x a)\sin(q_y a)$	$-2\alpha_1 \cos\left(\frac{q_x a}{2}\right)\cos\left(\frac{q_y a}{2}\right)$	$2\alpha_1 \sin\left(\frac{q_x a}{2}\right)\sin\left(\frac{q_y a}{2}\right)$
$2\alpha_3 \sin(q_x a)\sin(q_y a)$	$2\alpha_1 + 4\alpha_2 \sin^2\left(\frac{q_y a}{2}\right) +$ $2\alpha_3\left[1-\cos(q_x a)\cos(q_y a)\right]$	$2\alpha_1 \sin\left(\frac{q_x a}{2}\right)\sin\left(\frac{q_y a}{2}\right)$	$-2\alpha_1 \cos\left(\frac{q_x a}{2}\right)\cos\left(\frac{q_y a}{2}\right)$
$-2\alpha_1 \cos\left(\frac{q_x a}{2}\right)\cos\left(\frac{q_y a}{2}\right)$	$2\alpha_1 \sin\left(\frac{q_x a}{2}\right)\sin\left(\frac{q_y a}{2}\right)$	$2\alpha_1 + 4\alpha_2 \sin^2\left(\frac{q_x a}{2}\right) +$ $2\alpha_3\left[1-\cos(q_x a)\cos(q_y a)\right]$	$2\alpha_3 \sin(q_x a)\sin(q_y a)$
$2\alpha_1 \sin\left(\frac{q_x a}{2}\right)\sin\left(\frac{q_y a}{2}\right)$	$-2\alpha_1 \cos\left(\frac{q_x a}{2}\right)\cos\left(\frac{q_y a}{2}\right)$	$2\alpha_3 \sin(q_x a)\sin(q_y a)$	$2\alpha_1 + 4\alpha_2 \sin^2\left(\frac{q_y a}{2}\right) +$ $2\alpha_3\left[1-\cos(q_x a)\cos(q_y a)\right]$

Diatomic Basis: Solution and Phonon Bands

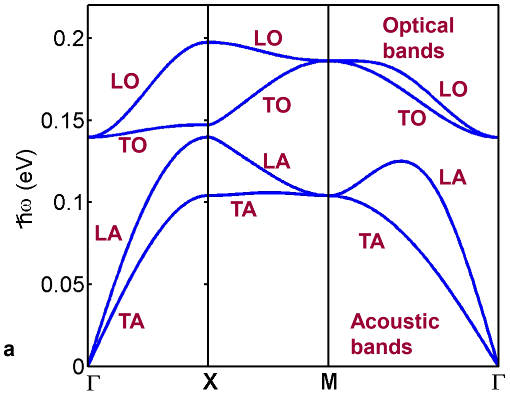
For calculations:

$2M_1 = M_2 = 4\times10^{-26}$ kg

$\alpha_1 = 300$ N/m

$\alpha_2 = 200$ N/m

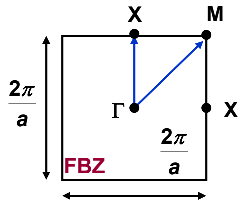
$\alpha_3 = 100$ N/m



One obtains:

- 2 optical phonon bands (that have a non-zero frequency at the zone center)

- 2 acoustic phonon bands (that have zero frequency at the zone center)



Longitudinal (LO) and Transverse (TO) Optical Phonons

Case I: $q_x \approx 0\,,\, q_y = 0$

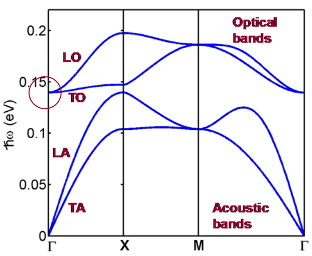
$$\frac{1}{M_r} = \frac{1}{M_1} + \frac{1}{M_2}$$

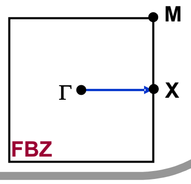
$$\omega_{LO}(q_x \approx 0) = \sqrt{\frac{2\alpha_1}{M_r}} \qquad \begin{bmatrix} u_{1x}(q_x) \\ u_{1y}(q_x) \\ u_{2x}(q_x) \\ u_{2y}(q_x) \end{bmatrix} = A \begin{bmatrix} 1 \\ 0 \\ -M_1/M_2 \\ 0 \end{bmatrix}$$

Longitudinal optical phonons: atomic motion in the direction of wave propagation and basis atoms move out of phase

$$\omega_{TO}(q_x \approx 0) = \sqrt{\frac{2\alpha_1}{M_r}} \qquad \begin{bmatrix} u_{1x}(q_x) \\ u_{1y}(q_x) \\ u_{2x}(q_x) \\ u_{2y}(q_x) \end{bmatrix} = A \begin{bmatrix} 0 \\ 1 \\ 0 \\ -M_1/M_2 \end{bmatrix}$$

Transverse optical phonons: atomic motion in the direction perpendicular to wave propagation and basis atoms move out of phase





Longitudinal (LA) and Transverse (TA) Acoustic Phonons

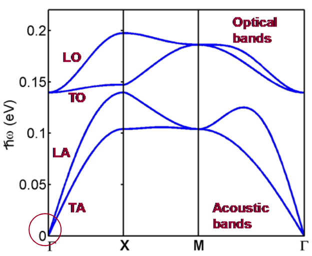
Case I: $q_x \approx 0\,,\, q_y = 0$

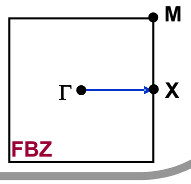
$$\omega_{LA}(q_x \approx 0) = ? \qquad \begin{bmatrix} u_{1x}(q_x) \\ u_{1y}(q_x) \\ u_{2x}(q_x) \\ u_{2y}(q_x) \end{bmatrix} = A \begin{bmatrix} 1 \\ 0 \\ 1 \\ 0 \end{bmatrix}$$

Longitudinal acoustic phonons: atomic motion in the direction of wave propagation and basis atoms move in phase

$$\omega_{TO}(q_x \approx 0) = ? \qquad \begin{bmatrix} u_{1x}(q_x) \\ u_{1y}(q_x) \\ u_{2x}(q_x) \\ u_{2y}(q_x) \end{bmatrix} = A \begin{bmatrix} 0 \\ 1 \\ 0 \\ 1 \end{bmatrix}$$

Transverse acoustic phonons: atomic motion in the direction perpendicular to wave propagation and basis atoms move in phase





Counting Degrees of Freedom and the Number of Phonon Bands

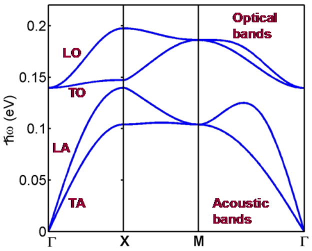
Periodic boundary conditions for a lattice of N_1xN_2 primitive cells imply:

$$\vec{q} = \alpha_1 \vec{b}_1 + \alpha_2 \vec{b}_2$$

$$\alpha_1 = \frac{m_1}{N_1} \quad \left\{ \text{where } -\frac{N_1}{2} < m \leq \frac{N_1}{2} \right.$$

$$\alpha_2 = \frac{m_2}{N_2} \quad \left\{ \text{where } -\frac{N_2}{2} < m_2 \leq \frac{N_2}{2} \right.$$

$\Rightarrow$There are N_1N_2 allowed wavevectors in the FBZ
$\Rightarrow$There are N_1N_2 phonon modes per phonon band



Counting degrees of freedom:

- There are $4N_1N_2$ degrees of freedom corresponding to the motion in 2D of $2N_1N_2$ atoms (2 atoms in each primitive cell)

- The total number of different phonon modes in the four bands is also $4N_1N_2$

Handout 19

Lattice Waves (Phonons) in 3D Crystals
Group IV and Group III-V Semiconductors
LO and TO Phonons in Polar Crystals
and
Macroscopic Models of Acoustic Phonons in Solids

In this lecture you will learn:

- Lattice waves (phonons) in 3D crystals
- Phonon bands in group IV and group III-V Semiconductors

- Macroscopic description of acoustic phonons from elasticity theory
- Stress, strain, and Hooke's law

Counting the Number of Phonon bands in 3D Crystals

Periodic boundary conditions for a lattice of N_1xN_2xN_3 primitive cells imply:

$$\vec{q} = \alpha_1 \vec{b}_1 + \alpha_2 \vec{b}_2 + \alpha_3 \vec{b}_3$$

$$\alpha_1 = m_1/N_1 \quad \{\text{where } -N_1/2 < m_1 \leq N_1/2$$

$$\alpha_2 = m_2/N_2 \quad \{\text{where } -N_2/2 < m_2 \leq N_2/2$$

$$\alpha_3 = m_3/N_3 \quad \{\text{where } -N_3/2 < m_3 \leq N_3/2$$

⇒There are $N_1N_2N_3$ allowed wavevectors in the FBZ
⇒There are $N_1N_2N_3$ phonon modes per phonon band

Counting degrees of freedom and the number of phonon bands: Monoatomic Basis

- There are $3N_1N_2N_3$ degrees of freedom corresponding to the motion in 3D of $N_1N_2N_3$ atoms

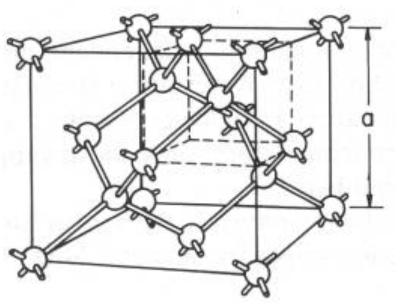
⇒The number of phonon bands must be 3 (two TA bands and one LA band)

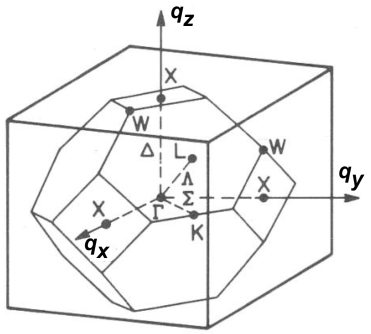
Counting degrees of freedom and the number of phonon bands: Diatomic Basis

- There are $6N_1N_2N_3$ degrees of freedom corresponding to the motion in 3D of $2N_1N_2N_3$ atoms

⇒The number of phonon bands must be 6 (two TA bands and one LA band for acoustic phonons and two TO bands and one LO band for optical phonons)

Phonon Bands in Silicon





Silicon has a FCC lattice with two basis atoms in one primitive cell

FBZ of Silicon

⇒The number of phonon bands must be 6; two TA bands and one LA band for acoustic phonons and two TO bands and one LO band for optical phonons

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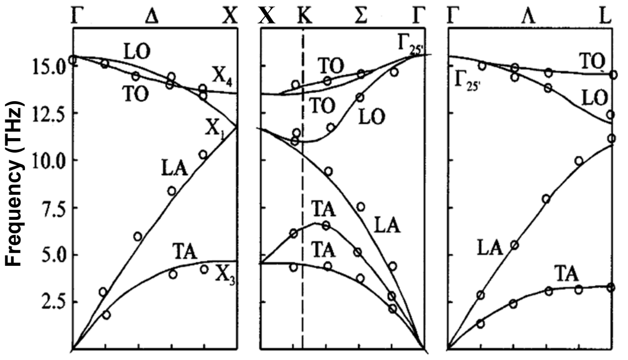
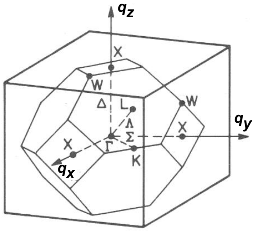
Phonon Bands in Silicon



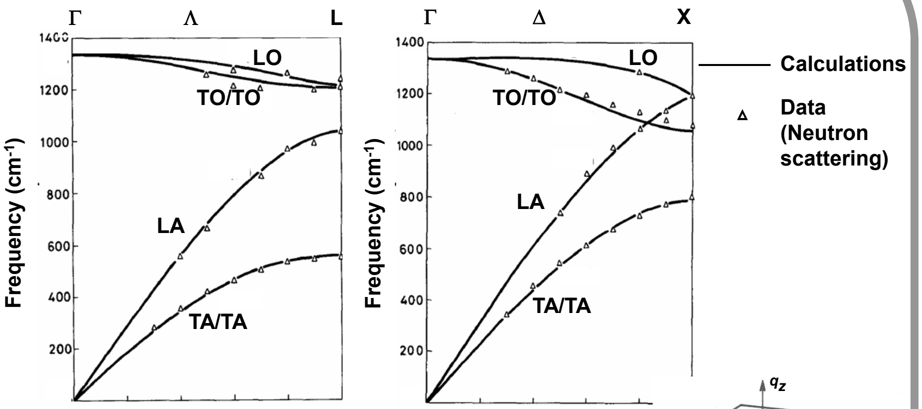
— Calculations

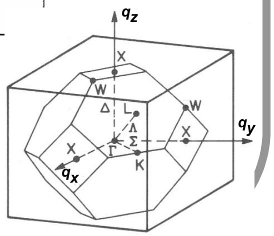
○ Data (Neutron scattering)



$$\hbar\omega_{LO}(q_x \approx 0) = \hbar\omega_{TO}(q_x \approx 0) = 64 \text{ meV}$$

Phonon Bands in Diamond





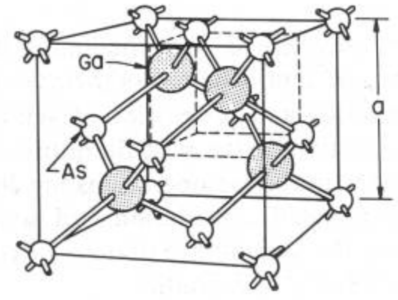
$$\hbar\omega_{LO}(q_x \approx 0) = \hbar\omega_{TO}(q_x \approx 0) = 165 \text{ meV}$$

Large!!

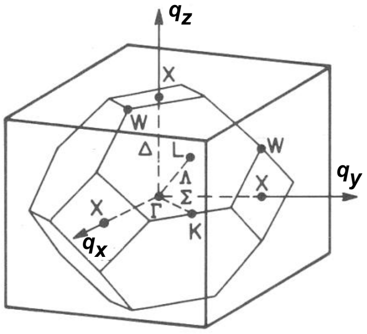
Phonon frequencies are also expressed in units of equivalent photon wavelength inverse:

$$\frac{\omega_{LO}(q_x \approx 0)}{2\pi c} = \frac{\omega_{TO}(q_x \approx 0)}{2\pi c} = 1330 \text{ cm}^{-1}$$

Phonon Bands in GaAs



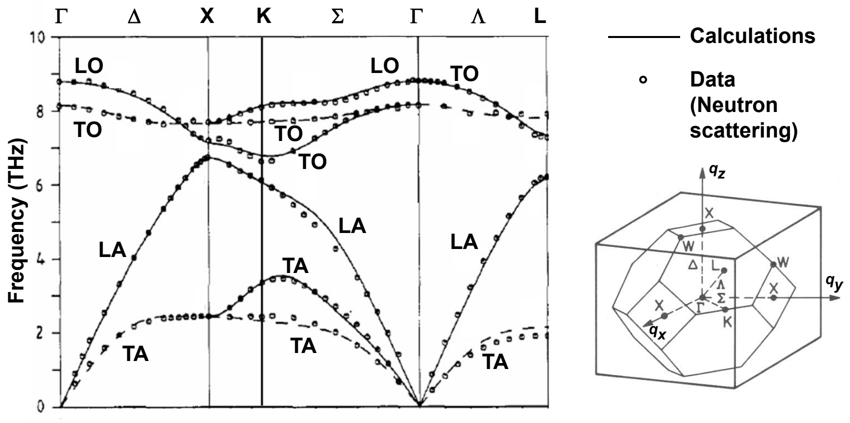
GaAs has a FCC lattice with two basis atoms in one primitive cell



FBZ of GaAs

⇒The number of phonon bands must be 6; two TA bands and one LA band for acoustic phonons and two TO bands and one LO band for optical phonons

Phonon Bands in GaAs

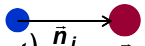


$$\hbar\omega_{LO}(q_x \approx 0) = 36\text{ meV}$$

$$\hbar\omega_{TO}(q_x \approx 0) = 33\text{ meV}$$

Optical Phonons in Polar Crystals

Consider a crystal, like GaAs, made up of two different kind of atoms with a polar covalent bond



$$\vec{u}_1(\vec{R}+\vec{d}_1,t) \quad \vec{n}_j \quad \vec{u}_2(\vec{R}+\vec{d}_1+\vec{n}_j,t)$$

When the atoms move, an oscillating charge dipole is created with a dipole moment given by:

$$\vec{p}_j(\vec{R},t) = f\left[\vec{u}_2(\vec{R}+\vec{d}_1+\vec{n}_j,t) - \vec{u}_1(\vec{R}+\vec{d}_1,t)\right]$$

The material polarization, or the dipole moment density, is then:

$$\vec{P}(\vec{R},t) = \frac{n}{Z}\sum_j \vec{p}_j(\vec{R},t) = \frac{nf}{Z}\sum_j\left[\vec{u}_2(\vec{R}+\vec{d}_1+\vec{n}_j,t) - \vec{u}_1(\vec{R}+\vec{d}_1,t)\right]$$

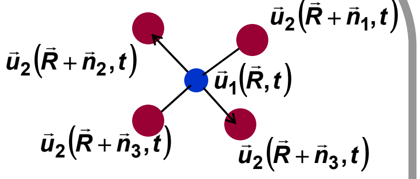
where:

$n = \dfrac{1}{\Omega_3} =$ Number of primitive cells per unit volume

$Z =$ Number of nearest neighbors

A non-zero polarization means an electric field!

Optical Phonons in Polar Crystals: D-Field and E-Field



A non-zero polarization means an electric field!
How do we find it?

The divergence of the D-field is zero inside the crystal:

$$\nabla.\vec{D} = \rho_u = 0$$

But inside the crystal:

$$\vec{D} = \varepsilon(\infty)\vec{E} + \vec{P}$$

$$\Rightarrow \nabla.\vec{E} = -\frac{\nabla.\vec{P}}{\varepsilon(\infty)}$$

Since:

$$\vec{P}(\vec{R},t) = \frac{n}{Z}\sum_j \vec{p}_j(\vec{R},t) = \frac{nf}{Z}\sum_j\left[\vec{u}_2(\vec{R}+\vec{d}_1+\vec{n}_j,t) - \vec{u}_1(\vec{R}+\vec{d}_1,t)\right]$$

Therefore:

$$\nabla.\vec{E}(\vec{R},t) = -\frac{\nabla.\vec{P}(\vec{R},t)}{\varepsilon(\infty)} \xrightarrow{\hspace{2cm}}$$

We must also have:

$$\nabla\times\vec{E}(\vec{R},t) = 0$$

Optical Phonons in Polar Crystals: Dynamical Equations

Dynamical equations (assuming only nearest neighbor interactions):

$$\frac{d^2\vec{u}_1(\vec{R}+\vec{d}_1,t)}{dt^2} = \frac{\alpha}{M_1}\sum_j\left[\left[\vec{u}_2(\vec{R}+\vec{d}_1+\vec{n}_j,t) - \vec{u}_1(\vec{R}+\vec{d}_1,t)\right].\,\hat{n}_j\right]\hat{n}_j - \frac{f}{M_1}\vec{E}(\vec{R},t)$$

$$\frac{d^2\vec{u}_2(\vec{R}+\vec{d}_2,t)}{dt^2} = -\frac{\alpha}{M_2}\sum_j\left[\left[\vec{u}_2(\vec{R}+\vec{d}_2,t) - \vec{u}_1(\vec{R}+\vec{d}_2-\vec{n}_j,t)\right].\,\hat{n}_j\right]\hat{n}_j + \frac{f}{M_2}\vec{E}(\vec{R},t)$$

Suppose:

$$\begin{bmatrix}\vec{u}_1(\vec{R}+\vec{d}_1,t)\\ \vec{u}_2(\vec{R}+\vec{d}_2,t)\end{bmatrix} = \begin{bmatrix}\vec{u}_1(\vec{q})e^{i\vec{q}.\vec{d}_1}\\ \vec{u}_2(\vec{q})e^{i\vec{q}.\vec{d}_2}\end{bmatrix} e^{i\vec{q}.\vec{R}-i\omega t} \qquad \begin{aligned}\vec{E}(\vec{R},t) &= \vec{E}(\vec{q})\,e^{i\vec{q}.\vec{R}-i\omega t}\\ \vec{P}(\vec{R},t) &= \vec{P}(\vec{q})\,e^{i\vec{q}.\vec{R}-i\omega t}\end{aligned}$$

We have:

$$\nabla\times\vec{E}(\vec{R},t) = 0 \quad\Rightarrow\quad \vec{q}\times\vec{E}(\vec{q}) = 0$$

We also have:

$$\nabla.\vec{E}(\vec{R},t) = -\frac{\nabla.\vec{P}(\vec{R},t)}{\varepsilon(\infty)} \quad\Rightarrow\quad \hat{q}.\vec{E}(\vec{q}) = -\frac{\vec{P}(\vec{q}).\hat{q}}{\varepsilon(\infty)}$$

The above two imply that the E-field has non-zero component only in the direction parallel to $\vec{q}$ given by:

$$\vec{E}(\vec{q}) = -\frac{\vec{P}(\vec{q}).\hat{q}}{\varepsilon(\infty)}\hat{q}$$

Optical Phonons in Polar Crystals: TO Phonons

Subtract the two equations and take the limit $q \approx 0$ to get:

$$-\omega^2\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right] = -\frac{\alpha}{M_r}\sum_j \left[\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right].\hat n_j\right]\hat n_j + \frac{f}{M_r}\vec E(\vec q)$$

Transverse Optical Phonons:

Take the cross-product of both sides with $\hat q$ to get:

$$-\omega^2\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right]\times\hat q = -\frac{\alpha}{M_r}\sum_j \left[\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right].\hat n_j\right]\hat n_j\times\hat q + \frac{f}{M_r}\vec E(\vec q)\times\hat q$$

$$-\omega^2\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right]\times\hat q = -\frac{b\alpha}{M_r}\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right]\times\hat q \qquad \left\{\begin{array}{l}\sum_j \hat n_j\,\hat n_j = b \\ \sum_j \left(\vec A.\hat n_j\right)\left(\hat n_j\times\hat q\right) = b\vec A\times\hat q\end{array}\right.$$

$$\Rightarrow \omega = \sqrt{\frac{b\alpha}{M_r}}$$

$$\Rightarrow \omega_{TO}(q\approx 0) = \sqrt{\frac{b\alpha}{M_r}}$$

For example in GaAs:

$$\vec n_1 = \frac{1}{\sqrt 3}\begin{bmatrix}1\\1\\1\end{bmatrix} \quad \vec n_2 = \frac{1}{\sqrt 3}\begin{bmatrix}-1\\-1\\1\end{bmatrix} \quad \vec n_3 = \frac{1}{\sqrt 3}\begin{bmatrix}-1\\1\\-1\end{bmatrix} \quad \vec n_4 = \frac{1}{\sqrt 3}\begin{bmatrix}1\\-1\\-1\end{bmatrix}$$

$$\Rightarrow \quad \sum_j \hat n_j\,\hat n_j = \frac{4}{3}\begin{bmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix} = \frac{4}{3}$$

Optical Phonons in Polar Crystals: LO Phonons

Again start from:

$$-\omega^2\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right] = -\frac{\alpha}{M_r}\sum_j \left[\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right].\hat n_j\right]\hat n_j + \frac{f}{M_r}\vec E(\vec q)$$

Longitudinal Optical Phonons:

Take the dot-product of both sides with $\hat q$ to get:

$$-\omega^2\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right].\hat q = -\frac{\alpha}{M_r}\sum_j \left[\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right].\hat n_j\right]\hat n_j.\hat q + \frac{f}{M_r}\vec E(\vec q).\hat q$$

$$-\omega^2\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right].\hat q = -\frac{b\alpha}{M_r}\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right].\hat q - \frac{nf^2}{M_r\varepsilon(\infty)}\left[\vec u_2(\vec q)-\vec u_1(\vec q)\right].\hat q$$

$$\Rightarrow \omega_{LO}(q\approx 0) = \sqrt{\frac{b\alpha}{M_r}+\frac{nf^2}{M_r\varepsilon(\infty)}} \qquad \left\{\begin{array}{l}\sum_j \hat n_j\,\hat n_j = b \\ \sum_j \left(\vec A.\hat n_j\right)\left(\hat n_j.\hat q\right) = b\vec A.\hat q\end{array}\right.$$

$$\Rightarrow \omega_{LO}^2(q\approx 0) - \omega_{TO}^2(q\approx 0) = \frac{nf^2}{M_r\varepsilon(\infty)}$$

$$\Rightarrow \omega_{LO}^2 - \omega_{TO}^2 = \frac{nf^2}{M_r\varepsilon(\infty)}$$

Optical Phonons in Polar Crystals: Dielectric Constant

Consider the response of polar optical phonons to an externally applied E-field
The total electric field (external plus internal) is:

$$\vec{E}\left(\vec{R},t\right)=\vec{E}(\vec{q})\,e^{i\vec{q}.\vec{R}-i\omega t} \qquad \left\{\ \vec{q}\approx 0\right.$$

We have:

$$-\omega^2[\vec{u}_2(\vec{q})-\vec{u}_1(\vec{q})]=-\frac{\alpha}{M_r}\sum_j[[\,\vec{u}_2(\vec{q})-\vec{u}_1(\vec{q})].\,\hat{n}_j]\,\hat{n}_j+\frac{f}{M_r}\vec{E}(\vec{q})$$

$$\Rightarrow[\vec{u}_2(\vec{q})-\vec{u}_1(\vec{q})]=-\frac{\frac{f}{M_r}\vec{E}(\vec{q})}{\omega^2-\omega_{TO}^2} \qquad \left\{\sum_j\hat{n}_j\,\hat{n}_j=b\right.$$

$$\Rightarrow\vec{P}(\vec{q})=nf[\vec{u}_2(\vec{q})-\vec{u}_1(\vec{q})]=-\frac{\frac{nf^2}{M_r}\vec{E}(\vec{q})}{\omega^2-\omega_{TO}^2}$$

The D-field is:

$$\vec{D}(\vec{q})=\varepsilon(\infty)\vec{E}(\vec{q})+\vec{P}(\vec{q})=\varepsilon(\omega)\vec{E}(\vec{q})$$

$$\Rightarrow D(\vec{q})=\left(\varepsilon(\infty)-\frac{nf^2/M_r}{\omega^2-\omega_{TO}^2}\right)\vec{E}(\vec{q})$$

$$\Rightarrow\varepsilon(\omega)=\varepsilon(\infty)-\frac{nf^2/M_r}{\omega^2-\omega_{TO}^2}$$

Optical Phonons in Polar Crystals: Lydanne-Sachs-Teller Relation

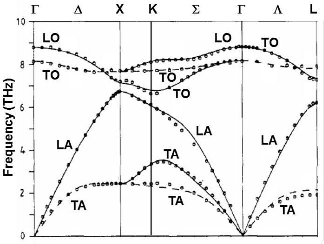
We have:

$$\varepsilon(\omega)=\varepsilon(\infty)-\frac{nf^2/M_r}{\omega^2-\omega_{TO}^2}$$

$$\Rightarrow\varepsilon(0)=\varepsilon(\infty)+\frac{nf^2/M_r}{\omega_{TO}^2} \longrightarrow$$

Low frequency dielectric constant

$$\Rightarrow\frac{nf^2}{M_r}=\omega_{TO}^2[\varepsilon(0)-\varepsilon(\infty)]$$



The LO-TO phonon frequency splitting was given by:

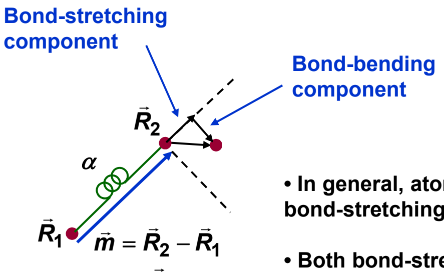
$$\Rightarrow\omega_{LO}^2-\omega_{TO}^2=\frac{nf^2}{M_r\varepsilon(\infty)}=\omega_{TO}^2\frac{[\varepsilon(0)-\varepsilon(\infty)]}{\varepsilon(\infty)}$$

$$\Rightarrow\omega_{LO}^2=\omega_{TO}^2\frac{\varepsilon(0)}{\varepsilon(\infty)}$$

The above relationship is called the Lydanne-Sachs-Teller relation
The above relation does not change if more than nearest-neighbor interactions are also included in the analysis
One can also write:

$$\varepsilon(\omega)=\varepsilon(\infty)-\frac{\omega_{TO}^2[\varepsilon(0)-\varepsilon(\infty)]}{\omega^2-\omega_{TO}^2}$$

Vector Dynamical Equations: Bond-Stretching and Bond-Bending



$$\vec{m} = \vec{R}_2 - \vec{R}_1$$

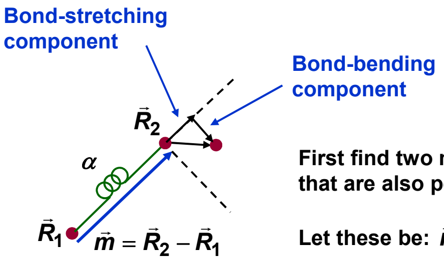
$$\hat{m} = \frac{\vec{m}}{|\vec{m}|}$$

- In general, atomic displacements can cause both bond-stretching and bond-bending
- Both bond-stretching and bond-bending give rise to restoring forces

Bond-stretching contribution:

$$M\frac{d^2\vec{u}(\vec{R}_1,t)}{dt^2} = \alpha\left[\left[\vec{u}(\vec{R}_1+\vec{m},t)-\vec{u}(\vec{R}_1,t)\right].\hat{m}\right]\hat{m}$$

Vector Dynamical Equations: Bond-Stretching and Bond-Bending



$$\vec{m} = \vec{R}_2 - \vec{R}_1$$

$$\hat{m} = \frac{\vec{m}}{|\vec{m}|}$$

First find two mutually orthogonal unit vectors that are also perpendicular to $\hat{m}$

Let these be: $\hat{n}_1$ and $\hat{n}_2$

Bond-stretching and bond-bending contributions:

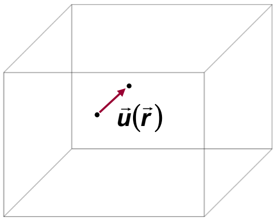
$$\begin{aligned} M\frac{d^2\vec{u}(\vec{R}_1,t)}{dt^2} &= \alpha\left[\left[\vec{u}(\vec{R}_1+\vec{m},t)-\vec{u}(\vec{R}_1,t)\right].\hat{m}\right]\hat{m} \\ &+\beta\left[\left[\vec{u}(\vec{R}_1+\vec{m},t)-\vec{u}(\vec{R}_1,t)\right].\hat{n}_1\right]\hat{n}_1 \\ &+\beta\left[\left[\vec{u}(\vec{R}_1+\vec{m},t)-\vec{u}(\vec{R}_1,t)\right].\hat{n}_2\right]\hat{n}_2 \end{aligned}$$

Macroscopic Description of Acoustic Phonons in Solids

Acoustic phonons can also be described using a macroscopic formalism based on the theory of elasticity

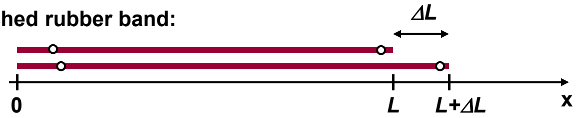
Let the local displacement of a solid from its equilibrium position be given by the vector

$$\vec{u}(\vec{r}) = \begin{bmatrix} u_x(\vec{r}) \\ u_y(\vec{r}) \\ u_z(\vec{r}) \end{bmatrix}$$



Strain Tensor:

Consider a stretched rubber band:



There is a uniform strain given by:

$$e_{xx} = \frac{\partial u_x(x)}{\partial x} = \frac{\Delta L}{L}$$

Stress and Strain

Strain Tensor:

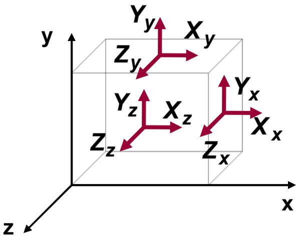
The strain tensor $\overline{\overline{e}}$ is defined by its 6 components:

$$e_{xx} = \frac{\partial u_x(\vec{r})}{\partial x} \quad e_{yy} = \frac{\partial u_y(\vec{r})}{\partial y} \quad e_{zz} = \frac{\partial u_z(\vec{r})}{\partial z}$$

$$e_{xy} = \frac{\partial u_x(\vec{r})}{\partial y} + \frac{\partial u_y(\vec{r})}{\partial x} \quad e_{yz} = \frac{\partial u_y(\vec{r})}{\partial z} + \frac{\partial u_z(\vec{r})}{\partial y} \quad e_{zx} = \frac{\partial u_z(\vec{r})}{\partial x} + \frac{\partial u_x(\vec{r})}{\partial z}$$

Stress Tensor:

Stress is the force acting per unit area on any plane of the solid
It is a tensor with 9 components (as shown)



For example, X_y is the force acting per unit area in the x-direction on a plane that has a normal vector pointing in the y-direction

Hooke's Law

Stress Tensor:

In solids with cubic symmetry, if the stress tensor produces no torque (and no angular acceleration) then one must have:

$$X_y = Y_x \qquad Y_z = Z_y \qquad Z_x = X_z$$

So there are only 6 independent stress tensor components:

$$X_x \quad Y_y \quad Z_z \quad Y_z \quad Z_x \quad X_y$$

Hooke's Law:

A fundamental theorem in the theory of elasticity is Hooke's law that says that strain is proportional to the stress and vice versa. Mathematically, the 6 stress tensor components are related to the 6 strain tensor components by a matrix:

$$\begin{bmatrix} X_x \\ Y_y \\ Z_z \\ Y_z \\ Z_x \\ X_y \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & \cdot & \cdot & c_{16} \\ c_{21} & c_{22} & \cdot & \cdot & \cdot & \cdot \\ c_{31} & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ c_{61} & c_{62} & \cdot & \cdot & \cdot & c_{66} \end{bmatrix} \begin{bmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ e_{yz} \\ e_{zx} \\ e_{xy} \end{bmatrix}$$

Elastic stiffness constants

Hooke's Law for Cubic Materials

In solids with cubic symmetry (SC, FCC, BCC) the matrix of elastic constants have only three independent components:

$$\begin{bmatrix} X_x \\ Y_y \\ Z_z \\ Y_z \\ Z_x \\ X_y \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{bmatrix} \begin{bmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ e_{yz} \\ e_{zx} \\ e_{xy} \end{bmatrix}$$

Elastic energy:

The elastic energy per unit volume of a strained cubic material is:

$$V = \frac{1}{2} c_{11}\left(e_{xx}^2 + e_{yy}^2 + e_{zz}^2\right) + c_{12}\left(e_{xx}e_{yy} + e_{yy}e_{zz} + e_{zz}e_{xx}\right) + c_{44}\left(e_{yz}^2 + e_{zx}^2 + e_{xy}^2\right)$$

Wave Equation for Acoustic Phonons in Cubic Solids

Consider a solid with density ρ

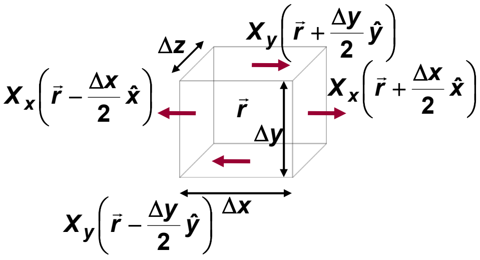
Consider a small volume of this solid that is in motion, as shown

We want to write Newton's second law for its motion in the x-direction

First consider only the force due to the stress tensor component X_x

$$\rho\,\Delta x\,\Delta y\,\Delta z\,\frac{\partial^2 u_x(\vec{r},t)}{\partial t^2}=\Delta y\,\Delta z\left[X_x\left(\vec{r}+\frac{\Delta x}{2}\hat{x}\right)-X_x\left(\vec{r}-\frac{\Delta x}{2}\hat{x}\right)\right]=\Delta x\,\Delta y\,\Delta z\,\frac{\partial X_x(\vec{r})}{\partial x}$$

$$\Rightarrow \rho\,\frac{\partial^2 u_x(\vec{r},t)}{\partial t^2}=\frac{\partial X_x(\vec{r})}{\partial x}$$



Now add the contribution of all forces acting in the x-direction:

$$\rho\,\frac{\partial^2 u_x(\vec{r},t)}{\partial t^2}=\frac{\partial X_x(\vec{r})}{\partial x}+\frac{\partial X_y(\vec{r})}{\partial y}+\frac{\partial X_z(\vec{r})}{\partial z}$$

Wave Equation for Acoustic Phonons in Cubic Solids

We have:

$$\rho\,\frac{\partial^2 u_x(\vec{r},t)}{\partial t^2}=\frac{\partial X_x(\vec{r})}{\partial x}+\frac{\partial X_y(\vec{r})}{\partial y}+\frac{\partial X_z(\vec{r})}{\partial z}$$

Similarly for acceleration in the y- and z-directions we get:

$$\rho\,\frac{\partial^2 u_y(\vec{r},t)}{\partial t^2}=\frac{\partial Y_x(\vec{r})}{\partial x}+\frac{\partial Y_y(\vec{r})}{\partial y}+\frac{\partial Y_z(\vec{r})}{\partial z}\qquad \rho\,\frac{\partial^2 u_z(\vec{r},t)}{\partial t^2}=\frac{\partial Z_x(\vec{r})}{\partial x}+\frac{\partial Z_y(\vec{r})}{\partial y}+\frac{\partial Z_z(\vec{r})}{\partial z}$$

Using the Hooke's law relation, the above equation for motion in the x-direction can be written as:

$$\begin{aligned}\rho\,\frac{\partial^2 u_x(\vec{r},t)}{\partial t^2}&=c_{11}\frac{\partial e_{xx}(\vec{r})}{\partial x}+c_{12}\left[\frac{\partial e_{yy}(\vec{r})}{\partial x}+\frac{\partial e_{zz}(\vec{r})}{\partial x}\right]+c_{44}\left[\frac{\partial e_{xy}(\vec{r})}{\partial y}+\frac{\partial e_{zx}(\vec{r})}{\partial z}\right]\\&=c_{11}\frac{\partial^2 u_x(\vec{r})}{\partial x^2}+c_{44}\left[\frac{\partial^2 u_x(\vec{r})}{\partial y^2}+\frac{\partial^2 u_x(\vec{r})}{\partial z^2}\right]+(c_{12}+c_{44})\left[\frac{\partial^2 u_y(\vec{r})}{\partial x\,\partial y}+\frac{\partial^2 u_z(\vec{r})}{\partial x\,\partial z}\right]\end{aligned}$$

Wave equation for acoustic phonons

Wave Equation for Acoustic Phonons in Cubic Solids

$$\rho \frac{\partial^2 u_x(\vec{r},t)}{\partial t^2} = c_{11}\frac{\partial^2 u_x(\vec{r})}{\partial x^2} + c_{44}\left[\frac{\partial^2 u_x(\vec{r})}{\partial y^2} + \frac{\partial^2 u_x(\vec{r})}{\partial z^2}\right] + (c_{12}+c_{44})\left[\frac{\partial^2 u_y(\vec{r})}{\partial x\,\partial y} + \frac{\partial^2 u_z(\vec{r})}{\partial x\,\partial z}\right]$$

LA phonons:

Consider a LA phonon wave propagating in the x-direction:

$$u_x(\vec{r},t) = A\,e^{i\,q_x x}e^{-i\,\omega\,t}$$

Plug the assumed solution in the wave equation to get:

$$\omega = \sqrt{\frac{c_{11}}{\rho}}\,q_x \quad \longrightarrow \quad \text{velocity of wave} = \sqrt{\frac{c_{11}}{\rho}}$$

TA phonons:

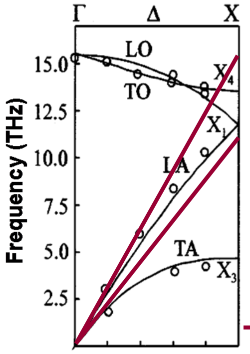
Consider a TA phonon wave propagating in the y-direction:

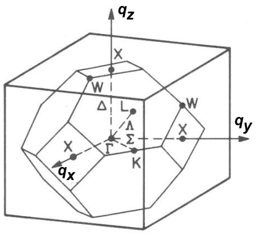
$$u_x(\vec{r},t) = A\,e^{i\,q_y y}e^{-i\,\omega\,t}$$

Plug the assumed solution in the wave equation to get:

$$\omega = \sqrt{\frac{c_{44}}{\rho}}\,q_y \quad \longrightarrow \quad \text{velocity of wave} = \sqrt{\frac{c_{44}}{\rho}}$$

Acoustic Phonons in Silicon





Results from elasticity theory

In Silicon:

$c_{11} = 1.66 \times 10^{11}$ N/m^2

$c_{12} = 0.64 \times 10^{11}$ N/m^2

$c_{44} = 0.80 \times 10^{11}$ N/m^2

$\rho = 2330$ kg/m^3

For LA phonons propagating in the Γ-X direction:

$$\text{velocity of wave} = \sqrt{\frac{c_{11}}{\rho}} = 8.44 \text{ km/sec}$$

For TA phonons propagating in the Γ-X direction:

$$\text{velocity of wave} = \sqrt{\frac{c_{44}}{\rho}} = 5.86 \text{ km/sec}$$

Wave Equation for Acoustic Phonons in Cubic Solids

$$\rho\frac{\partial^2 u_x(\vec{r},t)}{\partial t^2}=c_{11}\frac{\partial^2 u_x(\vec{r})}{\partial x^2}+c_{44}\left[\frac{\partial^2 u_x(\vec{r})}{\partial y^2}+\frac{\partial^2 u_x(\vec{r})}{\partial z^2}\right]+(c_{12}+c_{44})\left[\frac{\partial^2 u_y(\vec{r})}{\partial x\,\partial y}+\frac{\partial^2 u_z(\vec{r})}{\partial x\,\partial z}\right]$$

$$\rho\frac{\partial^2 u_y(\vec{r},t)}{\partial t^2}=c_{11}\frac{\partial^2 u_y(\vec{r})}{\partial y^2}+c_{44}\left[\frac{\partial^2 u_y(\vec{r})}{\partial z^2}+\frac{\partial^2 u_y(\vec{r})}{\partial x^2}\right]+(c_{12}+c_{44})\left[\frac{\partial^2 u_x(\vec{r})}{\partial x\,\partial y}+\frac{\partial^2 u_z(\vec{r})}{\partial z\,\partial y}\right]$$

Consider a phonon wave propagating in the direction: $\frac{\hat{x}+\hat{y}}{\sqrt{2}} \quad \Rightarrow \quad \vec{q}=q\frac{\hat{x}+\hat{y}}{\sqrt{2}}$

$$\begin{bmatrix}u_x(\vec{r},t)\\ u_y(\vec{r},t)\end{bmatrix}=\begin{bmatrix}u_x(\vec{q})\\ u_y(\vec{q})\end{bmatrix}e^{i\,\vec{q}\,.\,\vec{r}}e^{-i\,\omega\,t}$$

Plug the assumed solution in the wave equation to get two coupled equations:

$$\begin{bmatrix}\frac{q^2}{2}(c_{11}+c_{44}) & \frac{q^2}{2}(c_{12}+c_{44})\\ \frac{q^2}{2}(c_{12}+c_{44}) & \frac{q^2}{2}(c_{11}+c_{44})\end{bmatrix}\begin{bmatrix}u_x(\vec{q})\\ u_y(\vec{q})\end{bmatrix}=\rho\,\omega^2\begin{bmatrix}u_x(\vec{q})\\ u_y(\vec{q})\end{bmatrix}$$

Wave Equation for Acoustic Phonons in Cubic Solids

$$\begin{bmatrix}\frac{q^2}{2}(c_{11}+c_{44}) & \frac{q^2}{2}(c_{12}+c_{44})\\ \frac{q^2}{2}(c_{12}+c_{44}) & \frac{q^2}{2}(c_{11}+c_{44})\end{bmatrix}\begin{bmatrix}u_x(\vec{q})\\ u_y(\vec{q})\end{bmatrix}=\rho\,\omega^2\begin{bmatrix}u_x(\vec{q})\\ u_y(\vec{q})\end{bmatrix}$$

The two solutions are as follows:

LA phonon:

$$\omega=\sqrt{\frac{c_{11}+c_{12}+2c_{44}}{2\rho}}\,q \qquad \begin{bmatrix}u_x(\vec{q})\\ u_y(\vec{q})\end{bmatrix}=A\begin{bmatrix}1\\ 1\end{bmatrix}$$

TA phonon:

$$\omega=\sqrt{\frac{c_{11}-c_{12}}{2\rho}}\,q \qquad \begin{bmatrix}u_x(\vec{q})\\ u_y(\vec{q})\end{bmatrix}=A\begin{bmatrix}1\\ -1\end{bmatrix}$$

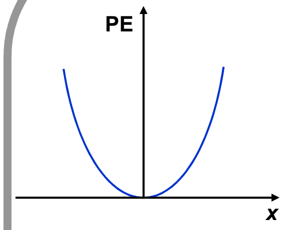
Handout 20

Quantization of Lattice Waves:
From Lattice Waves to Phonons

In this lecture you will learn:

- Simple harmonic oscillator in quantum mechanics
- Classical and quantum descriptions of lattice wave modes
- Phonons – what are they?

Classical Simple Harmonic Oscillator



Consider a particle of mass *m* in a parabolic potential

$$\text{KE} = \frac{p_x^2(t)}{2m} \qquad \text{PE} = V(\hat{x}) = \frac{1}{2} m \omega_o^2 \, x^2(t)$$

The total energy is:

$$E_{Total} = \frac{p_x^2(t)}{2m} + \frac{1}{2} m \omega_o^2 \, x^2(t)$$

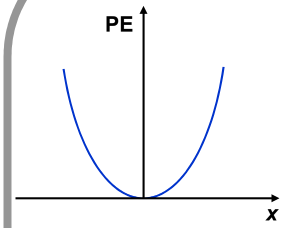
In quantum mechanics, the dynamical variables and observables become operators:

$$x(t) \Leftrightarrow \hat{x}$$

$$p_x(t) \Leftrightarrow \hat{p}_x$$

$$E_{Total} \Leftrightarrow \hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2} m \omega_o^2 \, \hat{x}^2$$

Quantum Simple Harmonic Oscillator Review - I



Consider a particle of mass *m* in a parabolic potential

$$\text{KE} = \frac{\hat{p}_x^2}{2m} \qquad \text{PE} = V(\hat{x}) = \frac{1}{2} m\omega_o^2\, \hat{x}^2$$

Hamiltonian operator is:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2} m\omega_o^2\, \hat{x}^2$$

The quantum mechanical commutation relations are:

$$[\, \hat{x}, \hat{p}_x \,] = i\,\hbar$$

Define two new operators:

$$\hat{a} = \sqrt{\frac{m\omega_o}{2\hbar}}\,\hat{x} + i\sqrt{\frac{1}{2m\,\hbar\omega_o}}\,\hat{p}_x$$

$$\hat{a}^{+} = \sqrt{\frac{m\omega_o}{2\hbar}}\,\hat{x} - i\sqrt{\frac{1}{2m\,\hbar\omega_o}}\,\hat{p}_x$$

Quantum Simple Harmonic Oscillator Review - II

$$\hat{a} = \sqrt{\frac{m\omega_o}{2\hbar}}\,\hat{x} + i\sqrt{\frac{1}{2m\,\hbar\omega_o}}\,\hat{p}_x \qquad \hat{a}^{+} = \sqrt{\frac{m\omega_o}{2\hbar}}\,\hat{x} - i\sqrt{\frac{1}{2m\,\hbar\omega_o}}\,\hat{p}_x$$

The quantum mechanical commutation relations are:

$$[\, \hat{x}, \hat{p}_x \,] = i\,\hbar \quad \Rightarrow \quad \left[\hat{a}, \hat{a}^{+}\right] = 1$$

The Hamiltonian operator can be written as:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2} m\omega_o^2\, \hat{x}^2 = \hbar\,\omega_o\left(\hat{a}^{+}\hat{a} + \frac{1}{2}\right)$$

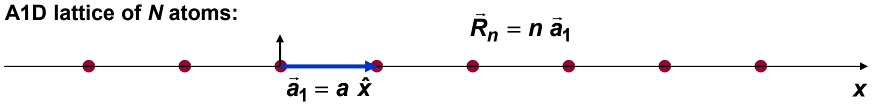
The Hamiltonian operator has eigenstates $|n\rangle$ that satisfy:

$$\hat{a}^{+}\hat{a}\,|n\rangle = n\,|n\rangle \qquad \{\, n = 0,1,2,3............$$

$$\hat{H}\,|n\rangle = \hbar\,\omega_o\left(\hat{a}^{+}\hat{a} + \frac{1}{2}\right)|n\rangle = \hbar\,\omega_o\left(n + \frac{1}{2}\right)|n\rangle$$

Lattice Waves in a 1D Crystal: Classical Description

A1D lattice of *N* atoms:



Potential Energy:

$$V = V_{EQ} + \frac{1}{2}\sum_k\sum_j K(\vec{R}_j\,,\vec{R}_k)\,u(\vec{R}_j,t)\,u(\vec{R}_k,t)$$

$$= \frac{1}{2}\sum_k\sum_j K(\vec{R}_j\,,\vec{R}_k)\,u(\vec{R}_j,t)\,u(\vec{R}_k,t)$$

$$\left\{ K(\vec{R}_j\,,\vec{R}_k) = \left.\frac{\partial^2 V}{\partial u(\vec{R}_j)\,\partial u(\vec{R}_k)}\right|_{EQ} \right.$$

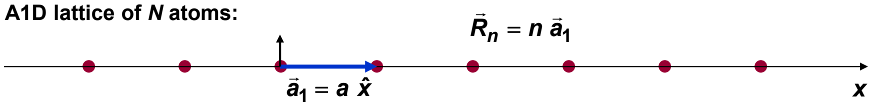
Choose the zero of energy so the constant term V_{EQ} goes away

Kinetic Energy:

$$\text{KE} = \sum_j \frac{M}{2}\left(\frac{du(\vec{R}_j,t)}{dt}\right)^2$$

Lattice Waves in a 1D Crystal: Classical Description

A1D lattice of *N* atoms:



Potential Energy:

$$V = \frac{1}{2}\sum_k\sum_j K(\vec{R}_j\,,\vec{R}_k)\,u(\vec{R}_j,t)\,u(\vec{R}_k,t)$$

$$K(\vec{R}_k\,,\vec{R}_j) = -\alpha\,\delta_{j,k+1} - \alpha\,\delta_{j,k-1} + 2\alpha\,\delta_{j,k} \longrightarrow$$

Nearest-neighbor interaction

$K(\vec{R}_j\,,\vec{R}_k)$ is always a function of only the difference $\vec{R}_j - \vec{R}_k$

$$\Rightarrow\; V = \frac{1}{2}\sum_k\sum_j K(\vec{R}_j - \vec{R}_k)\,u(\vec{R}_j,t)\,u(\vec{R}_k,t)$$

Lattice Waves in a 1D Crystal: Classical Description

The energy for the entire crystal becomes:

Atomic displacements coupled in the PE term

$$E = \text{KE} + \text{PE}$$

$$= \sum_j \frac{M}{2}\left(\frac{d\,u(\vec{R}_j,t)}{dt}\right)^2 + \frac{1}{2}\sum_k\sum_j K(\vec{R}_j-\vec{R}_k)\,u(\vec{R}_j,t)\,u(\vec{R}_k,t)$$

The atomic displacement can be expanded in terms of all the lattice wave modes:

$$u(\vec{R}_n,t) = \sum_{\vec{q}\text{ in FBZ}} \text{Re}\left[u(\vec{q})\,e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega(\vec{q})\,t}\right]$$

$$= \sum_{\vec{q}\text{ in FBZ}} \frac{u(\vec{q})}{2}\,e^{i\,\vec{q}\,.\,\vec{R}_n}\,e^{-i\,\omega(\vec{q})\,t} + \frac{u^*(\vec{q})}{2}\,e^{-i\,\vec{q}\,.\,\vec{R}_n}\,e^{i\,\omega(\vec{q})\,t}$$

$$= \sum_{\vec{q}\text{ in FBZ}} \frac{u(\vec{q},t)}{2}\,e^{i\,\vec{q}\,.\,\vec{R}_n} + \frac{u^*(\vec{q},t)}{2}\,e^{-i\,\vec{q}\,.\,\vec{R}_n}$$

$$= \sum_{\vec{q}\text{ in FBZ}} \frac{u(\vec{q},t)}{2}\,e^{i\,\vec{q}\,.\,\vec{R}_n} + \frac{u^*(-\vec{q},t)}{2}\,e^{i\,\vec{q}\,.\,\vec{R}_n}$$

$$= \sum_{\vec{q}\text{ in FBZ}} U(\vec{q},t)\,e^{i\,\vec{q}\,.\,\vec{R}_n} \qquad \left\{\; U(-\vec{q},t) = U^*(\vec{q},t)\right.$$

Lattice Waves in a 1D Crystal: Classical Description

Take the expansion in terms of the lattice wave modes:

$$u(\vec{R}_n,t) = \sum_{\vec{q}\text{ in FBZ}} U(\vec{q},t)\,e^{i\,\vec{q}\,.\,\vec{R}_n} \qquad \left\{\; U(-\vec{q},t) = U^*(\vec{q},t)\right.$$

And plug it into the expression for the energy:

$$E = \sum_j \frac{M}{2}\left(\frac{d\,u(\vec{R}_j,t)}{dt}\right)^2 + \frac{1}{2}\sum_k\sum_j K(\vec{R}_j-\vec{R}_k)\,u(\vec{R}_j,t)\,u(\vec{R}_k,t)$$

The KE term becomes:

$$\sum_j \frac{M}{2}\left(\frac{d\,u(\vec{R}_j,t)}{dt}\right)^2 = \sum_{\vec{q}\text{ in FBZ}} \frac{NM}{2}\,\frac{dU(\vec{q},t)}{dt}\,\frac{dU^*(\vec{q},t)}{dt}$$

The PE term becomes:

$$\frac{1}{2}\sum_k\sum_j K(\vec{R}_j-\vec{R}_k)\,u(\vec{R}_j,t)\,u(\vec{R}_k,t) = \sum_{\vec{q}\text{ in FBZ}} \frac{NM\,\omega^2(\vec{q})}{2}\,U(\vec{q},t)\,U^*(\vec{q},t)$$

where: $\omega^2(\vec{q}) = \dfrac{1}{M}\sum_j K(\vec{R}_j)\,e^{i\,\vec{q}\,.\,\vec{R}_j} = \dfrac{4\alpha}{M}\sin^2\!\left(\dfrac{\vec{q}\,.\,\vec{a}_1}{2}\right)$

From Classical to Quantum Description

So we have finally:

$$E = \sum_{j} \frac{M}{2}\left(\frac{d\, u(\vec{R}_j,t)}{dt}\right)^2 + \frac{1}{2}\sum_{k}\sum_{j} K(\vec{R}_j - \vec{R}_k)\, u(\vec{R}_j,t)\, u(\vec{R}_k,t)$$

$$= \sum_{\vec{q}\,\text{in FBZ}} \left[\frac{NM}{2} \frac{dU(\vec{q},t)}{dt} \frac{dU^*(\vec{q},t)}{dt} + \frac{NM}{2}\omega^2(\vec{q})\, U(\vec{q},t)\, U^*(\vec{q},t) \right]$$

Lattice wave amplitudes uncoupled in the PE term

Going from classical to quantum description:

The atomic displacements and the atomic momenta become operators:

$$u(\vec{R}_n,t) \;\Rightarrow\; \hat{u}(\vec{R}_n)$$

$$M\frac{du(\vec{R}_n,t)}{dt} \;\Rightarrow\; \hat{p}(\vec{R}_n)$$

Commutation relations are:

$$\left[\hat{u}(\vec{R}_n),\, \hat{p}(\vec{R}_n)\right] = i\,\hbar$$

From Classical to Quantum Description

The amplitudes of lattice waves are now also operators:

Classical: $u(\vec{R}_n,t) = \sum_{\vec{q}\,\text{in FBZ}} U(\vec{q},t)\, e^{i\,\vec{q}\,.\,\vec{R}_n}$ $\quad \left\{\; U(-\vec{q},t) = U^*(\vec{q},t) \right.$

Quantum: $\hat{u}(\vec{R}_n) = \sum_{\vec{q}\,\text{in FBZ}} \hat{U}(\vec{q})\, e^{i\,\vec{q}\,.\,\vec{R}_n}$ $\quad \left\{\; \hat{U}(-\vec{q}) = \hat{U}^+(\vec{q},t) \right.$

Classical: $p(\vec{R}_n,t) = \sum_{\vec{q}\,\text{in FBZ}} P(\vec{q},t)\, e^{i\,\vec{q}\,.\,\vec{R}_n}$ $\quad \left\{\; P(-\vec{q},t) = P^*(\vec{q},t) \right.$

Quantum: $\hat{p}(\vec{R}_n) = \sum_{\vec{q}\,\text{in FBZ}} \hat{P}(\vec{q})\, e^{i\,\vec{q}\,.\,\vec{R}_n}$ $\quad \left\{\; \hat{P}(-\vec{q}) = \hat{P}^+(\vec{q}) \right.$

The commutation relations for the lattice wave amplitudes are:

$$\left[\hat{u}(\vec{R}_j),\, \hat{p}(\vec{R}_j)\right] = i\,\hbar \quad \text{can hold only if} \quad \left[\hat{U}(\vec{q}),\, \hat{P}^+(\vec{q}\,')\right] = \frac{i\hbar}{N}\delta_{\vec{q},\vec{q}\,'}$$

The Hamiltonian operator in terms of the lattice wave amplitude operators is:

$$\hat{H} = \sum_{\vec{q}\,\text{in FBZ}} \left[\frac{N}{2M}\hat{P}(\vec{q})\, P^+(\vec{q}) + \frac{NM}{2}\omega^2(\vec{q})\, \hat{U}(\vec{q},t)\, \hat{U}^+(\vec{q},t) \right]$$

From Classical to Quantum Description

Define two new operators:

$$\hat{a}(\vec{q}) = \sqrt{\frac{NM\omega(\vec{q})}{2\hbar}}\,\hat{U}(\vec{q}) + i\sqrt{\frac{N}{2M\,\hbar\omega(\vec{q})}}\hat{P}(\vec{q})$$

$$\hat{a}^{+}(\vec{q}) = \sqrt{\frac{NM\omega(\vec{q})}{2\hbar}}\,\hat{U}^{+}(\vec{q}) - i\sqrt{\frac{N}{2M\,\hbar\omega(\vec{q})}}\hat{P}^{+}(\vec{q})$$

The commutation relations are:

$$\left[\hat{U}(\vec{q})\,,\,\hat{P}^{+}(\vec{q}\,')\right] = \frac{i\hbar}{N}\delta_{\vec{q}\,,\,\vec{q}\,'} \qquad \Rightarrow \qquad \left[\,\hat{a}(\vec{q})\,,\hat{a}^{+}(\vec{q}\,')\,\right] = \delta_{\vec{q}\,,\,\vec{q}\,'}$$

Note the inverse expressions:

$$\hat{U}(\vec{q}) = \sqrt{\frac{\hbar}{2NM\omega(\vec{q})}}\left[\,\hat{a}(\vec{q}) + \hat{a}^{+}(-\vec{q})\,\right]$$

$$\hat{P}(\vec{q}) = -i\sqrt{\frac{M\,\hbar\omega(\vec{q})}{2N}}\left[\,\hat{a}(\vec{q}) - \hat{a}^{+}(-\vec{q})\,\right]$$

From Classical to Quantum Description

Use the expressions:

$$\hat{U}(\vec{q}) = \sqrt{\frac{\hbar}{2NM\omega(\vec{q})}}\left[\,\hat{a}(\vec{q}) + \hat{a}^{+}(-\vec{q})\,\right]$$

$$\hat{P}(\vec{q}) = -i\sqrt{\frac{M\,\hbar\omega(\vec{q})}{2N}}\left[\,\hat{a}(\vec{q}) - \hat{a}^{+}(-\vec{q})\,\right]$$

in the Hamiltonian operator:

$$\hat{H} = \sum_{\vec{q}\text{ in FBZ}}\left[\frac{N}{2M}\hat{P}(\vec{q})\,P^{+}(\vec{q}) + \frac{NM}{2}\omega^{2}(\vec{q})\hat{U}(\vec{q},t)\,\hat{U}^{+}(\vec{q},t)\right]$$

to get:

$$\hat{H} = \sum_{\vec{q}\text{ in FBZ}}\hbar\,\omega(\vec{q})\left(\hat{a}^{+}(\vec{q})\,\hat{a}(\vec{q}) + \frac{1}{2}\right)$$

From Classical to Quantum Description

The final answer:

$$\hat{H} = \sum_{\vec{q}\ \text{in FBZ}} \hbar\, \omega(\vec{q}) \left(\hat{a}^{+}(\vec{q})\, \hat{a}(\vec{q}) + \frac{1}{2} \right)$$

and the commutation relations

$$\left[\hat{a}(\vec{q}) , \hat{a}^{+}(\vec{q}) \right] = 1$$

tell us that:

1) The Hamiltonians of different lattice wave modes are uncoupled
2) The Hamiltonian of each lattice mode resembles that of a simple harmonic oscillator

Finally, the atomic displacements can be expanded in terms of the phonon creation and destruction operators

$$\begin{aligned} \hat{u}\left(\vec{R}_j\right) &= \sum_{\vec{q}\ \text{in FBZ}} \hat{U}(\vec{q})\, e^{i\,\vec{q}\,.\,\vec{R}_j} \\ &= \sum_{\vec{q}\ \text{in FBZ}} \sqrt{\frac{\hbar}{2NM\omega(\vec{q})}} \left[\hat{a}(\vec{q}) + \hat{a}^{+}(-\vec{q}) \right] e^{i\,\vec{q}\,.\,\vec{R}_j} \end{aligned}$$

What are Phonons?

Consider the Hamiltonian of just a single lattice wave mode:

$$\hat{H} = \hbar\, \omega(\vec{q}) \left(\hat{a}^{+}(\vec{q})\, \hat{a}(\vec{q}) + \frac{1}{2} \right)$$

In analogy to the simple harmonic oscillator, its eigenstates, and the corresponding eigenenergies, must be of the form:

$$\left| n_{\vec{q}} \right\rangle \qquad \left\{ \text{where} \quad n_{\vec{q}} = 0,1,2,3............ \right.$$

$$\hat{H} \left| n_{\vec{q}} \right\rangle = \hbar\, \omega(\vec{q}) \left(\hat{a}^{+}(\vec{q})\, \hat{a}(\vec{q}) + \frac{1}{2} \right) \left| n_{\vec{q}} \right\rangle = \hbar\, \omega(\vec{q}) \left(n_{\vec{q}} + \frac{1}{2} \right) \left| n_{\vec{q}} \right\rangle$$

This eigenstate corresponds to $n_{\vec{q}}$ phonons in the lattice wave mode

- A phonon corresponds to the minimum amount by which the energy of a lattice wave mode can be increased or decreased – it is the quantum of lattice wave energy

- A lattice wave mode with $n_{\vec{q}}$ phonons means the total energy of the lattice wave above the ground state energy of $\hbar\, \omega(\vec{q})/2$ is $n_{\vec{q}}\ \hbar\, \omega(\vec{q})$

- The ground state energy is not zero but equals $\hbar\, \omega(\vec{q})/2$ and corresponds to quantum fluctuations of atoms around their equilibrium positions (but no phonons)

What are Phonons?

In general the quantum state of all the lattice wave modes can be written as follows:

$$|\psi\rangle = |n_{\vec{q}_1}\rangle |n_{\vec{q}_2}\rangle |n_{\vec{q}_3}\rangle |n_{\vec{q}_4}\rangle \ldots\ldots\ldots\ldots\ldots\ldots |n_{\vec{q}_N}\rangle = \prod_{\vec{q}\ \mathrm{in\ FZB}} |n_{\vec{q}}\rangle$$

where the wavevectors run over all the *N* lattice wave modes in the FBZ, and the total energy for this quantum state is:

$$\hat{H}|\psi\rangle = \sum_{\vec{q}\ \mathrm{in\ FBZ}} \hbar\,\omega(\vec{q})\left(\hat{a}^{+}(\vec{q})\,\hat{a}(\vec{q}) + \frac{1}{2}\right)|\psi\rangle$$

$$= \sum_{\vec{q}\ \mathrm{in\ FBZ}} \hbar\,\omega(\vec{q})\left(n_{\vec{q}} + \frac{1}{2}\right)|\psi\rangle$$

"Phonons are to lattice waves as photons are to electromagnetic waves"

Hamiltonian for Multiple Phonon Bands

If the crystal has multiple phonon bands (TA, LA, TO, etc) then it can be shown that the Hamiltonian can be written as follows:

$$\hat{H} = \sum_{\eta} \sum_{\vec{q}\ \mathrm{in\ FBZ}} \hbar\,\omega_{\eta}(\vec{q})\left(\hat{a}_{\eta}^{+}(\vec{q})\,\hat{a}_{\eta}(\vec{q}) + \frac{1}{2}\right)$$

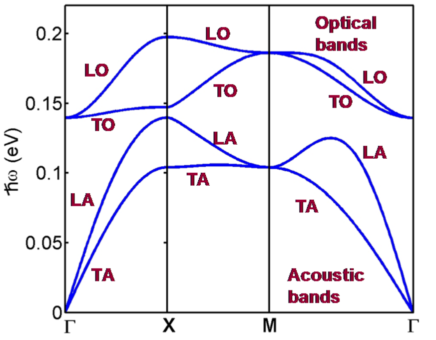
where the summation over "η" represents the summation over different phonon bands.

$\eta = 1 \Rightarrow$ **TA**

$\eta = 2 \Rightarrow$ **LA**

$\eta = 3 \Rightarrow$ **TO**

$\eta = 4 \Rightarrow$ **LO**



Phonons bands of a 2D diatomic crystal

Handout 21

Phonon Thermal Statistics and Heat Capacities

In this lecture you will learn:

- Phonon occupation statistics
- Bose-Einstein distribution
- Phonon density of states in 1D, 2D, and 3D
- Phonon thermal energy and heat capacity of solids

Peter Debye
Born: 1884 (Netherlands)
Died: 1966 (Ithaca, NY)

A Single Lattice Wave Mode

Consider the Hamiltonian of just a single lattice wave mode:

$$\hat{H} = \hbar\,\omega(\vec{q})\left(\hat{a}^{+}(\vec{q})\,\hat{a}(\vec{q}) + \frac{1}{2}\right)$$

Its eigenstates, and the corresponding eigenenergies, are:

$$|n\rangle \qquad \{\text{ where } \quad n = 0,1,2,3............$$

$$\begin{aligned}\hat{H}|n\rangle &= \hbar\,\omega(\vec{q})\left(\hat{a}^{+}(\vec{q})\,\hat{a}(\vec{q}) + \frac{1}{2}\right)|n\rangle \\ &= \hbar\,\omega(\vec{q})\left(n + \frac{1}{2}\right)|n\rangle \\ &= E(n)\,|n\rangle\end{aligned}$$

The state $|n\rangle$ corresponds to "n" phonons in the lattice wave mode

A Single Lattice Wave Mode in Thermal Equilibrium

$$\hat{H}|n\rangle = \hbar\,\omega(\vec{q})\left(n+\frac{1}{2}\right)|n\rangle = E(n)\,|n\rangle$$

Thermal Equilibrium

In thermal equilibrium, let *P*(*n*) be the probability that there are "*n*" phonons in this lattice wave mode

P(*n*) must be related to the energy corresponding to the "*n*" phonons:

$$P(n) \propto e^{-\frac{E(n)}{KT}} = e^{-\frac{\hbar\,\omega(\vec{q})(n+1/2)}{KT}} \longrightarrow (1)$$

P(*n*) must be normalized properly:

$$\sum_{n=0}^{\infty} P(n) = 1 \longrightarrow (2)$$

(1) and (2) give:

$$P(n) = e^{-\frac{\hbar\,\omega(\vec{q})n}{KT}}\left[1-e^{-\frac{\hbar\,\omega(\vec{q})}{KT}}\right]$$

Bose-Einstein Distribution

The probability distribution given by,

$$P(n) = e^{-\frac{\hbar\,\omega(\vec{q})n}{KT}}\left[1-e^{-\frac{\hbar\,\omega(\vec{q})}{KT}}\right]$$

is called the Bose-Einstein distribution

Average Phonon Number:

One can calculate the average phonon number in equilibrium:

$$\langle n\rangle = \sum_{n=0}^{\infty} n\,P(n) = \frac{1}{e^{\hbar\,\omega(\vec{q})/KT}-1}$$

Average phonon number in any lattice wave mode depends on the phonon energy

Limiting Cases:

$$KT \gg \hbar\omega(\vec{q}) \;\Rightarrow\; \langle n\rangle = \frac{1}{e^{\hbar\,\omega(\vec{q})/KT}-1} \approx \frac{KT}{\hbar\omega(\vec{q})} \;\Rightarrow\; \langle E\rangle = \hbar\omega(\vec{q})\langle n\rangle \approx KT$$

Classical equipartition theorem

$$KT \ll \hbar\omega(\vec{q}) \;\Rightarrow\; \langle n\rangle = \frac{1}{e^{\hbar\,\omega(\vec{q})/KT}-1} \approx e^{-\hbar\,\omega(\vec{q})/KT}$$

Classical Equipartition Theorem

Every independent quadratic term in position or momentum in the expression for the energy of a system has an average value equal to *KT*/2 at temperature *T*

- Only holds when classical statistics apply - which is generally the case at high enough temperatures

Example: A Free Particle in 1D

$$E = \frac{p_x^2}{2m} \quad \Rightarrow \quad \langle E \rangle = \frac{1}{2} KT$$

Example: A Free Particle in 3D

$$E = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \quad \Rightarrow \quad \langle E \rangle = \frac{3}{2} KT$$

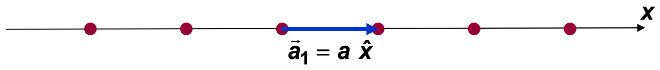
Example: A Classical Simple Harmonic Oscillator in 1D

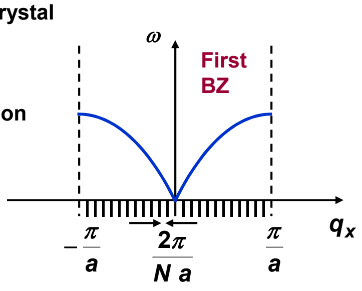
$$E = \frac{p_x^2}{2m} + \frac{1}{2} k x^2 \quad \Rightarrow \quad \langle E \rangle = KT$$

Example: A Single Lattice Wave Mode of a 1D Crystal

$$E = \frac{N}{2M} P(\vec{q},t)\, P^*(\vec{q},t) + \frac{NM}{2} \omega^2(\vec{q})\, U(\vec{q},t)\, U^*(\vec{q},t) \quad \Rightarrow \quad \langle E \rangle = KT$$

Acoustic Phonons in 1D: Density of States





Consider acoustic phonons in a *N*-primitive-cell 1D crystal of length *L*:

$$L = N\,a$$

First we need to figure out how to convert a summation over all lattice wave modes of the form:

$$\sum_{q_x \text{ in FBZ}}$$

into an integral for the form:

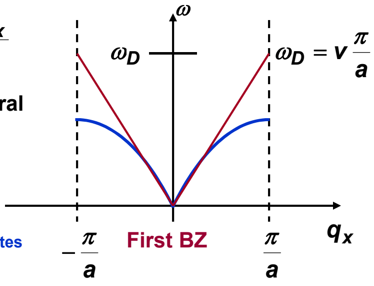
$$\int_{-\pi/a}^{\pi/a} dq_x$$

We now that there are *N* different allowed wavevector values in FBZ (in interval 2π/*a*)
So in interval dq_x there must be (*Na*/2π) dq_x different wavevector values:

$$\Rightarrow \quad \sum_{q_x \text{ in FBZ}} \quad \rightarrow \quad Na \int_{-\pi/a}^{\pi/a} \frac{dq_x}{2\pi} \quad \rightarrow \quad L \int_{-\pi/a}^{\pi/a} \frac{dq_x}{2\pi}$$

Acoustic Phonons in 1D: Density of States

$$\Rightarrow \sum_{q_x \text{ in FBZ}} \rightarrow Na\int_{-\pi/a}^{\pi/a}\frac{dq_x}{2\pi} \rightarrow L\int_{-\pi/a}^{\pi/a}\frac{dq_x}{2\pi}$$



Now we need to figure out how to convert an integral of the form:

$$L\int_{-\pi/a}^{\pi/a}\frac{dq_x}{2\pi}$$

into an integral over frequency of the form:

$$L\int_0^{?}d\omega\ g_{1D}(\omega)$$

Density of states

We need to know the dispersion of the phonons. We approximate it by a linear function:

$$\omega = v\, q_x$$

Therefore:

$$L\int_{-\pi/a}^{\pi/a}\frac{dq_x}{2\pi} \rightarrow 2\,L\int_0^{\pi/a}\frac{dq_x}{2\pi} \rightarrow \frac{L}{\pi}\int_0^{\omega_D}\left|\frac{dq_x}{d\omega}\right|d\omega \rightarrow L\int_0^{\omega_D}d\omega\,\frac{1}{\pi\, v}$$

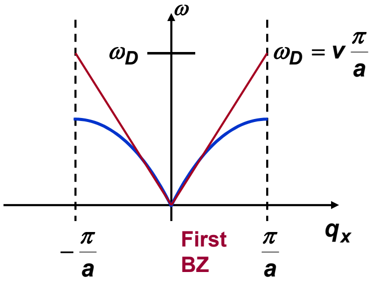
The density of states function $g_{1D}(\omega)$ is the number of phonon modes per unit frequency interval per unit length:

$$g_{1D}(\omega) = \frac{1}{\pi\, v}$$

Acoustic Phonons in 1D: Debye Frequency

We know that:

$$\sum_{q_x \text{ in FBZ}} = N$$



Since:

$$\sum_{q_x \text{ in FBZ}} = L\int_0^{\omega_D}d\omega\ g_{1D}(\omega)$$

We must have:

$$L\int_0^{\omega_D}d\omega\ g_{1D}(\omega) = N \longrightarrow (1)$$

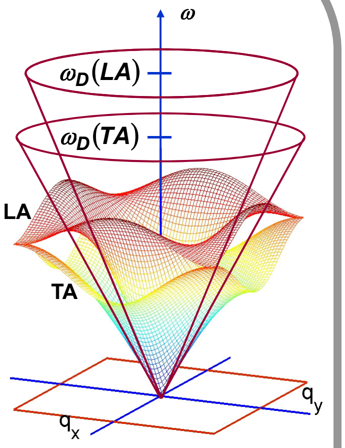
Since:

$$\omega_D = v\frac{\pi}{a} \qquad g_{1D}(\omega) = \frac{1}{\pi\, v}$$

It can be verified that (1) above holds

The frequency ω_D is called the Debye frequency (after Peter Debye – Cornell University). It is chosen to ensure that the total number of phonon modes are conserved when going from q-space integrals to frequency domain integrals. In 1D this is automatic.

Acoustic Phonons in 2D: Density of States



Consider acoustic phonons in a *N*-primitive-cell 2D crystal of area *A*

We need to go from a q-space integral to a frequency integral:

$$\sum_{\vec{q}\text{ in FBZ}} \rightarrow A\int_0^{\omega_D} d\omega\, g_{2D}(\omega)$$

We need to know the dispersion for the 2 acoustic phonon bands. We assume that for both phonon bands the dispersion is linear:

$$\omega = v_\eta\, q \qquad \{\, \eta = 1,2 \quad \text{for} \quad \text{LA, TA}$$

For each phonon band we get:

$$\sum_{\vec{q}\text{ in FBZ}} \rightarrow A\int_{FBZ}\frac{d^2\vec{q}}{(2\pi)^2} \rightarrow A\int_0^{?}\frac{2\pi\, q\, dq}{(2\pi)^2}$$

$$\rightarrow \frac{A}{2\pi}\int_0^{\omega_D} q\left|\frac{dq}{d\omega}\right| d\omega \rightarrow A\int_0^{\omega_D} d\omega\,\frac{\omega}{2\pi\, v_\eta^2} \longrightarrow g_{2D}(\omega) = \frac{\omega}{2\pi\, v_\eta^2}$$

The question is what is ω_D ?

Acoustic Phonons in 2D: Debye Frequency

To find ω_D we count and conserve the total number of phonon modes in each band:

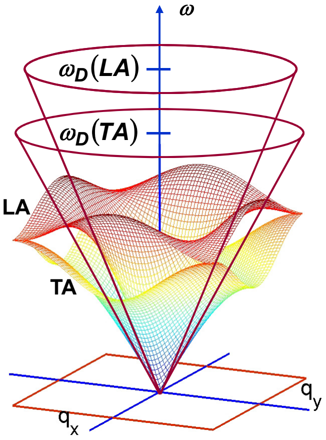
$$\sum_{\vec{q}\text{ in FBZ}} = N$$

$$\Rightarrow A\int_0^{\omega_D} d\omega\,\frac{\omega}{2\pi\, v_\eta^2} = N$$

$$\Rightarrow A\frac{\omega_D^2}{4\pi\, v_\eta^2} = N$$

$$\Rightarrow \omega_D = \sqrt{4\pi\, v_\eta^2\frac{N}{A}}$$

Each phonon band has a different Debye frequency



Acoustic Phonons in 3D: Density of States

Consider acoustic phonons in a *N*-primitive-cell 3D crystal of volume *V*

We need to go from a q-space integral to a frequency integral:

$$\sum_{\vec{q}\ \text{in FBZ}} \rightarrow V \int_0^{\omega_D} d\omega \, g_{3D}(\omega)$$

We need to know the dispersion for the 3 acoustic phonon bands. We assume that for all 3 phonon bands the dispersion is linear:

$$\omega = v_\eta \, q \qquad \{ \eta = 1,2,3 \quad \text{for} \quad \text{LA, TA, TA}$$

For each phonon band we get:

$$\sum_{\vec{q}\ \text{in FBZ}} \rightarrow V \int_{FBZ} \frac{d^3\vec{q}}{(2\pi)^3} \rightarrow V \int_0^{?} \frac{4\pi \, q^2 \, dq}{(2\pi)^3}$$

$$\rightarrow \frac{V}{2\pi^2} \int_0^{\omega_D} q^2 \left| \frac{dq}{d\omega} \right| d\omega \rightarrow V \int_0^{\omega_D} d\omega \, \frac{\omega^2}{2\pi^2 \, v_\eta^3} \longrightarrow g_{3D}(\omega) = \frac{\omega^2}{2\pi^2 \, v_\eta^3}$$

The question is what is ω_D ?

Acoustic Phonons in 3D: Debye Frequency

To find ω_D we count and conserve the total number of phonon modes in each band:

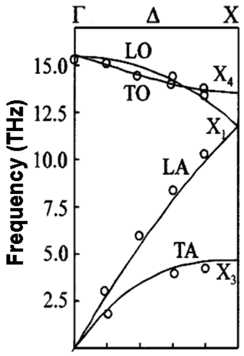
$$\sum_{\vec{q}\ \text{in FBZ}} = N$$

$$\Rightarrow V \int_0^{\omega_D} d\omega \, \frac{\omega^2}{2\pi^3 \, v_\eta^3} = N$$

$$\Rightarrow V \frac{\omega_D^3}{6\pi^2 \, v_\eta^2} = N$$

$$\Rightarrow \omega_D = \left(6\pi^2 \, v_\eta^3 \frac{N}{V} \right)^{1/3}$$

Each phonon band has a different Debye frequency



Silicon Phonon Bands

Silicon:

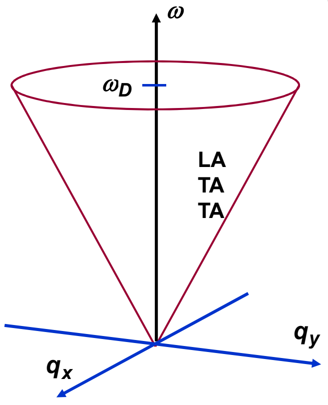
In Silicon the TA phonon velocity is 5.86 km/s. The corresponding Debye frequency is 13.4 THz. The LA phonon velocity is 8.44 km/s. The corresponding Debye frequency is 19.3 THz.

Acoustic Phonons in 3D: Thermal Energy

Consider acoustic phonons in a *N*-primitive-cell 3D crystal of volume *V*

Also assume that all three acoustic phonon modes have the same velocity (for simplicity)

$$\omega = v\,q \qquad \{\text{for}\quad \text{LA, TA, TA}$$



Then for each phonon band we have:

$$g_{3D}(\omega) = \frac{\omega^2}{2\pi^2 v^3}$$

The energy *u* of the lattice per unit volume at temperature *T* can be written as:

3 degenerate phonon bands

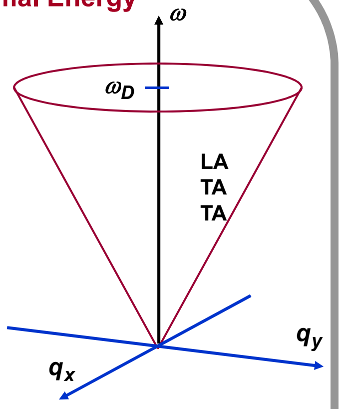
$$u = 3\times\frac{1}{V}\sum_{\vec{q}\ \text{in FBZ}} \hbar\omega(\vec{q})\left\langle n_{\vec{q}}\right\rangle$$

$$= 3\times\int_0^{\omega_D} d\omega\, g_{3D}(\omega)\frac{\hbar\omega}{e^{\hbar\omega/KT}-1}$$

$$= \frac{3\hbar}{2\pi^2 v^3}\int_0^{\omega_D} d\omega\,\frac{\omega^3}{e^{\hbar\omega/KT}-1}$$

$$\left\{\omega_D = \left(6\pi^2 v^3\frac{N}{V}\right)^{1/3}\right.$$

Acoustic Phonons in 3D: Thermal Energy



$$u = \frac{3\hbar}{2\pi^2 v^3}\int_0^{\omega_D} d\omega\,\frac{\omega^3}{e^{\hbar\omega/KT}-1}$$

Define dimensionless variable "*x*" as:

$$x = \frac{\hbar\omega}{KT} \qquad \Rightarrow \qquad x_D = \frac{\hbar\omega_D}{KT}$$

To get:

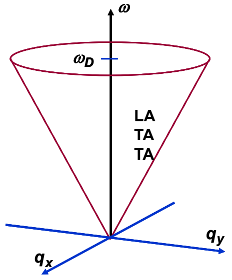
$$u = \frac{3}{2\pi^2(\hbar v)^3}(KT)^4\int_0^{x_D} dx\,\frac{x^3}{e^x-1}$$

$$\boxed{\text{Case I: } KT \ll \hbar\omega_D \quad \Rightarrow \quad x_D \gg 1}$$

$$u = \frac{3}{2\pi^2(\hbar v)^3}(KT)^4\int_0^{\infty} dx\,\frac{x^3}{e^x-1} = \frac{3}{2\pi^2(\hbar v)^3}(KT)^4\left(\frac{\pi^4}{15}\right) = \frac{\pi^2 (KT)^4}{10\,(\hbar v)^3}$$

Specific Heat or Heat Capacity: $C = \dfrac{du}{dT} = \dfrac{2\pi^2 K^4 (T)^3}{5\,(\hbar v)^3}$ ⟶ Debye's famous T^3 law

Acoustic Phonons in 3D: Debye Temperature



The low temperature limit:

$$KT << \hbar\omega_D$$

can also be written as:

$$T << \theta_D$$

Where θ_D is the Debye temperature:

$$\theta_D = \frac{\hbar\omega_D}{K}$$

The Debye frequency thus defines a natural temperature scale for the phonon energetics

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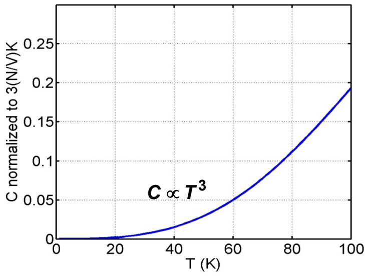
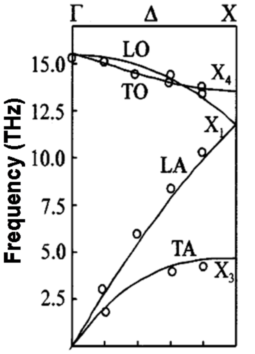
Silicon Heat Capacity

Silicon Heat Capacity





Silicon Phonon Bands

In silicon where the Debye frequency for TA phonons is 13.4 THz, the corresponding Debye temperature is 643 K. The Debye frequency for LA phonons is 19.3 THz and the corresponding Debye temperature is 926 K

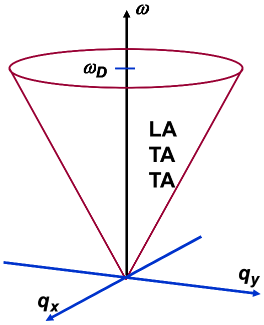
The T^3 law for heat capacity holds well in Silicon for temperatures less than 50 K (much less than the Debye temperature of any phonon band)

$$\omega_D(LA) = 19.3 \text{ THz}$$
$$\theta_D(LA) = 926 \text{ K}$$

$$\omega_D(TA) = 13.4 \text{ THz}$$
$$\theta_D(TA) = 643 \text{ K}$$

Acoustic Phonons in 3D: Classical Equipartition Theorem

Case II: $KT >> \hbar\omega_D \quad \Rightarrow \quad T >> \theta_D$



$$u = \frac{3}{2\pi^2(\hbar v)^3}(KT)^4 \int_0^{x_D} dx \, \frac{x^3}{e^x - 1}$$

$$\Rightarrow \quad e^x - 1 \approx x$$

$$u = \frac{3}{2\pi^2(\hbar v)^3}(KT)^4 \int_0^{x_D} dx \, x^2 = \frac{3}{2\pi^2(\hbar v)^3}(KT)^4 \frac{x_D^3}{3}$$

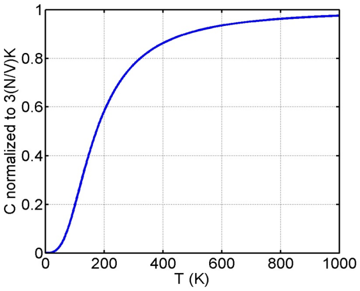
$$= \frac{KT}{2\pi^2 v^3}\omega_D^3 = 3\left(\frac{N}{V}\right)KT \qquad \left\{ \omega_D = \left(6\pi^2 v^3 \frac{N}{V}\right)^{1/3} \right.$$

Physical explanation: There are *N*/*V* phonon modes per band per unit volume and each mode has energy equal to *KT* as per the classical equipartition theorem

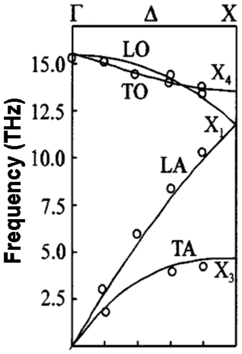
Specific Heat: $C = \frac{du}{dT} = 3\left(\frac{N}{V}\right)K \longrightarrow$ Dulong and Petit Law (1819)

Silicon Heat Capacity

Silicon Heat Capacity



The Heat capacity approaches 3(*N*/*V*)*K* as the temperature exceeds the Debye temperature of all acoustic phonon bands



Silicon Phonon Bands

$\omega_D(LA) = 19.3$ THz
$\theta_D(LA) = 926$ K

$\omega_D(TA) = 13.4$ THz
$\theta_D(TA) = 643$ K

Optical Phonons in 1D: Einstein Model and Density of States

Consider optical phonons in a *N*-primitive-cell 1D crystal of length *L*

Let the optical phonon frequency be $\omega_{LO}(\vec{q})$

We want to be able to write:

$$\sum_{q_x \text{ in FBZ}} \overset{?}{=} L\int_0^{\infty} d\omega \; g_{1D}(\omega)$$

We suppose that all optical phonon modes in FBZ have the same frequency ω_{LO} **(i.e. the phonon band is completely flat - Einstein model):**

$$\Rightarrow \quad g_{1D}(\omega) \propto C\,\delta(\omega-\omega_{LO}) \longrightarrow \text{What is } C\,?$$

We know that:

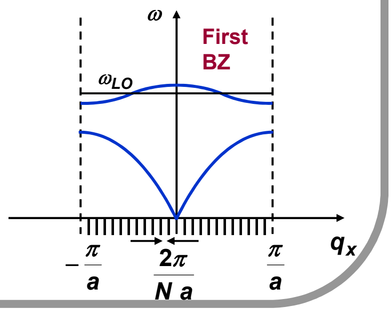
$$\sum_{q_x \text{ in FBZ}} = N$$

Therefore:

$$L\int_0^{\infty} d\omega \; g_{1D}(\omega) = N \qquad \Rightarrow \qquad C = \frac{N}{L}$$

Finally:

$$g_{1D}(\omega) = \frac{N}{L}\,\delta(\omega-\omega_{LO})$$



Optical Phonons in 2D and 3D: Einstein Model

Consider optical phonons in a *N*-primitive-cell 2D (or 3D) crystal of area *A* (or volume *V*)

For each optical phonon band we want to be able to write:

$$\sum_{\vec{q} \text{ in FBZ}} \overset{?}{=} A\int_0^{\infty} d\omega \; g_{2D}(\omega) \quad \text{or} \quad \sum_{\vec{q} \text{ in FBZ}} \overset{?}{=} V\int_0^{\infty} d\omega \; g_{3D}(\omega)$$

We suppose that each optical phonon band is completely flat and every phonon mode in a band has the same frequency ω_η

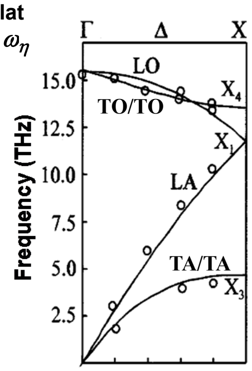
$$\omega = \omega_\eta \qquad \{\, \eta = 1,2,3 \;\; \text{for} \;\; \text{LO, TO, TO}$$

$$g_{2D}(\omega) = \frac{N}{A}\,\delta(\omega-\omega_\eta) \quad \text{or} \quad g_{3D}(\omega) = \frac{N}{V}\,\delta(\omega-\omega_\eta)$$

On can check that the number of phonon modes per band is conserved:

$$A\int_0^{\infty} d\omega \; g_{2D}(\omega) = N \quad \text{or} \quad V\int_0^{\infty} d\omega \; g_{3D}(\omega) = N$$

Silicon Phonon Bands



Heat Capacity of Optical Phonons in 2D: Einstein Model

Consider a material with two atoms per primitive cell in 2D
⇒ There must be 2 optical phonons bands in 2D (LO and TO)

Suppose the optical phonon frequencies are ω_{LO} and ω_{TO}. Assuming Einstein model:

$$g_{2D-LO}(\omega)=\frac{N}{A}\delta(\omega-\omega_{LO}) \qquad g_{2D-TO}(\omega)=\frac{N}{A}\delta(\omega-\omega_{LO})$$

Total energy per unit area in both the optical phonon modes is:

$$\begin{aligned}u &= \frac{1}{A}\sum_{\vec{q}\text{ in FBZ}}\hbar\omega_{LO}(\vec{q})\langle n_{\vec{q}}\rangle + \frac{1}{A}\sum_{\vec{q}\text{ in FBZ}}\hbar\omega_{TO}(\vec{q})\langle n_{\vec{q}}\rangle \\ &= \int_0^\infty d\omega\, g_{2D-LO}(\omega)\frac{\hbar\omega}{e^{\hbar\omega/KT}-1} + \int_0^\infty d\omega\, g_{2D-TO}(\omega)\frac{\hbar\omega}{e^{\hbar\omega/KT}-1} \\ &= \frac{N}{A}\frac{\hbar\omega_{LO}}{e^{\hbar\omega_{LO}/KT}-1} + \frac{N}{A}\frac{\hbar\omega_{TO}}{e^{\hbar\omega_{TO}/KT}-1}\end{aligned}$$

The heat capacity is:

$$C=\frac{du}{dT}=\frac{N}{A}K\frac{e^{\hbar\omega_{LO}/KT}}{\left(e^{\hbar\omega_{LO}/KT}-1\right)^2}\left(\frac{\hbar\omega_{LO}}{KT}\right)^2 + \frac{N}{A}K\frac{e^{\hbar\omega_{TO}/KT}}{\left(e^{\hbar\omega_{TO}/KT}-1\right)^2}\left(\frac{\hbar\omega_{TO}}{KT}\right)^2$$

Appendix: Classical Equipartition Theorem

According to the canonical ensemble of statistical physics, a system at temperature *T* will have energy *E* with the probability given by:

$$P(E)=\frac{1}{Z}e^{-\frac{E}{KT}}$$

The constant *Z* is determined by adding the probabilities for all possible states of the system and equating the result to unity

1D Example: Consider a free particle in 1D with the energy given by:

$$E=\frac{p_x^2}{2m}$$

The probability that the particle at temperature *T* will have momentum p_x is then:

$$P(p_x)=\frac{1}{Z}e^{-\frac{p_x^2/2m}{KT}}$$

We must have:

$$\int_{-\infty}^{\infty}dp_x\;P(p_x)=1 \quad\Rightarrow\quad Z=\sqrt{2\pi\, mKT}$$

Appendix: Classical Equipartition Theorem

So we finally have for the probability distribution of the particle momentum:

$$P(p_x)=\frac{1}{\sqrt{2\pi\, mKT}}\,e^{-\frac{p_x^2/2m}{KT}}$$

The average energy of the particle is then:

$$\int_{-\infty}^{\infty} dp_x\,\frac{p_x^2}{2m}\,P(p_x)=\frac{1}{2}KT$$

General Proof:

Consider a system whose total energy can be written in terms of various independent momenta and displacements as follows:

$$E=\sum_j a_j p_j^2+\sum_j b_j u_j^2$$

The probability that the system will have some specific values for all the displacements and momenta is:

$$P(p_1,p_2,\ldots\ldots u_1,u_2,\ldots\ldots)=\frac{1}{Z}\,e^{-\frac{\sum_j a_j p_j^2+\sum_j b_j u_j^2}{KT}}$$

Appendix: Classical Equipartition Theorem

$$P(p_1,p_2,\ldots\ldots u_1,u_2,\ldots\ldots)=\frac{1}{Z}\,e^{-\frac{\sum_j a_j p_j^2+\sum_j b_j u_j^2}{KT}}$$

The constant *Z* is determined by requiring:

$$\int_{-\infty}^{\infty}\prod_j\left(dp_j\right)\,\prod_r\left(du_r\right)\;P(p_1,p_2,\ldots\ldots u_1,u_2,\ldots\ldots)=1$$

It then follows that the average value of any one particular quadratic term in the expression for the total energy of the system is:

$$\left\langle a_n p_n^2\right\rangle=\int_{-\infty}^{\infty}\prod_j\left(dp_j\right)\,\prod_r\left(du_r\right)\;a_n p_n^2\;\;P(p_1,p_2,\ldots\ldots u_1,u_2,\ldots\ldots)=\frac{1}{2}KT$$

$$\left\langle b_n u_n^2\right\rangle=\int_{-\infty}^{\infty}\prod_j\left(dp_j\right)\,\prod_r\left(du_r\right)\;b_n u_n^2\;\;P(p_1,p_2,\ldots\ldots u_1,u_2,\ldots\ldots)=\frac{1}{2}KT$$

The above results follow from the properties of standard Gaussian integrals

Handout 24

The Effective Mass Theorem and the Effective Mass Schrodinger Equation

In this lecture you will learn:

- Electron states in crystals with weak potential perturbations
- The effective mass theorem
- The effective mass Schrodinger equation
- The donor and acceptor impurity levels in crystals

G. H. Wannier, Phys. Rev., 52, 191 (1937).
J. C. Slater, Phys. Rev., 76, 1592 (1949).
J. M. Luttinger and W. Kohn, Phys. Rev., 97, 869 (1955).

Perturbed Electrons in Energy Bands

1) The quantum states of an electron in a crystal are given by Bloch functions that obey the Schrodinger equation:

$$\hat{H}\,\psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})$$

where the wavevector $\vec{k}$ is confined to the FBZ and "*n*" is the band index

2) Under a lattice translation, Bloch functions obey the relation:

$$\psi_{n,\vec{k}}(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi_{n,\vec{k}}(\vec{r})$$

Now we ask the following question: if an external potential is added to the crystal Hamiltonian,

$$\hat{H} + U(\vec{r})$$

then what happens? How do the electrons behave? How do we find the new energies and eigenstates?

$$\left[\,\hat{H} + U(\vec{r})\,\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

The external potential could represent, for example, an applied E-field or an applied B-field, or potentials due to impurity atoms, or inhomogeneous nanostructures

Some Preliminaries

Statement of problem: Need to solve,

$$\left[\hat{H} + U(\vec{r})\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

As always, we will start from a completely different point to solve the problem stated above

Recall that the energy bands are lattice-periodic in the reciprocal space,

$$E_n\left(\vec{k}+\vec{G}\right) = E_n\left(\vec{k}\right)$$

When a function in real space is lattice-periodic, we can expand it in a Fourier series,

$$V\left(\vec{r}+\vec{R}\right) = V(\vec{r}) \quad \Rightarrow \quad V(\vec{r}) = \sum_j V\left(\vec{G}_j\right) e^{i\,\vec{G}_j\,.\,\vec{r}}$$

⇒ When a function is lattice-periodic in reciprocal space, we can also expand it in Fourier series of the form,

$$E_n\left(\vec{k}+\vec{G}\right) = E_n\left(\vec{k}\right) \quad \Rightarrow \quad E_n\left(\vec{k}\right) = \sum_j E_n\left(\vec{R}_j\right) e^{i\,\vec{R}_j\,.\,\vec{k}}$$

A Brief Review

$$E_n\left(\vec{k}+\vec{G}\right) = E_n\left(\vec{k}\right) \quad \Rightarrow \quad E_n\left(\vec{k}\right) = \sum_j E_n\left(\vec{R}_j\right) e^{i\,\vec{R}_j\,.\,\vec{k}}$$

Recall the operator:

$$\hat{E}_n(-i\nabla) = \sum_j E_n\left(\vec{R}_j\right) e^{\vec{R}_j\,.\,\nabla}$$

When we apply this operator to a Bloch function from the same band (i.e. the *n*-th band) we got:

$$\begin{aligned}
\hat{E}_n(-i\nabla)\,\psi_{n,\vec{k}}(\vec{r}) &= \sum_j E_n\left(\vec{R}_j\right) e^{\vec{R}_j\,.\,\nabla}\;\psi_{n,\vec{k}}(\vec{r}) \\
&= \sum_j E_n\left(\vec{R}_j\right)\;\psi_{n,\vec{k}}\left(\vec{r}+\vec{R}_j\right) \\
&= \sum_j E_n\left(\vec{R}_j\right) e^{i\,\vec{k}\,.\,\vec{R}_j}\;\psi_{n,\vec{k}}(\vec{r}) \\
&= E_n\left(\vec{k}\right)\;\psi_{n,\vec{k}}(\vec{r})
\end{aligned}$$

The result above implies that the action of the operator $\hat{E}_n(-i\nabla)$ on a Bloch function belonging to the same band is that of the Hamiltonian!

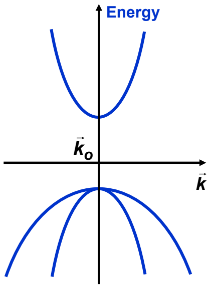
$$E_n(-i\nabla)\,\psi_{n,\vec{k}}(\vec{r}) = \hat{H}\,\psi_{n,\vec{k}}(\vec{r}) = E_n\left(\vec{k}\right)\psi_{n,\vec{k}}(\vec{r})$$

Solution Strategy

Now we come back to the problem:

$$\left[\hat{H} + U(\vec{r})\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

We want to see how the Bloch function $\psi_{n,\vec{k}_o}(\vec{r})$ is perturbed by the potential.



We write the solution as a superposition using Bloch functions from the same *n*-th band :

$$\psi(\vec{r}) = \sum_{\vec{k}\text{ near }\vec{k}_o} c(\vec{k})\,\psi_{n,\vec{k}}(\vec{r})$$

to get,

$$\left[\hat{H} + U(\vec{r})\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$
$$\Rightarrow \left[\hat{E}_n(-i\nabla) + U(\vec{r})\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

where we have replaced the Hamiltonian operator by $\hat{E}_n(-i\nabla)$

We are seeking a solution near a particular point $\vec{k}_o$ in k-space. For example, near a band extremum. For $\vec{k}$ near $\vec{k}_o$ we can approximate all Bloch functions as,

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\,\vec{k}\,.\,\vec{r}}\,u_{n,\vec{k}}(\vec{r}) \approx e^{i\,\vec{k}\,.\,\vec{r}}\,u_{n,\vec{k}_o}(\vec{r}) = e^{i\,(\vec{k}-\vec{k}_o)\,.\,\vec{r}}\,\psi_{n,\vec{k}_o}(\vec{r})$$

The Envelope Function

$$\begin{aligned}\psi(\vec{r}) &= \sum_{\vec{k}\text{ near }\vec{k}_o} c(\vec{k})\,\psi_{n,\vec{k}}(\vec{r}) \\ &= \sum_{\vec{k}\text{ near }\vec{k}_o} c(\vec{k})\,e^{i\,(\vec{k}-\vec{k}_o)\,.\,\vec{r}}\,\psi_{n,\vec{k}_o}(\vec{r}) \\ &= \left[\sum_{\vec{k}\text{ near }\vec{k}_o} c(\vec{k})\,e^{i\,(\vec{k}-\vec{k}_o)\,.\,\vec{r}}\right]\psi_{n,\vec{k}_o}(\vec{r}) \\ &= \phi(\vec{r})\;\psi_{n,\vec{k}_o}(\vec{r})\end{aligned}$$

The above expression shows that we are approximating the solution as a product of a Bloch function and another (unknown) function $\phi(\vec{r})$ which is called the envelope function. By construction the envelope function is slowly varying in space (on atomic scale).

We use the above form of the solution in the equation,

$$\left[\hat{E}_n(-i\nabla) + U(\vec{r})\right]\phi(\vec{r})\,\psi_{n,\vec{k}_o}(\vec{r}) = E\,\phi(\vec{r})\,\psi_{n,\vec{k}_o}(\vec{r})$$

First we look at:

$$\hat{E}_n(-i\nabla)\;\phi(\vec{r})\,\psi_{n,\vec{k}_o}(\vec{r})$$

The Effective Mass Schrodinger Equation

$$\begin{aligned}
\hat{E}_n(-i\nabla)\,\phi(\vec{r})\,\psi_{n,\vec{k}_o}(\vec{r}) &= \sum_j E_n(\vec{R}_j)\,e^{\vec{R}_j\,.\,\nabla}\,\phi(\vec{r})\,\psi_{n,\vec{k}_o}(\vec{r}) \\
&= \sum_j E_n(\vec{R}_j)\;\phi(\vec{r}+\vec{R}_j)\,\psi_{n,\vec{k}_o}(\vec{r}+\vec{R}_j) \\
&= \sum_j E_n(\vec{R}_j)\,e^{i\,\vec{k}_o\,.\,\vec{R}_j}\;\phi(\vec{r}+\vec{R}_j)\,\psi_{n,\vec{k}_o}(\vec{r}) \\
&= \psi_{n,\vec{k}_o}(\vec{r})\sum_j E_n(\vec{R}_j)\,e^{i\,\vec{k}_o\,.\,\vec{R}_j}\;\phi(\vec{r}+\vec{R}_j) \\
&= \psi_{n,\vec{k}_o}(\vec{r})\sum_j E_n(\vec{R}_j)\,e^{i\,\vec{k}_o\,.\,\vec{R}_j}\;e^{\vec{R}_j\,.\,\nabla}\;\phi(\vec{r}) \\
&= \psi_{n,\vec{k}_o}(\vec{r})\sum_j E_n(\vec{R}_j)\,e^{i\,(\vec{k}_o-i\nabla)\,.\,\vec{R}_j}\;\phi(\vec{r}) \\
&= \psi_{n,\vec{k}_o}(\vec{r})\,\hat{E}_n(\vec{k}_o-i\nabla)\,\phi(\vec{r})
\end{aligned}$$

This implies:

$$\left[\,\hat{E}_n(-i\nabla)+U(\vec{r})\,\right]\phi(\vec{r})\,\psi_{n,\vec{k}_o}(\vec{r}) = E\;\phi(\vec{r})\,\psi_{n,\vec{k}_o}(\vec{r})$$

$$\Rightarrow \psi_{n,\vec{k}_o}(\vec{r})\left[\,\hat{E}_n(\vec{k}_o-i\nabla)+U(\vec{r})\,\right]\phi(\vec{r}) = E\;\phi(\vec{r})\,\psi_{n,\vec{k}_o}(\vec{r})$$

The Effective Mass Theorem

Finally we have the following equation for the envelope function:

$$\boxed{\left[\,\hat{E}_n(\vec{k}_o-i\nabla)+U(\vec{r})\,\right]\phi(\vec{r}) = E\;\phi(\vec{r})}$$

The effective mass theorem states the following:

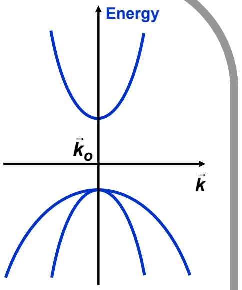
a) In the presence of a weak perturbing potential the solution for electron states near $\vec{k}_o$ in k-space can be represented as a product of a slowly varying envelope function and a Bloch function

$$\psi(\vec{r}) = \phi(\vec{r})\;\psi_{n,\vec{k}_o}(\vec{r})$$

b) The slowly varying envelope function obeys the effective mass Schrodinger equation:

$$\left[\,\hat{E}_n(\vec{k}_o-i\nabla)+U(\vec{r})\,\right]\phi(\vec{r}) = E\;\phi(\vec{r})$$

The Envelope Function

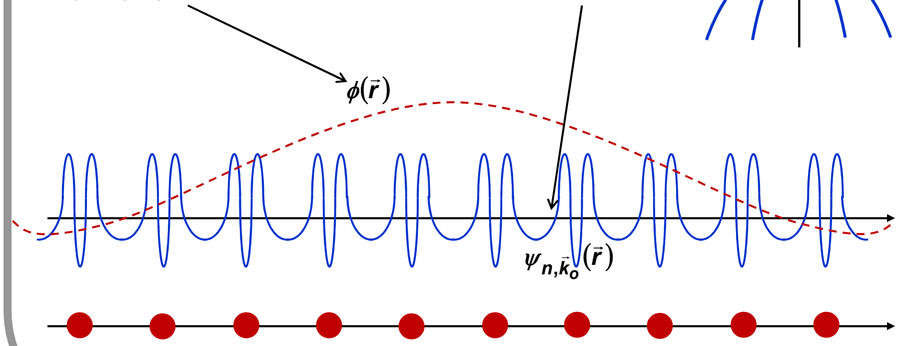


$$\left[\,\hat{E}_n\left(\vec{k}_o - i\nabla\right) + U(\vec{r})\,\right]\phi(\vec{r}) = E\,\phi(\vec{r})$$

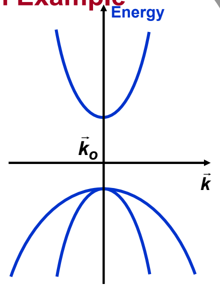
Electron wavefunction → $\psi(\vec{r}) = \phi(\vec{r})\;\psi_{n,\vec{k}_o}(\vec{r})$

Slowly varying envelope function

Bloch function



The Effective Mass Schrodinger Equation: An Example



Consider a conduction energy band with the dispersion:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2 (k_x - k_{ox})^2}{2m_{xx}} + \frac{\hbar^2 \left(k_y - k_{oy}\right)^2}{2m_{yy}} + \frac{\hbar^2 (k_z - k_{oz})^2}{2m_{zz}}$$

Now suppose an external potential $U(\vec{r})$ is present. The electron states near the conduction band bottom in the presence of the external potential are described by the effective mass equation:

$$\left[\,\hat{E}_c\left(\vec{k}_o - i\nabla\right) + U(\vec{r})\,\right]\phi(\vec{r}) = E\,\phi(\vec{r})$$

Note that one has to make the following replacements in the energy dispersion relation:

$$E_c(\vec{k}) \rightarrow \hat{E}_c\left(\vec{k}_o - i\nabla\right) \quad\Rightarrow\quad \boxed{k_x \rightarrow k_{ox} - i\frac{\partial}{\partial x} \qquad k_y \rightarrow k_{oy} - i\frac{\partial}{\partial y} \qquad k_z \rightarrow k_{oz} - i\frac{\partial}{\partial z}}$$

The operator $\hat{E}_c\left(\vec{k}_o - i\nabla\right)$ is then:

$$E_c\left(\vec{k}_o - i\nabla\right) = E_c - \frac{\hbar^2}{2m_{xx}}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m_{yy}}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m_{zz}}\frac{\partial^2}{\partial z^2}$$

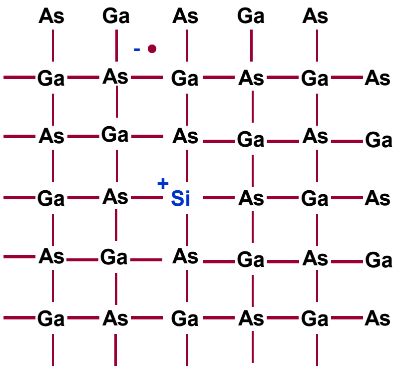
The effective mass Shrodinger equation becomes:

$$\left[-\frac{\hbar^2}{2m_{xx}}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m_{yy}}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m_{zz}}\frac{\partial^2}{\partial z^2} + E_c + U(\vec{r})\right]\phi(\vec{r}) = E\,\phi(\vec{r})$$

Donor Impurities in Semiconductors

One of the earliest applications of the effective mass theorem was the donor and acceptor impurity states and energy levels in semiconductors

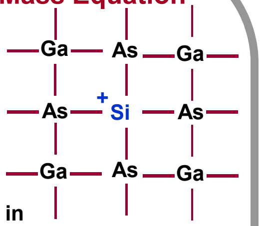
Consider a semiconductor (say GaAs) in which one Ga atom site is occupied by a Si atom, as shown:



- Silicon has one more electron in the outermost shell compared to Ga (4 in Si compared to 3 in Ga)

- Since only 3 electrons are needed to form co-valent bonds with the nearby As atoms, the extra electron does not participate in bonding and can drift away leaving behind a positively charged Si atom

Donor Impurities in Semiconductors: Effective Mass Equation

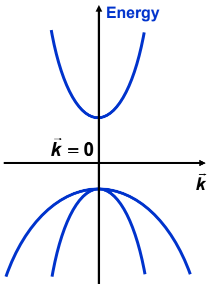


The positively charged Si atoms presents a Coulomb potential to the lattice. Therefore the potential energy is:

Attractive positive potential: $U(\vec{r}) = -\dfrac{e^2}{4\pi\,\varepsilon_s\,|\vec{r}|}$

We need to figure out how the electron states and energy levels in the conduction band are modified because of this Coulomb potential

$$\left[\hat{H} + U(\vec{r})\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$



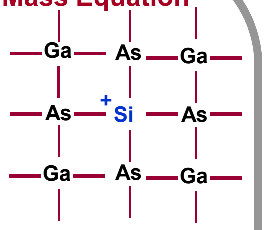
We are interested in how the states near the conduction band bottom get modified, so we assume

$$\psi(\vec{r}) = \phi(\vec{r})\;\psi_{c,\vec{k}_o=0}(\vec{r})$$

And we know that the envelope function satisfies the effective mass Schrodinger equation

$$\left[\hat{E}_c\left(\vec{k}_o - i\nabla\right) + U(\vec{r})\right]\phi(\vec{r}) = E\,\phi(\vec{r})$$

Donor Impurities in Semiconductors: Effective Mass Equation



We seek a solution near the conduction band bottom at $\vec{k}_o = 0$:

$$\Rightarrow \left[\hat{E}_c(-i\nabla)+U(\vec{r})\right]\phi(\vec{r}) = E\,\phi(\vec{r})$$

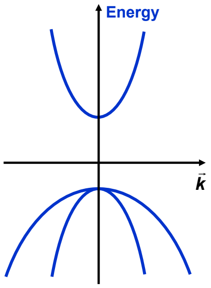
The conduction band dispersion in GaAs implies:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_e} \quad \Rightarrow \quad E_c\left(\cancelto{0}{\vec{k}_o} - i\nabla\right) = E_c(-i\nabla) = E_c - \frac{\hbar^2\nabla^2}{2m_e}$$

So we get the equation:

$$\left[E_c - \frac{\hbar^2\nabla^2}{2m_e} - \frac{e^2}{4\pi\,\varepsilon_s\,r}\right]\phi(\vec{r}) = E\,\phi(\vec{r})$$

$$\Rightarrow \left[-\frac{\hbar^2\nabla^2}{2m_e} - \frac{e^2}{4\pi\,\varepsilon_s\,r}\right]\phi(\vec{r}) = (E - E_c)\,\phi(\vec{r})$$

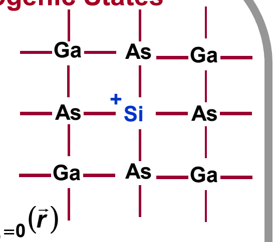


The above equation looks like the Schrodinger equation for an electron in a hydrogen atom with the exceptions that:

i)The mass is the effective mass m_e instead of the free-electron mass m

ii)The dielectric constant is ε_s instead of ε_o

Donor Impurities in Semiconductors: Hydrogenic States



$$\left[-\frac{\hbar^2\nabla^2}{2m_e} - \frac{e^2}{4\pi\,\varepsilon_s\,r}\right]\phi(\vec{r}) = (E - E_c)\,\phi(\vec{r})$$

Solutions are:

$$\phi(\vec{r}) = \phi_{n\ell m}(\vec{r}) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$$

Remember that the actual wavefunction is: $\psi(\vec{r}) = \phi(\vec{r})\ \psi_{c,\vec{k}_o=0}(\vec{r})$

Where:

1) n is a positive integer ≥ 1 $(n = 1,2,......)$
2) ℓ is a postive integer $< n$ $(\ell = 0,1,2,......(n-1)$ for s, p, d, f, ...)
3) m is an integer such that $|m| \leq \ell$ $(m = -\ell,...-1,0,+1,....+\ell)$

The corresponding energy eigenvalues are:

$$E - E_c = -\frac{E_o}{n^2} \xrightarrow{\qquad\qquad} n = 1,2,3......$$

$$\Rightarrow \quad E = E_c - \frac{E_o}{n^2}$$

$$\left\{ \; E_o = \frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_s}\right)^2 \right.$$

Donor Impurities in Semiconductors: Hydrogenic States

$$E = E_c - \frac{E_o}{n^2} \longrightarrow n = 1,2,3\ldots\ldots$$

$$\left\{\begin{aligned} E_o &= \frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_s}\right)^2 \\ &= (13.6\text{ eV})\left(\frac{m_e}{m}\right)\left(\frac{\varepsilon_o}{\varepsilon_s}\right)^2 \end{aligned}\right.$$

Ground state (lowest energy state):

$$\Rightarrow \quad n = 1 \quad \ell = 0 \quad m = 0$$

$$E = E_c - E_o$$

$$\phi_{1s}(\vec{r}) = \phi_{n=1\;\ell=0\;m=0}(\vec{r}) = \frac{1}{\sqrt{\pi\, a_o^3}}\, e^{-r/a_o}$$

$$\left\{\begin{aligned} a_o &= \left(\frac{4\pi\varepsilon_s}{e^2}\right)\frac{\hbar^2}{m_e} \\ &= (0.53\text{ A})\left(\frac{\varepsilon_s}{\varepsilon_o}\right)\left(\frac{m}{m_e}\right) \end{aligned}\right.$$

Effective Bohr radius

In GaAs: $m_e = .067\, m$ and $\varepsilon_s = 12.4\, \varepsilon_o$

$$E = E_c - E_o = E_c - (13.6\text{ eV})\left(\frac{m_e}{m}\right)\left(\frac{\varepsilon_o}{\varepsilon_s}\right)^2 \approx E_c - 5.9\ \text{meV}$$

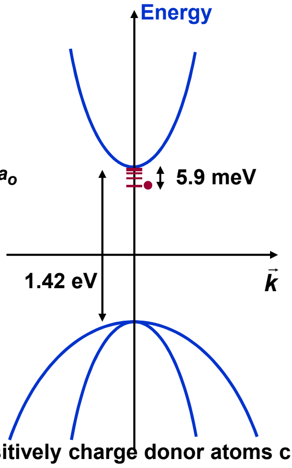
$$a_o = (0.53\text{ A})\left(\frac{\varepsilon_s}{\varepsilon_o}\right)\left(\frac{m}{m_e}\right) \approx 98\text{ A} \longrightarrow$$ Very large!

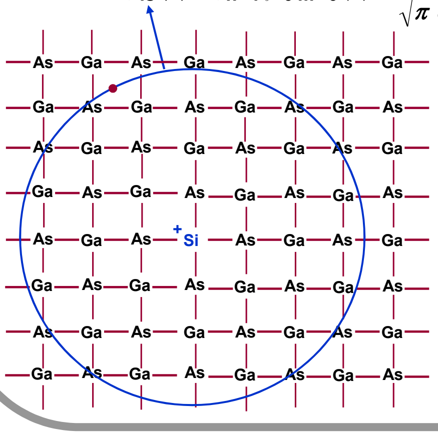
Donor Impurities in Semiconductors: Hydrogenic States

$$E = E_c - \frac{(13.6\text{ eV})}{n^2}\left(\frac{m_e}{m}\right)\left(\frac{\varepsilon_o}{\varepsilon_s}\right)^2 \approx E_c - \frac{5.9\ \text{meV}}{n^2}$$

$$a_o = (0.53\text{ A})\left(\frac{\varepsilon_s}{\varepsilon_o}\right)\left(\frac{m}{m_e}\right) \approx 98\text{ A}$$

$$\phi_{1s}(\vec{r}) = \phi_{n=1\;\ell=0\;m=0}(\vec{r}) = \frac{1}{\sqrt{\pi\, a_o^3}}\, e^{-r/a_o}$$

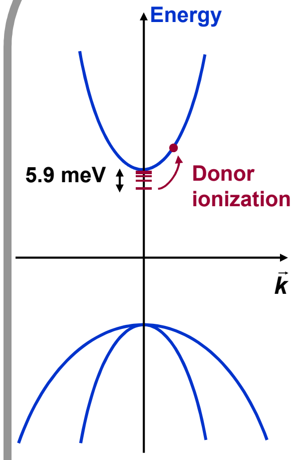




The positively charge donor atoms create new quantum states whose energies are slightly below the conduction band edge and whose wavefunctions are localized near the donor atom

$$\psi(\vec{r}) = \phi_{1s}(\vec{r})\ \psi_{c,\vec{k}_o=0}(\vec{r})$$

Donor Impurities in Semiconductors: N-Type Doping



- At very low temperatures the electron resides in the donor energy level and the donor atom is neutral
- At room temperature, the electron in the donor energy level can acquire enough energy to jump to the conduction band

When this happens the donor is said to have ionized

- Once in the conduction band the electron can move around and is no longer localized at the donor atom
- Donor impurities can therefore be used to dope semiconductors n-type

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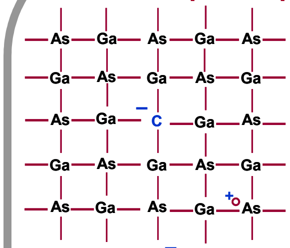
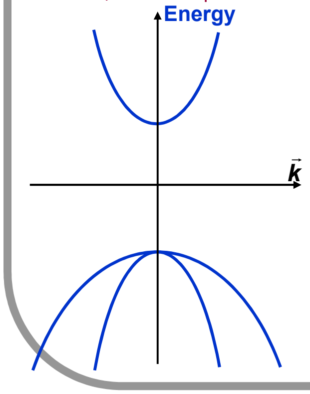
Acceptor Impurities in Semiconductors: P-Type Doping





Consider a semiconductor (say GaAs) in which one As atom site is occupied by a carbon atom, as shown:

- C has one less electron in the outermost shell compared to As (4 in C compared to 5 in As)
- Since 4 electrons are needed to form covalent bonds with the nearby Ga atoms, the required electron is taken from the valence band resulting in a negatively charged C atom and a hole in the valence band

Solution: $\psi(\vec{r}) = \phi(\vec{r})\ \psi_{hh,\vec{k}_o=0}(\vec{r})$

$$\Rightarrow \left[\hat{E}_{hh}(-i\nabla) + U(\vec{r})\right]\phi(\vec{r}) = E\ \phi(\vec{r})$$

Negative repulsive potential: $U(\vec{r}) = +\dfrac{e^2}{4\pi\,\varepsilon_s\,|\vec{r}|}$

hh-band dispersion: $E_{hh}(\vec{k}) = E_v - \dfrac{\hbar^2 k^2}{2m_{hh}}$

$$\Rightarrow \quad E_{hh}(-i\nabla) = E_v + \frac{\hbar^2\nabla^2}{2m_{hh}}$$

Acceptor Impurities in Semiconductors: P-Type Doping

The effective mass Schrodinger equation becomes:

$$\left[E_v + \frac{\hbar^2\nabla^2}{2m_{hh}} + \frac{e^2}{4\pi\,\varepsilon_s\,|\vec{r}|}\right]\phi(\vec{r}) = E\,\phi(\vec{r})$$

Rearrange:

$$\left[-\frac{\hbar^2\nabla^2}{2m_{hh}} - \frac{e^2}{4\pi\,\varepsilon_s\,|\vec{r}|}\right]\phi(\vec{r}) = (-E+E_v)\,\phi(\vec{r})$$

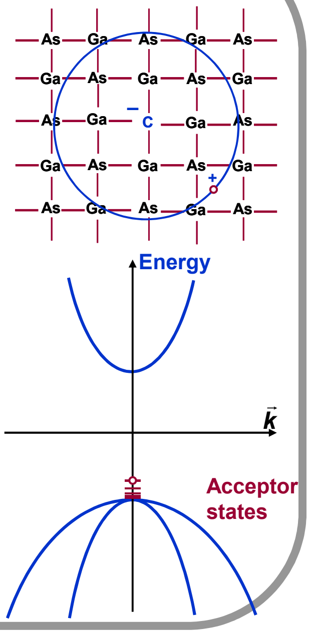
Again we end up with a Schrodinger-like equation for a Hydrogen atom which has the solution:

$$\phi(\vec{r}) = \phi_{n\ell m}(\vec{r}) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$$

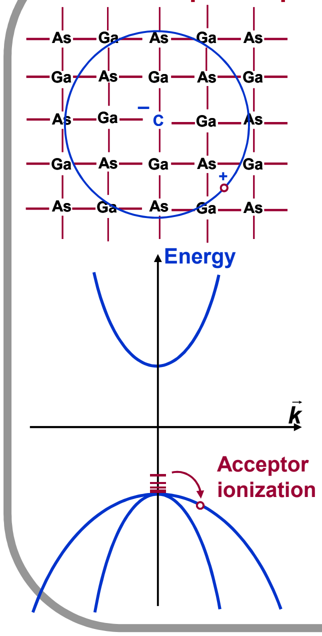
$$-E+E_v = -\frac{E_o}{n^2}$$

$$\Rightarrow \quad E = E_v + \frac{E_o}{n^2}$$

$$\left\{\begin{aligned} E_o &= \frac{m_{hh}}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_s}\right)^2 \\ &= (13.6\text{ eV})\left(\frac{m_{hh}}{m}\right)\left(\frac{\varepsilon_o}{\varepsilon_s}\right)^2 \end{aligned}\right.$$

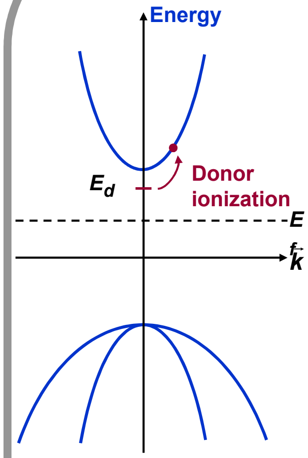


Acceptor Impurities in Semiconductors: P-Type Doping



- Acceptor atom gives rise to hydrogenic energy levels near the valence band maximum
- At very low temperatures the hole resides in the acceptor energy level and the acceptor atom location is overall neutral
- At room temperature, the hole in the acceptor energy level can acquire enough energy to jump to the valence band
When this happens the acceptor is said to have ionized
- Once in the valence band the hole can move around and is no longer localized at the acceptor atom
- Acceptor impurities can therefore be used to dope semiconductors p-type

Donor Ionization Statistics



In the grand canonical ensemble the probability of a system to have total particles *N* and total energy *E* is:

$$P(N,E) = A\,e^{-(E-E_f N)/KT}$$

The donor level can have the following possible states:

1) No electrons present

$$P(N=0,E=0) = A$$

2) One spin-up electron present

$$P(N=1,E=E_d) = A\,e^{-(E_d-E_f)/KT}$$

3) One spin-down electron present

$$P(N=1,E=E_d) = A\,e^{-(E_d-E_f)/KT}$$

4) Two or more electrons present

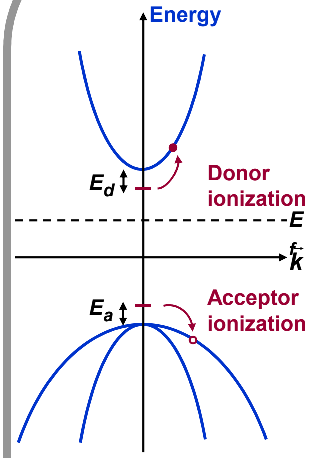
$$P(N>1,E) = 0 \longrightarrow$$

Coulomb repulsion does not allow it

Sum of all probabilities should equal unity:

$$\Rightarrow A\left[1+2\,e^{-(E_d-E_f)/KT}\right]=1 \quad \Rightarrow \quad A=\frac{1}{1+2\,e^{-(E_d-E_f)/KT}}$$

Donor Ionization Statistics



Probability that the donor level is ionized = Probability that the donor level has no electrons

$$= P(N=0,E=0)$$

$$= A$$

$$= \frac{1}{1+2\,e^{-(E_d-E_f)/KT}}$$

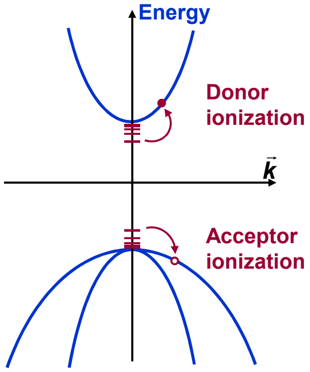
If the total donor impurity concentration is N_d then the concentration of ionized donors N^+_d is equal to:

$$N_d^+ = \frac{N_d}{1+2\,e^{-(E_d-E_f)/KT}}$$

For acceptors we have a similar relation:

$$N_a^- = \frac{N_a}{1+2\,e^{(E_a-E_f)/KT}}$$

Carrier Statistics in Doped Semiconductors



Consider a semiconductor that is doped with both donor and acceptor impurity atoms

- The total charge must be zero:

$$N_d^+ - N_a^- + p - n = 0$$

The above equation can be used to find the position of the equilibrium Fermi level since every term depends on the Fermi level position (one equation in one unknown)

$$N_d^+ = \frac{N_d}{1 + 2\, e^{-(E_d - E_f)/KT}}$$

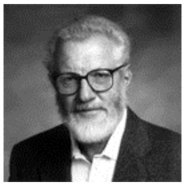
$$N_a^- = \frac{N_a}{1 + 2\, e^{(E_a - E_f)/KT}}$$

Handout 25

Semiconductor Heterostructures

In this lecture you will learn:

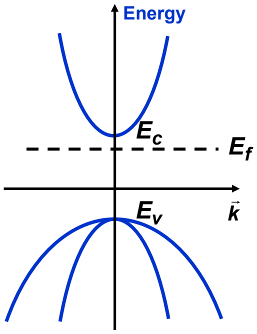
- Energy band diagrams in real space
- Semiconductor heterostructures and heterojunctions
- Electron affinity and work function
- Heterojunctions in equilibrium
- Electrons at Heterojunctions



Herbert Kroemer
(1920-)
Nobel Prize 2000 for
the Semiconductor
Heterostructure Laser

Band Diagrams in Real Space - I

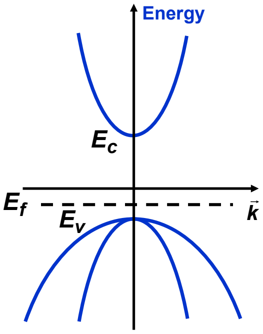
N-type semiconductor



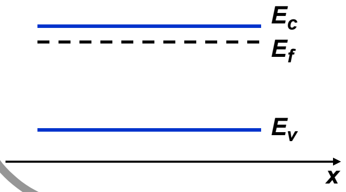
$$n = N_c\, e^{-(E_c - E_f)/KT}$$

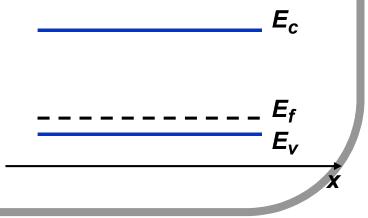
$$p = N_v\, e^{-(E_f - E_v)/KT}$$

P-type semiconductor



For devices, it is useful to draw the conduction and valence band edges in real space:





Band Diagrams in Real Space - II

Electrostatic potential and electric field:

An electrostatic potential (and an electric field) can be present in a crystal:

$$\phi(\vec{r}) \quad \text{and} \quad \vec{E}(\vec{r}) = -\nabla\phi(\vec{r})$$

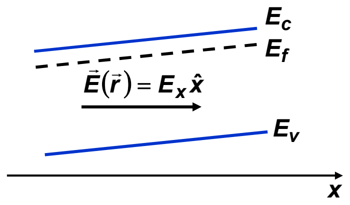
The total energy of an electron in a crystal is then given not just by the energy band dispersion $E_n(\vec{k})$ but also includes the potential energy coming from the potential:

$$E_n(\vec{k}) \rightarrow E_n(\vec{k}) - e\phi(\vec{r})$$

Therefore, the conduction and valence band edges also become position dependent:

$$E_c \rightarrow E_c - e\phi(\vec{r}) \qquad E_v \rightarrow E_v - e\phi(\vec{r})$$

Example: Uniform x-directed electric field

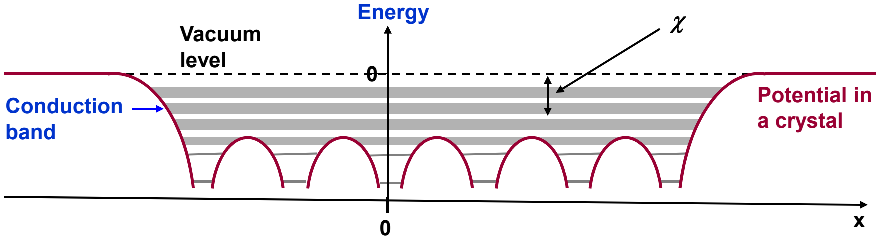


N-type semiconductor

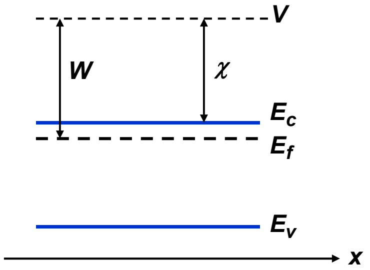
$$\vec{E}(\vec{r}) = E_x\hat{x}$$
$$\phi(\vec{r}) = \phi(x=0) - E_x x$$
$$E_c(x) = E_c(x=0) + eE_x x$$

Electron Affinity and Work Function

Electron affinity "χ" is the energy required to remove an electron from the bottom of the conduction band to outside the crystal, i.e. the vacuum level



Work function "W" is the energy required to remove an electron from the Fermi level to the vacuum level

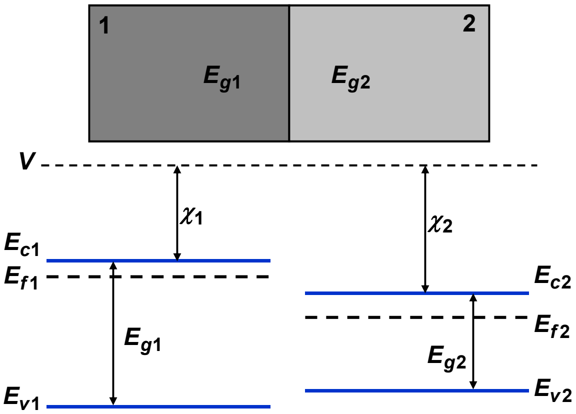


- Work function changes with doping but affinity is a constant for a given material

Semiconductor N-N Heterostructure: Electron Affinity Rule

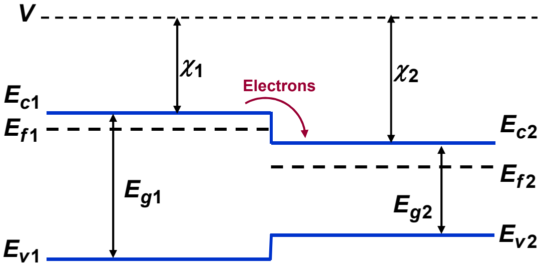
Heterostructure: A semiconductor structure in which more than one semiconductor material is used and the structure contains interfaces or junctions between two different semiconductors

Consider the following heterostructure interface between a wide bandgap and a narrow bandgap semiconductor (both n-type):



The **electron affinity rule** tells how the energy band edges of the two semiconductors line up at a hetero-interface

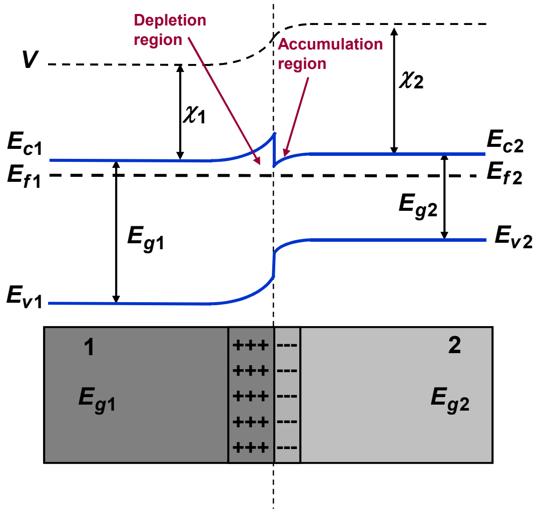
Semiconductor N-N Heterojunction



Something is wrong here: the Fermi level (the chemical potential) has to be the same everywhere in equilibrium (i.e. a flat line)

- Once a junction is made, electrons will flow from the side with higher Fermi level (1) to the side with lower Fermi level (2)

Semiconductor N-N Heterojunction: Equilibrium



- Electrons will flow from the side with higher Fermi level (1) to the side with lower Fermi level (2)

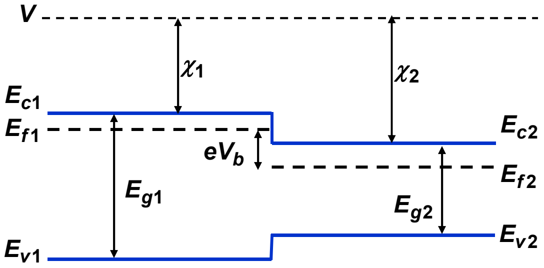
- Electron flow away from semiconductor (1) will result in a region at the interface which is depleted of electrons (depletion region). Because of positively charged donor atoms, the depletion region has net positive charge density

- Electron flow into semiconductor (2) will result in a region at the interface which has an accumulation of electrons (accumulation region). The accumulation region has net negative charge density

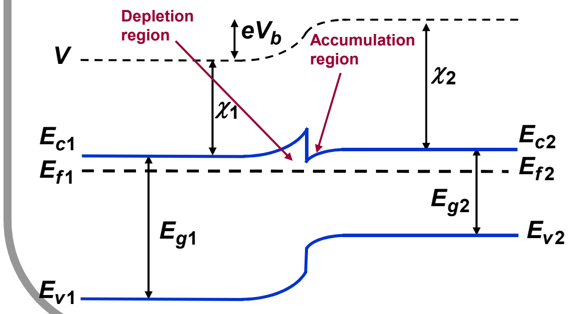
Note: the vacuum level follows the electrostatic potential:

$$V(x) = V(x=0) - e\,[\,\phi(x) - \phi(x=0)\,]$$

Semiconductor N-N Heterojunction: Equilibrium



- Electron flow from semiconductor (1) to semiconductor (2) continues until the electric field due to the formation of depletion and accumulation regions becomes so large that the Fermi levels on both sides become the same

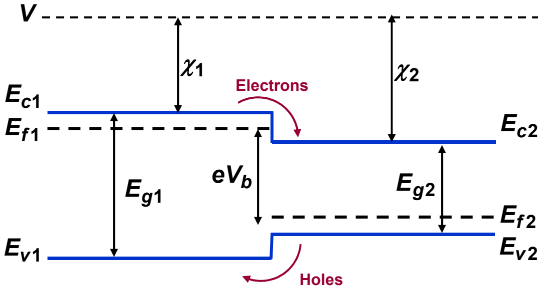


- In equilibrium, because of the electric field at the interface, there is a potential difference between the two sides – called the built-in voltage

- The built-in voltage is related to the difference in the Fermi levels before the equilibrium was established:

$$eV_b = E_{f1} - E_{f2}$$

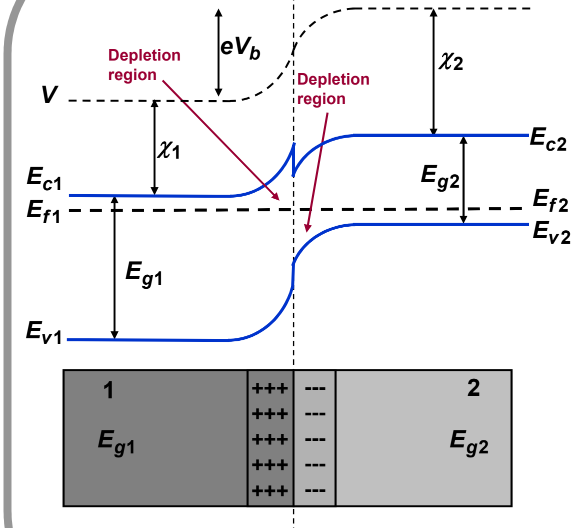
Semiconductor P-N Heterojunction



Once a junction is made:

- **Electrons will flow from the side with higher Fermi level (1) to the side with lower Fermi level (2)**
- **Holes will flow from the side with lower Fermi level (2) to the side with higher Fermi level (1)**

Semiconductor P-N Heterojunction: Equilibrium

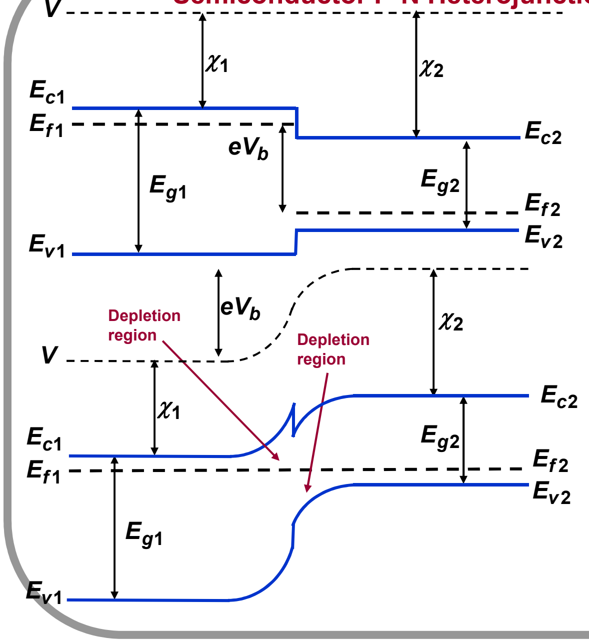


- **Electron flow away from semiconductor (1) will result in a region at the interface which is depleted of electrons (depletion region). Because of positively charged donor atoms, the depletion region has net positive charge density**
- **Hole flow away from semiconductor (2) will result in a region at the interface which is depleted of holes (depletion region). Because of negatively charged acceptor atoms, the depletion region has net negative charge density**

Note: **the vacuum level follows the electrostatic potential:**

$$V(x) = V(x=0) - e\,[\,\phi(x) - \phi(x=0)\,]$$

Semiconductor P-N Heterojunction: Equilibrium



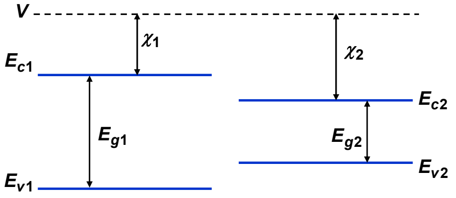
- Electron flow from semiconductor (1) to semiconductor (2) and hole flow from semiconductor (2) to semiconductor (1) continues until the electric field due to the formation of depletion regions becomes so large that the Fermi levels on both sides become the same

- The built-in voltage is related to the difference in the Fermi levels before the equilibrium was established:

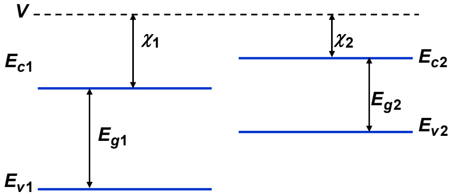
$$eV_b = E_{f1} - E_{f2}$$

Types of Semiconductor Heterojunctions

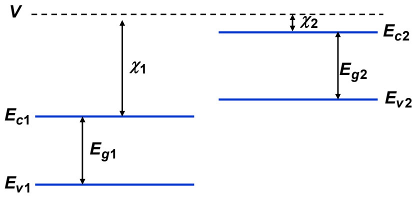
Type-I: Straddling gap



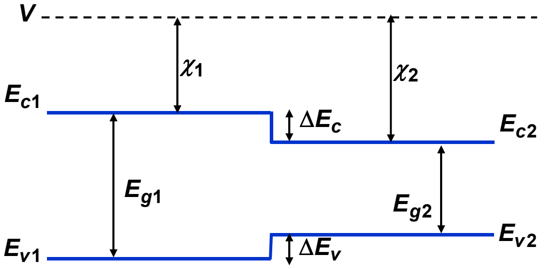
Type-II: Staggered gap



Type-III: Broken gap



Band Offsets in Heterojunctions

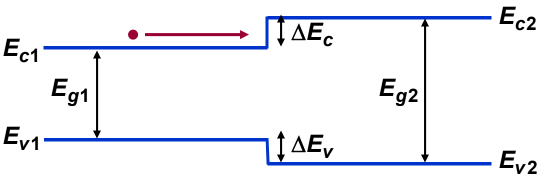


The conduction and valence band offsets are determined as follows:

$$\Delta E_c = \chi_2 - \chi_1$$

$$\Delta E_v = \Delta E_g - \Delta E_c = \left(E_{g1} - E_{g2}\right) - \Delta E_c$$

Electrons at Heterojunctions



Question: What happens to the electron that approaches the interface (as shown)? How does it see the band offset? Does it bounce back? Does it go on the under side?

The **effective mass equation** can be used to answer all the above questions

In semiconductor 1:

$$\psi_1(\vec{r}) = \phi_1(\vec{r})\ \psi_{c1,\vec{k}_o}(\vec{r})$$

$$\left[\,\hat{E}_{c1}\left(\vec{k}_o - i\nabla\right) + U(\vec{r})\,\right]\phi_1(\vec{r}) = E\ \phi_1(\vec{r})$$

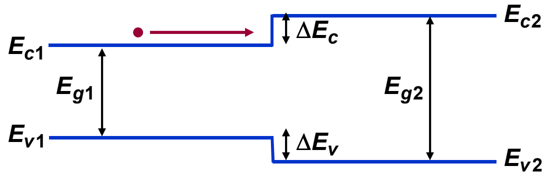
In semiconductor 2:

$$\psi_2(\vec{r}) = \phi_2(\vec{r})\ \psi_{c2,\vec{k}_o}(\vec{r})$$

$$\left[\,\hat{E}_{c2}\left(\vec{k}_o - i\nabla\right) + U(\vec{r})\,\right]\phi_2(\vec{r}) = E\ \phi_2(\vec{r})$$

Electrons at Heterojunctions; Effect of Band Offsets

$U(\vec r) = 0$



Assume for the electron in the conduction band of semiconductor 1:

$$E_{c1}(\vec k) = E_{c1} + \frac{\hbar^2 k^2}{2m_{e1}} \qquad \psi_1(\vec r) = \phi_1(\vec r)\ \psi_{c1,\vec k_o=0}(\vec r)$$

$$\Rightarrow \left[-\frac{\hbar^2}{2m_{e1}}\nabla^2 + E_{c1} \right] \phi_1(\vec r) = E\ \phi_1(\vec r)$$

And for the electron in semiconductor 2:

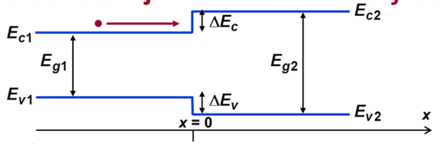
$$E_{c2}(\vec k) = E_{c2} + \frac{\hbar^2 k^2}{2m_{e2}} \qquad \psi_2(\vec r) = \phi_2(\vec r)\ \psi_{c2,\vec k_o=0}(\vec r)$$

$$\Rightarrow \left[-\frac{\hbar^2}{2m_{e2}}\nabla^2 + E_{c2} \right] \phi_2(\vec r) = E\ \phi_2(\vec r)$$

Notice that the conduction band edge energy (i.e. E_{c1} or E_{c2}) appears as a constant potential in the effective mass Schrodinger equation

Conduction band offset at the heterojunction therefore appears like a potential step to the electron

Electrons at Heterojunctions: Boundary Conditions



(1) Continuity of the wavefunction at the boundary:

$$\psi_1(\vec r)\big|_{x=0} = \psi_2(\vec r)\big|_{x=0}$$

If one assumes: $\psi_{c1,\vec k_o}(\vec r) \approx \psi_{c2,\vec k_o}(\vec r)$ ⇨ $\boxed{\phi_1(\vec r)\big|_{x=0} = \phi_2(\vec r)\big|_{x=0}}$

(2) Continuity of the normal component of the probability current at the boundary:

In text book quantum mechanics **the probability current** is defined as:

$$\vec J(\vec r) = \psi^*(\vec r)\frac{\hbar}{2im}\nabla\psi(\vec r) + c.c. = \psi^*(\vec r)\frac{\hbar}{2im}\nabla\psi(\vec r) - \psi(\vec r)\frac{\hbar}{2im}\nabla\psi^*(\vec r)$$

Or in shorter component notation:

$$J_\alpha(\vec r) = \psi^*(\vec r)\frac{\hbar}{2im}\partial_\alpha\psi(\vec r) + c.c.$$

Probability current is always continuous across a boundary

We need an expression for the probability current in terms of the envelope function

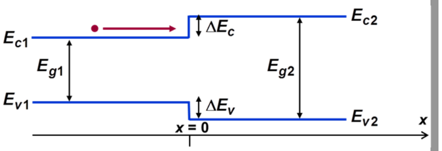
Electrons at Heterojunctions: Boundary Conditions

Probability Current: In a material with energy band dispersion given by:

$$E_n(\vec{k}) = E_n + \frac{\hbar^2}{2}(\vec{k}-\vec{k}_o).M^{-1}.(\vec{k}-\vec{k}_o) = E_n + \sum_{\alpha,\beta} \frac{\hbar^2}{2m_{\alpha\beta}}(k_\alpha - k_{o\alpha})(k_\beta - k_{o\beta})$$

The expression for the electron probability current (in terms of the envelope function) is:

$$J_\alpha(\vec{r}) = \sum_\beta \phi^*(\vec{r}) \frac{\hbar}{2im_{\alpha\beta}} \partial_\beta \phi(\vec{r}) + \text{c.c.}$$



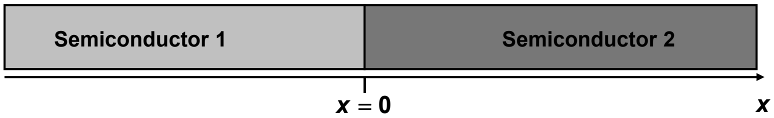
Continuity of the probability current:

The continuity of the **normal component** of the probability current across a heterojunction gives another boundary condition for the envelope function:

$$\boxed{\sum_\beta \frac{1}{m_{x\beta 1}} \partial_\beta \phi_1(\vec{r})\Big|_{x=0} = \sum_\beta \frac{1}{m_{x\beta 2}} \partial_\beta \phi_2(\vec{r})\Big|_{x=0}}$$

For: $$M^{-1} = \begin{bmatrix} 1/m_{xx} & & \\ & 1/m_{yy} & \\ & & 1/m_{zz} \end{bmatrix} \Longrightarrow \frac{1}{m_{xx1}} \frac{\partial \phi_1(\vec{r})}{\partial x}\Big|_{x=0} = \frac{1}{m_{xx2}} \frac{\partial \phi_2(\vec{r})}{\partial x}\Big|_{x=0}$$

Electrons at Heterojunctions: Boundary Conditions



(1) Continuity of the envelope function at the boundary:

$$\boxed{\phi_1(\vec{r})\big|_{x=0} = \phi_2(\vec{r})\big|_{x=0}}$$

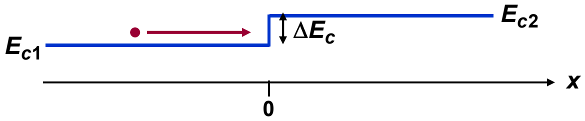
(2) Continuity of the normal component of the probability current at the boundary:

$$\boxed{\sum_\beta \frac{1}{m_{x\beta 1}} \partial_\beta \phi_1(\vec{r})\Big|_{x=0} = \sum_\beta \frac{1}{m_{x\beta 2}} \partial_\beta \phi_2(\vec{r})\Big|_{x=0}}$$

If in both the materials the inverse effective mass matrix is diagonal then this boundary condition becomes:

$$M^{-1} = \begin{bmatrix} 1/m_{xx} & & \\ & 1/m_{yy} & \\ & & 1/m_{zz} \end{bmatrix} \Longrightarrow \frac{1}{m_{xx1}} \frac{\partial \phi_1(\vec{r})}{\partial x}\Big|_{x=0} = \frac{1}{m_{xx2}} \frac{\partial \phi_2(\vec{r})}{\partial x}\Big|_{x=0}$$

The Effective Mass Theory for Heterojunctions



Assume in semiconductor (1):

$$\vec{k}_o = 0$$

$$E_{c1}(\vec{k}) = E_{c1} + \frac{\hbar^2 k_x^2}{2m_{x1}} + \frac{\hbar^2 k_y^2}{2m_{y1}} + \frac{\hbar^2 k_z^2}{2m_{z1}}$$

Assume in semiconductor (2):

$$\vec{k}_o = 0$$

$$E_{c2}(\vec{k}) = E_{c2} + \frac{\hbar^2 k_x^2}{2m_{x2}} + \frac{\hbar^2 k_y^2}{2m_{y2}} + \frac{\hbar^2 k_z^2}{2m_{z2}}$$

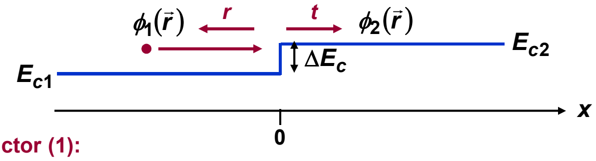
In semiconductor (1):

$$\left[\hat{E}_{c1}(\vec{k}_o - i\nabla) + U(\vec{r})\right]\phi_1(\vec{r}) = E\,\phi_1(\vec{r})$$

$$\Rightarrow \left[\hat{E}_{c1}(-i\nabla)\right]\phi_1(\vec{r}) = E\,\phi_1(\vec{r})$$

$$\Rightarrow \left[-\frac{\hbar^2}{2m_{x1}}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m_{y1}}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m_{z1}}\frac{\partial^2}{\partial z^2} + E_{c1}\right]\phi_1(\vec{r}) = E\,\phi_1(\vec{r})$$

The Effective Mass Theory for Heterojunctions



In semiconductor (1):

$$\left[-\frac{\hbar^2}{2m_{x1}}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m_{y1}}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m_{z1}}\frac{\partial^2}{\partial z^2} + E_{c1}\right]\phi_1(\vec{r}) = E\,\phi_1(\vec{r})$$

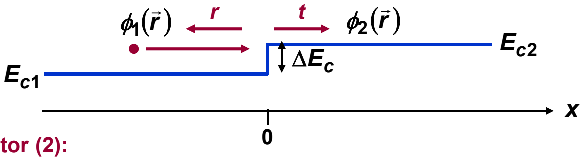
Assume a plane wave solution: $\phi_1(\vec{r}) = e^{i\left(k_{x1}x + k_y y + k_z z\right)}$

Plug it in to get: $E = E_{c1} + \dfrac{\hbar^2 k_{x1}^2}{2m_{x1}} + \dfrac{\hbar^2 k_y^2}{2m_{y1}} + \dfrac{\hbar^2 k_z^2}{2m_{z1}}$ $\longrightarrow$ **A plane wave solution works**

We expect a reflected wave also so we write the total solution in semiconductor (1) as:

$$\phi_1(\vec{r}) = e^{i\left(k_{x1}x + k_y y + k_z z\right)} + r\,e^{i\left(-k_{x1}x + k_y y + k_z z\right)}$$

The Effective Mass Theory for Heterojunctions



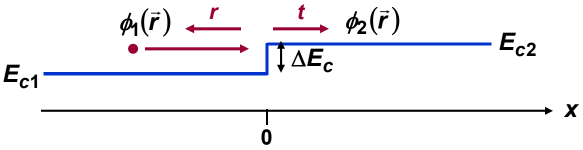
In semiconductor (2):

$$\left[-\frac{\hbar^2}{2m_{x2}}\frac{\partial^2}{\partial x^2}-\frac{\hbar^2}{2m_{y2}}\frac{\partial^2}{\partial y^2}-\frac{\hbar^2}{2m_{z2}}\frac{\partial^2}{\partial z^2}+E_{c2}\right]\phi_2(\vec{r})=E\,\phi_2(\vec{r})$$

Assume a plane wave solution: $\phi_2(\vec{r})=t\,e^{i\left(k_{x2}x+k_yy+k_zz\right)}$

Plug it in to get: $E=E_{c2}+\frac{\hbar^2k_{x2}^2}{2m_{x2}}+\frac{\hbar^2k_y^2}{2m_{y2}}+\frac{\hbar^2k_z^2}{2m_{z2}}$ ⟶ **A plane wave solution works here also**

Boundary Conditions at Heterojunctions



$$\phi_1(\vec{r})=e^{i\left(k_{x1}x+k_yy+k_zz\right)}+r\,e^{i\left(-k_{x1}x+k_yy+k_zz\right)}\longrightarrow E=E_{c1}+\frac{\hbar^2k_{x1}^2}{2m_{x1}}+\frac{\hbar^2k_y^2}{2m_{y1}}+\frac{\hbar^2k_z^2}{2m_{z1}}$$

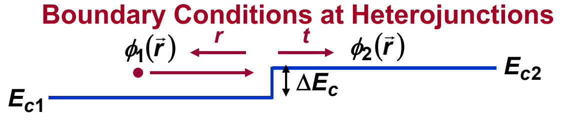
$$\phi_2(\vec{r})=t\,e^{i\left(k_{x2}x+k_yy+k_zz\right)}\longrightarrow E=E_{c2}+\frac{\hbar^2k_{x2}^2}{2m_{x2}}+\frac{\hbar^2k_y^2}{2m_{y2}}+\frac{\hbar^2k_z^2}{2m_{z2}}$$

(1) Envelope functions must be continuous at the interface:

$$\phi_1(x=0)=\phi_2(x=0)$$
$$\Rightarrow e^{i\left(k_yy+k_zz\right)}+r\,e^{i\left(k_yy+k_zz\right)}=t\,e^{i\left(k_yy+k_zz\right)}$$
$$\Rightarrow 1+r=t$$

Note that this boundary condition can only be satisfied if the components of the wavevector parallel to the interface are the same on both sides

Boundary Conditions at Heterojunctions



$$\phi_1(\vec r) = e^{i(k_{x1}x+k_y y+k_z z)} + r\, e^{i(-k_{x1}x+k_y y+k_z z)} \longrightarrow E = E_{c1} + \frac{\hbar^2 k_{x1}^2}{2m_{x1}} + \frac{\hbar^2 k_y^2}{2m_{y1}} + \frac{\hbar^2 k_z^2}{2m_{z1}}$$

$$\phi_2(\vec r) = t\, e^{i(k_{x2}x+k_y y+k_z z)} \longrightarrow E = E_{c2} + \frac{\hbar^2 k_{x2}^2}{2m_{x2}} + \frac{\hbar^2 k_y^2}{2m_{y2}} + \frac{\hbar^2 k_z^2}{2m_{z2}}$$

Energy conservation:

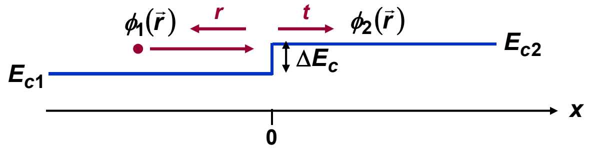
$$E = E_{c1} + \frac{\hbar^2 k_{x1}^2}{2m_{x1}} + \frac{\hbar^2 k_y^2}{2m_{y1}} + \frac{\hbar^2 k_z^2}{2m_{z1}} = E_{c2} + \frac{\hbar^2 k_{x2}^2}{2m_{x2}} + \frac{\hbar^2 k_y^2}{2m_{y2}} + \frac{\hbar^2 k_z^2}{2m_{z2}}$$

$$\Rightarrow \frac{\hbar^2 k_{x2}^2}{2m_{x2}} = \frac{\hbar^2 k_{x1}^2}{2m_{x1}} - \Delta E_c - \frac{\hbar^2 k_y^2}{2}\left(\frac{1}{m_{y2}} - \frac{1}{m_{y1}}\right) - \frac{\hbar^2 k_z^2}{2}\left(\frac{1}{m_{z2}} - \frac{1}{m_{z1}}\right)$$

$$\Rightarrow \frac{\hbar^2 k_{x2}^2}{2m_{x2}} = \frac{\hbar^2 k_{x1}^2}{2m_{x1}} - \Delta V_{eff}(k_y, k_z)$$

Note that the effective barrier height depends on the band offset as well as the parallel components of the wavevector

Boundary Conditions at Heterojunctions



$$\phi_1(\vec r) = e^{i(k_{x1}x+k_y y+k_z z)} + r\, e^{i(-k_{x1}x+k_y y+k_z z)} \longrightarrow E = E_{c1} + \frac{\hbar^2 k_{x1}^2}{2m_{x1}} + \frac{\hbar^2 k_y^2}{2m_{y1}} + \frac{\hbar^2 k_z^2}{2m_{z1}}$$

$$\phi_2(\vec r) = t\, e^{i(k_{x2}x+k_y y+k_z z)} \longrightarrow E = E_{c2} + \frac{\hbar^2 k_{x2}^2}{2m_{x2}} + \frac{\hbar^2 k_y^2}{2m_{y2}} + \frac{\hbar^2 k_z^2}{2m_{z2}}$$

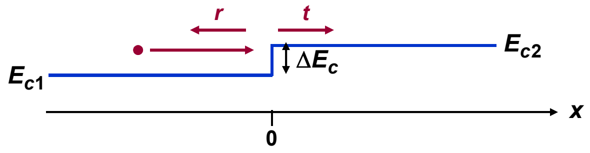
(2) Probability current must be continuous at the interface:

$$\left.\frac{1}{m_{x1}}\frac{\partial\phi_1}{\partial x}\right|_{x=0} = \left.\frac{1}{m_{x2}}\frac{\partial\phi_2}{\partial x}\right|_{x=0} \longrightarrow \left\{\text{Conservation of probability current at the interface}\right.$$

$$\Rightarrow \frac{ik_{x1}}{m_{x1}}\left(e^{i(k_y y+k_z z)} - r\, e^{i(k_y y+k_z z)}\right) = \frac{ik_{x2}}{m_{x2}}\, t\, e^{i(k_y y+k_z z)}$$

$$\Rightarrow \frac{k_{x1}}{m_{x1}}(1-r) = \frac{k_{x2}}{m_{x2}}\, t$$

Transmission and Reflection at Heterojunctions



We have two equations in two unknowns:

$$1+r=t \qquad \frac{k_{x1}}{m_{x1}}(1-r)=\frac{k_{x2}}{m_{x2}}t$$

The solution is:

$$t=\frac{2}{1+m_{x1}k_{x2}/m_{x2}k_{x1}} \qquad r=\frac{1-m_{x1}k_{x2}/m_{x2}k_{x1}}{1+m_{x1}k_{x2}/m_{x2}k_{x1}}$$

Where:

$$\frac{\hbar^2 k_{x2}^2}{2m_{x2}}=\frac{\hbar^2 k_{x1}^2}{2m_{x1}}-\Delta V_{eff}\left(k_y,k_z\right)$$

Special case: If the RHS in the above equation is negative, then k_{x2} becomes imaginary and the wavefunction decays exponentially for x>0 (in semiconductor 2). In this case:

$$|r|=1$$

and the electron is completely reflected from the hetero-interface

Handout 26

2D Nanostructures: Semiconductor Quantum Wells

In this lecture you will learn:

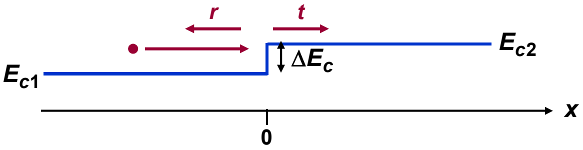
- Effective mass equation for heterojunctions
- Electron reflection and transmission at interfaces
- Semiconductor quantum wells
- Density of states in semiconductor quantum wells


Leo Esaki (1925-)
Nobel Prize


Nick Holonyak Jr. (1928-)


Charles H. Henry (1937-)

Transmission and Reflection at Heterojunctions



The solution is:

$$t = \frac{2}{1 + m_{x1}k_{x2}/m_{x2}k_{x1}} \qquad r = \frac{1 - m_{x1}k_{x2}/m_{x2}k_{x1}}{1 + m_{x1}k_{x2}/m_{x2}k_{x1}}$$

Where:

$$\frac{\hbar^2 k_{x2}^2}{2m_{x2}} = \frac{\hbar^2 k_{x1}^2}{2m_{x1}} - \Delta E_c - \frac{\hbar^2 k_y^2}{2}\left(\frac{1}{m_{y2}} - \frac{1}{m_{y1}}\right) - \frac{\hbar^2 k_z^2}{2}\left(\frac{1}{m_{z2}} - \frac{1}{m_{z1}}\right)$$

$$\Rightarrow \frac{\hbar^2 k_{x2}^2}{2m_{x2}} = \frac{\hbar^2 k_{x1}^2}{2m_{x1}} - \Delta V_{eff}\left(k_y, k_z\right)$$

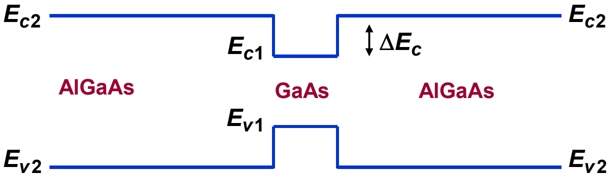
Special case: If the RHS in the above equation is negative, then k_{x2} becomes imaginary and the wavefunction decays exponentially for x>0 (in semiconductor 2). In this case:

$$|r| = 1$$

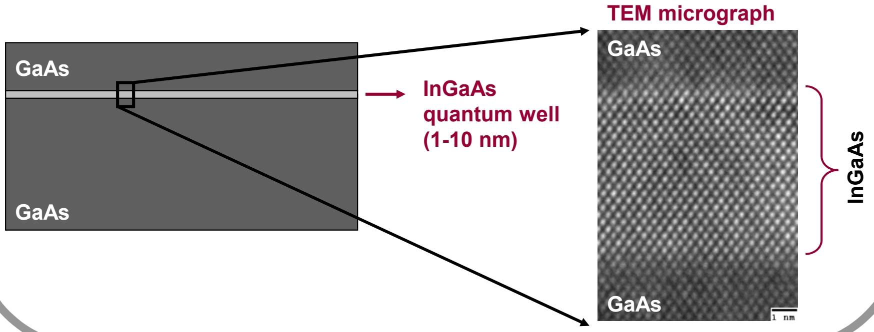
and the electron is completely reflected from the hetero-interface

Semiconductor Quantum Wells

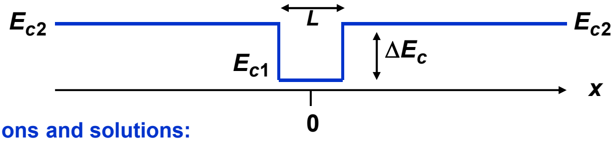
A thin (~1-10 nm) narrow bandgap material sandwiched between two wide bandgap materials



Semiconductor quantum wells can be composed of pretty much any semiconductor from the groups II, III, IV, V, and VI of the periodic table



Semiconductor Quantum Well: Conduction Band Solution



Assumptions and solutions:

$$E_{c1}(\vec{k}) = E_{c1} + \frac{\hbar^2 k^2}{2m_e}$$

$$\left[\hat{E}_{c1}(-i\nabla)\right]\phi_1(\vec{r}) = E\,\phi_1(\vec{r})$$

$$\Rightarrow \left[-\frac{\hbar^2\nabla^2}{2m_e} + E_{c1}\right]\phi_1(\vec{r}) = E\,\phi_1(\vec{r})$$

Symmetric

$$\phi_1(\vec{r}) = A\begin{cases} \cos(k_x x)\,e^{i(k_y y + k_z z)} \\ \sin(k_x x)\,e^{i(k_y y + k_z z)} \end{cases}$$

Anti-symmetric

$$E_{c2}(\vec{k}) = E_{c2} + \frac{\hbar^2 k^2}{2m_e}$$

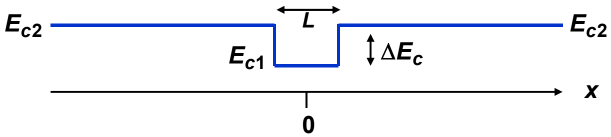
$$\left[\hat{E}_{c2}(-i\nabla)\right]\phi_2(\vec{r}) = E\,\phi_2(\vec{r})$$

$$\Rightarrow \left[-\frac{\hbar^2\nabla^2}{2m_e} + E_{c2}\right]\phi_2(\vec{r}) = E\,\phi_2(\vec{r})$$

$$\phi_2(\vec{r}) = B\begin{cases} e^{-\alpha(x-L/2)}\,e^{i(k_y y + k_z z)} \\ e^{-\alpha(x-L/2)}\,e^{i(k_y y + k_z z)} \end{cases} \quad x \ge L/2$$

$$\phi_2(\vec{r}) = B\begin{cases} e^{\alpha(x+L/2)}\,e^{i(k_y y + k_z z)} \\ -e^{\alpha(x+L/2)}\,e^{i(k_y y + k_z z)} \end{cases} \quad x \le -L/2$$

Semiconductor Quantum Well: Conduction Band Solution



Energy conservation condition:

$$E = E_{c1} + \frac{\hbar^2\left(k_x^2 + k_\parallel^2\right)}{2m_e} = E_{c2} + \frac{\hbar^2\left(-\alpha^2 + k_\parallel^2\right)}{2m_e}$$

$$\left\{ k_\parallel^2 = k_y^2 + k_z^2 \right.$$

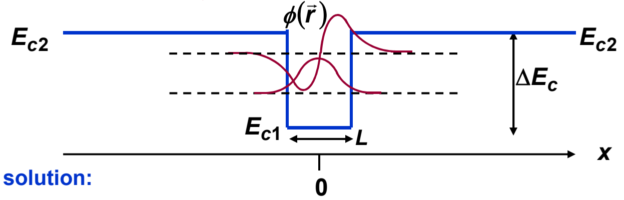
$$\Rightarrow \alpha = \sqrt{\frac{2m_e}{\hbar^2}\Delta E_c - k_x^2}$$

The two unknowns *A* and *B* can be found by imposing the continuity of the wavefunction condition and the probability current continuity condition to get the following conditions for the wavevector k_x:

$$\begin{cases} \tan\left(\frac{k_x L}{2}\right) = \frac{\alpha}{k_x} = \frac{\sqrt{\frac{2m_e}{\hbar^2}\Delta E_c - k_x^2}}{k_x} \\ -\cot\left(\frac{k_x L}{2}\right) = \frac{\alpha}{k_x} = \frac{\sqrt{\frac{2m_e}{\hbar^2}\Delta E_c - k_x^2}}{k_x} \end{cases}$$

Wavevector k_x cannot be arbitrary!
Its value must satisfy these transcendental equations

Semiconductor Quantum Well: Conduction Band Solution

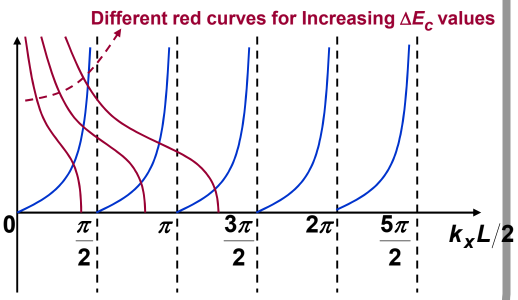


Graphical solution:

$$\begin{cases} \tan\left(\frac{k_x L}{2}\right) = \frac{\alpha}{k_x} = \frac{\sqrt{\frac{2m_e}{\hbar^2}\Delta E_c - k_x^2}}{k_x} \\ -\cot\left(\frac{k_x L}{2}\right) = \frac{\alpha}{k_x} = \frac{\sqrt{\frac{2m_e}{\hbar^2}\Delta E_c - k_x^2}}{k_x} \end{cases}$$

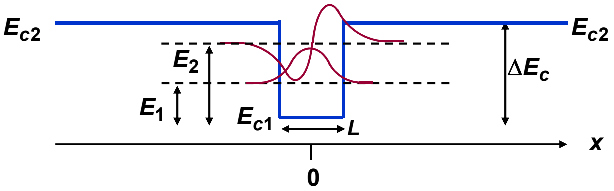
In the limit $\Delta E_c \to \infty$ the values of k_x are:

$$k_x = p\pi/L \quad (p = 1,2,3........$$


Different red curves for Increasing ΔE_c values

- Values of k_x are quantized
- Only a finite number of solutions are possible – depending on the value of ΔE_c

Electrons in Quantum Wells: A 2D Fermi Gas



Since values of k_x are quantized, the energy dispersion can be written as:

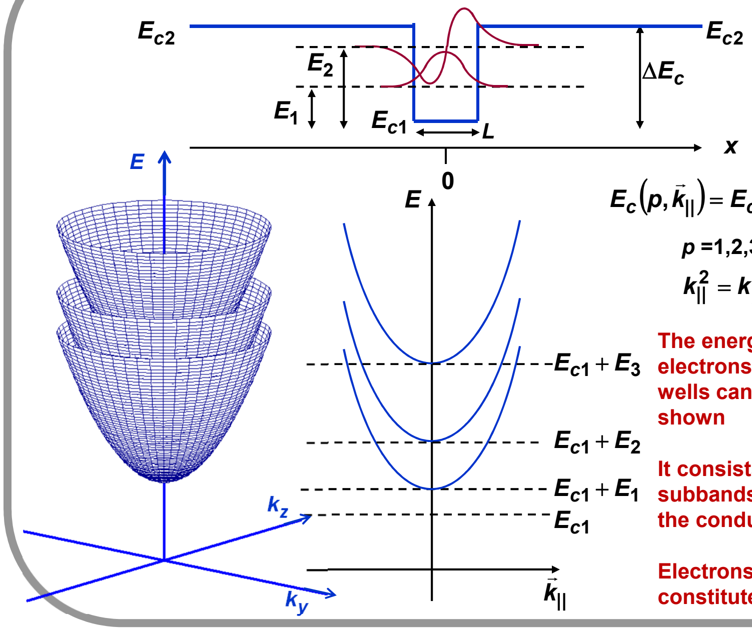
$$E = E_{c1} + \frac{\hbar^2 k_x^2}{2m_e} + \frac{\hbar^2 k_{||}^2}{2m_e} \qquad \left\{ k_{||}^2 = k_y^2 + k_z^2 \right.$$

$$= E_{c1} + E_p + \frac{\hbar^2 k_{||}^2}{2m_e} \longrightarrow \qquad p = 1,2,3……..$$

In the limit $\Delta E_c \to \infty$ the values of E_p are: $E_p = \frac{\hbar^2}{2m_e}\left(\frac{p\pi}{L}\right)^2$ **p = 1,2,3……..**

- **We say that the motion in the x-direction is quantized (the energy associated with that motion can only take a discrete set of values)**
- **The freedom of motion is now available only in the y and z directions (i.e. in directions that are in the plane of the quantum well)**
- **Electrons in the quantum well are essentially a two dimensional Fermi gas!**

Energy Subbands in Quantum Wells



$$E_c\left(p, \vec{k}_{||}\right) = E_{c1} + E_p + \frac{\hbar^2 k_{||}^2}{2m_e}$$

p =1,2,3……..

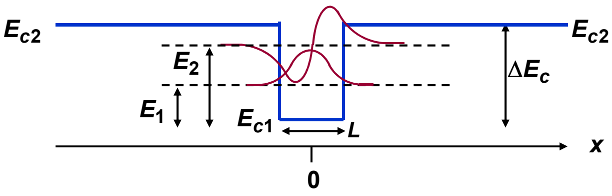
$$k_{||}^2 = k_y^2 + k_z^2$$

The energy dispersion for electrons in the quantum wells can be plotted as shown

It consists of energy subbands (i.e. subbands of the conduction band)

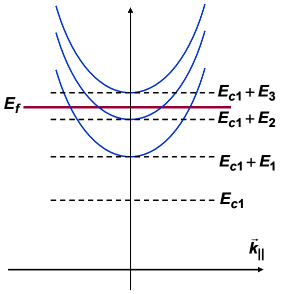
Electrons in each subband constitute a 2D Fermi gas

Density of States in Quantum Wells



Suppose, given a Fermi level position E_f, we need to find the electron density:
We can add the electron present in each subband as follows:

$$n = \sum_p 2 \times \int \frac{d^2\vec{k}_{||}}{(2\pi)^2} f\left(E_c\left(p,\vec{k}_{||}\right) - E_f\right)$$



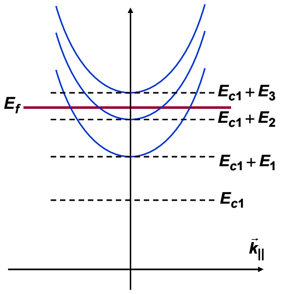
If we want to write the above as:

$$n = \int_{E_{c1}}^{\infty} dE \; g_{QW}(E) \, f(E - E_f)$$

Then the question is what is the density of states $g_{QW}(E)$?

Density of States in Quantum Wells

$$E_c\left(p,\vec{k}_{||}\right) = E_{c1} + E_p + \frac{\hbar^2 k_{||}^2}{2m_e}$$



Start from:

$$n = \sum_p 2 \times \int \frac{d^2\vec{k}_{||}}{(2\pi)^2} f\left(E_c\left(p,\vec{k}_{||}\right) - E_f\right)$$

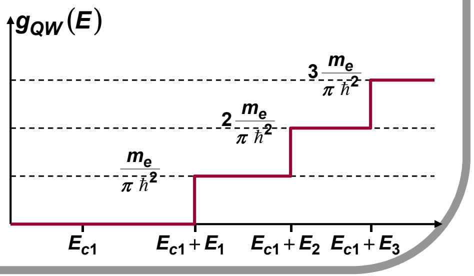
And convert the k-space integral to energy space:

$$n = \sum_p \int_{E_{c1}+E_p}^{\infty} dE \left(\frac{m_e}{\pi\hbar^2}\right) f(E - E_f)$$

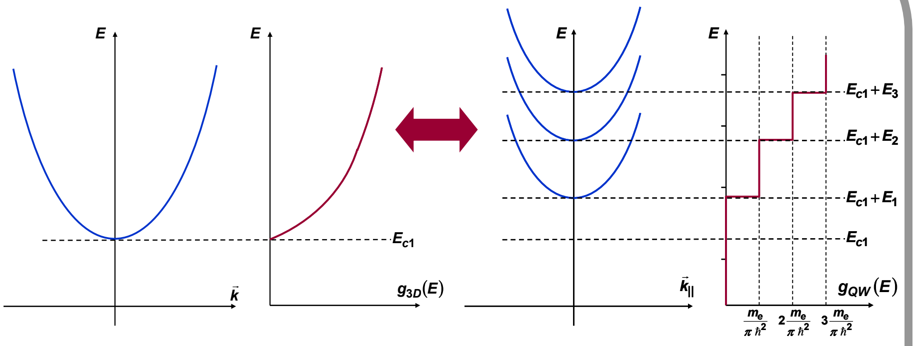
$$= \int_{E_{c1}}^{\infty} dE \; \sum_p \left(\frac{m_e}{\pi\hbar^2}\right) \theta\left(E - E_{c1} - E_p\right) f(E - E_f)$$

This implies:

$$g_{QW}(E) = \sum_p \left(\frac{m_e}{\pi\hbar^2}\right) \theta\left(E - E_{c1} - E_p\right)$$



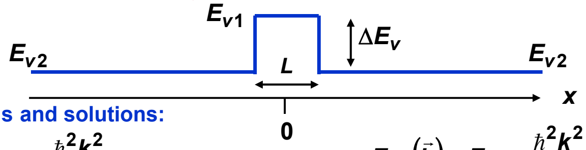
Density of States: From Bulk (3D) to QW (2D)



The modification of the density of states by quantum confinement in nanostructures can be used to:

i) Control and design custom energy levels for laser and optoelectronic applications
ii) Control and design carrier scattering rates, recombination rates, mobilities, for electronic applications
iii) Achieve ultra low-power electronic and optoelectronic devices

Semiconductor Quantum Well: Valence Band Solution



Assumptions and solutions:

$$E_{v1}(\vec{k}) = E_{v1} - \frac{\hbar^2 k^2}{2m_h}$$

$$\left[\hat{E}_{v1}(-i\nabla)\ \right]\phi_1(\vec{r}) = E\ \phi_1(\vec{r})$$

$$\Rightarrow \left[+\frac{\hbar^2\nabla^2}{2m_h} + E_{v1}\right]\phi_1(\vec{r}) = E\ \phi_1(\vec{r})$$

$$\Rightarrow \left[-\frac{\hbar^2\nabla^2}{2m_h} - E_{v1}\right]\phi_1(\vec{r}) = -E\ \phi_1(\vec{r})$$

Symmetric

$$\phi_1(\vec{r}) = A\begin{cases}\cos(k_x x)e^{i(k_y y + k_z z)} \\ \sin(k_x x)e^{i(k_y y + k_z z)}\end{cases}$$

Anti-symmetric

$$E_{v2}(\vec{k}) = E_{v2} - \frac{\hbar^2 k^2}{2m_v}$$

$$\left[\hat{E}_{v2}(-i\nabla)\ \right]\phi_2(\vec{r}) = E\ \phi_2(\vec{r})$$

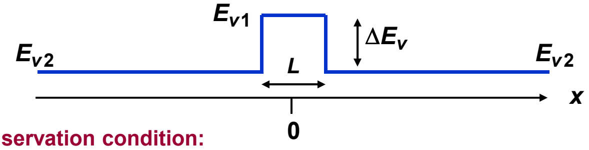
$$\Rightarrow \left[+\frac{\hbar^2\nabla^2}{2m_h} + E_{v2}\right]\phi_2(\vec{r}) = E\ \phi_2(\vec{r})$$

$$\Rightarrow \left[-\frac{\hbar^2\nabla^2}{2m_h} - E_{v2}\right]\phi_2(\vec{r}) = -E\ \phi_2(\vec{r})$$

$$\phi_2(\vec{r}) = B\begin{cases}e^{-\alpha\,(x-L/2)}\ e^{i(k_y y + k_z z)} \\ e^{-\alpha\,(x-L/2)}\ e^{i(k_y y + k_z z)}\end{cases} \qquad x \geq L/2$$

$$\phi_2(\vec{r}) = B\begin{cases}e^{\alpha\,(x+L/2)}\ e^{i(k_y y + k_z z)} \\ -\,e^{\alpha\,(x+L/2)}\ e^{i(k_y y + k_z z)}\end{cases} \qquad x \leq -L/2$$

Semiconductor Quantum Well: Valence Band Solution



Energy conservation condition:

$$E = E_{v1} - \frac{\hbar^2\left(k_x^2 + k_\parallel^2\right)}{2mh} = E_{v2} - \frac{\hbar^2\left(-\alpha^2 + k_\parallel^2\right)}{2m_e}$$

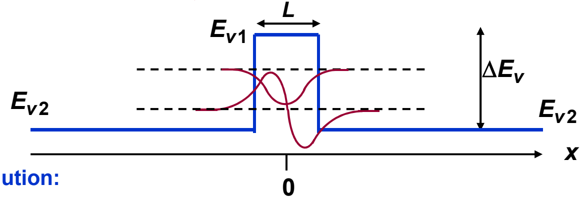
$$\Rightarrow \alpha = \sqrt{\frac{2m_h}{\hbar^2}\Delta E_v - k_x^2}$$

The two unknowns *A* and *B* can be found by imposing the continuity of the wavefunction condition and the probability current conservation condition to get the following conditions for the wavevector k_x:

$$\begin{cases} \tan\left(\frac{k_x L}{2}\right) = \frac{\alpha}{k_x} = \frac{\sqrt{\frac{2m_h}{\hbar^2}\Delta E_v - k_x^2}}{k_x} \\ -\cot\left(\frac{k_x L}{2}\right) = \frac{\alpha}{k_x} = \frac{\sqrt{\frac{2m_h}{\hbar^2}\Delta E_v - k_x^2}}{k_x} \end{cases}$$

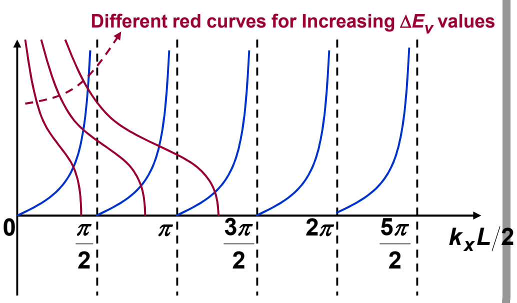
Wavevector k_x cannot be arbitrary!

Semiconductor Quantum Well: Valence Band Solution



Graphical solution:

$$\begin{cases} \tan\left(\frac{k_x L}{2}\right) = \frac{\alpha}{k_x} = \frac{\sqrt{\frac{2m_h}{\hbar^2}\Delta E_v - k_x^2}}{k_x} \\ -\cot\left(\frac{k_x L}{2}\right) = \frac{\alpha}{k_x} = \frac{\sqrt{\frac{2m_h}{\hbar^2}\Delta E_v - k_x^2}}{k_x} \end{cases}$$

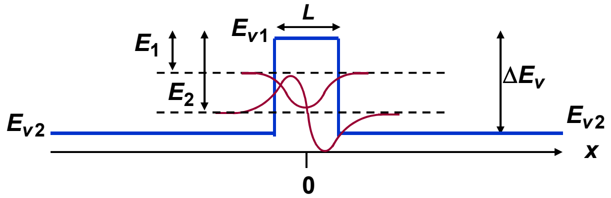


In the limit $\Delta E_v \rightarrow \infty$ the values of k_x are:

$$k_x = p\pi/L \quad (p = 1,2,3\ldots\ldots$$

- Values of k_x are quantized
- Only a finite number of solutions are possible – depending on the value of ΔE_v

Semiconductor Quantum Wells: A 2D Fermi Gas



Since values of k_x are quantized, the energy dispersion can be written as:

$$E = E_{v1} - \frac{\hbar^2 k_x^2}{2m_h} - \frac{\hbar^2 k_{||}^2}{2m_h}$$

$$= E_{v1} - E_p - \frac{\hbar^2 k_{||}^2}{2m_h} \longrightarrow \quad p = 1,2,3\ldots\ldots$$

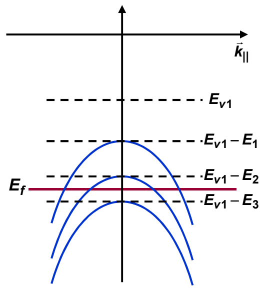
Light-hole/heavy-hole degeneracy breaks!

In the limit $\Delta E_v \to \infty$ the values of E_p are: $E_p = \frac{\hbar^2}{2m_h}\left(\frac{p\pi}{L}\right)^2 \qquad p = 1,2,3\ldots\ldots$

- We say that the motion in the x-direction is quantized (the energy associated with that motion can only take a discrete set of values)
- The freedom of motion is now available only in the y and z directions (i.e. in directions that are in the plane of the quantum well)
- Electrons (or holes) in the quantum well are essentially a two dimensional Fermi gas!

Density of States in Quantum Wells: Valence Band

$$E_v\left(p,\vec{k}_{||}\right) = E_{v1} - E_p - \frac{\hbar^2 k_{||}^2}{2m_h}$$



Start from:

$$p = \sum_p 2 \times \int \frac{d^2\vec{k}_{||}}{(2\pi)^2}\left[1 - f\left(E_v\left(p,\vec{k}_{||}\right) - E_f\right)\right]$$

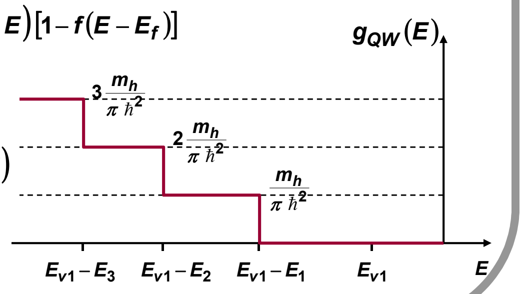
And convert the k-space integral to energy space:

$$p = \sum_p \int_{-\infty}^{E_{v1}-E_p} dE \left(\frac{m_h}{\pi\hbar^2}\right)\left[1 - f(E - E_f)\right]$$

$$= \int_{-\infty}^{E_{v1}} dE \sum_p \left(\frac{m_h}{\pi\hbar^2}\right)\theta\left(E_{v1} - E_p - E\right)\left[1 - f(E - E_f)\right]$$

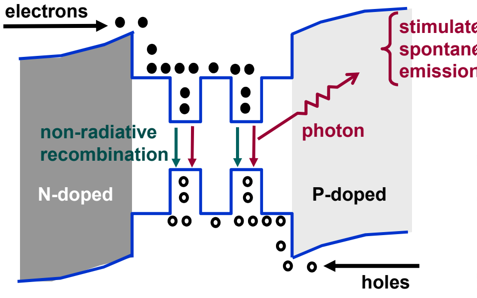
This implies:

$$g_{QW}(E) = \sum_p \left(\frac{m_h}{\pi\hbar^2}\right)\theta\left(E_{v1} - E_p - E\right)$$

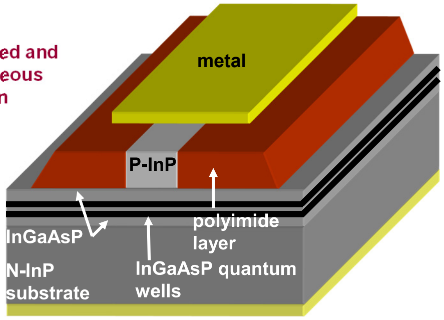


Example (Photonics): Semiconductor Quantum Well Lasers

A quantum well laser (band diagram)

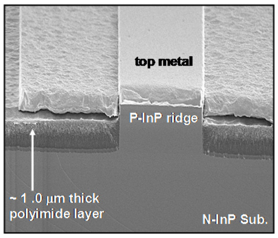


A ridge waveguide laser structure



Some advantages of quantum wells for laser applications:

- Low laser threshold currents due to reduced density of states
- High speed laser current modulation due to large differential gain
- Ability to control emission wavelength via quantum size effect



All lasers used in fiber optical communication systems are semiconductor quantum well lasers

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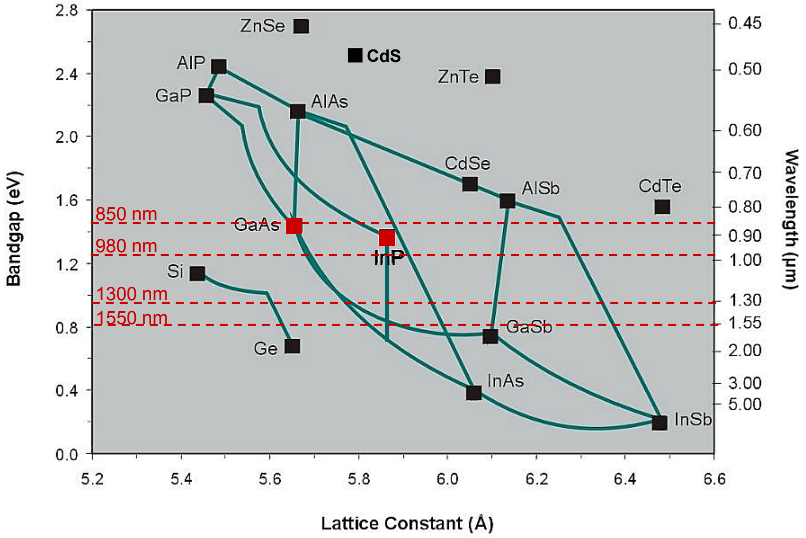
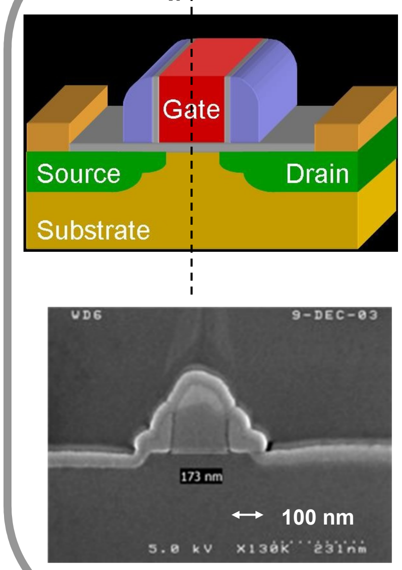
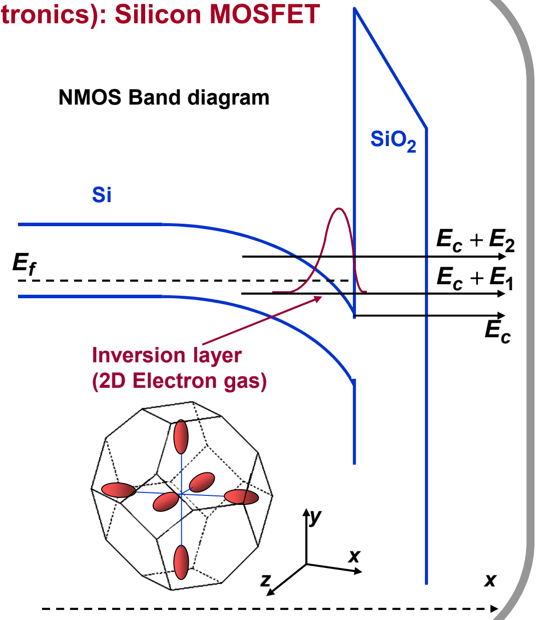
Compound Semiconductors and their Alloys: Groups IV, III-V, II-VI



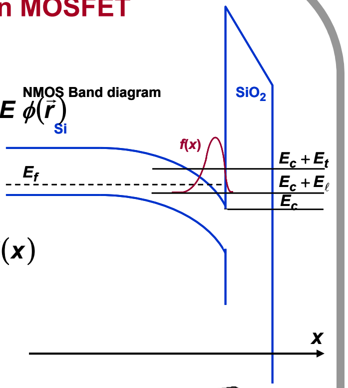
Example (Electronics): Silicon MOSFET



A 50 nm gate MOS transistor



Example (Electronics): Silicon MOSFET



For minima 1 and 2:

$$\left[-\frac{\hbar^2}{2m_\ell}\frac{\partial^2}{\partial x^2}-\frac{\hbar^2}{2m_t}\frac{\partial^2}{\partial y^2}-\frac{\hbar^2}{2m_t}\frac{\partial^2}{\partial z^2}+E_c+\vec{U}(\vec{r})\right]\phi(\vec{r})=E\,\phi(\vec{r})$$

$$\phi(\vec{r})=f(x)e^{ik_y z+ik_z z}$$

$$\left[-\frac{\hbar^2}{2m_\ell}\frac{\partial^2}{\partial x^2}+U(\vec{r})\right]f(x)=\left(E-E_c-\frac{\hbar^2k_y^2}{2m_t}--\frac{\hbar^2k_z^2}{2m_t}\right)f(x)$$

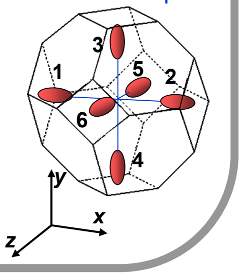
$$\Rightarrow E=E_c+E_\ell+\frac{\hbar^2k_y^2}{2m_t}+\frac{\hbar^2k_z^2}{2m_t}$$

For minima 3 and 4:

$$\phi(\vec{r})=g(x)e^{ik_y z+ik_z z}$$

$$\left[-\frac{\hbar^2}{2m_t}\frac{\partial^2}{\partial x^2}+U(\vec{r})\right]g(x)=\left(E-E_c-\frac{\hbar^2k_y^2}{2m_\ell}--\frac{\hbar^2k_z^2}{2m_t}\right)g(x)$$

$$\Rightarrow E=E_c+E_t+\frac{\hbar^2k_y^2}{2m_\ell}+\frac{\hbar^2k_z^2}{2m_t}\quad\longrightarrow\quad\left\{\,E_t>E_\ell\right.$$



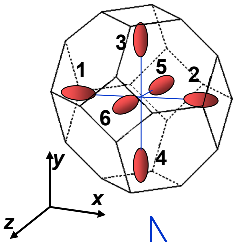
Example (Electronics): Silicon MOSFET

For minima 5 and 6:

$$\phi(\vec{r}) = g(x)\, e^{ik_y z + ik_z z}$$

$$\left[-\frac{\hbar^2}{2m_t}\frac{\partial^2}{\partial x^2} + U(\vec{r})\right] g(x) = \left(E - E_c - \frac{\hbar^2 k_y^2}{2m_t} - - \frac{\hbar^2 k_z^2}{2m_\ell}\right) g(x)$$

$$\Rightarrow E = E_c + E_t + \frac{\hbar^2 k_y^2}{2m_t} + \frac{\hbar^2 k_z^2}{2m_\ell} \longrightarrow \left\{ E_t > E\ell \right.$$

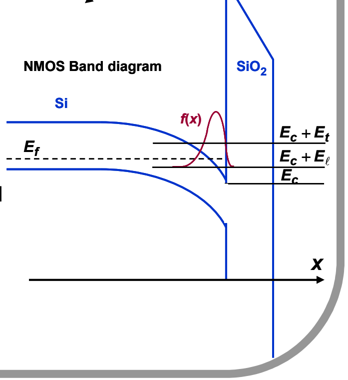


Advantage of Quantum Confinement and Quantization:

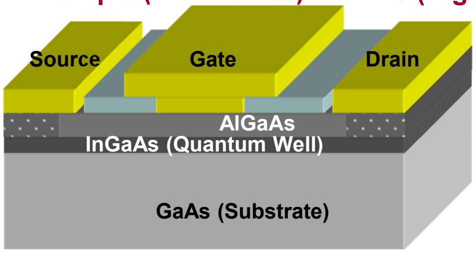
- As a result of quantum confinement the degeneracy among the states in the 6 valleys or pockets is lifted

- Most of the electrons (at least at low temperatures) occupy the two valleys (1 & 2) with the lower quantized energy (i.e. E_ℓ)

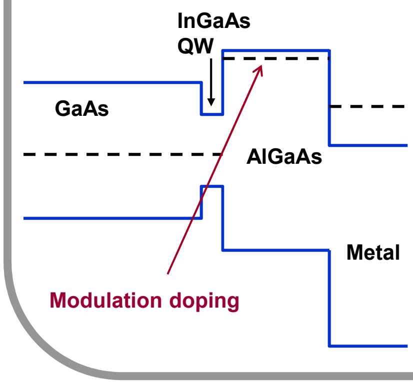
- Electrons in the lower energy valleys have a lighter mass (i.e. m_t) in the directions parallel to the interface (*y-z* plane) and, therefore, a higher mobility



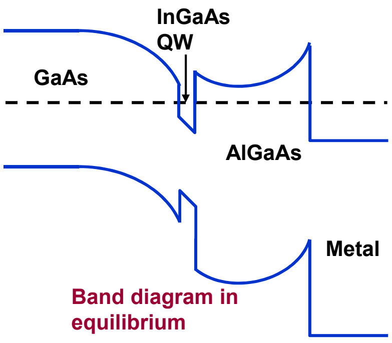
Example (Electronics): HEMTs (High Electron Mobility Transistors)



The HEMT operates like a MOS transistor:
The application of a positive or negative bias on the gate can increase or decrease the electron density in the quantum well channel thereby changing the current density



Modulation doping



Band diagram in equilibrium

Handout 27

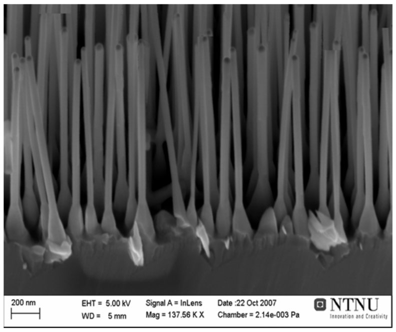
1D and 0D Nanostructures: Semiconductor Quantum Wires and Quantum Dots

In this lecture you will learn:

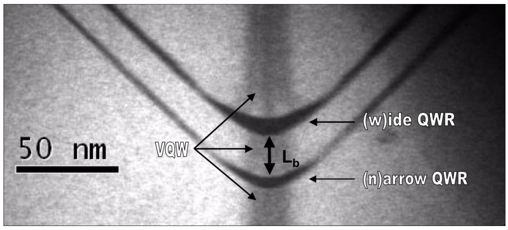
- Semiconductor quantum wires and dots
- Density of states in semiconductor quantum wires and dots

Charles H. Henry (1937-)

1D Nanostructures: Semiconductor Quantum Wires

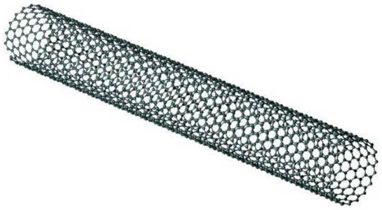


SEM of 20 nm diameter GaAs nanowires

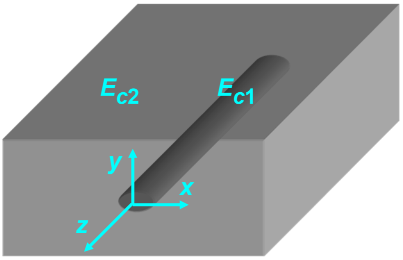


GaAs/AlGaAs quantum wires grown by electron waveguide confinement

A carbon nanotube (rolled up graphene):



Semiconductor Quantum Wires



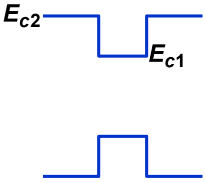
$$\Delta E_c = E_{c2} - E_{c1}$$

Inside:

$$E_{c1}(\vec{k}) = E_{c1} + \frac{\hbar^2 k^2}{2m_e}$$

Outside:

$$E_{c2}(\vec{k}) = E_{c2} + \frac{\hbar^2 k^2}{2m_e}$$



Inside:

$$\left[\hat{E}_{c1}(-i\nabla)\ \right]\phi_1(\vec{r}) = E\,\phi_1(\vec{r}) \quad\Rightarrow\quad \left[E_{c1} - \frac{\hbar^2\nabla^2}{2m_e}\right]\phi_1(\vec{r}) = E\,\phi_1(\vec{r})$$

Outside:

$$\left[\hat{E}_{c2}(-i\nabla)\ \right]\phi_2(\vec{r}) = E\,\phi_2(\vec{r}) \quad\Rightarrow\quad \left[E_{c2} - \frac{\hbar^2\nabla^2}{2m_e}\right]\phi_2(\vec{r}) = E\,\phi_2(\vec{r})$$

Assumed solutions:

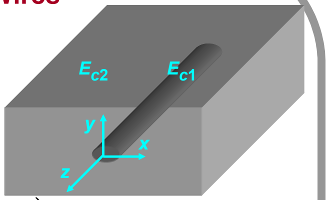
Inside:

$$\phi_1(\vec{r}) = A\,f_1(x,y)\,e^{i\,k_z\,z}$$

Outside:

$$\phi_2(\vec{r}) = A\,f_2(x,y)\,e^{i\,k_z\,z}$$

Semiconductor Quantum Wires



Inside:

Plug in the assumed solution:

$$\left[E_{c1} - \frac{\hbar^2\nabla^2}{2m_e}\right] f_1(x,y)\,e^{ik_z z} = E\,f_1(x,y)\,e^{ik_z z}$$

$$\Rightarrow \left[E_{c1} + \frac{\hbar^2 k_z^2}{2m_e} - \frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial y^2}\right] f_1(x,y) = E\,f_1(x,y)$$

$$\Rightarrow \left[-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial y^2}\right] f_1(x,y) = \left(E - E_{c1} - \frac{\hbar^2 k_z^2}{2m_e}\right) f_1(x,y)$$

Outside:

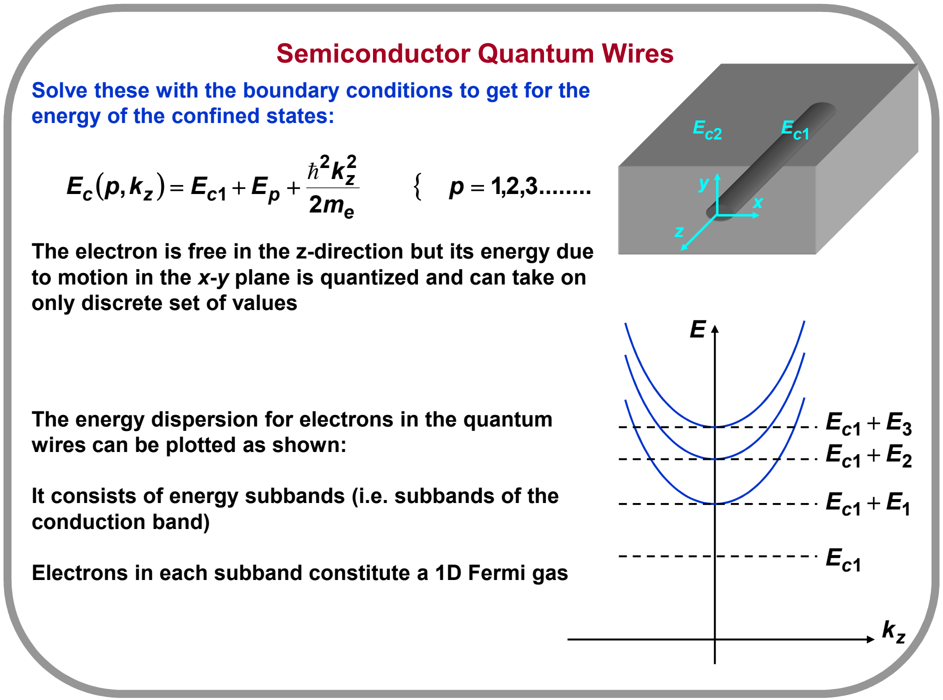
$$\left[-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial y^2}\right] f_2(x,y) = \left(E - E_{c2} - \frac{\hbar^2 k_z^2}{2m_e}\right) f_2(x,y)$$

Boundary conditions at the inside-outside boundary:

$$f_1(x,y)\big|_{\text{boundary}} = f_2(x,y)\big|_{\text{boundary}}$$

$$\frac{1}{m_e}\nabla f_1(x,y).\hat{n}\,\Big|_{\text{boundary}} = \frac{1}{m_e}\nabla f_2(x,y).\hat{n}\,\Big|_{\text{boundary}}$$

$\left\{\ \hat{n}\right.$ is the unit vector normal to the boundary



Semiconductor Quantum Wires

Solve these with the boundary conditions to get for the energy of the confined states:

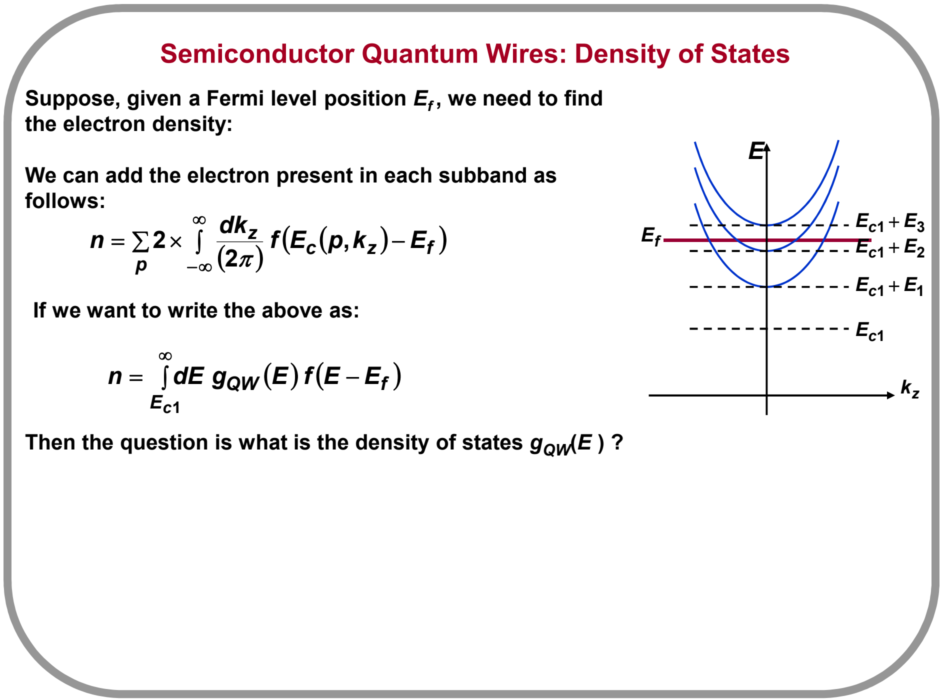
$$E_c(p,k_z)=E_{c1}+E_p+\frac{\hbar^2k_z^2}{2m_e} \qquad \{ \quad p=1,2,3........$$

The electron is free in the z-direction but its energy due to motion in the *x-y* plane is quantized and can take on only discrete set of values

The energy dispersion for electrons in the quantum wires can be plotted as shown:

It consists of energy subbands (i.e. subbands of the conduction band)

Electrons in each subband constitute a 1D Fermi gas



Semiconductor Quantum Wires: Density of States

Suppose, given a Fermi level position E_f, we need to find the electron density:

We can add the electron present in each subband as follows:

$$n=\sum_p 2\times\int_{-\infty}^{\infty}\frac{dk_z}{(2\pi)}\,f\left(E_c(p,k_z)-E_f\right)$$

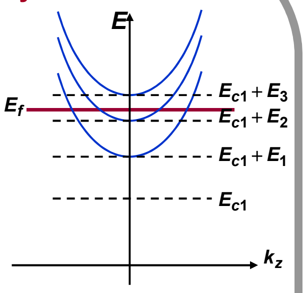
If we want to write the above as:

$$n=\int_{E_{c1}}^{\infty}dE\;g_{QW}(E)\,f(E-E_f)$$

Then the question is what is the density of states $g_{QW}(E)$?

Semiconductor Quantum Wires: Density of States

$$E_c(p,k_z) = E_{c1} + E_p + \frac{\hbar^2 k_z^2}{2m_e}$$



Start from:

$$n = \sum_p 2\times \int_{-\infty}^{\infty} \frac{dk_z}{(2\pi)}\, f\left(E_c(p,k_z)-E_f\right)$$

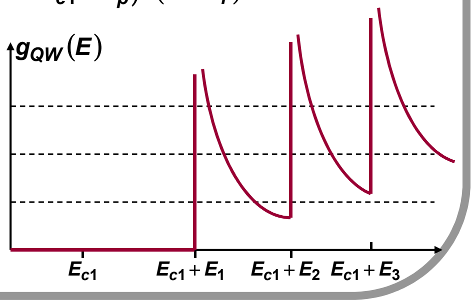
And convert the k-space integral to energy space:

$$n = \sum_p \int_{E_{c1}+E_p}^{\infty} dE \sqrt{\frac{2m_e}{\pi^2\hbar^2\left(E-E_{c1}-E_p\right)}}\, f(E-E_f)$$

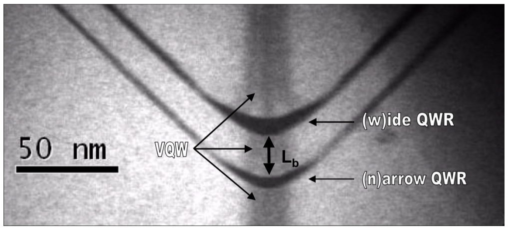
$$= \int_{E_{c1}}^{\infty} dE \sum_p \sqrt{\frac{2m_e}{\pi^2\hbar^2\left(E-E_{c1}-E_p\right)}}\, \theta\left(E-E_{c1}-E_p\right) f(E-E_f)$$

This implies:

$$g_{QW}(E) = \sum_p \sqrt{\frac{2m_e}{\pi^2\hbar^2\left(E-E_{c1}-E_p\right)}} \times \theta\left(E-E_{c1}-E_p\right)$$

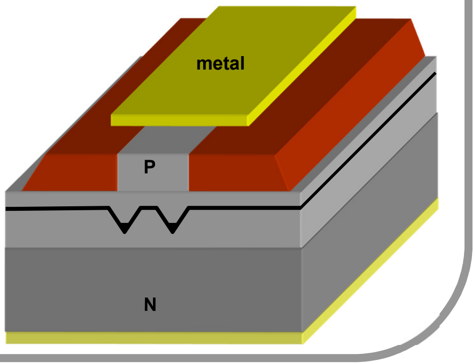


Semiconductor Quantum Wire Lasers

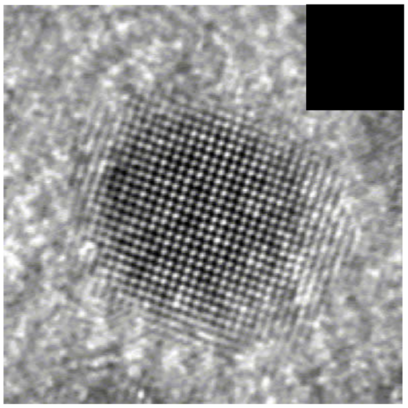


GaAs/AlGaAs quantum wires grown by electron waveguide confinement

A Ridge Waveguide Laser Structure

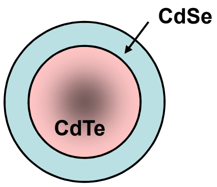


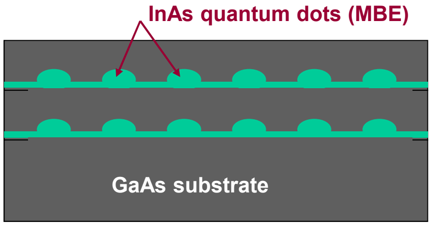
0D Nanostructures: Semiconductor Quantum Dots


[redacted]

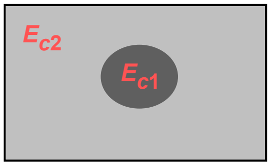
TEM of a PbS quantum dot

Core-shell colloidal quantum dots (Mostly II-VI semiconductors)

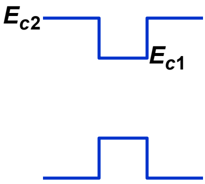




Semiconductor Quantum Dots



$$\Delta E_c = E_{c2} - E_{c1}$$



Inside:

$$E_{c1}(\vec{k}) = E_{c1} + \frac{\hbar^2 k^2}{2m_e}$$

Outside:

$$E_{c2}(\vec{k}) = E_{c2} + \frac{\hbar^2 k^2}{2m_e}$$

Inside:

$$\left[\hat{E}_{c1}(-i\nabla)\right]\phi_1(\vec{r}) = E\,\phi_1(\vec{r}) \quad \Rightarrow \quad \left[E_{c1} - \frac{\hbar^2\nabla^2}{2m_e}\right]\phi_1(\vec{r}) = E\,\phi_1(\vec{r})$$

Outside:

$$\left[\hat{E}_{c2}(-i\nabla)\right]\phi_2(\vec{r}) = E\,\phi_2(\vec{r}) \quad \Rightarrow \quad \left[E_{c2} - \frac{\hbar^2\nabla^2}{2m_e}\right]\phi_2(\vec{r}) = E\,\phi_2(\vec{r})$$

Assumed solutions:

Inside:

$$\phi_1(\vec{r}) = A\,f_1(x,y,z)$$

Outside:

$$\phi_2(\vec{r}) = A\,f_2(x,y,z)$$

Semiconductor Quantum Dots

Boundary conditions at the inside-outside boundary:

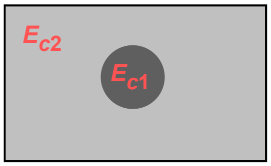
$$f_1(x,y,z)\big|_{\text{boundary}} = f_2(x,y,z)\big|_{\text{boundary}}$$

$$\frac{1}{m_e}\nabla f_1(x,y,z).\hat{n}\,\Big|_{\text{boundary}} = \frac{1}{m_e}\nabla f_2(x,y,z).\hat{n}\,\Big|_{\text{boundary}}$$

$\hat{n}$ is the unit vector normal to the boundary

Solve these with the boundary conditions to get for the energy of the confined states:

$$E_c(p) = E_{c1} + E_p \quad \{ \quad p = 1,2,3........$$



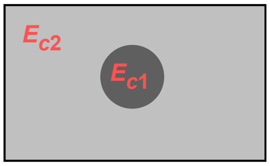
In the limit $\Delta E_c \rightarrow \infty$ the lowest energy level value for a spherical dot of radius R is:

$$E_1 = \frac{\hbar^2}{2m_e}\left(\frac{\pi}{R}\right)^2$$

The electron is not free in any direction and its energy due to motion is quantized and can take on only discrete set of values

---

Semiconductor Quantum Dots: Density of States



Suppose, given a Fermi level position E_f, we need to find the electron number N:

We can add the electron present in each level as follows:

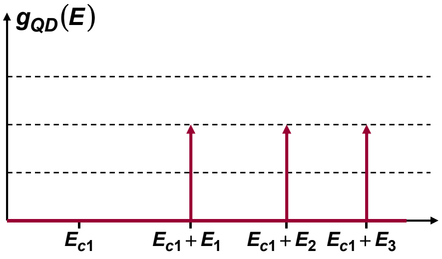
$$N = \sum_p 2 \times f(E_c(p) - E_f)$$

If we want to write the above as:

$$N = \int_{E_{c1}}^{\infty} dE\; g_{QD}(E)\, f(E - E_f)$$

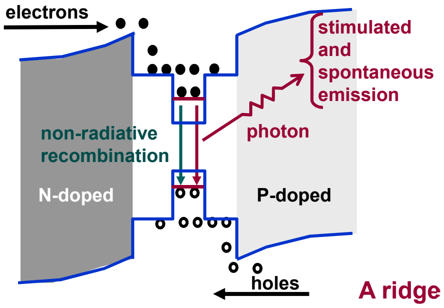
Then the question is what is the density of states $g_{QW}(E)$?

$$g_{QD}(E) = 2 \times \sum_p \delta(E - E_c(p))$$



Because the dot is such a small system, at many times concept of a Fermi level may not even be appropriate!!

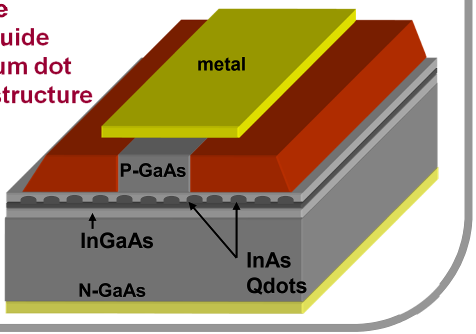
Semiconductor Quantum Dot Lasers (III-V Materials)



Some advantages of 0D quantum dots for laser applications:

- Ultralow laser threshold currents due to reduced density of states
- High speed laser current modulation due to large differential gain
- Small wavelength chirp in direct current modulation
- Ability to control emission wavelength via quantum size effect

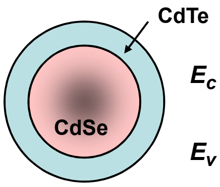
A ridge waveguide quantum dot laser structure



- Only 2 electrons can occupy a single quantum dot energy level in the conduction band

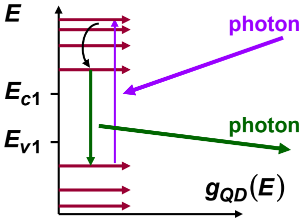
- Only 2 holes can occupy a single quantum dot energy level in the valence band

Colloidal Quantum Dots: Wonders of Quantum Size Effect



$$E_c(1) \approx E_c + \frac{\hbar^2}{2m_e}\left(\frac{\pi}{R}\right)^2$$

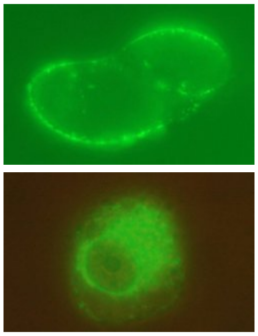
$$E_v(1) \approx E_v - \frac{\hbar^2}{2m_h}\left(\frac{\pi}{R}\right)$$



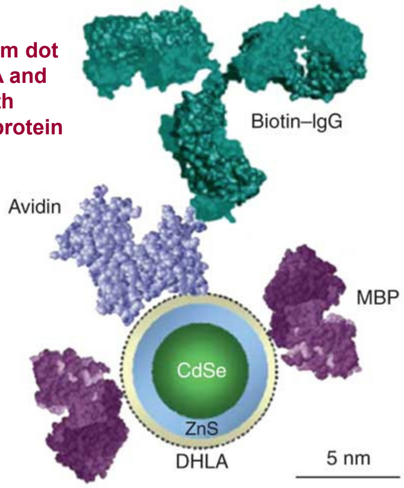
Photoluminescence from CdSe/ZnS (core-shell colloidal) quantum dots of different sizes (~2-6 nm) pumped with the same laser

Photoluminescence from CdTe/CdSe (core-shell colloidal) quantum dots of different sizes

Quantum Dots: Biology Applications



CdSe/ZnS quqntum dot coated with DHLA and functionalized with maltose binding protein (MBP) and Avidin

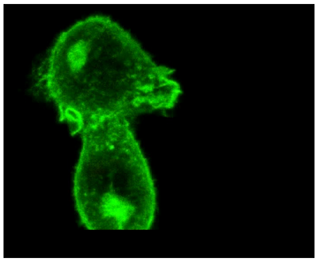


Motion of quantum-dot-attached-RNA into cells monitored by the luminescence (the quantum dots used are CdSe (core) and ZnS (shell)

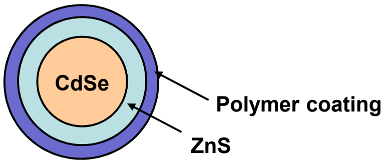
Quantum Dots: Biology Applications

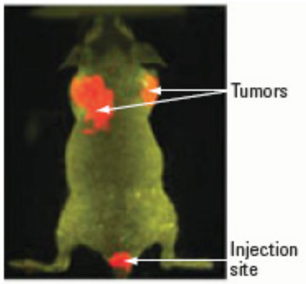
Invitro microscopy of the binding of EGF to erbB1

erB1 bound to eGFP (enhanced green fluorescent protein)
EGF (epidermal growth factor) bound to quantum dot
Movie shows binding of EGF tagged with fluorescent quantum dots to erB1 tagged with the green fluorescent protein



Nat. Biotechnol., 22, 198-203 (2004)

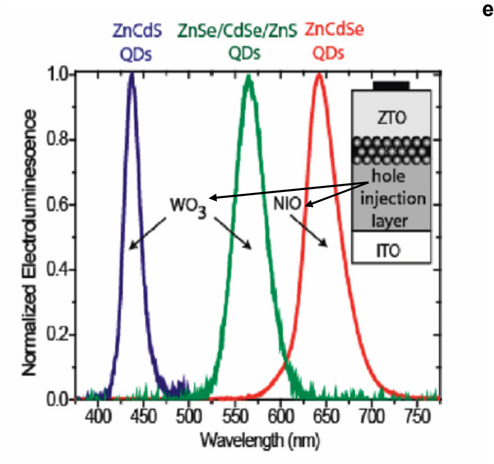




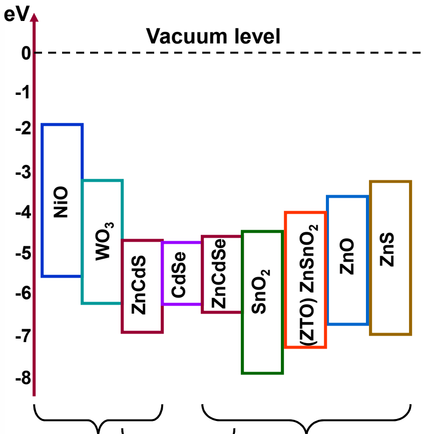
Imaging of antibody (PSMA) coated quantum dots targeting cancer tumors cells

Nat. Biotechnol., 22, 969 (2004)

Colloidal Quantum Dot Electrically Pumped LEDs



Bulovic et. al. (2010)



Possible hole injection layers

Quantum dot (QD)

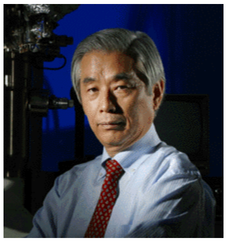
Possible electron injection layers

Handout 31

Carbon Nanotubes: Physics and Applications

In this lecture you will learn:

- Carbon nanotubes
- Energy subbands in nanotubes
- Device applications of nanotubes



Sumio Iijima
(Meijo University, Japan))

Paul L. McEuen
(Cornell University)

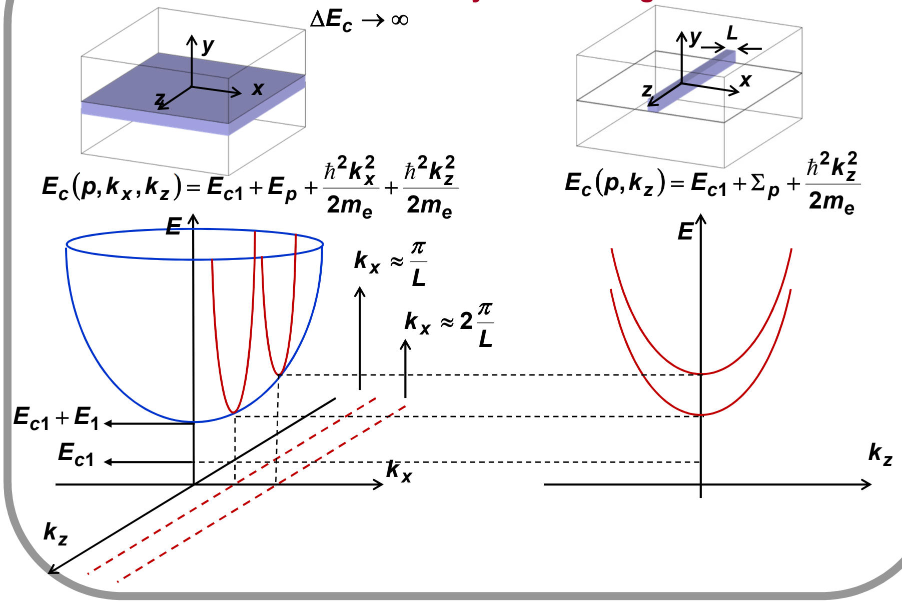
Mildred Dresselhaus
(MIT)

Another Look at Quantum Confinement: Going to Reduced Dimensions by Band Slicing

Quantum Well

Quantum Wire

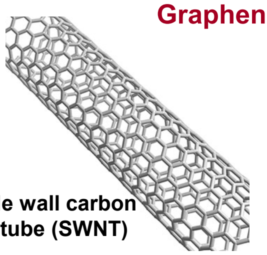
$\Delta E_c \rightarrow \infty$



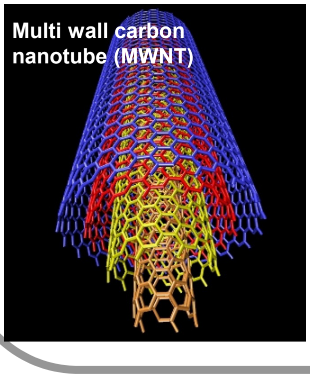
$$E_c(p,k_x,k_z) = E_{c1} + E_p + \frac{\hbar^2 k_x^2}{2m_e} + \frac{\hbar^2 k_z^2}{2m_e}$$

$$E_c(p,k_z) = E_{c1} + \Sigma_p + \frac{\hbar^2 k_z^2}{2m_e}$$

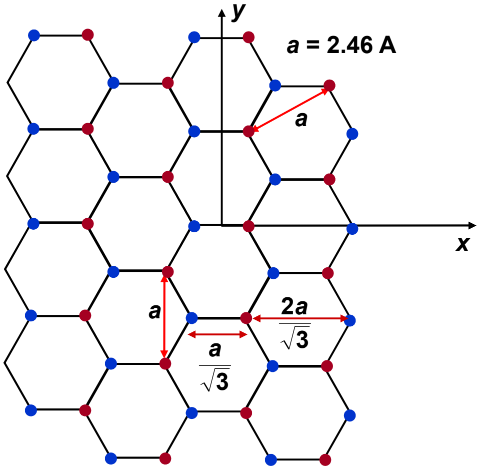
Graphene and Carbon Nanotubes



Single wall carbon nanotube (SWNT)



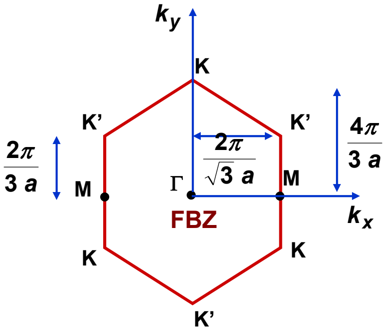
Multi wall carbon nanotube (MWNT)

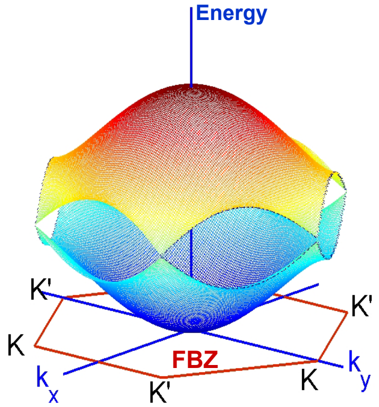


- Carbon nanotubes are rolled up graphene sheets
- Graphene sheets can be rolled in many different ways to yield different kinds of nanotubes with very different properties

Graphene: π-Energy Bands

Recall the energy bands of graphene:



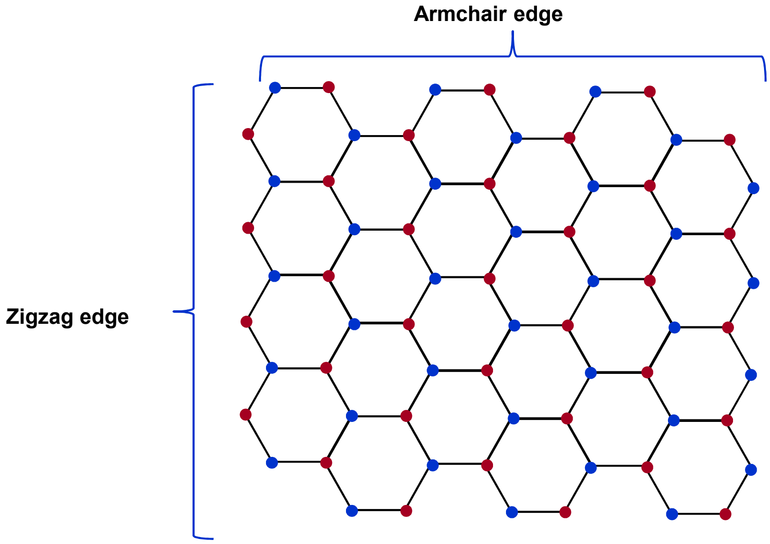


$$E(\vec{k}) = E_p \pm V_{pp\pi} \left| f(\vec{k}) \right|$$

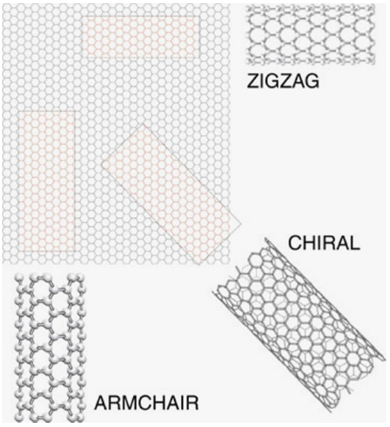
$$f(\vec{k}) = e^{i\vec{k}.\vec{n}_1} + e^{i\vec{k}.\vec{n}_2} + e^{i\vec{k}.\vec{n}_3}$$

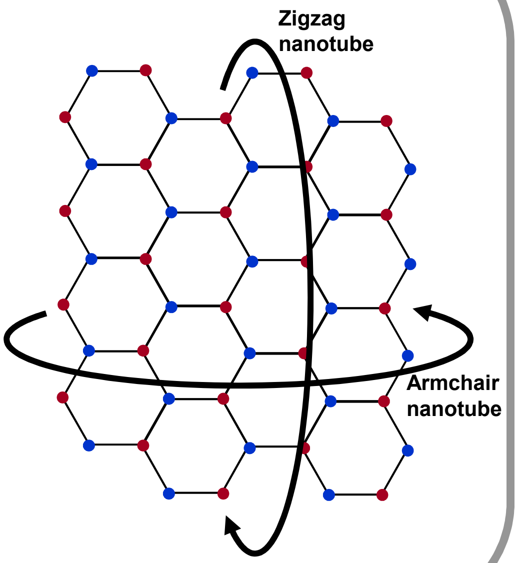
$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}.\vec{r}} u_{n,\vec{k}}(\vec{r}) = e^{i(k_x x + k_y y)} u_{n,\vec{k}}(\vec{r})$$

Graphene Edges

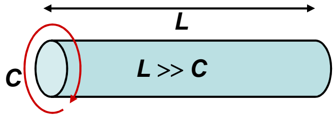


Rolling Up Graphene





Zigzag Nanotubes: Crystal Momentum Quantization



Circumference of the zigzag nanotube:

$$C = ma \qquad \{m = 2,3,4.......$$

Boundary condition on the wavefunction:

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i(k_x x + k_y y)} u_{n,\vec{k}}(\vec{r})$$

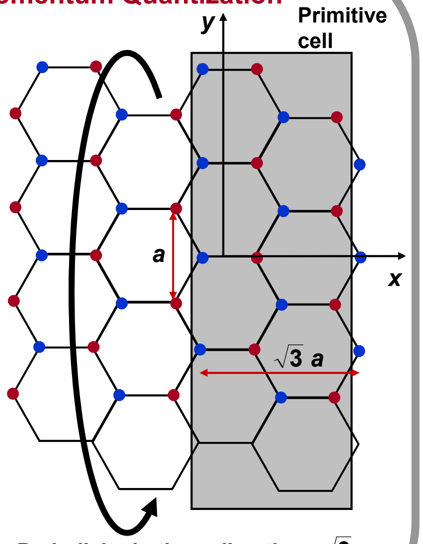
The wavefunction must be continuous along the circumference after one complete roundtrip:

$$\psi_{n,\vec{k}}(x, y + C, z) = \psi_{n,\vec{k}}(x, y, z)$$

$$\Rightarrow \quad e^{ik_y C} = 1$$

$$\Rightarrow \quad k_y = \frac{2\pi\, n}{C} \qquad \{n = \text{integer, range?}$$

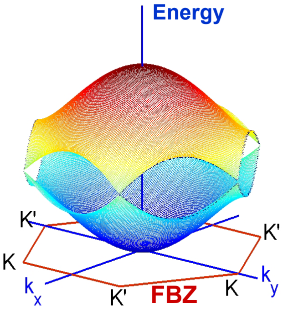
The crystal momentum in the y-direction (in direction transverse to the nanotube length) has quantized values



Periodicity in the x-direction: $\sqrt{3}\,a$

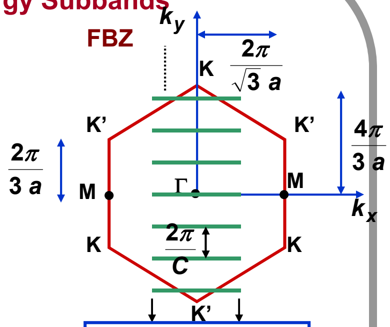
Number of atoms in the primitive cell: $4m$

Zigzag Nanotubes: 1D Energy Subbands



Obtain all the 1D subbands of the nanotube by taking cross sections of the 2D energy band dispersion of graphene

$$E(\vec{k}) = E_p \pm V_{pp\pi} \left| f(\vec{k}) \right|$$



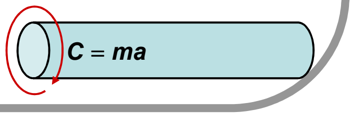
$$\boxed{-\frac{\pi}{\sqrt{3}a} < k_x \le \frac{\pi}{\sqrt{3}a}}$$

One will obtain two subbands (one from the conduction and one from the valence band) for each quantized value of k_y

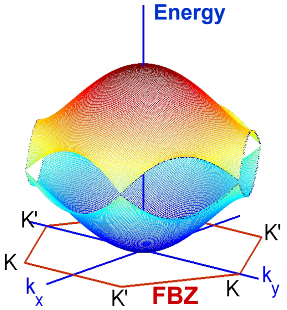
But number of bands = number of orbitals per primitive cell = $4m$

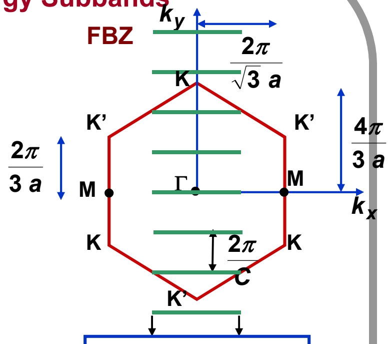
$\Rightarrow$ Number of distinct quantized k_y values must equal $2m$

$$\boxed{k_y = \frac{2\pi\, n}{C} \qquad \{n = -(m-1), ... -1, 0, +1, ..., m}$$

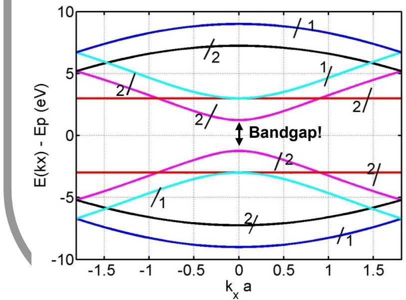


Zigzag Nanotubes: 1D Energy Subbands





$$-\frac{\pi}{\sqrt{3}a} < k_x \le \frac{\pi}{\sqrt{3}a}$$



Suppose $C = 4a$ (i.e. $m = 4$)

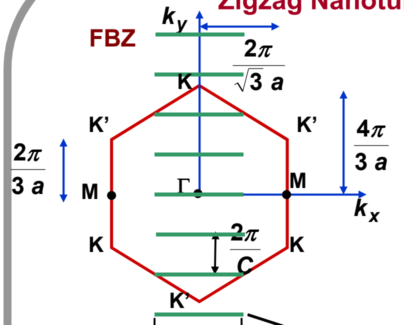
$$\Rightarrow \quad k_y = \frac{2\pi\, n}{C} = \frac{\pi\, n}{2a} \quad \{ n = -3,-2,-1,0,1,2,3,4$$

$$E(\vec{k}) = E_p \pm V_{pp\pi}\left|f(\vec{k})\right| \longrightarrow$$ 16 1D subbands total

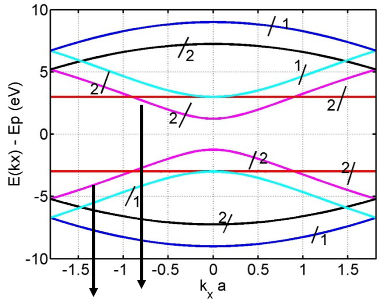
Lower 8 subbands will be completely full at T=0K

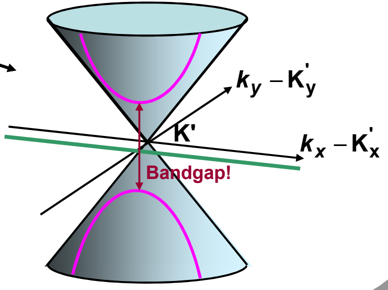
The nanotube is a semiconductor!

Zigzag Nanotubes: 1D Energy Subbands



$$-\frac{\pi}{\sqrt{3}a} < k_x \le \frac{\pi}{\sqrt{3}a}$$



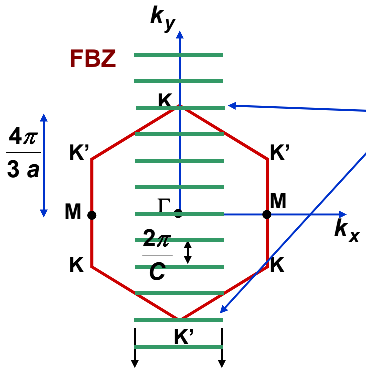


The bandgap appears because the quantized k_y value is such that the "green line" misses the K-point

When: $R >> a$ (R = radius of nanotube)

$$E_g \approx \frac{2\hbar v}{3R} \propto \frac{1}{R}$$

Zigzag Nanotubes: Semiconductor and Metallic Behavior

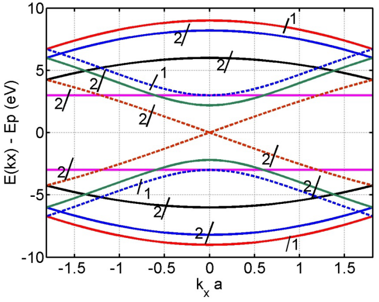


$$-\frac{\pi}{\sqrt{3}a} < k_x \le \frac{\pi}{\sqrt{3}a}$$

Suppose $C = 6a$ (i.e. $m = 6$)

$$\Rightarrow \quad k_y = \frac{2\pi\, n}{C} = \frac{\pi\, n}{3a} \quad \{n = -5, \ldots -1, 0, 1, \ldots 6$$

Two lines for $n=\pm 4$ pass through the Dirac points



24 1D subbands total, 12 lower ones will be completely filled at T=0K, and there is no bandgap!

- All zigzag nanotubes for which $m = 3p$ (p any integer) will have a zero bandgap

⇒ All zigzag nanotubes with radius $R = C/2\pi = 3pa/2\pi$ (p any integer) will have a zero bandgap

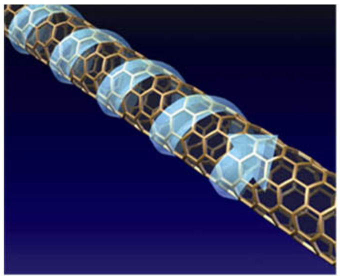
---

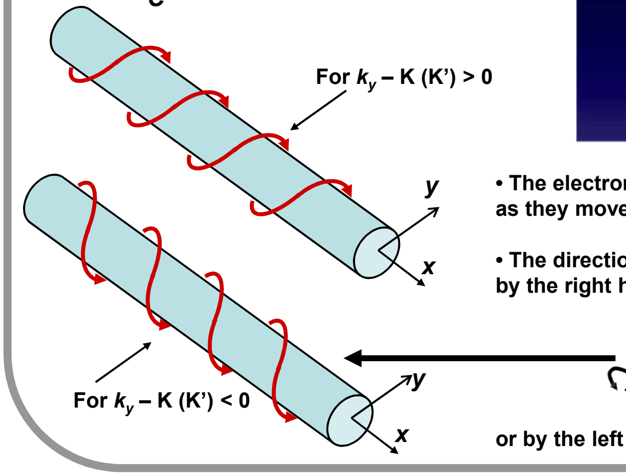
Motion of Conduction Band Bottom Electrons in Zigzag Nanotubes

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i(k_x x + k_y y)}\, u_{n,\vec{k}}(\vec{r})$$

$$\Rightarrow \quad e^{i k_y C} = 1$$

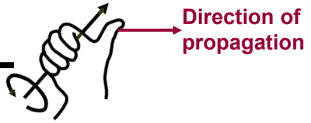
$$\Rightarrow \quad k_y = \frac{2\pi\, n}{C} \quad \{n = -(m-1), \ldots \ldots -1, 0, +1, \ldots \ldots, m$$





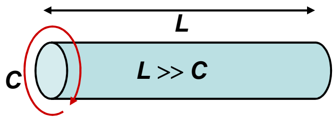
- The electrons coil around the nanotube as they move forward

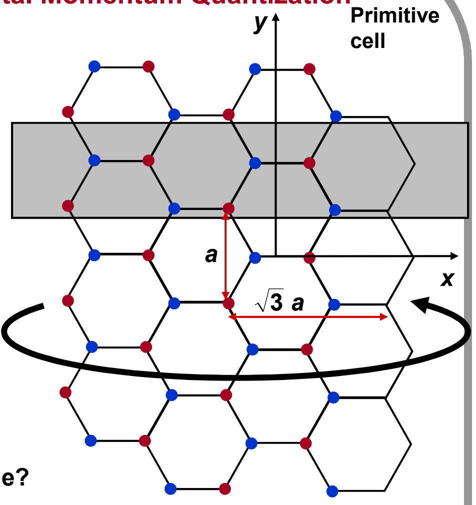
- The direction of coiling can be given by the right hand rule:



or by the left hand rule

Armchair Nanotubes: Crystal Momentum Quantization





Circumference of the armchair nanotube:

$$C = m\sqrt{3}\,a \qquad \{m = 2,3,4.......$$

Boundary condition on the wavefunction:

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i(k_x x + k_y y)}\,u_{n,\vec{k}}(\vec{r})$$

The wavefunction must be continuous along the circumference

$$\Rightarrow \quad e^{ik_x C} = 1$$

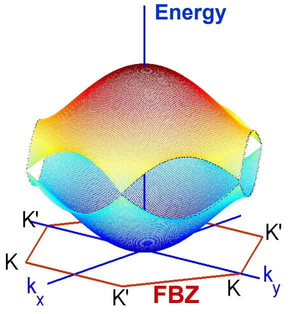
$$\Rightarrow \quad k_x = \frac{2\pi\, n}{C} \qquad \{n = \text{integer, range?}$$

The crystal momentum in the x-direction (in direction transverse to the nanotube length) has quantized values

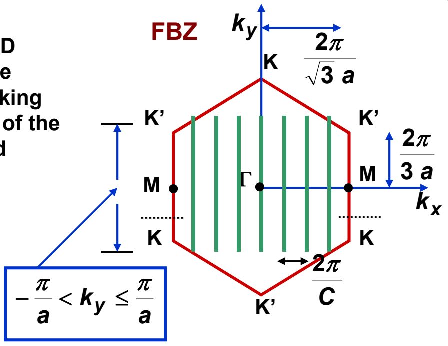
Periodicity in the y-direction: a

Number of atoms in the primitive cell: $4m$

Armchair Nanotubes: 1D Energy Subbands



Obtain all the 1D subbands of the nanotube by taking cross sections of the 2D energy band dispersion of graphene



$$-\frac{\pi}{a} < k_y \le \frac{\pi}{a}$$

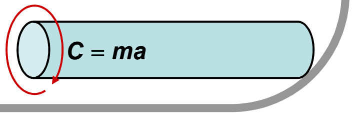
$$E(\vec{k}) = E_p \pm V_{pp\pi}\,\left|f(\vec{k})\right|$$

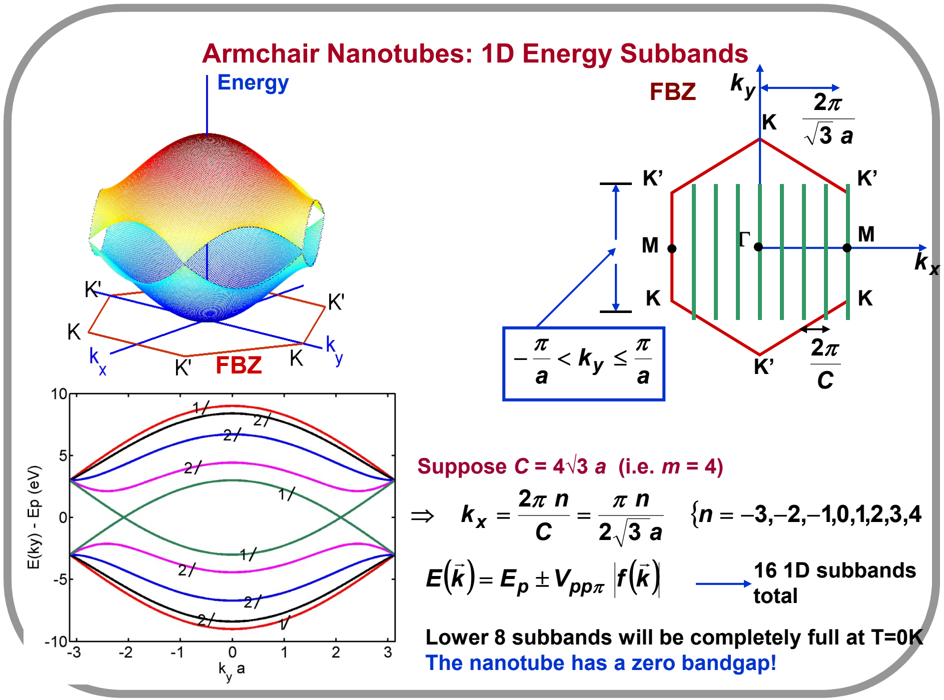
One will obtain two bands for each quantized value of k_x

But number of bands = number of orbitals in the primitive cell = $4m$

⇒ Number of distinct quantized k_x values must equal $2m$

$$\boxed{k_x = \frac{2\pi\, n}{C} \qquad \{n = -(m-1),.......-1,0,+1,.......,m}$$





Armchair Nanotubes: 1D Energy Subbands

$$-\frac{\pi}{a} < k_y \le \frac{\pi}{a}$$

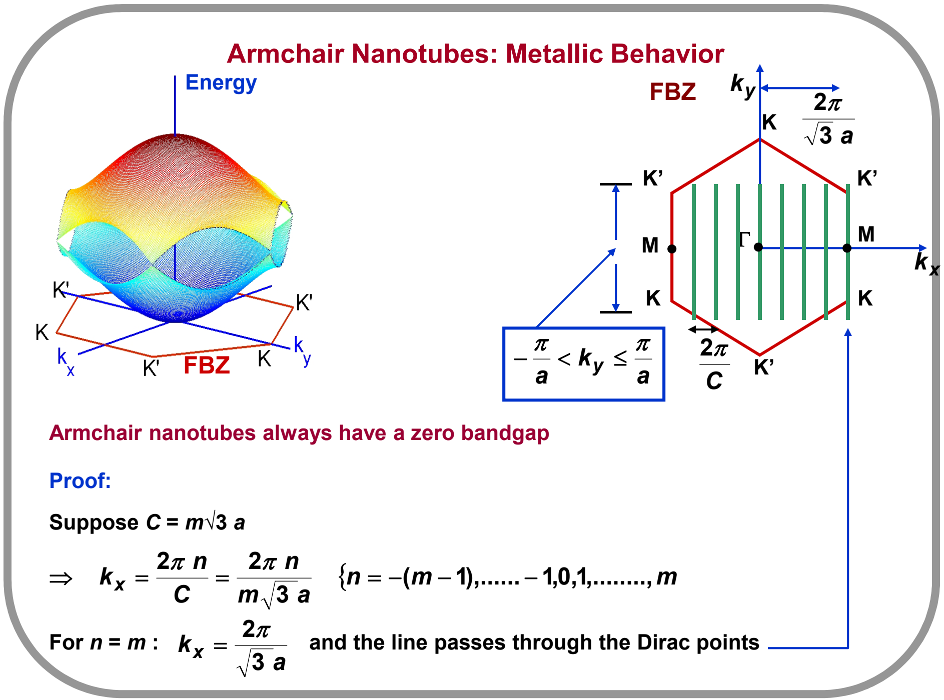
Suppose $C = 4\sqrt{3}\,a$ (i.e. $m = 4$)

$$\Rightarrow \quad k_x = \frac{2\pi\, n}{C} = \frac{\pi\, n}{2\sqrt{3}\,a} \quad \{n = -3,-2,-1,0,1,2,3,4$$

$$E(\vec{k}) = E_p \pm V_{pp\pi}\left|f(\vec{k})\right| \longrightarrow$$ 16 1D subbands total

Lower 8 subbands will be completely full at T=0K

The nanotube has a zero bandgap!



Armchair Nanotubes: Metallic Behavior

$$-\frac{\pi}{a} < k_y \le \frac{\pi}{a}$$

Armchair nanotubes always have a zero bandgap

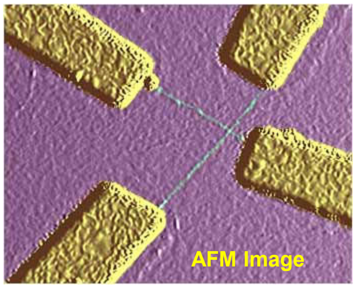
Proof:

Suppose $C = m\sqrt{3}\,a$

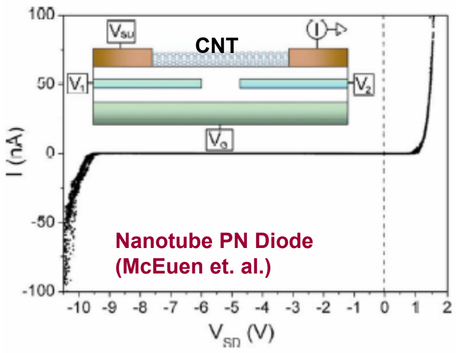
$$\Rightarrow \quad k_x = \frac{2\pi\, n}{C} = \frac{2\pi\, n}{m\sqrt{3}\,a} \quad \{n = -(m-1),\ldots\ldots -1,0,1,\ldots\ldots\ldots, m$$

For $n = m$: $k_x = \frac{2\pi}{\sqrt{3}\,a}$ and the line passes through the Dirac points

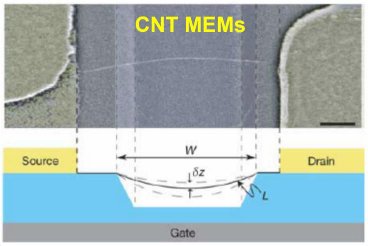
Carbon Nanotubes: Applications



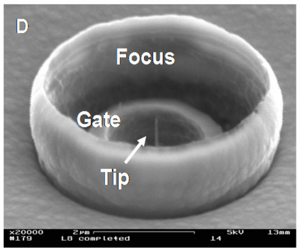
AFM Image



Nanotube PN Diode (McEuen et. al.)

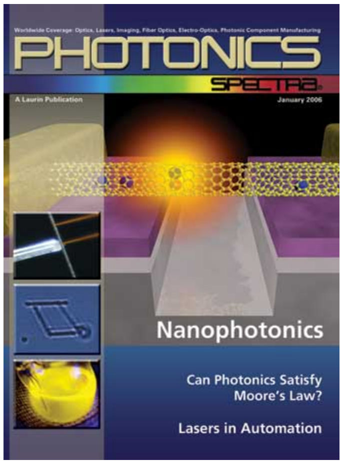


CNT MEMs

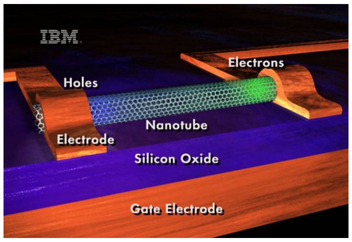


CNT field emission tips for electron guns

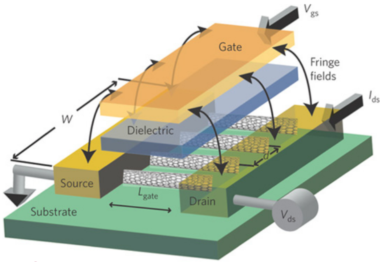
Carbon Nanotubes: Applications



Carbon Nanotube LEDs (IBM)

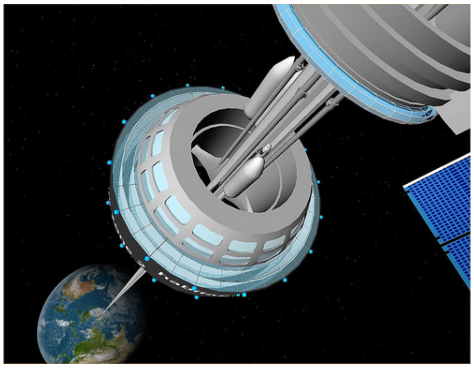


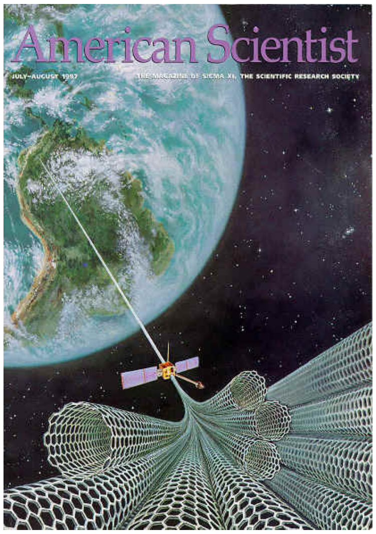
Carbon Nanotube FET (IBM)



Carbon Nanotube FET (Burke et. al.)

Carbon Nanotubes: Applications





One main obstacle to making a space elevator is finding a material for the cable that is strong enough to withstand a huge amount of tension. Some scientists think that cables made from carbon nanotubes could be the answer……

Carbon Nanotube Space Elevator !!

Handout 29

Optical Transitions in Solids, Optical Gain, and Semiconductor Lasers

In this lecture you will learn:

- Electron-photon Hamiltonian in solids
- Optical transition matrix elements
- Optical absorption coefficients
- Stimulated absorption and stimulated emission
- Optical gain in semiconductors
- Semiconductor heterostructure lasers

Interactions Between Light and Solids

The basic interactions between light and solids cover a wide variety of topics that can include:

- Interband electronic transitions in solids
- Intraband electronic transitions and intersubband electronic transitions
- Plasmons and plasmon-polaritons
- Surface plasmons
- Excitons and exciton-polaritons
- Phonon and phonon-polaritons
- Nonlinear optics
- Quantum optics
- Optical spintronics

Fermi's Golden Rule: A Review

Consider a Hamiltonian with the following eigenstates and eigenenergies:

$$\hat{H}_o \, |\psi_m\rangle = E_m \, |\psi_m\rangle \qquad \{ \; m = \text{integer}$$

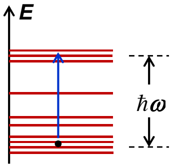
Now suppose a time dependent externally applied potential is added to the Hamiltonian:

$$\hat{H} = \hat{H}_o + \hat{V}_\uparrow \, e^{-i\omega t} + \hat{V}_\downarrow \, e^{i\omega t}$$

Suppose at time $t = 0$ an electron was in some initial state k: $|\psi(t=0)\rangle = |\psi_p\rangle$

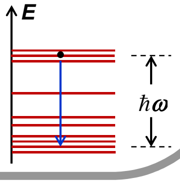
Fermi's golden rule tells that the rate at which the electron absorbs energy $\hbar\omega$ from the time-dependent potential and makes a transition to some higher energy level is given by:

$$W_\uparrow(p) = \frac{2\pi}{\hbar} \sum_m \left| \langle \psi_m | \hat{V}_\uparrow | \psi_p \rangle \right|^2 \delta\left(E_m - E_p - \hbar\omega\right)$$



The rate at which the electron gives away energy $\hbar\omega$ to the time-dependent potential and makes a transition to some lower energy level is given by:

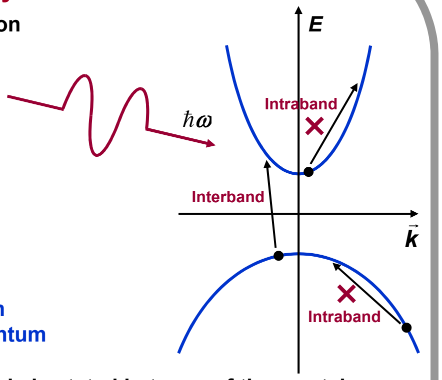
$$W_\downarrow(p) = \frac{2\pi}{\hbar} \sum_m \left| \langle \psi_m | \hat{V}_\downarrow | \psi_p \rangle \right|^2 \delta\left(E_m - E_p + \hbar\omega\right)$$



Optical Transitions in Solids: Energy and Momentum Conservation

For an electron to absorb energy from a photon energy conservation implies:

$$\underbrace{E_m(\vec{k}_f)}_{\text{Final energy}} = \underbrace{E_n(\vec{k}_i)}_{\text{Initial energy}} + \underbrace{\hbar\omega}_{\text{Photon energy}}$$



Momentum conservation implies:

$$\underbrace{\hbar\,\vec{k}_f}_{\text{Final momentum}} = \underbrace{\hbar\,\vec{k}_i}_{\text{Initial momentum}} + \underbrace{\hbar\,\vec{q}}_{\text{Photon momentum}}$$

Note that the momentum conservation principle is stated in terms of the crystal momentum of the electrons. This principle will be derived later.

Intraband photonic transitions are not possible:

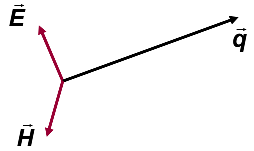
For parabolic bands, it can be shown that intraband optical transitions cannot satisfy both energy and momentum conservation and are therefore not possible

Electromagnetic Wave Basics

Consider an electromagnetic wave passing through a solid with electric field given by:

$$\vec{E}(\vec{r},t) = -\hat{n}\, E_o \sin(\vec{q}\,.\,\vec{r} - \omega\, t)$$

The vector potential associated with the field is:



$$\vec{E}(\vec{r},t) = -\frac{\partial \vec{A}(\vec{r},t)}{\partial t} \quad \Rightarrow \quad \vec{A}(\vec{r},t) = \hat{n}\,\frac{E_o}{\omega}\cos(\vec{q}\,.\,\vec{r} - \omega\, t)$$

$$= \hat{n}\, A_o \cos(\vec{q}\,.\,\vec{r} - \omega\, t)$$

The divergence of the field is zero:

$$\nabla\,.\,\vec{E}(\vec{r},t) = \nabla\,.\,\vec{A}(\vec{r},t) = 0$$

The power per unit area or the Intensity of the field is given by the Poynting vector:

$$\vec{I} = \left\langle \vec{S}(\vec{r},t) \right\rangle = \left\langle \vec{E}(\vec{r},t) \times \vec{H}(\vec{r},t) \right\rangle = \hat{q}\,\frac{E_o^2}{2\eta} = \hat{q}\,\frac{\omega^2 A_o^2}{2\eta} \qquad \left\{ \eta = \sqrt{\frac{\mu_o}{\varepsilon}} = \frac{\eta_o}{n} \right.$$

The photon flux per unit area is:

$$F = \frac{\left|\vec{I}\right|}{\hbar\omega} = \frac{\omega\, A_o^2}{2\eta\hbar}$$

Electron-Photon Hamiltonian in Solids

Consider electrons in a solid. The eigenstates (Bloch functions) and eigenenergies satisfy:

$$\hat{H}_o \left|\psi_{n,\vec{k}}\right\rangle = E_n\!\left(\vec{k}\right)\left|\psi_{n,\vec{k}}\right\rangle$$

where:

$$\hat{H}_o = \frac{\hat{\vec{P}}\,.\,\hat{\vec{P}}}{2m} + V_{lattice}\!\left(\hat{\vec{r}}\right)$$

In the presence of E&M fields the Hamiltonian is:

$$\hat{H} = \frac{\left[\hat{\vec{P}} + e\vec{A}\!\left(\hat{\vec{r}},t\right)\right]^2}{2m} + V_{lattice}\!\left(\hat{\vec{r}}\right) \qquad \left\{ \vec{A}(\vec{r},t) = \hat{n}\, A_o \cos(\vec{q}\,.\,\vec{r} - \omega\, t) \right.$$

$$= \frac{\hat{\vec{P}}\,.\,\hat{\vec{P}}}{2m} + V_{lattice}\!\left(\hat{\vec{r}}\right) + \frac{e}{2m}\,\hat{\vec{P}}\,.\,\vec{A}\!\left(\hat{\vec{r}},t\right) + \frac{e}{2m}\,\vec{A}\!\left(\hat{\vec{r}},t\right).\,\hat{\vec{P}} + \cancel{\frac{e^2}{2m}\,\vec{A}\!\left(\hat{\vec{r}},t\right).\,\vec{A}\!\left(\hat{\vec{r}},t\right)}$$

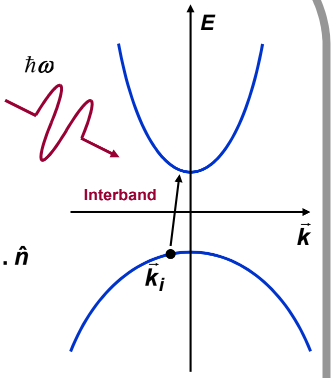
Assume small

$$\approx \hat{H}_o + \frac{e}{2m}\,\hat{\vec{P}}\,.\,\vec{A}\!\left(\hat{\vec{r}},t\right) + \frac{e}{2m}\,\vec{A}\!\left(\hat{\vec{r}},t\right).\,\hat{\vec{P}}$$

$$= \hat{H}_o + \frac{e}{m}\,\vec{A}\!\left(\hat{\vec{r}},t\right).\,\hat{\vec{P}} \quad \longrightarrow \quad \left\{ \text{Provided: } \nabla\,.\,\vec{A}(\vec{r},t) = 0 \right.$$

$$= \hat{H}_o + \frac{e\,A_o\left[\, e^{i\vec{q}\,.\,\hat{\vec{r}} - i\,\omega\,t} + e^{-i\vec{q}\,.\,\hat{\vec{r}} + i\,\omega\,t} \,\right]}{2m}\,\hat{n}\cdot\hat{\vec{P}}$$

Optical Interband Transitions in Solids



$$\hat{H}_o\left|\psi_{n,\vec{k}}\right\rangle = E_n\left(\vec{k}\right)\left|\psi_{n,\vec{k}}\right\rangle$$

$$\hat{H} = \hat{H}_o + \frac{e\,A_o\left[\,e^{i\vec{q}\,.\,\hat{\vec{r}}-i\,\omega\,t} + e^{-i\vec{q}\,.\,\hat{\vec{r}}+i\,\omega\,t}\,\right]}{2m}\,\hat{\vec{P}}\,.\,\hat{n}$$

Comparison with:

$$\hat{H} = \hat{H}_o + \hat{V}_{\uparrow}\,e^{-i\omega t} + \hat{V}_{\downarrow}\,e^{i\omega t}$$

gives:

$$\hat{V}_{\uparrow} = \frac{e\,A_o e^{i\vec{q}\,.\,\hat{\vec{r}}}}{2m}\,\hat{\vec{P}}\,.\,\hat{n} \qquad \hat{V}_{\downarrow} = \frac{e\,A_o e^{-i\vec{q}\,.\,\hat{\vec{r}}}}{2m}\,\hat{\vec{P}}\,.\,\hat{n}$$

Suppose at time $t = 0$ the electron was sitting in the valence band with crystal momentum $\vec{k}_i$:

$$\left|\psi(t=0)\right\rangle = \left|\psi_{v,\vec{k}_i}\right\rangle$$

The transition rate to states in the conduction band is given by the Fermi's golden rule:

$$W_{\uparrow}\left(\vec{k}_i\right) = \frac{2\pi}{\hbar}\sum_{\vec{k}_f}\left|\left\langle\psi_{c,\vec{k}_f}\right|\hat{V}_{\uparrow}\left|\psi_{v,\vec{k}_i}\right\rangle\right|^2\,\delta\left(E_c\left(\vec{k}_f\right) - E_v\left(\vec{k}_i\right) - \hbar\omega\right)$$

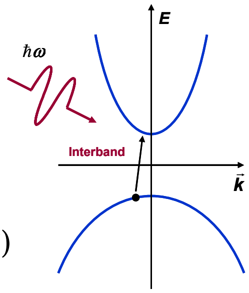
The summation is over all possible final states in the conduction band that have the same spin as the initial state. Energy conservation is enforced by the delta function.

Optical Matrix Element

$$W_{\uparrow}\left(\vec{k}_i\right) = \frac{2\pi}{\hbar}\sum_{\vec{k}_f}\left|\left\langle\psi_{c,\vec{k}_f}\right|\hat{V}_{\uparrow}\left|\psi_{v,\vec{k}_i}\right\rangle\right|^2\,\delta\left(E_c\left(\vec{k}_f\right) - E_v\left(\vec{k}_i\right) - \hbar\omega\right)$$

$$= \frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2\sum_{\vec{k}_f}\left|\left\langle\psi_{c,\vec{k}_f}\right|e^{i\vec{q}\,.\,\hat{\vec{r}}}\,\hat{\vec{P}}\,.\,\hat{n}\left|\psi_{v,\vec{k}_i}\right\rangle\right|^2\,\delta\left(E_c\left(\vec{k}_f\right) - E_v\left(\vec{k}_i\right) - \hbar\omega\right)$$

Now consider the matrix element:



$$\left\langle\psi_{c,\vec{k}_f}\right|e^{i\vec{q}\,.\,\hat{\vec{r}}}\hat{\vec{P}}\,.\,\hat{n}\left|\psi_{v,\vec{k}_i}\right\rangle$$

$$= \int d^3\vec{r}\;\psi^*_{c,\vec{k}_f}\left(\vec{r}\right)\quad e^{i\vec{q}\,.\,\vec{r}}\;\hat{\vec{P}}\,.\,\hat{n}\quad\psi_{v,\vec{k}_i}\left(\vec{r}\right)$$

$$= \int d^3\vec{r}\;e^{-i\vec{k}_f\,.\,\vec{r}}u^*_{c,\vec{k}_f}\left(\vec{r}\right)\quad e^{i\vec{q}\,.\,\vec{r}}\;\hat{\vec{P}}\,.\,\hat{n}\quad e^{i\vec{k}_i\,.\,\vec{r}}u_{v,\vec{k}_i}\left(\vec{r}\right)$$

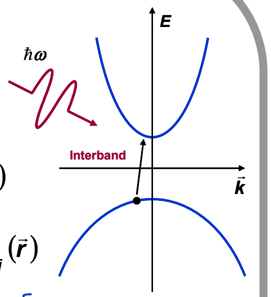
$$= \int d^3\vec{r}\;e^{-i\vec{k}_f\,.\,\vec{r}}u^*_{c,\vec{k}_f}\left(\vec{r}\right)\quad e^{i\vec{q}\,.\,\vec{r}}\;e^{i\vec{k}_i\,.\,\vec{r}}\left(\hat{\vec{P}} + \cancelto{0}{\hbar\vec{k}_i}\right).\,\hat{n}\quad u_{v,\vec{k}_i}\left(\vec{r}\right)$$

$$= \int d^3\vec{r}\;\underbrace{e^{-i\vec{k}_f\,.\,\vec{r}}}\,\overbrace{u^*_{c,\vec{k}_f}\left(\vec{r}\right)}\quad \underbrace{e^{i\vec{q}\,.\,\vec{r}}}\;\underbrace{e^{i\vec{k}_i\,.\,\vec{r}}}\;\hat{\vec{P}}\,.\,\hat{n}\quad \overbrace{u_{v,\vec{k}_i}\left(\vec{r}\right)}$$

Rapidly varying in space

Slowly varying in space

Optical Matrix Element



$$\left\langle \psi_{c,\vec{k}_f} \right| e^{i\vec{q}\cdot\hat{\vec{r}}}\,\hat{\vec{P}}\cdot\hat{n} \left| \psi_{v,\vec{k}_i} \right\rangle$$

$$= \int d^3\vec{r}\; e^{-i\vec{k}_f\cdot\vec{r}}\, u^*_{c,\vec{k}_f}(\vec{r}) \quad e^{i\vec{q}\cdot\vec{r}}\; e^{i\vec{k}_i\cdot\vec{r}}\; \hat{\vec{P}}\cdot\hat{n}\;\; u_{v,\vec{k}_i}(\vec{r})$$

$$= \sum_{\vec{R}_j} e^{i\left(\vec{k}_i+\vec{q}-\vec{k}_f\right)\cdot\vec{R}_j} \int_{j\text{-th primitive cell}} d^3\vec{r} \quad u^*_{c,\vec{k}_f}(\vec{r}) \;\; \hat{\vec{P}}\cdot\hat{n} \;\; u_{v,\vec{k}_i}(\vec{r})$$

$$= \sum_{\vec{R}_j} e^{i\left(\vec{k}_i+\vec{q}-\vec{k}_f\right)\cdot\vec{R}_j} \int_{\text{any one primitive cell}} d^3\vec{r} \quad u^*_{c,\vec{k}_f}(\vec{r}) \;\; \hat{\vec{P}}\cdot\hat{n} \;\; u_{v,\vec{k}_i}(\vec{r})$$

$$= N\delta_{\vec{k}_i+\vec{q}\,,\,\vec{k}_f} \int_{\text{any one primitive cell}} d^3\vec{r} \quad u^*_{c,\vec{k}_f}(\vec{r}) \;\; \hat{\vec{P}}\cdot\hat{n} \;\; u_{v,\vec{k}_i}(\vec{r})$$

$$= \delta_{\vec{k}_i+\vec{q}\,,\,\vec{k}_f} \int_{\text{entire crystal}} d^3\vec{r}\;\; u^*_{c,\vec{k}_f}(\vec{r}) \;\; \hat{\vec{P}}\cdot\hat{n} \;\; u_{v,\vec{k}_i}(\vec{r})$$

$$= \delta_{\vec{k}_i+\vec{q}\,,\,\vec{k}_f}\; \vec{P}_{cv}\cdot\hat{n}$$

N = number of primitive cells in the crystal

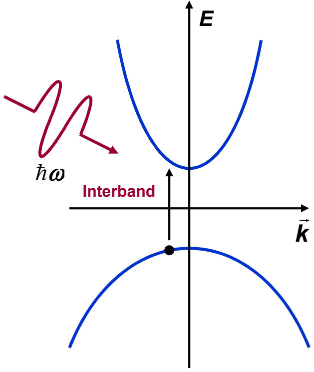
Interband momentum matrix element

Crystal Momentum Selection Rule

$$W_{\uparrow}\left(\vec{k}_i\right) = \frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2 \sum_{\vec{k}_f} \left| \left\langle \psi_{c,\vec{k}_f} \right| e^{i\vec{q}\cdot\hat{\vec{r}}}\,\hat{\vec{P}}\cdot\hat{n} \left| \psi_{v,\vec{k}_i} \right\rangle \right|^2 \delta\!\left(E_c\left(\vec{k}_f\right) - E_v\left(\vec{k}_i\right) - \hbar\omega\right)$$

$$= \frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2 \sum_{\vec{k}_f} \left|\vec{P}_{cv}\cdot\hat{n}\right|^2 \delta_{\vec{k}_i+\vec{q}\,,\,\vec{k}_f}\; \delta\!\left(E_c\left(\vec{k}_f\right) - E_v\left(\vec{k}_i\right) - \hbar\omega\right)$$

$$= \frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2 \left|\vec{P}_{cv}\cdot\hat{n}\right|^2 \delta\!\left(E_c\left(\vec{k}_i+\vec{q}\right) - E_v\left(\vec{k}_i\right) - \hbar\omega\right)$$



Crystal Momentum Selection Rule:

We have the crystal momentum selection rule:

$$\boxed{\vec{k}_f = \vec{k}_i + \vec{q}}$$

The wave vector of the photons is very small since the speed of light is very large

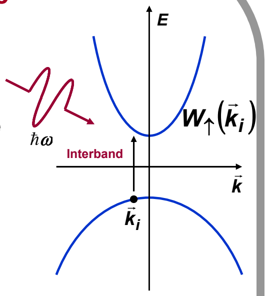
Therefore, one may assume that:

$$\boxed{\vec{k}_f \approx \vec{k}_i} \longrightarrow$$

Optical transitions are vertical in k-space

Transition Rates per Unit Volume

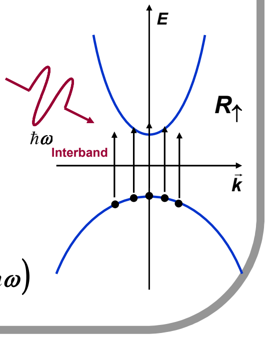
$$W_{\uparrow}(\vec{k}_i)=\frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2 \left|\vec{P}_{cv}\ .\ \hat{n}\right|^2 \ \delta\left(E_c(\vec{k}_i)-E_v(\vec{k}_i)-\hbar\omega\right)$$



Generally one is not interested in the transition rate for any one particular initial electron state but in the number of transitions happening per unit volume of the material per second

The upward transition $R_{\uparrow}$ rate per unit volume is obtained by summing over all the possible initial states per unit volume weighed by the occupation probability of the initial state and by the probability that the final state is empty:

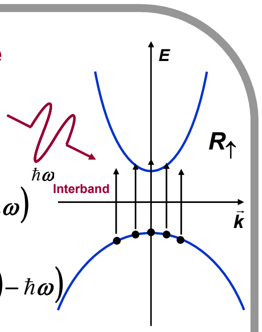
$$R_{\uparrow}(\omega)=\frac{2}{V}\times\sum_{\vec{k}_i}W_{\uparrow}(\vec{k}_i)\,f_v(\vec{k}_i)\left[1-f_c(\vec{k}_i)\right]$$



If we assume, as in an intrinsic semiconductor, that the valence band is full and the conduction band is empty of electrons, then:

$$\begin{aligned}R_{\uparrow}(\omega)&=\frac{2}{V}\times\sum_{\vec{k}_i}W_{\uparrow}(\vec{k}_i)\\&=\frac{2}{V}\times\sum_{\vec{k}_i}\frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2 \left|\vec{P}_{cv}\ .\ \hat{n}\right|^2 \ \delta\left(E_c(\vec{k}_i)-E_v(\vec{k}_i)-\hbar\omega\right)\end{aligned}$$

Transition Rates per Unit Volume



$$\begin{aligned}R_{\uparrow}(\omega)&=\frac{2}{V}\times\sum_{\vec{k}_i}\frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2 \left|\vec{P}_{cv}\ .\ \hat{n}\right|^2 \ \delta\left(E_c(\vec{k}_i)-E_v(\vec{k}_i)-\hbar\omega\right)\\&=2\times\int_{FBZ}\frac{d^3\vec{k}_i}{(2\pi)^3}\ \frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2 \left|\vec{P}_{cv}\ .\ \hat{n}\right|^2 \delta\left(E_c(\vec{k}_i)-E_v(\vec{k}_i)-\hbar\omega\right)\\&=\frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2 \left\langle\left|\vec{P}_{cv}\ .\ \hat{n}\right|^2\right\rangle\ 2\times\int_{FBZ}\frac{d^3\vec{k}_i}{(2\pi)^3}\ \delta\left(E_c(\vec{k}_i)-E_v(\vec{k}_i)-\hbar\omega\right)\\&=\frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2 \left\langle\left|\vec{P}_{cv}\ .\ \hat{n}\right|^2\right\rangle\ \underbrace{2\times\int_{FBZ}\frac{d^3\vec{k}}{(2\pi)^3}\ \delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)}_{\text{Joint density of states}}\end{aligned}$$

The integral in the expression above is similar to the density of states integral:

Suppose: $E_c(\vec{k})=E_c+\dfrac{\hbar^2k^2}{2m_e}$

Then: $g_{3D}(E)=2\times\displaystyle\int_{FBZ}\frac{d^3\vec{k}}{(2\pi)^3}\ \delta\left(E_c(\vec{k})-E\right)=\frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\sqrt{E-E_c}$

Transition Rates per Unit Volume and Joint Density of States

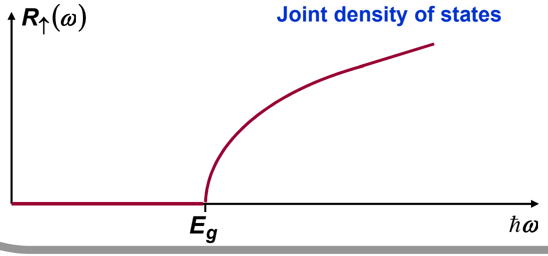
$$R_{\uparrow}(\omega)=\frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\,2\times\int_{FBZ}\frac{d^3\vec{k}}{(2\pi)^3}\,\delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)$$

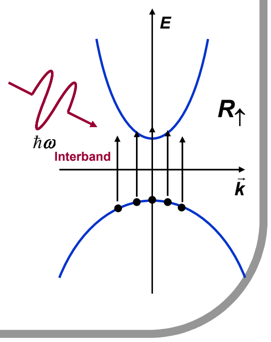
Suppose: $E_c(\vec{k})=E_c+\dfrac{\hbar^2k^2}{2m_e}$ $\qquad E_v(\vec{k})=E_v-\dfrac{\hbar^2k^2}{2m_h}$

Then: $E_c(\vec{k})-E_v(\vec{k})=E_c-E_v+\dfrac{\hbar^2k^2}{2}\left(\dfrac{1}{m_e}+\dfrac{1}{m_h}\right)=E_g+\dfrac{\hbar^2k^2}{2m_r}$

Reduced effective mass

$$R_{\uparrow}(\omega)=\frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\underbrace{\frac{1}{2\pi^2}\left(\frac{2m_r}{\hbar^2}\right)^{3/2}\sqrt{\hbar\omega-E_g}}_{\text{Joint density of states}}$$





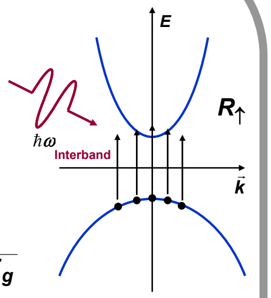
Transition Rates per Unit Volume

$$R_{\uparrow}(\omega)=\frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\frac{1}{2\pi^2}\left(\frac{2m_r}{\hbar^2}\right)^{3/2}\sqrt{\hbar\omega-E_g}$$

The power per unit area or the Intensity of the E&M wave is:

$$I=\frac{\omega^2A_o^2}{2\eta}$$

$$R_{\uparrow}(\omega)=\frac{2\pi}{\hbar}\left(\frac{e}{2m}\right)^2\left(\frac{2\eta I}{\omega^2}\right)\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\frac{1}{2\pi^2}\left(\frac{2m_r}{\hbar^2}\right)^{3/2}\sqrt{\hbar\omega-E_g}$$

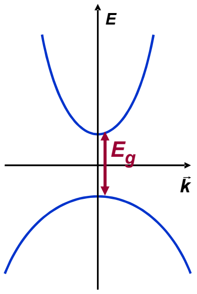


Interband Momentum Matrix Elements:

Recall the result from homework 7:

$$\frac{1}{m_r}=\left(\frac{1}{m_e}+\frac{1}{m_h}\right)=\frac{4}{m^2}\frac{\left|\vec{P}_{cv}\cdot\hat{n}\right|^2}{E_g}$$

The above result assumed diagonal isotropic conduction and valence bands and also that no other bands are present, and is therefore oversimplified



Momentum Matrix Elements

In bulk III-V semiconductors with cubic symmetry, the average value of the momentum matrix element is usually expressed in terms of the energy E_p as,

$$\left\langle \left| \vec{P}_{cv} \cdot \hat{n} \right|^2 \right\rangle = \frac{m E_p}{6}$$

Note that the momentum matrix elements are independent of the direction of light polarization!

Parameters at 300K	GaAs	AlAs	InAs	InP	GaP
Ep (eV)	25.7	21.1	22.2	20.7	22.2

Transition Rates per Unit Volume and the Absorption or Loss Coefficient

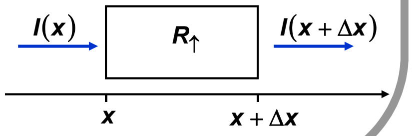
Because of transitions photons will be lost from the E&M wave traveling inside the solid. This loss will result in decay of the wave Intensity with distance travelled:

$$\Rightarrow I(x) = e^{-\alpha x}\, I(x=0)$$

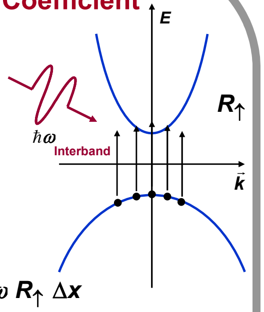
$$\Rightarrow \frac{I(x)}{dx} = -\alpha\, I(x)$$

$$\Rightarrow I(x+\Delta x) - I(x) = -\underset{\uparrow}{\alpha}\; \Delta x\, I(x)$$

Loss coefficient or absorption coefficient

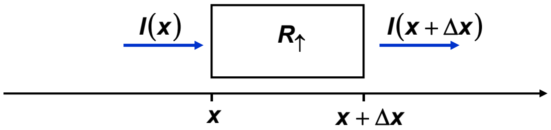


Transition Rates per Unit Volume and Loss Coefficient



$$\Rightarrow I(x+\Delta x) - I(x) = -\alpha\; \Delta x\, I(x)$$

The wave power loss (per unit area) in small distance Δx is $\alpha\, \Delta x\, I(x)$



The wave power loss in small distance Δx must also equal: $\hbar\omega\, R_\uparrow\, \Delta x$

Therefore:

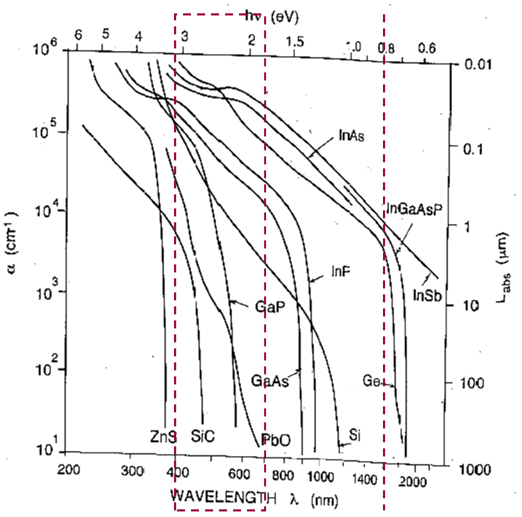
$$\hbar\omega\, R_\uparrow\, \Delta x = \alpha\, \Delta x\, I$$

$$\Rightarrow \alpha(\omega) = \frac{\hbar\omega\, R_\uparrow(\omega)}{I} = 2\pi \left(\frac{e}{2m}\right)^2 \left(\frac{2\eta}{\omega}\right) \left|\vec{P}_{cv} \cdot \hat{n}\right|^2 \frac{1}{2\pi^2} \left(\frac{2m_r}{\hbar^2}\right)^{3/2} \sqrt{\hbar\omega - E_g}$$

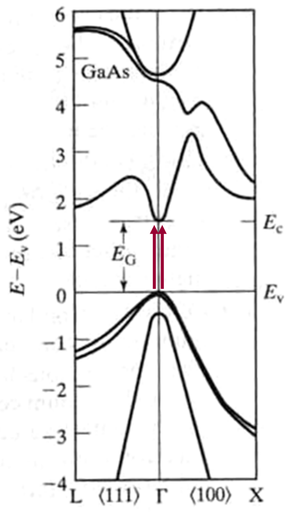
$$= \left(\frac{e}{m}\right)^2 \frac{\pi}{\varepsilon_o\, n\omega\, c} \left|\vec{P}_{cv} \cdot \hat{n}\right|^2 \frac{1}{2\pi^2} \left(\frac{2m_r}{\hbar^2}\right)^{3/2} \sqrt{\hbar\omega - E_g}$$

Values of $\alpha(\omega)$ for most semiconductors can range from a few hundred cm^{-1} to hundred thousand cm^{-1}

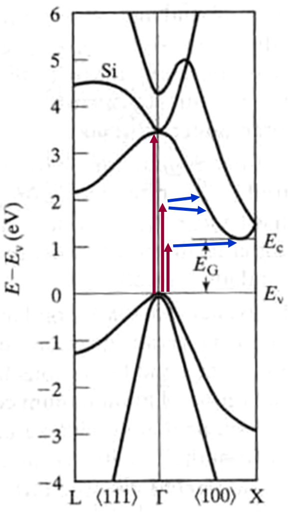
Loss Coefficient of Semiconductors



Direct Bandgap and Indirect Bandgap Semiconductors



Direct bandgap
(Direct optical transitions)



Direct bandgap
(Indirect phonon-assisted transitions)

$$\frac{1}{m_r} = \left(\frac{1}{m_h} + \frac{1}{m_e}\right)$$

If m_e approaches $-m_h$, then m_r becomes very large

Then, $\alpha \propto (m_r)^{3/2}$ also becomes very large

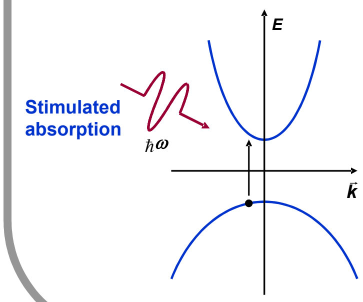
Stimulated Absorption and Stimulated Emission

Throwing back in the occupation factors one can write more generally:

$$R_{\uparrow}(\omega)=\frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2 \left\langle \left|\vec{P}_{cv}\,.\,\hat{n}\right|^2\right\rangle \; 2\times\int_{FBZ}\frac{d^3\vec{k}}{(2\pi)^3}\, f_v(\vec{k})\left[1-f_c(\vec{k})\right]\delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)$$

Stimulated Absorption:

The process of photon absorption is called stimulated absorption (because, quite obviously, the process is initiated by the incoming radiation or photons some of which eventually end up getting absorbed)



An incoming photon can also cause the reverse process in which an electron makes a downward transition

This reverse process is initiated by the term in Hamiltonian that has the $e^{i\omega t}$ time dependence:

$$\hat{H}=\hat{H}_o+\hat{V}_{\uparrow}\,e^{-i\omega t}+\hat{V}_{\downarrow}\,e^{i\omega t}$$

$$\hat{V}_{\uparrow}=\frac{e\,A_o e^{i\vec{q}\,.\,\hat{\vec{r}}}}{2m}\,\hat{\vec{P}}\,.\,\hat{n} \qquad \hat{V}_{\downarrow}=\frac{e\,A_o e^{-i\vec{q}\,.\,\hat{\vec{r}}}}{2m}\,\hat{\vec{P}}\,.\,\hat{n}$$

Stimulated Emission and Spontaneous Emission

Following the same procedure as for stimulated absorption, one can write the rate per unit volume for the downward transitions as:

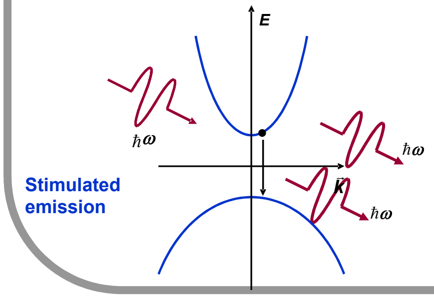
$$R_{\downarrow}(\omega)=\frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2 \left\langle \left|\vec{P}_{cv}\,.\,\hat{n}\right|^2\right\rangle \; 2\times\int_{FBZ}\frac{d^3\vec{k}}{(2\pi)^3}\, f_c(\vec{k})\left[1-f_v(\vec{k})\right]\delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)$$

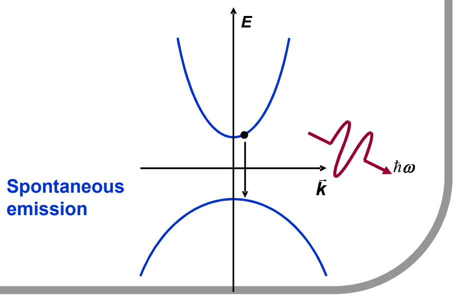
Stimulated Emission:

In the downward transition, the electron gives off its energy to the electromagnetic field, i.e. it emits a photon! The process of photon emission caused by incoming radiation (or by other photons) is called stimulated emission.

Spontaneous Emission:

Electrons can also make downward transitions even in the absence of any incoming radiation (or photons). This process is called spontaneous emission.





Stimulated Absorption and Stimulated Emission

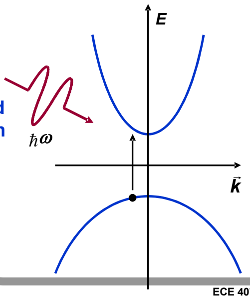
The net stimulated electronic transition rate is the difference between the stimulated emission and stmulated absorption rates:

$$R_\uparrow(\omega)-R_\downarrow(\omega)=\frac{2\pi}{\hbar}\left(\frac{eA_o}{2m}\right)^2\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\;2\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\left[f_v(\vec{k})-f_c(\vec{k})\right]\delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)$$

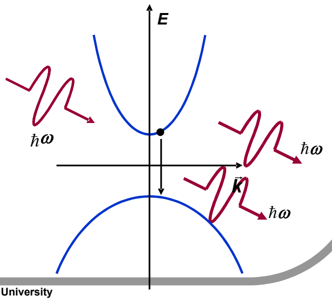
And the more accurate expression for the loss coefficient is then:

$$\alpha(\omega)=\frac{\hbar\omega\left(R_\uparrow(\omega)-R_\downarrow(\omega)\right)}{I}$$

$$=\left(\frac{e}{m}\right)^2\frac{\pi}{\varepsilon_o n\omega c}\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\;2\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\left[f_v(\vec{k})-f_c(\vec{k})\right]\delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)$$



Stimulated absorption



Stimulated emission

Optical Gain in Semiconductors

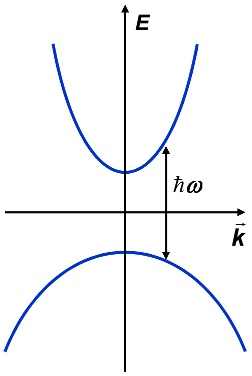
$$\alpha(\omega)=\left(\frac{e}{m}\right)^2\frac{\pi}{\varepsilon_o n\omega c}\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\;2\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\left[f_v(\vec{k})-f_c(\vec{k})\right]\delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)$$

Note that the Intensity decays as: $I(x)=e^{-\alpha x}\,I(x=0)$

What if α were to become negative? Optical gain !!

$$\alpha(\omega)<0\quad\Rightarrow\quad R_\downarrow(\omega)>R_\uparrow(\omega)$$

A negative value of α implies optical gain (as opposed to optical loss) and means that stimulated emission rate exceeds stimulated absorption rate



Optical gain is possible if:

$$f_v(\vec{k})-f_c(\vec{k})<0\qquad\text{for}\qquad E_c(\vec{k})-E_v(\vec{k})=\hbar\omega$$
$$\Rightarrow f_c(\vec{k})-f_v(\vec{k})>0\qquad\text{for}\qquad E_c(\vec{k})-E_v(\vec{k})=\hbar\omega$$

Optical Gain in Semiconductors

Optical gain is only possible in non-equilibrium situations when the electron and hole Fermi levels are not the same

Suppose:

$$f_c(\vec{k}) = f\left(E_c(\vec{k}) - E_{fe}\right) = \frac{1}{1 + e^{\left(E_c(\vec{k}) - E_{fe}\right)/KT}}$$

$$f_v(\vec{k}) = f\left(E_v(\vec{k}) - E_{fh}\right) = \frac{1}{1 + e^{\left(E_v(\vec{k}) - E_{fh}\right)/KT}}$$

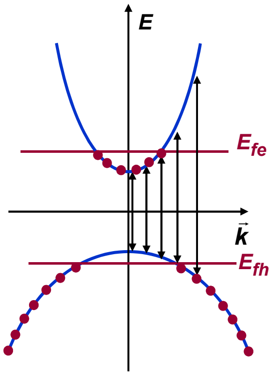
$$E_c(\vec{k}) - E_v(\vec{k}) = \hbar\omega$$

Then the condition for optical gain at frequency ω is:

$$f\left(E_c(\vec{k}) - E_{fe}\right) - f\left(E_v(\vec{k}) - E_{fh}\right) > 0$$

$$\Rightarrow E_{fe} - E_{fh} > E_c(\vec{k}) - E_v(\vec{k})$$

$$\Rightarrow E_{fe} - E_{fh} > \hbar\omega$$

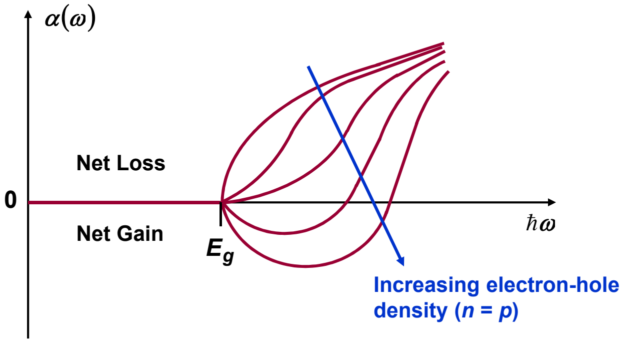


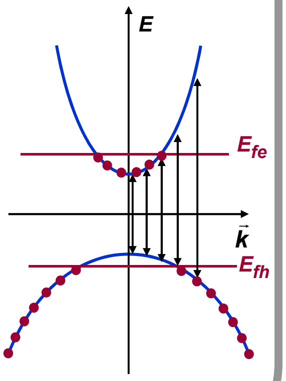
The above is the condition for population inversion (lots of electrons in the conduction band and lots of holes in the valence band)

Optical Gain in Semiconductors

The loss coefficient is a function of frequency:

$$\alpha(\omega) = \left(\frac{e}{m}\right)^2 \frac{\pi}{\varepsilon_o n\omega\, c} \left\langle \left|\vec{P}_{cv} \cdot \hat{n}\right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3} \left[f_v(\vec{k}) - f_c(\vec{k})\right] \delta\left(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega\right)$$

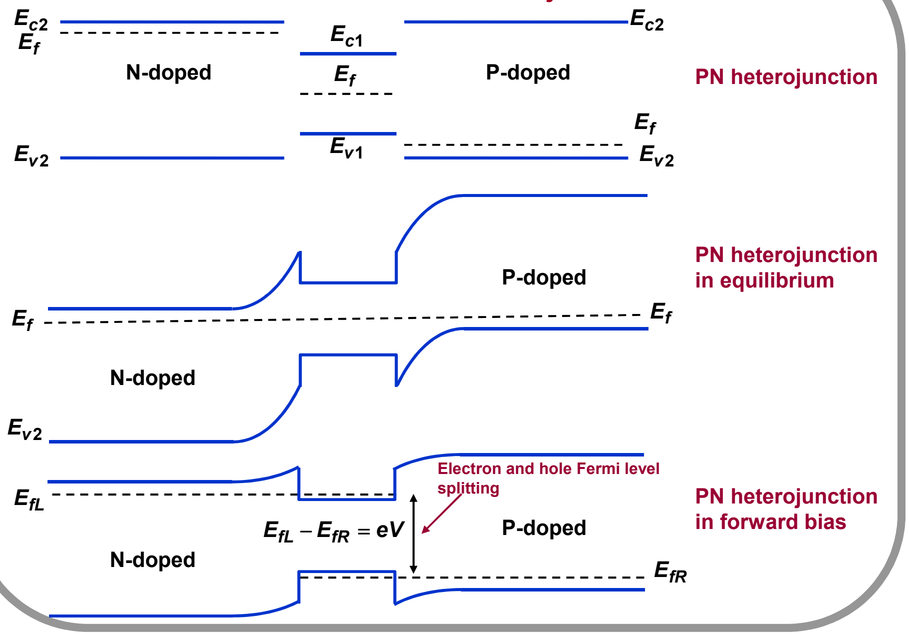




Optical gain for frequencies for which:

$$E_g < \hbar\omega < E_{fe} - E_{fh}$$

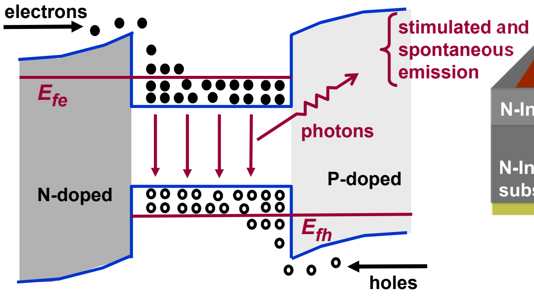
Semiconductor PN Heterojunctions



Semiconductor Heterostructure Lasers

A Heterostructure Laser (Band Diagram)

Non-equilibrium electron and hole populations can be sustained in a forward bias pn junction

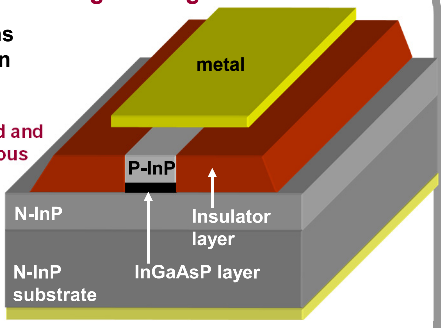


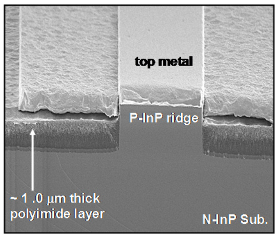
$$E_{fe} - E_{fh} > \hbar\omega$$

$$\Rightarrow \quad eV > \hbar\omega$$

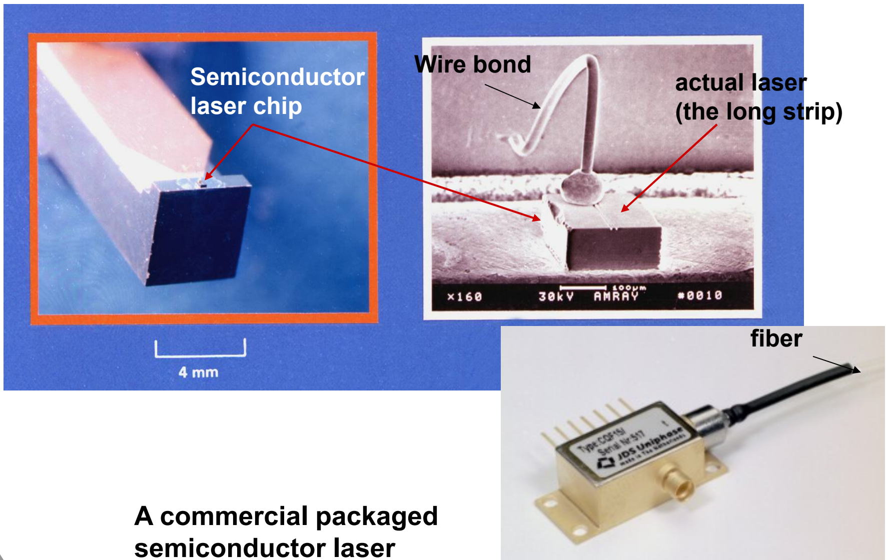
All lasers used in fiber optical communications are semiconductor lasers

A Ridge Waveguide Laser Structure





Semiconductor Heterostructure Lasers



A commercial packaged semiconductor laser

Handout 30

Optical Processes in Solids and the Dielectric Constant

In this lecture you will learn:

- Linear response functions
- Kramers-Kronig relations
- Dielectric constant of solids
- Interband and Intraband contributions to the dielectric constant of solids

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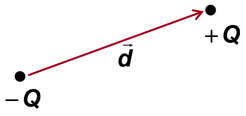
Charge Dipole, Dipole Moment, and Polarization Density

A charge dipole consists of a negative and a positive charge separated by some distance:

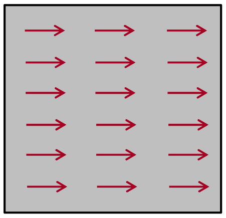


Dipole moment of a charge dipole is a vector $\vec{p}$ such that:

$$\vec{p} = |Q|\,\vec{d}$$

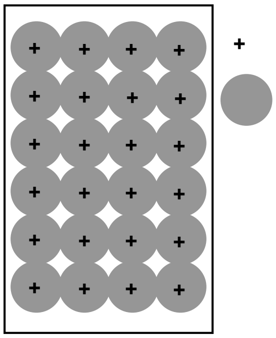
Polarization density vector $\vec{P}$ of a medium consisting of charge dipoles is the product of the number N of dipoles per unit volume (i.e. dipole density) and the strength of each dipole given by $\vec{p}$:

$$\vec{P} = N\vec{p} = N|Q|\vec{d}$$



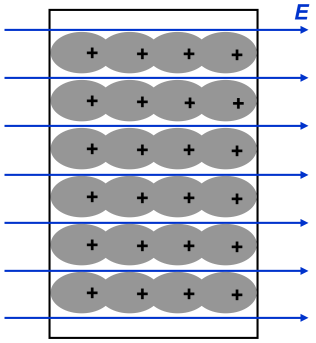
Dielectric Constant of Non-Polar Materials

Non-Polar Dielectric Material (Non-polar Insulator or Intrinsic Semiconductor)


+ +ve nucleus

-ve electron cloud (valence band and core electrons)

Dielectric in an E-field



Material gets polarized when placed in an electric field (i.e. develops charge dipoles) because the electron cloud shifts relative to the nuclei

$\vec{P} =$ Polarization density (# of dipoles per unit volume times the strength of one dipole)

$$\vec{P}_e = \varepsilon_o \chi_e \vec{E}$$

$$\vec{D} = \varepsilon_o \vec{E} + \vec{P}_e = \varepsilon \vec{E}$$

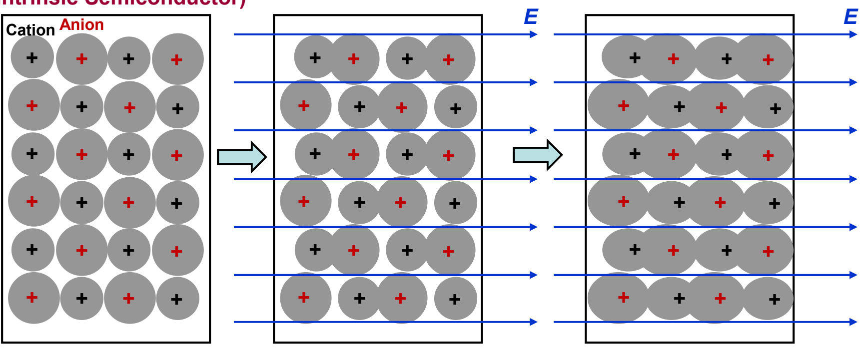
$$\varepsilon = \varepsilon_o (1 + \chi_e)$$

Dielectric Constant of Polar Materials

Polar Dielectric Material (Polar Insulator or Intrinsic Semiconductor)

The phonon contribution to Polarization

The total (phonon + electron) contribution to Polarization



In polar materials, material polarization in an E-field has two contributions:

a) The phonon contribution: $\vec{P}_{ph} = \varepsilon_o \chi_{ph} \vec{E}$

b) The electron contribution: $\vec{P}_e = \varepsilon_o \chi_e \vec{E}$

$$\Rightarrow \vec{D} = \varepsilon_o \vec{E} + \vec{P}_e + P_{ph} = \varepsilon_o (1 + \chi_e + \chi_{ph}) \vec{E}$$

$$\Rightarrow \varepsilon = \varepsilon_o (1 + \chi_e + \chi_{ph})$$

Dielectric Constant of Materials: Phonon and Electron Contributions

In general, the susceptibilities are frequency dependent:

$$\varepsilon(\omega)=\varepsilon_o\left(1+\chi_e(\omega)+\chi_{ph}(\omega)\right)$$

Electrons respond much faster than the lattice

If one is working at frequencies that are too small compared to the characteristic frequencies of $\chi_e(\omega)$ then one may make the approximation:

$$\varepsilon(\omega)=\varepsilon_o\left(1+\chi_e(0)+\chi_{ph}(\omega)\right)$$

If we define:

$$\varepsilon(\infty)=\varepsilon_o\left(1+\chi_e(0)\right) \qquad \varepsilon(0)=\varepsilon_o\left(1+\chi_e(0)+\chi_{ph}(0)\right)$$

then for small frequencies:

$$\varepsilon(\omega)=\varepsilon(\infty)+\varepsilon_o\,\chi_{ph}(\omega)$$

Comparing with the expression in handout 19: $\varepsilon(\omega)=\varepsilon(\infty)-\dfrac{nf^2/M_r}{\omega^2-\omega_{TO}^2}$

gives us:

$$\varepsilon_o\,\chi_{ph}(\omega)=-\frac{nf^2/M_r}{\omega^2-\omega_{TO}^2}$$

And we have finally:

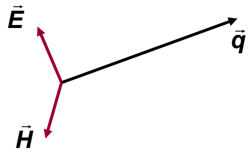
$$\varepsilon(\omega)=\varepsilon_o\left(1+\chi_e(\omega)\right)-\frac{nf^2/M_r}{\omega^2-\omega_{TO}^2}=\varepsilon_o\left(1+\chi_e(\omega)\right)-\omega_{TO}^2\,\frac{\left(\varepsilon(0)-\varepsilon(\infty)\right)}{\omega^2-\omega_{TO}^2}$$

We now find the electronic contribution

High Frequency Dielectric Constant of Solids

Consider a sinusoidal E&M wave of frequency ω propagating in a solid:

$$\vec{E}(\vec{r},t)=\hat{n}\,E_o\cos(\vec{q}\cdot\vec{r}-\omega\,t)=\text{Re}\left\{\vec{E}(\vec{r},\omega)\,e^{-i\,\omega\,t}\right\}$$



Where the electric field "phasor" is:

$$\vec{E}(\vec{r},\omega)=\hat{n}\,E_o\,e^{i\,\vec{q}\cdot\vec{r}}$$

Similarly, the magnetic field phasor is:

$$\vec{H}(\vec{r},\omega)=(\hat{q}\times\hat{n})\,H_o\,e^{i\,\vec{q}\cdot\vec{r}}$$

And the two field are related by the two Maxwell equations:

$$\nabla\times\vec{E}(\vec{r},\omega)=i\omega\,\mu_o\vec{H}(\vec{r},\omega) \qquad \text{Faraday's Law}$$

$$\nabla\times\vec{H}(\vec{r},\omega)=-i\omega\,\varepsilon(\omega)\,\vec{E}(\vec{r},\omega) \qquad \text{Ampere's Law}$$

These two equations together give the dispersion relation of the E&M wave:

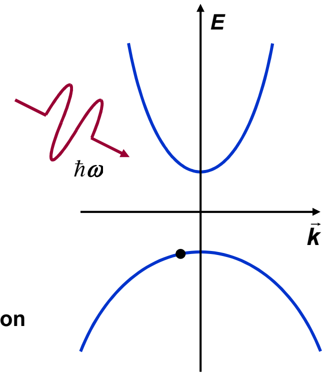
$$\omega=\frac{|\vec{q}|}{\sqrt{\varepsilon(\omega)\,\mu_o}}=q\,\frac{c}{\sqrt{\varepsilon(\omega)/\varepsilon_o}}$$

Strategy to Calculate the Dielectric Constant of Materials

1) Start with the Hamiltonian describing the interaction of the electrons with the electromagnetic field:

$$\hat{H} = \hat{H}_o + \frac{e\, A_o \left[e^{i\vec{q}\,.\,\hat{\vec{r}} - i\,\omega\, t} + e^{-i\vec{q}\,.\,\hat{\vec{r}} + i\,\omega\, t} \right]}{2m}\, \hat{\vec{P}}\,.\,\hat{n}$$

$$\hat{H}_o \left| \psi_{n,\vec{k}} \right\rangle = E_n\left(\vec{k}\right) \left| \psi_{n,\vec{k}} \right\rangle$$



2) Find out how the electron wavefunctions (i.e. Bloch functions) get modified using standard first order perturbation theory:

$$\left| \psi_{n,\vec{k}} \right\rangle_{\text{new}} = \left| \psi_{n,\vec{k}} \right\rangle + \sum_m \sum_{\vec{k}'} c_{m,\vec{k}'}(t) \left| \psi_{m,\vec{k}'} \right\rangle$$

3) From the modified wavefunctions, calculate the electron charge density, and then the dipole density

The above procedure, although doable, is a little complicated and we will use an alternate approach!

Refractive Index of Solids

The refractive index of a material is defined as: $n(\omega) = \sqrt{\frac{\varepsilon(\omega)}{\varepsilon_o}}$

The wave dispersion relation is then: $\omega = q\,\frac{c}{n(\omega)}$

And the electric field phasor can be written as:

$$\vec{E}(\vec{r},\omega) = \hat{n}\, E_o\, e^{i\,\vec{q}\,.\,\vec{r}} = \hat{n}\, E_o\, e^{i\frac{\omega\, n(\omega)}{c}\hat{q}\,.\,\vec{r}}$$

The refractive index usually has real and imaginary parts:

$$n(\omega) = n'(\omega) + i\, n''(\omega)$$

The electric field phasor is then:

$$\vec{E}(\vec{r},\omega) = \hat{n}\, E_o\, e^{i\frac{\omega\, n'(\omega)}{c}\hat{q}\,.\,\vec{r}}\, \underbrace{e^{-\frac{\omega\, n''(\omega)}{c}\hat{q}\,.\,\vec{r}}}$$

The imaginary part of the index describes wave decay (or wave amplification if gain is present)

Imaginary Part of the Refractive Index and the Loss Coefficient

We have already seen that stimulated absorption results in a wave to decay in a medium (optical loss):

$$\vec{E}(\vec{r},\omega) \propto e^{-\frac{\alpha(\omega)}{2}\hat{q}\,.\,\vec{r}}$$

Where:

$$\alpha(\omega) = \frac{\hbar\omega\,(R_{\uparrow} - R_{\downarrow})}{P}$$

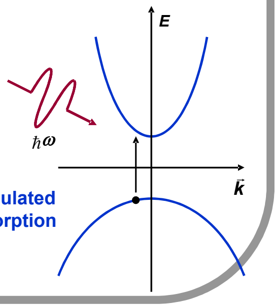
$$= \left(\frac{e}{m}\right)^2 \frac{\pi}{\varepsilon_o n'\,\omega\, c} \left\langle \left|\vec{P}_{cv}\,.\,\hat{n}\right|^2 \right\rangle \; 2\times \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3} \left[f_v(\vec{k}) - f_c(\vec{k})\right] \delta\left(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega\right)$$

But we also have:

$$\vec{E}(\vec{r},\omega) \;\propto\; e^{-\frac{\omega\, n''(\omega)}{c}\hat{q}\,.\,\vec{r}}$$

This means the imaginary part of the refractive index is:

$$\boxed{n''(\omega) = \frac{c}{\omega}\,\frac{\alpha(\omega)}{2}}$$



Stimulated absorption

High Frequency Dielectric Constant of Solids: Imaginary Part

The refractive index of a material is defined as: $n(\omega) = \sqrt{\dfrac{\varepsilon(\omega)}{\varepsilon_o}}$

Therefore, using the fact that: $|n''(\omega)| << |n'(\omega)|$

$$\varepsilon(\omega) = \varepsilon_o\, n^2(\omega) = \varepsilon_o\,[\; n'(\omega) + i n''(\omega)\;]^2 \approx \varepsilon_o\,[\; n'(\omega)\;]^2 + i2\;\varepsilon_o n'(\omega) n''(\omega)$$

$$\Rightarrow \varepsilon'(\omega) + i\varepsilon''(\omega) = \varepsilon_o\,[\; n'(\omega)\;]^2 + i2\;\varepsilon_o n'(\omega) n''(\omega)$$

This implies:

$$\boxed{\varepsilon''(\omega) \approx 2\varepsilon_o n'(\omega) n''(\omega)} \qquad \text{and} \qquad \boxed{\varepsilon'(\omega) \approx \varepsilon_o[\; n'(\omega)\;]^2}$$

Using the expression for the imaginary part of the refractive index we get:

$$\varepsilon''(\omega) = \left(\frac{e}{m}\right)^2 \frac{\pi}{\omega^2} \left\langle \left|\vec{P}_{cv}\,.\,\hat{n}\right|^2 \right\rangle \; 2\times \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3} \left[f_v(\vec{k}) - f_c(\vec{k})\right] \delta\left(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega\right)$$

Question: What is the real part of the dielectric constant?

Linear Response Functions

Linear Response Functions:

In a linear time invariant (LTI) system, the stimulus phasor $S(\omega)$ is related to the response phasor $R(\omega)$ by a linear response function $\gamma(\omega)$:

$$R(\omega) = \gamma(\omega)\, S(\omega) \qquad \left\{ \gamma(\omega) = \gamma'(\omega) + i\, \gamma''(\omega) \right.$$

The linear system must satisfy the following two properties:

i) It must be causal (system cannot respond before the stimulus is applied)
ii) A real stimulus $S(t)$ must result in a real response $R(t)$ (with no imaginary component)

The second condition gives:

$$\gamma(-\omega) = \gamma^{*}(\omega) \quad \Rightarrow \quad \gamma'(-\omega) = \gamma'(\omega) \quad \textbf{and} \quad \gamma''(-\omega) = -\gamma''(\omega)$$

Most responses of solids are expressed in terms of linear response functions. Examples include:

Conductivity: $\sigma(\omega) \longrightarrow \vec{J}(\vec{r},\omega) = \sigma(\omega)\, \vec{E}(\vec{r},\omega)$

Dielectric Constant: $\varepsilon(\omega) \longrightarrow \vec{D}(\vec{r},\omega) = \varepsilon(\omega)\, E(\vec{r},\omega)$

Linear Response Functions and Kramers-Kronig Relations

The two conditions, listed on previous slide, dictate that the real and imaginary parts of any response function cannot be independent – they must be RELATED!

$$R(\omega) = \gamma(\omega)\, S(\omega) \qquad \left\{ \gamma(\omega) = \gamma'(\omega) + i\, \gamma''(\omega) \right.$$

This relationship between the real and the imaginary parts of the response functions is captured by the Kramers-Kronig relations:

$$\boxed{\begin{aligned} \gamma''(\omega) &= 4\int_0^{\infty} \frac{d\omega'}{2\pi}\, [\gamma'(\omega') - \gamma'(\infty)] \frac{\omega}{\omega^2 - \omega'^2} && \longrightarrow \quad (1) \\ \gamma'(\omega) - \gamma'(\infty) &= -4\int_0^{\infty} \frac{d\omega'}{2\pi}\, \gamma''(\omega') \frac{\omega'}{\omega^2 - \omega'^2} && \longrightarrow \quad (2) \end{aligned}}$$

- **If one knows the real part for all frequencies, then one can find the imaginary part using Kramers-Kronig relations**

- **Conversely, if one knows the imaginary part for all frequencies, then one can find the real part using Kramers-Kronig relations**

PROOF OF KRAMERS-KRONIG RELATIONS GIVEN IN APPENDIX

High Frequency Dielectric Constant of Solids: Real Part

We have:

$$\boxed{\varepsilon''(\omega)=\left(\frac{e}{m}\right)^2\frac{\pi}{\omega^2}\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\,2\times\int_{FBZ}\frac{d^3\vec{k}}{(2\pi)^3}\left[f_v(\vec{k})-f_c(\vec{k})\right]\delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)}$$

And from the Kramers-Kronig relations we know:

$$\varepsilon'(\omega)-\varepsilon'(\infty)=-4\int_0^{\infty}\frac{d\omega'}{2\pi}\,\varepsilon''(\omega')\frac{\omega'}{\omega^2-\omega'^2}\xrightarrow{\qquad\qquad}\left\{\varepsilon'(\infty)=\varepsilon_o\right.$$

$$\Rightarrow\varepsilon'(\omega)-\varepsilon_o=-2\left(\frac{e}{m}\right)^2\hbar^2\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\,2\times\int_{FBZ}\frac{d^3\vec{k}}{(2\pi)^3}\left[f_v(\vec{k})-f_c(\vec{k})\right]\frac{\left(E_c(\vec{k})-E_v(\vec{k})\right)^{-1}}{(\hbar\omega)^2-\left(E_c(\vec{k})-E_v(\vec{k})\right)^2}$$

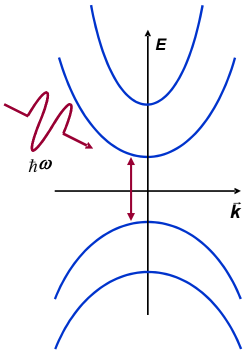
$$\boxed{\Rightarrow\varepsilon'(\omega)=\varepsilon_o-2\left(\frac{e}{m}\right)^2\hbar^2\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\,2\times\int_{FBZ}\frac{d^3\vec{k}}{(2\pi)^3}\left[f_v(\vec{k})-f_c(\vec{k})\right]\frac{\left(E_c(\vec{k})-E_v(\vec{k})\right)^{-1}}{(\hbar\omega)^2-\left(E_c(\vec{k})-E_v(\vec{k})\right)^2}}$$

High Frequency Dielectric Constant of Solids

$$\boxed{\varepsilon'(\omega)=\varepsilon_o-2\left(\frac{e}{m}\right)^2\hbar^2\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\,2\times\int_{FBZ}\frac{d^3\vec{k}}{(2\pi)^3}\left[f_v(\vec{k})-f_c(\vec{k})\right]\frac{\left(E_c(\vec{k})-E_v(\vec{k})\right)^{-1}}{(\hbar\omega)^2-\left(E_c(\vec{k})-E_v(\vec{k})\right)^2}}$$

$$\boxed{\varepsilon''(\omega)=\left(\frac{e}{m}\right)^2\frac{\pi}{\omega^2}\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\,2\times\int_{FBZ}\frac{d^3\vec{k}}{(2\pi)^3}\left[f_v(\vec{k})-f_c(\vec{k})\right]\delta\left(E_c(\vec{k})-E_v(\vec{k})-\hbar\omega\right)}$$

- Note that our expression for dielectric constant takes into account interband transitions involving only a single valence band and a single conduction band
- A more realistic expression would include interband transitions among all bands of the solid



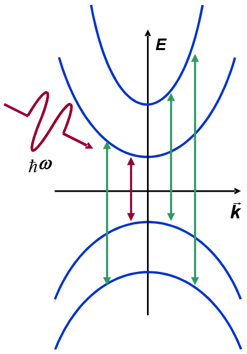
High Frequency Dielectric Constant of Solids

$$\varepsilon''(\omega)=\left(\frac{e}{m}\right)^2\frac{\pi}{\omega^2}\sum_{r,s}\;2\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\left|\vec{P}_{rs}\cdot\hat{n}\right|^2\left[f_s(\vec{k})-f_r(\vec{k})\right]\delta\left(E_r(\vec{k})-E_s(\vec{k})-\hbar\omega\right)$$

$$\varepsilon'(\omega)=\varepsilon_o-2\left(\frac{e}{m}\right)^2\hbar^2\sum_{r,s}\;2\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\left|\vec{P}_{rs}\cdot\hat{n}\right|^2\left[f_s(\vec{k})-f_r(\vec{k})\right]\frac{\left(E_r(\vec{k})-E_s(\vec{k})\right)^{-1}}{(\hbar\omega)^2-\left(E_r(\vec{k})-E_s(\vec{k})\right)^2}$$

- **The above expression includes contributions from interband transitions among all pairs of bands of the solid**

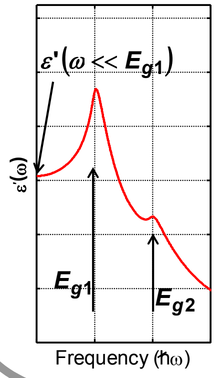
- **Usually the most important and dominant contribution at frequencies of interest comes from interband transitions between the highest occupied bands (i.e. the valence bands) and the lowest unoccupied band (i.e. the conduction bands)**

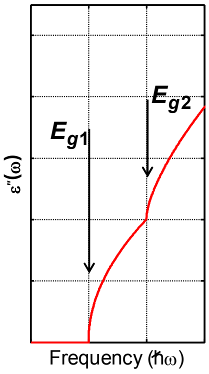


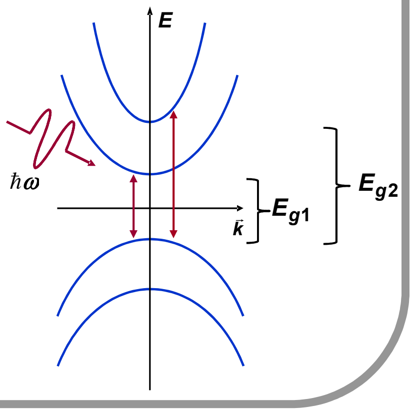
Bandgaps and the High Frequency Dielectric Constant

$$\varepsilon''(\omega)=\left(\frac{e}{m}\right)^2\frac{\pi}{\omega^2}\sum_{r,s}\;2\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\left|\vec{P}_{rs}\cdot\hat{n}\right|^2\left[f_s(\vec{k})-f_r(\vec{k})\right]\delta\left(E_r(\vec{k})-E_s(\vec{k})-\hbar\omega\right)$$

$$\varepsilon'(\omega)=\varepsilon_o-2\left(\frac{e}{m}\right)^2\hbar^2\sum_{r,s}\;2\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\left|\vec{P}_{rs}\cdot\hat{n}\right|^2\left[f_s(\vec{k})-f_r(\vec{k})\right]\frac{\left(E_r(\vec{k})-E_s(\vec{k})\right)^{-1}}{(\hbar\omega)^2-\left(E_r(\vec{k})-E_s(\vec{k})\right)^2}$$



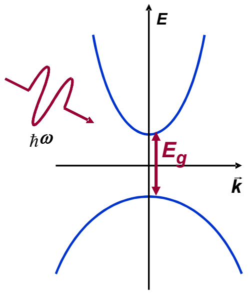




Bandgaps and the High Frequency Dielectric Constant

$$\varepsilon'(\omega)=\varepsilon_o-2\left(\frac{e}{m}\right)^2\hbar^2\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle\;2\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\left[f_v(\vec{k})-f_c(\vec{k})\right]\frac{\left(E_c(\vec{k})-E_v(\vec{k})\right)^{-1}}{(\hbar\omega)^2-\left(E_c(\vec{k})-E_v(\vec{k})\right)^2}$$

Make some very rough estimates:



$$\text{Suppose: } \hbar\omega \ll E_g$$

$$E_c(\vec{k})-E_v(\vec{k})\approx E_g$$

$$f_v(\vec{k})\approx 1 \qquad f_c(\vec{k})\approx 0$$

$$\Rightarrow \varepsilon'(\omega)\approx\varepsilon_o+2\left(\frac{e}{m}\right)^2\hbar^2\frac{\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle}{E_g^3}\;2\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\,f_v(\vec{k})$$

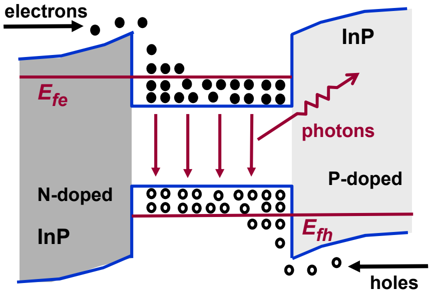
$$\approx\varepsilon_o+\frac{(e\hbar)^2}{2}\left(\frac{1}{m_e}+\frac{1}{m_h}\right)\frac{n_v}{E_g^2}$$

Remember the relation from your homework 7: $\left(\frac{1}{m_e}+\frac{1}{m_h}\right)=\frac{4}{m^2}\frac{\left\langle\left|\vec{P}_{cv}\cdot\hat{n}\right|^2\right\rangle}{E_g}$

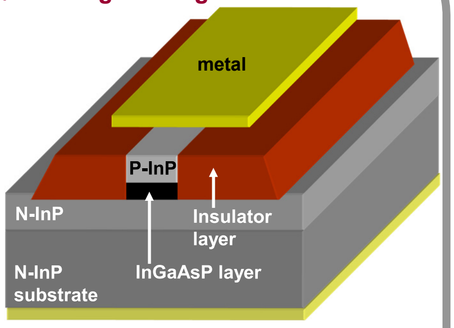
⇒ Materials with larger bandgaps will have smaller real parts of dielectric constants (and, therefore, smaller real parts of refractive indices)

Semiconductor Heterostructure Lasers

A Heterostructure Laser (Band Diagram)



A Ridge Waveguide Laser Structure

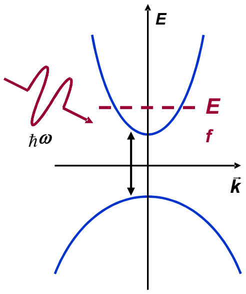


In semiconductor heterostructure laser, the wider bandgap material has smaller refractive index than the narrower bandgap material

The combination of narrow and wide bandgap materials act like a dielectric optical waveguide that confines and guides the photons

The heterostructure not only confines the carriers but it also confines the photons!!

Dielectric Constant: Case of Non-Zero Conductivity



We have obtained an expression for the dielectric constant that incorporated interband optical processes and phonons

What if the material also contained large densities of electrons or holes or both (i.e. what if the material was doped and conductive)?

Go back to Maxwell equations:

$$\nabla\times\vec{E}(\vec{r},\omega)=i\omega\,\mu_o\vec{H}(\vec{r},\omega) \qquad \text{Faraday's Law}$$

$$\nabla\times\vec{H}(\vec{r},\omega)=\vec{J}(\omega)-i\omega\,\varepsilon(\omega)\,\vec{E}(\vec{r},\omega) \qquad \text{Ampere's Law}$$

New term (current density due to electrons or holes or both)

$$\vec{J}(\omega)=\sigma(\omega)\,\vec{E}(\omega)$$

$$\Rightarrow\nabla\times\vec{H}(\vec{r},\omega)=\sigma(\omega)\,\vec{E}(\omega)-i\omega\,\varepsilon(\omega)\,\vec{E}(\vec{r},\omega)$$

$$\Rightarrow\nabla\times\vec{H}(\vec{r},\omega)=-i\omega\,\varepsilon_{eff}(\omega)\,\vec{E}(\vec{r},\omega)$$

Where:

$$\varepsilon_{eff}(\omega)=\varepsilon(\omega)+i\,\frac{\sigma(\omega)}{\omega}$$

→ The second term is the intraband or the free-carrier contribution

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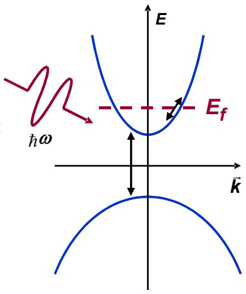
Dielectric Constant: Non-Zero Conductivity



We have:

$$\varepsilon_{eff}(\omega)=\varepsilon(\omega)+i\,\frac{\sigma(\omega)}{\omega}$$

Use the Drude model for the frequency dependent conductivity:

The equation for the electron drift velocity is (assuming parabolic/isotropic bands in 3D):

$$m_e\frac{d\vec{v}}{dt}-\frac{m_e\vec{v}}{\tau}=-e\,\vec{E}$$

In phasor notation (assuming a sinusoidal electric field):

$$\vec{v}(\omega)=-\frac{e\tau/m_e}{1-i\omega\tau}\,\vec{E}(\omega)$$

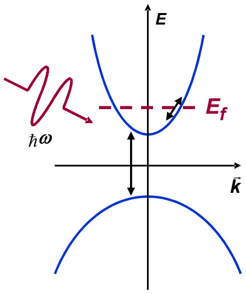
The current density is:

$$\vec{J}(\omega)=n\,e\,\vec{v}(\omega)=\sigma(\omega)\,\vec{E}(\omega)$$

where:

$$\sigma(\omega)=\frac{n\,e^2\tau/m_e}{1-i\omega\tau}$$

Dielectric Constant: Non-Zero Conductivity



Assuming non-zero densities for both electrons and holes the total conductivity becomes:

$$\sigma(\omega)=\frac{n\,e^2\tau/m_e}{1-i\omega\tau}+\frac{p\,e^2\tau/m_h}{1-i\omega\tau}$$

We have:

$$\varepsilon_{eff}(\omega)=\varepsilon(\omega)+i\frac{\sigma(\omega)}{\omega}$$

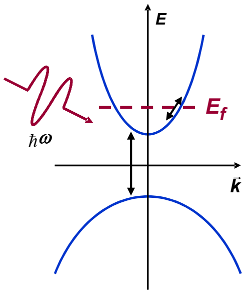
Therefore:

$$\boxed{\varepsilon_{eff}(\omega)=\underbrace{\varepsilon(\omega)}_{\text{Interband optical processes and phonons}}+\underbrace{i\frac{ne^2\tau/m_e}{\omega(1-i\omega\tau)}+i\frac{pe^2\tau/m_h}{\omega(1-i\omega\tau)}}_{\text{Intraband optical processes}}}$$

The Plasma Frequency

Suppose we have a metal or a n-doped semiconductor for which:

$$\omega\tau \gg 1$$
$$\omega \gg \omega_{TO},\omega_{LO}$$
$$\hbar\omega \ll E_g$$



Then we have:

$$\varepsilon_{eff}(\omega)=\varepsilon(\omega)+i\frac{ne^2\tau/m_e}{\omega(1-i\omega\tau)}+i\cancelto{0}{\frac{pe^2\tau/m_h}{\omega(1-i\omega\tau)}}$$
$$=\varepsilon(\infty)+i\frac{ne^2\tau/m_e}{\omega(1-i\omega\tau)}\approx\varepsilon(\infty)-\frac{ne^2/m_e}{\omega^2}$$
$$=\varepsilon(\infty)\left(1-\frac{\omega_p^2}{\omega^2}\right)$$

Where the plasma frequency is defined as:

$$\omega_p=\sqrt{\frac{ne^2}{\varepsilon(\infty)\,m_e}}\longrightarrow\begin{cases}\text{For metals:}\\ \quad \omega_p/2\pi\ \sim 4\times10^{15}\ \text{Hz}\ \ \text{(UV-blue light frequency)}\\ \text{For semiconductors:}\\ \quad \omega_p/2\pi\ \sim 10^{11}-10^{13}\ \text{Hz}\ \ \text{(Terahertz frequency)}\end{cases}$$

Putting Everything Together

$$\varepsilon_{eff}(\omega) = \varepsilon(\omega) + i\frac{\sigma(\omega)}{\omega} = \varepsilon_o\left(1 + \chi_e(\omega) + \chi_{ph}(\omega)\right) + i\frac{\sigma(\omega)}{\omega}$$

$$= \varepsilon_o + \underbrace{\varepsilon_o\chi_e(\omega)}_{\text{Electronic part (Interband)}} + \underbrace{\varepsilon_o\chi_{ph}(\omega)}_{\text{Phononic part}} + \underbrace{i\frac{\sigma(\omega)}{\omega}}_{\text{Conductivity part (electronic intraband part or the free carrier part)}}$$

Electronic Parts:

$$\varepsilon_o\chi_e(\omega) = -2\left(\frac{e}{m}\right)^2\hbar^2 \sum_{r,s} 2\times\int_{\text{FBZ}}\frac{d^3\vec{k}}{(2\pi)^3}\left|\vec{P}_{rs}\cdot\hat{n}\right|^2\left[f_s(\vec{k}) - f_r(\vec{k})\right]\frac{\left(E_r(\vec{k}) - E_s(\vec{k})\right)^{-1}}{(\hbar\omega + i\eta)^2 - \left(E_r(\vec{k}) - E_s(\vec{k})\right)^2}$$

$$i\frac{\sigma(\omega)}{\omega} = i\frac{ne^2\tau/m_e}{\omega(1 - i\omega\tau)} + i\frac{pe^2\tau/m_h}{\omega(1 - i\omega\tau)}$$

First line is the interband part and the second line is the inraband or the free-carrier part

Second line is non-zero only for conducting materials and has no zero frequency limit

Phononic Part:

$$\varepsilon_o\chi_{ph}(\omega) = -\frac{nf^2/M_r}{\omega^2 - \omega_{TO}^2}$$

Polaritons

Polaritons consist of electromagnetic waves coupled with some material wave or material excitation

It is the name given to the phenomena where electromagnetic energy becomes strongly coupled with material degrees of freedom

Some common examples of polaritons are:

1) Phonon-Polaritons

Electromagnetic waves become strongly coupled with the optical phonons of a polar medium

2) Plasmon-Polaritons

Electromagnetic waves become strongly coupled with the plasma waves of a conducting medium

3) Exciton-Polaritons

Electromagnetic waves become strongly coupled with excitons (bound electron-hole pairs)

Transverse and Longitudinal Polaritons

For any medium: $\vec{D} = \varepsilon_o \vec{E} + \vec{P} = \varepsilon(\omega)\vec{E} \qquad \rho_p = -\nabla.\vec{P}$

$$\nabla.\vec{E} = \frac{\rho_u + \rho_p}{\varepsilon_o} \qquad \nabla.\vec{D} = \frac{\rho_u}{\varepsilon_o}$$

Longitudinal Polaritons:

In longitudinal polaritons, the E-field has a non-zero divergence but the D-field has a zero divergence:

$$\nabla.\vec{E} = \frac{\rho_u + \rho_p}{\varepsilon_o} = \frac{\rho_p}{\varepsilon_o} \neq 0 \qquad \nabla.\vec{D} = \frac{\rho_u}{\varepsilon_o} = 0 \qquad \Rightarrow \qquad \rho_p = -\nabla.\vec{P} \neq 0$$

If the E-field has a wave-like form: $\vec{E} = \hat{n} E_o e^{i\vec{q}.\vec{r} - i\omega t}$

Then: $\nabla.\vec{E} \neq 0 \qquad \Rightarrow \qquad \vec{q}.\hat{n} \neq 0$

⇒ E-field has a non-zero component in the direction of wave propagation

Transverse Polaritons:

In transverse polaritons, the E-field and the D-field both have a zero divergence:

$$\nabla.\vec{E} = 0 \qquad \nabla.\vec{D} = 0 \qquad \Rightarrow \qquad \rho_p = 0$$

If the E-field has a wave-like form: $\vec{E} = \hat{n} E_o e^{i\vec{q}.\vec{r} - i\omega t}$

Then: $\nabla.\vec{E} = 0 \qquad \Rightarrow \qquad \vec{q}.\hat{n} = 0$

⇒ E-field has no component in the direction of wave propagation

---

Longitudinal Polaritons

Suppose the E-field has a wave-like form:

$$\vec{E} = \hat{n} E_o e^{i\vec{q}.\vec{r} - i\omega t}$$

The D-field is given as:

$$\vec{D} = \varepsilon_o \vec{E} + \vec{P} = \varepsilon_{eff}(\omega)\vec{E}$$

For longitudinal polaritons we must have:

$$\nabla.\vec{E} \neq 0$$
$$\nabla.\vec{D} = \varepsilon_{eff}(\omega)\nabla.\vec{E} = 0$$

The only way that both these equations can hold is if the frequency of the longitudinal polaritons is such that:

$$\varepsilon_{eff}(\omega) = 0$$

The above equation gives the frequency of the longitudinal polaritons

Longitudinal Polaritons

Longitudinal Phonon-Polaritons: Consider a non-conducting polar medium (polar semiconductor or a polar insulator) whose dielectric constant at frequencies much smaller than the material bandgap energies is approximately,

$$\varepsilon_{eff}(\omega) = \varepsilon(\infty) - \frac{nf^2/M_r}{\omega^2 - \omega_{TO}^2} = \varepsilon(\infty) - \omega_{TO}^2 \frac{(\varepsilon(0) - \varepsilon(\infty))}{\omega^2 - \omega_{TO}^2} = \varepsilon(\infty)\left[\frac{\omega^2 - \omega_{LO}^2}{\omega^2 - \omega_{TO}^2}\right]$$

The condition, $\varepsilon_{eff}(\omega) = 0$ gives:

$$\omega = \omega_{LO}$$

The longitudinal phonon-polaritons are just the polar longitudinal optical phonons!

Longitudinal Plasmon-Polaritons: Consider a conducting medium (like gold, silver) whose dielectric constant at frequencies much larger than the phonon frequencies but much smaller than the material bandgap energies is approximately,

$$\varepsilon_{eff}(\omega) = \varepsilon(\infty) + i\frac{\sigma(\omega)}{\omega} = \varepsilon(\infty) + i\frac{ne^2\tau/m_e}{\omega(1 - i\omega\tau)} \approx \varepsilon(\infty) - \frac{ne^2/m_e}{\omega^2} \qquad \{\ \omega\tau >> 1$$

The condition, $\varepsilon_{eff}(\omega) = 0$ gives:

$$\omega = \omega_p = \sqrt{\frac{ne^2}{\varepsilon(\infty) m_e}}$$

The longitudinal plasmon-polaritons are just the plasma waves!

Transverse Polaritons

Suppose the E-field has a wave-like form:

$$\vec{E} = \hat{n} E_o e^{i\vec{q}.\vec{r} - i\omega t} \qquad \{\ \nabla.\vec{E} = 0 \quad \Rightarrow \quad \vec{q}.\hat{n} = 0$$

The D-field is given as:

$$\vec{D} = \varepsilon_o \vec{E} + \vec{P} = \varepsilon_{eff}(\omega)\vec{E}$$

For transverse polaritons we must have:

$$\nabla.\vec{E} = \nabla.\vec{D} = 0$$

The electromagnetic wave equation when $\nabla.\vec{E} = 0$ is:

$$\nabla \times \nabla \times \vec{E} = \omega^2 \mu_o \varepsilon_{eff}(\omega)\vec{E}$$
$$\Rightarrow \nabla\left(\cancelto{0}{\nabla.\vec{E}}\right) - \nabla^2\vec{E} = \omega^2 \mu_o \varepsilon_{eff}(\omega)\vec{E}$$
$$\Rightarrow -\nabla^2\vec{E} = \omega^2 \mu_o \varepsilon_{eff}(\omega)\vec{E}$$

The plane wave is a solution of the wave equation if:

$$\omega^2 \frac{\varepsilon_{eff}(\omega)}{\varepsilon_o} = q^2 c^2$$

The above equation gives the dispersion of the transverse polaritons

Transverse Phonon-Polaritons

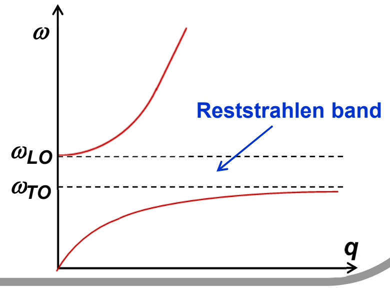
Consider a non-conducting polar medium (polar semiconductor or a polar insulator) whose dielectric constant at frequencies much smaller than the material bandgap energies is approximately,

$$\varepsilon_{eff}(\omega)=\varepsilon(\infty)-\frac{nf^2/M_r}{\omega^2-\omega_{TO}^2}=\varepsilon(\infty)-\omega_{TO}^2\frac{(\varepsilon(0)-\varepsilon(\infty))}{\omega^2-\omega_{TO}^2}=\varepsilon(\infty)\left[\frac{\omega^2-\omega_{LO}^2}{\omega^2-\omega_{TO}^2}\right]$$

The dispersion relation: $\omega^2\frac{\varepsilon_{eff}(\omega)}{\varepsilon_o}=q^2c^2$

gives the following equation:

$$\omega^4-\omega^2\left(\omega_{LO}^2+q^2c^2\,\varepsilon_o/\varepsilon(\infty)\right)+q^2c^2\omega_{TO}^2\,\varepsilon_o/\varepsilon(\infty)=0$$



The resulting dispersion relation is plotted in the Figure

Note that there is a band of frequencies in which no electromagnetic wave can propagate in the medium
(no propagating wave mode exists)

This band is called the Restsrahlen band

Transverse Plasmon-Polaritons

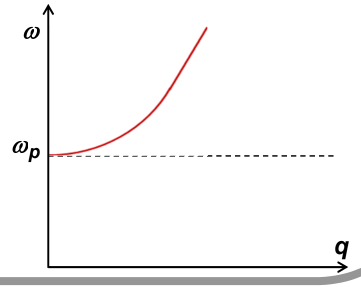
Consider a conducting medium (like gold, silver) whose dielectric constant at frequencies much larger than the phonon frequencies but much smaller than the material bandgap energies is approximately,

$$\varepsilon_{eff}(\omega)=\varepsilon(\infty)+i\frac{\sigma(\omega)}{\omega}=\varepsilon(\infty)+i\frac{ne^2\tau/m_e}{\omega(1-i\omega\tau)}\approx\varepsilon(\infty)-\frac{ne^2/m_e}{\omega^2}\qquad\{\ \omega\tau>>1$$

The dispersion relation: $\omega^2\frac{\varepsilon_{eff}(\omega)}{\varepsilon_o}=q^2c^2$

gives the following equation:

$$\omega^2=\omega_p^2+q^2c^2\frac{\varepsilon_o}{\varepsilon(\infty)}\qquad\left\{\ \omega_p=\sqrt{\frac{ne^2}{\varepsilon(\infty)m_e}}\right.$$



The resulting dispersion relation is plotted in the Figure

Note that no electromagnetic wave can propagate in the medium with a frequency smaller than the plasma frequency

APPENDIX: Kramers-Kronig Relations (Proof)

In a linear time invariant (LTI) system, the stimulus phasor $S(\omega)$ is related to the response phasor $R(\omega)$ by:

$$R(\omega)=\gamma(\omega)\,S(\omega)$$

The linear response function is $\gamma(\omega)$: $\quad \gamma(\omega)=\gamma'(\omega)+i\,\gamma''(\omega)$

Reality:

Real inputs must result in a real response. This condition gives:

$$\gamma(-\omega)=\gamma^{*}(\omega) \quad \Rightarrow \quad \gamma'(-\omega)=\gamma'(\omega) \quad \text{and} \quad \gamma''(-\omega)=-\gamma''(\omega)$$

Causality:

Inverse FT gives: $\quad R(t)=\int_{-\infty}^{\infty}dt'\;\gamma(t-t')\,S(t') \qquad \left\{\gamma(t-t')=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\;\gamma(\omega)\,e^{-i\,\omega\,(t-t')}\right.$

Causality implies that the system cannot exhibit response to an input before the input occurs:

$$\gamma(t-t')=0 \qquad \text{for} \quad t<t'$$

which gives: $\quad R(t)=\int_{-\infty}^{t}dt'\;\gamma(t-t')\,S(t')$

Infinite Frequency Response:

No physical system can respond at infinite frequencies, so:

$$\gamma(\omega\to\infty)=0$$

Kramers-Kronig Relations (Proof)

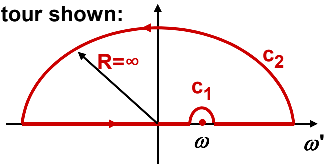
The causality condition is:

$$\gamma(t)=0 \qquad \text{for} \quad t<0$$

The function $\gamma(\omega)$, when considered as an analytic function in the complex plane, cannot have any pole in the upper half of the complex plane for the causality condition to hold

Consider the following contour integral over the contour shown:

$$\oint\frac{d\omega'}{2\pi}\frac{\gamma(\omega')}{\omega-\omega'}$$



Since there are no poles in the upper half plane, the closed contour contains no poles, and the contour integral must be zero

$$\oint\frac{d\omega'}{2\pi}\frac{\gamma(\omega')}{\omega-\omega'}=0$$

$$\Rightarrow \int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\frac{\gamma(\omega')}{\omega-\omega'}+\int_{c_1}\frac{d\omega'}{2\pi}\frac{\gamma(\omega')}{\omega-\omega'}+\cancelto{0}{\int_{c_2}\frac{d\omega'}{2\pi}\frac{\gamma(\omega')}{\omega-\omega'}}=0$$

$$\Rightarrow \int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\frac{\gamma(\omega')}{\omega-\omega'}+\frac{i}{2}\gamma(\omega)=0$$

Kramers-Kronig Relations (Proof)

$$\Rightarrow \quad \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{\gamma(\omega')}{\omega-\omega'} = -\frac{i}{2}\gamma(\omega)$$

Matching the real and imaginary parts on both sides gives:

$$\gamma'(\omega) = -2\int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{\gamma''(\omega')}{\omega-\omega'} = -4\int_{0}^{\infty} \frac{d\omega'}{2\pi}\, \gamma''(\omega')\, \frac{\omega'}{\omega^2-\omega'^2}$$

$$\gamma''(\omega) = 2\int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{\gamma'(\omega')}{\omega-\omega'} = 4\int_{0}^{\infty} \frac{d\omega'}{2\pi}\, \gamma'(\omega')\, \frac{\omega}{\omega^2-\omega'^2}$$

Where the following relations have been used to get the second integrals:

$$\gamma'(-\omega) = \gamma'(\omega) \quad \text{and} \quad \gamma''(-\omega) = -\gamma''(\omega)$$

In cases where the real part of $\gamma(\omega)$ may not be zero at infinite frequencies, as it happened in the case of the dielectric constant, we just repeat the entire procedure from the beginning with $\gamma(\omega) - \gamma'(\infty)$ instead of $\gamma(\omega)$ to get:

$$\gamma''(\omega) = 4\int_{0}^{\infty} \frac{d\omega'}{2\pi}\, \left[\gamma'(\omega') - \gamma'(\infty)\right] \frac{\omega}{\omega^2-\omega'^2}$$

$$\gamma'(\omega) - \gamma'(\infty) = -4\int_{0}^{\infty} \frac{d\omega'}{2\pi}\, \gamma''(\omega') \frac{\omega'}{\omega^2-\omega'^2}$$

Polaritons

Polaritons consist of electromagnetic waves coupled with some material wave or material excitation

It is the name given to the phenomena where electromagnetic energy becomes strongly coupled with material degrees of freedom

Some common examples of polaritons are:

1) Phonon-Polaritons

Electromagnetic waves become strongly coupled with the optical phonons of a polar medium

2) Plasmon-Polaritons

Electromagnetic waves become strongly coupled with the plasma waves of a conducting medium

3) Exciton-Polaritons

Electromagnetic waves become strongly coupled with excitons (bound electron-hole pairs)

Maxwell's Equations for Polarizable Media

For any medium, Maxwell's equations are:

$$\vec{D} = \varepsilon_o \vec{E} + \vec{P} = \varepsilon_{eff}(\omega)\vec{E} \qquad \rho_p = -\nabla . \vec{P}$$

$$\nabla . \vec{E} = \frac{\rho_u + \rho_p}{\varepsilon_o} \qquad \nabla . \vec{D} = \frac{\rho_u}{\varepsilon_o}$$

$\rho_p =$ Charge density due to material polarization (paired charge density)

$\rho_u =$ Charge density due to free unpaired charge

When a medium is subjected to an electric field, it can polarize and charge dipoles are created and the charge density associated with these dipoles is described by ρ_p

External charge placed inside a medium is described by ρ_u

Longitudinal and Transverse Polaritons

Longitudinal Polaritons:

In longitudinal polaritons, the E-field has a non-zero divergence but the D-field has a zero divergence:

$$\nabla.\vec{E} = \frac{\rho_u + \rho_p}{\varepsilon_o} = \frac{\rho_p}{\varepsilon_o} \neq 0 \qquad \nabla.\vec{D} = \frac{\rho_u}{\varepsilon_o} = 0 \qquad \Rightarrow \qquad \rho_p = -\nabla.\vec{P} \neq 0$$

If the E-field has a wave-like form: $\vec{E} = \hat{n}E_o e^{i\vec{q}.\vec{r} - i\omega t}$

Then: $\nabla.\vec{E} \neq 0 \quad \Rightarrow \quad \vec{q}.\hat{n} \neq 0$

⇒ E-field has a non-zero component in the direction of wave propagation

Transverse Polaritons:

In transverse polaritons, the E-field and the D-field both have a zero divergence:

$$\nabla.\vec{E} = 0 \qquad \nabla.\vec{D} = 0 \qquad \Rightarrow \qquad \rho_p = 0$$

If the E-field has a wave-like form: $\vec{E} = \hat{n}E_o e^{i\vec{q}.\vec{r} - i\omega t}$

Then: $\nabla.\vec{E} = 0 \quad \Rightarrow \quad \vec{q}.\hat{n} = 0$

⇒ E-field has no component in the direction of wave propagation

Longitudinal Polaritons

Suppose the E-field has a wave-like form:

$$\vec{E} = \hat{n}E_o e^{i\vec{q}.\vec{r} - i\omega t}$$

The D-field is given as:

$$\vec{D} = \varepsilon_o\vec{E} + \vec{P} = \varepsilon_{eff}(\omega)\vec{E}$$

For longitudinal polaritons we must have:

$$\nabla.\vec{E} \neq 0$$
$$\nabla.\vec{D} = \varepsilon_{eff}(\omega)\nabla.\vec{E} = 0$$

The only way that both these equations can hold is if the frequency of the longitudinal polaritons is such that at that frequency:

$$\varepsilon_{eff}(\omega) = 0$$

The above equation gives the frequency of the longitudinal polaritons

Longitudinal Polaritons

Longitudinal Phonon-Polaritons: Consider a non-conducting polar medium (polar semiconductor or a polar insulator) whose dielectric constant at frequencies much smaller than the material bandgap energies is approximately,

$$\varepsilon_{eff}(\omega)=\varepsilon(\infty)-\frac{nf^2/M_r}{\omega^2-\omega_{TO}^2}=\varepsilon(\infty)-\omega_{TO}^2\frac{(\varepsilon(0)-\varepsilon(\infty))}{\omega^2-\omega_{TO}^2}=\varepsilon(\infty)\left[\frac{\omega^2-\omega_{LO}^2}{\omega^2-\omega_{TO}^2}\right]$$

The condition, $\varepsilon_{eff}(\omega)=0$ gives:

$$\omega=\omega_{LO}$$

The longitudinal phonon-polaritons are just the polar longitudinal optical phonons!

Longitudinal Plasmon-Polaritons: Consider a conducting medium (like gold, silver) whose dielectric constant at frequencies much larger than the phonon frequencies but much smaller than the material bandgap energies is approximately,

$$\varepsilon_{eff}(\omega)=\varepsilon(\infty)+i\frac{\sigma(\omega)}{\omega}=\varepsilon(\infty)+i\frac{ne^2\tau/m_e}{\omega(1-i\omega\tau)}\approx\varepsilon(\infty)-\frac{ne^2/m_e}{\omega^2} \qquad \{\ \omega\tau>>1$$

The condition, $\varepsilon_{eff}(\omega)=0$ gives:

$$\omega=\omega_p=\sqrt{\frac{ne^2}{\varepsilon(\infty)m_e}}$$

The longitudinal plasmon-polaritons are just the plasma waves!

Transverse Polaritons

Suppose the E-field has a wave-like form:

$$\vec{E}=\hat{n}E_o e^{i\vec{q}.\vec{r}-i\omega t} \qquad \{\ \nabla.\vec{E}=0 \quad \Rightarrow \quad \vec{q}.\hat{n}=0$$

The D-field is given as:

$$\vec{D}=\varepsilon_o\vec{E}+\vec{P}=\varepsilon_{eff}(\omega)\vec{E}$$

For transverse polaritons we must have:

$$\nabla.\vec{E}=\nabla.\vec{D}=0$$

The electromagnetic wave equation when $\nabla.\vec{E}=0$ is:

$$\nabla\times\nabla\times\vec{E}=\omega^2\mu_o\varepsilon_{eff}(\omega)\vec{E}$$

$$\Rightarrow\nabla\left(\cancelto{0}{\nabla.\vec{E}}\right)-\nabla^2\vec{E}=\omega^2\mu_o\varepsilon_{eff}(\omega)\vec{E}$$

$$\Rightarrow-\nabla^2\vec{E}=\omega^2\mu_o\varepsilon_{eff}(\omega)\vec{E}$$

The plane wave is a solution of the wave equation if:

$$\omega^2\frac{\varepsilon_{eff}(\omega)}{\varepsilon_o}=q^2c^2$$

The above equation gives the dispersion of the transverse polaritons

Transverse Phonon-Polaritons

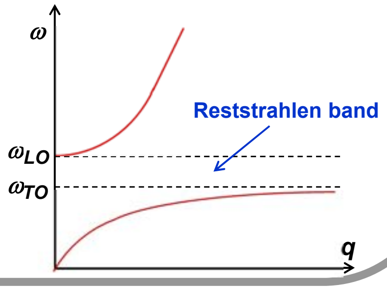
Consider a non-conducting polar medium (polar semiconductor or a polar insulator) whose dielectric constant at frequencies much smaller than the material bandgap energies is approximately,

$$\varepsilon_{eff}(\omega) = \varepsilon(\infty) - \frac{nf^2/M_r}{\omega^2 - \omega_{TO}^2} = \varepsilon(\infty) - \omega_{TO}^2 \frac{(\varepsilon(0) - \varepsilon(\infty))}{\omega^2 - \omega_{TO}^2} = \varepsilon(\infty)\left[\frac{\omega^2 - \omega_{LO}^2}{\omega^2 - \omega_{TO}^2}\right]$$

The dispersion relation: $\omega^2 \frac{\varepsilon_{eff}(\omega)}{\varepsilon_o} = q^2 c^2$

gives the following equation:

$$\omega^4 - \omega^2\left(\omega_{LO}^2 + q^2c^2\,\varepsilon_o/\varepsilon(\infty)\right) + q^2c^2\omega_{TO}^2\,\varepsilon_o/\varepsilon(\infty) = 0$$



The resulting dispersion relation is plotted in the Figure

Note that there is a band of frequencies in which no electromagnetic wave can propagate in the medium
(no propagating transverse wave mode exists)
This band is called the Restsrahlen band

Transverse Plasmon-Polaritons

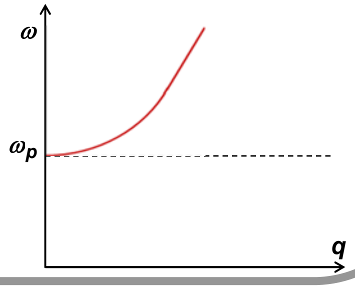
Consider a conducting medium (like gold, silver) whose dielectric constant at frequencies much larger than the phonon frequencies but much smaller than the material bandgap energies is approximately,

$$\varepsilon_{eff}(\omega) = \varepsilon(\infty) + i\frac{\sigma(\omega)}{\omega} = \varepsilon(\infty) + i\frac{ne^2\tau/m_e}{\omega(1 - i\omega\tau)} \approx \varepsilon(\infty) - \frac{ne^2/m_e}{\omega^2} \qquad \{\ \omega\tau >> 1$$

The dispersion relation: $\omega^2 \frac{\varepsilon_{eff}(\omega)}{\varepsilon_o} = q^2 c^2$

gives the following equation:

$$\omega^2 = \omega_p^2 + q^2c^2\frac{\varepsilon_o}{\varepsilon(\infty)} \qquad \left\{\ \omega_p = \sqrt{\frac{ne^2}{\varepsilon(\infty)m_e}}\right.$$



The resulting dispersion relation is plotted in the Figure

Note that no transverse electromagnetic wave can propagate in the medium with a frequency smaller than the plasma frequency

Handout 22

Electron Transport: The Boltzmann Equation

In this lecture you will learn:

- Non-equilibrium distribution functions
- The Liouville equation
- The Boltzmann equation
- Relaxation time approximation
- Scattering beyond the relaxation time approximation

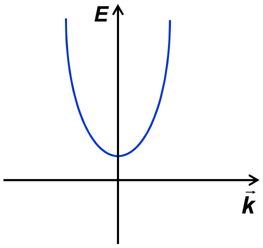
Ludwig Eduard Boltzmann
(1844-1906)

Note on Notation

In this handout, unless states otherwise, we will assume a conduction band with a dispersion given by:

$$E(\vec{k}) = E_c + \frac{\hbar^2}{2}\vec{k}^T \,.\, M^{-1} \,.\, \vec{k}$$

$$\Rightarrow \quad \vec{v}(\vec{k}) = M^{-1} \,.\, \hbar\,\vec{k}$$



Momentum Equation with Scattering and Problems

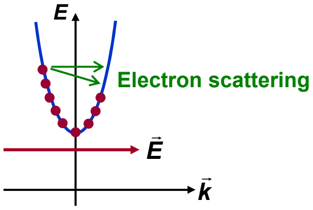
In any energy band the electrons obey the dynamical equation:

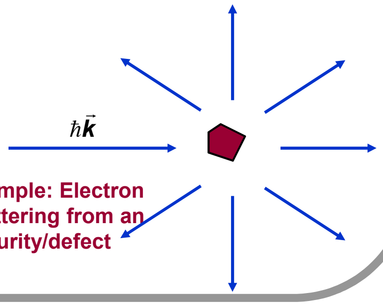
$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}$$

In the presence of scattering, we wrote:

$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E} - \left(\frac{\hbar\vec{k}(t) - \hbar\vec{k}}{\tau}\right)$$

- We need a more general and rigorous description of electron scattering than is captured by adding damping to the momentum equation





Example: Electron scattering from an impurity/defect

The Non-Equilibrium Distribution Function

In thermal equilibrium, the electron distribution (or the electron occupation probability) is given by the Fermi-Dirac distribution:

$$f_o(\vec{k}) = \frac{1}{1 + e^{(E(\vec{k}) - E_f)/KT}}$$

And the electron density can be written as:

$$n = 2 \times \int_{FBZ} \frac{d^d\vec{k}}{(2\pi)^d}\, f_o(\vec{k})$$

We generalize this concept to non-equilibrium situations (which happen, for example, when electric fields are applied from outside)

The electron distribution (or occupation probability) more generally is given by a time-dependent distribution function:

$$f(\vec{k},t)$$

that also obeys:

$$n = 2 \times \int_{FBZ} \frac{d^d\vec{k}}{(2\pi)^d}\, f(\vec{k},t)$$

The Non-Equilibrium Distribution Function

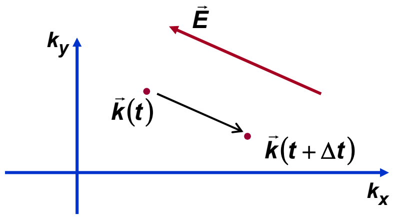
Consider a single electron state in k-space in the presence of an electric field

Assume no scattering

$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}$$

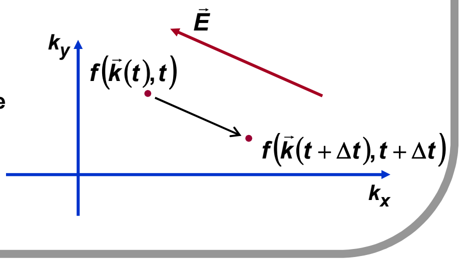
$$\Rightarrow \vec{k}(t) = \vec{k}(t=0) - \frac{e}{\hbar}\vec{E}t$$

$$\Rightarrow \vec{k}(t+\Delta t) = \vec{k}(t=0) - \frac{e}{\hbar}\vec{E}(t+\Delta t)$$



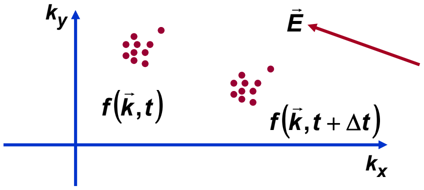
Suppose there exists a time dependent function $f(\vec{k},t)$ that gives the probability of electron occupying any state in k-space

$$\Rightarrow f\left(\vec{k}(t+\Delta t),t+\Delta t\right) = f\left(\vec{k}(t),t\right)$$



Case of No Scattering: Liouville Equation

Question: How does the non-equilibrium distribution function behave in time in the absence of scattering?



Consider an initial non-equilibrium distribution at time "t", as shown

There is also an applied electric field, as shown

In time "Δt" each electron would have moved according to the dynamical equation:

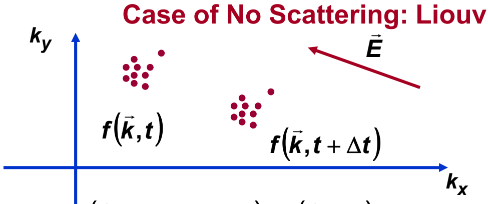
$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E} \qquad \begin{cases} \vec{k}(t) = \text{initial momentum value} \\ \vec{k}(t+\Delta t) = \text{final momentum value} \end{cases}$$

The distribution at time "$t+\Delta t$" must obey the equation:

$$f\left(\vec{k}(t+\Delta t),t+\Delta t\right) = f\left(\vec{k}(t),t\right)$$

This is because in time "Δt" the electron with initial momentum $\vec{k}(t)$ would have gone over to the state with momentum $\vec{k}(t+\Delta t)$

Case of No Scattering: Liouville Equation



$$\boxed{\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}}$$

We have: $f\left(\vec{k}(t+\Delta t), t+\Delta t\right) = f\left(\vec{k}(t), t\right)$

$$\Rightarrow \quad f\left(\vec{k}(t) + \frac{d\vec{k}(t)}{dt}\Delta t, t+\Delta t\right) = f\left(\vec{k}(t), t\right) \longrightarrow \left[\ \vec{k}(t) \text{ is arbitrary}\right.$$

$$\Rightarrow \quad f\left(\vec{k} + \frac{d\vec{k}(t)}{dt}\Delta t, t+\Delta t\right) = f\left(\vec{k}, t\right)$$

$$\Rightarrow \quad f\left(\vec{k},t\right) + \nabla_{\vec{k}} f\left(\vec{k},t\right) . \frac{d\vec{k}(t)}{dt}\Delta t + \frac{\partial f\left(\vec{k},t\right)}{\partial t}\Delta t = f\left(\vec{k},t\right)$$

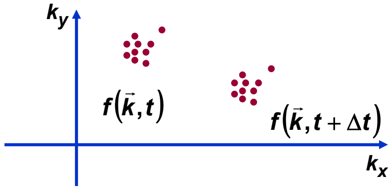
The above equation implies that the underlined term must be zero:

$$\boxed{\frac{\partial f\left(\vec{k},t\right)}{\partial t} + \nabla_{\vec{k}} f\left(\vec{k},t\right) . \frac{d\vec{k}(t)}{dt} = 0} \longrightarrow \text{Liouville equation}$$

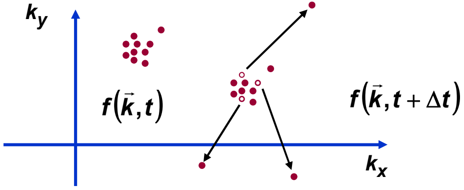
Describes the deterministic evolution of electron distribution in k-space

Boltzmann's Equation: Liouville Equation with Scattering

No Scattering



With Scattering



Now we have:

$$f\left(\vec{k}(t+\Delta t), t+\Delta t\right) = f\left(\vec{k}(t), t\right) + \{\text{changes due to scattering}\}\Delta t$$

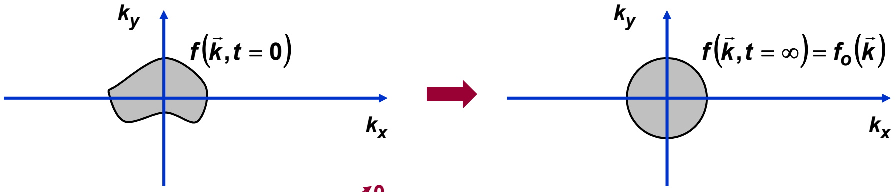
$$\Rightarrow f\left(\vec{k} + \frac{d\vec{k}(t)}{dt}\Delta t, t+\Delta t\right) = f\left(\vec{k}, t+\Delta t\right) + \{\text{changes due to scattering}\}\Delta t$$

$$\Rightarrow f\left(\vec{k},t\right) + \nabla_{\vec{k}} f\left(\vec{k},t\right) . \frac{d\vec{k}(t)}{dt}\Delta t + \frac{\partial f\left(\vec{k},t\right)}{\partial t}\Delta t = f\left(\vec{k},t\right) + \{\text{changes due to scattering}\}\Delta t$$

$$\Rightarrow \boxed{\underbrace{\frac{\partial f\left(\vec{k},t\right)}{\partial t} + \nabla_{\vec{k}} f\left(\vec{k},t\right) . \frac{d\vec{k}(t)}{dt}}_{\text{Deterministic evolution}} = \underbrace{\{\text{changes due to scattering}\}}_{\text{Non-deterministic evolution}}} \longrightarrow \text{Boltzmann's equation}$$

Relaxation Time Approximation

Suppose no external fields are applied: $\vec{E}=0$
The initial non-equilibrium distribution is given: $f(\vec{k},t=0)$
Scattering must eventually restore the equilibrium distribution function



$$\frac{\partial f(\vec{k},t)}{\partial t}+\nabla_{\vec{k}} f(\vec{k},t).\cancelto{0}{\frac{d\vec{k}(t)}{dt}}=\{\text{changes due to scattering}\}$$

$$\Rightarrow \frac{\partial f(\vec{k},t)}{\partial t}=\{\text{changes due to scattering}\}$$

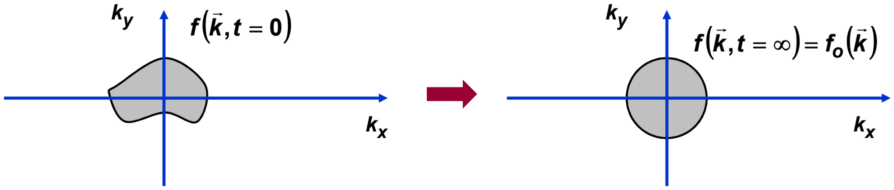
Scattering must "relax" the non-equilibrium distribution to the equilibrium Fermi-Dirac distribution at time *t* = ∞

Question: What should be the form of the expression on the RHS in the Boltzmann equation so that equilibrium Fermi-Dirac distribution is indeed restored at time *t* = ∞

Relaxation Time Approximation

Case I:

Suppose no external fields are applied: $\vec{E}=0$
The initial non-equilibrium distribution is given: $f(\vec{k},t=0)$



In the relaxation time approximation, the RHS is assumed to be as follows:

$$\frac{\partial f(\vec{k},t)}{\partial t}=\{\text{changes due to scattering}\}=-\frac{\left[f(\vec{k},t)-f_o(\vec{k})\right]}{\tau}$$

$$\Rightarrow \quad \frac{\partial f(\vec{k},t)}{\partial t}=-\frac{\left[f(\vec{k},t)-f_o(\vec{k})\right]}{\tau}$$

Solution is: $f(\vec{k},t)=f(\vec{k},t=0)e^{-t/\tau}+f_o(\vec{k})\left[1-e^{-t/\tau}\right]$

As $t\rightarrow\infty\ ,\ f(\vec{k},t)\rightarrow f_o(\vec{k})$

DC External Electric Field

When the external field is not zero, than we get:

$$\frac{\partial f(\vec{k},t)}{\partial t} + \nabla_{\vec{k}} f(\vec{k},t) . \frac{d\vec{k}(t)}{dt} = -\frac{\left[f(\vec{k},t) - f_o(\vec{k}) \right]}{\tau}$$

Case II:

Suppose a DC external field is applied: $\vec{E}$

The steady state distribution function is desired

Since: $\frac{d\,\vec{k}(t)}{dt} = -\frac{e\,\vec{E}}{\hbar}$

and since in steady state the distribution function cannot depend on time, we have:

$$\cancelto{0}{\frac{\partial f(\vec{k})}{\partial t}} - \nabla_{\vec{k}} f(\vec{k}) . \frac{e\,\vec{E}}{\hbar} = -\frac{\left[f(\vec{k}) - f_o(\vec{k}) \right]}{\tau}$$

$$\Rightarrow \quad f(\vec{k}) = f_o(\vec{k}) + \nabla_{\vec{k}} f(\vec{k}) . \frac{e\,\tau\,\vec{E}}{\hbar}$$

We will keep terms that are linear in the applied field (assuming the applied field is small) and so the distribution in the second term on the RHS can be approximated by the equilibrium distribution:

$$f(\vec{k}) \approx f_o(\vec{k}) + \nabla_{\vec{k}} f_o(\vec{k}) . \frac{e\,\tau\,\vec{E}}{\hbar}$$

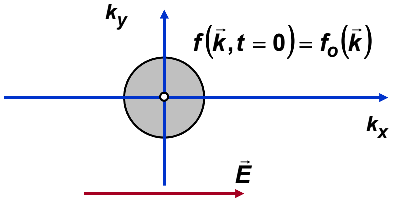
→ Final answer

DC External Electric Field

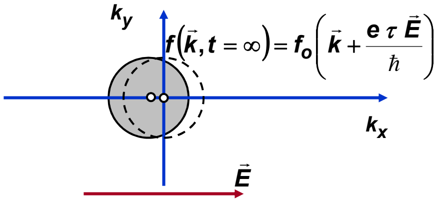
The final answer: $f(\vec{k}) \approx f_o(\vec{k}) + \nabla_{\vec{k}} f_o(\vec{k}) . \frac{e\,\tau\,\vec{E}}{\hbar}$ → 1st two terms of a Taylor expansion

can also be written approx. as: $f(\vec{k}) \approx f_o\left(\vec{k} + \frac{e\,\tau\,\vec{E}}{\hbar} \right)$ → Shifted equilibrium distribution

Initial Distribution



Steady State Distribution



Shifted equilibrium distribution
SAME AS BEFORE!

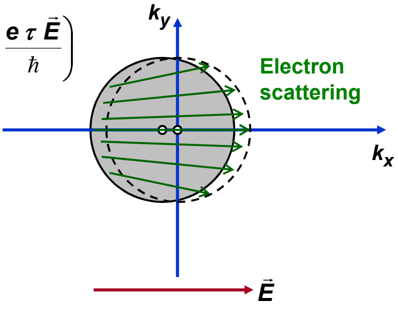
Everything from here onwards is the same as discussed earlier……………

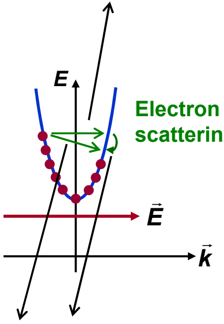
DC External Electric Field

Steady state distribution: $f(\vec{k}) \approx f_o\left(\vec{k} + \frac{e\,\tau\,\vec{E}}{\hbar}\right)$ → Shifted equilibrium distribution

Steady State Distribution

$$f(\vec{k}, t = \infty) = f_o\left(\vec{k} + \frac{e\,\tau\,\vec{E}}{\hbar}\right)$$





DC External Electric Field – Current Density

$$f(\vec{k}) \approx f_o(\vec{k}) + \nabla_{\vec{k}} f_o(\vec{k}) . \frac{e\,\tau\,\vec{E}}{\hbar} \approx f_o\left(\vec{k} + \frac{e\,\tau\,\vec{E}}{\hbar}\right)$$

Example: Consider the conduction band of a semiconductor with the following dispersion:

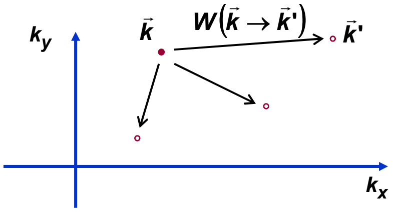
$$\boxed{E(\vec{k}) = E_c + \frac{\hbar^2}{2}\vec{k}^T . M^{-1} . \vec{k} \qquad\qquad \vec{v}(\vec{k}) = M^{-1} . \hbar\,\vec{k}}$$

The current density becomes:

$$\begin{aligned}\vec{J} &= -2\,e \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d}\, f(\vec{k})\,\vec{v}(\vec{k}) = -2\,e \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d}\, f_o\left(\vec{k} + \frac{e\tau\,\vec{E}}{\hbar}\right)\vec{v}(\vec{k}) \\ &= -2\,e \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d}\, f_o(\vec{k})\,\vec{v}\left(\vec{k} - \frac{e\tau\,\vec{E}}{\hbar}\right) = -2\,e \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d}\, f_o(\vec{k})\, M^{-1} . \hbar\left(\vec{k} - \frac{e\tau\,\vec{E}}{\hbar}\right) \\ &= e^2\tau\;\; 2 \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d}\, f_o(\vec{k})\, M^{-1} . \vec{E} \\ &= n\,e^2\tau\, M^{-1} . \vec{E} \\ &= \bar{\bar{\sigma}} . \vec{E}\end{aligned}$$

Scattering Rates

Consider a single electron state in k-space:



The electron in the initial state $\vec{k}$ can scatter to another state $\vec{k}'$ with a scattering rate given by $W(\vec{k}\rightarrow\vec{k}')$ due to phonons, defects, impurities, etc.

But to get the actual transition rate one must weigh $W(\vec{k}\rightarrow\vec{k}')$ by the probabilities that the final state is empty and the initial state is occupied:

$$R(\vec{k}\rightarrow\vec{k}')=W(\vec{k}\rightarrow\vec{k}')\,f(\vec{k},t)\left[1-f(\vec{k}',t)\right]$$

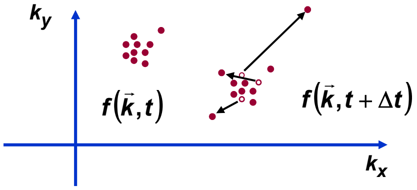
Total transition rate out of the state $\vec{k}$:

$$\sum_{\vec{k}'}R(\vec{k}\rightarrow\vec{k}')=\sum_{\vec{k}'}W(\vec{k}\rightarrow\vec{k}')\,f(\vec{k},t)\left[1-f(\vec{k}',t)\right]$$

Total transition into the state $\vec{k}$:

$$\sum_{\vec{k}'}R(\vec{k}'\rightarrow\vec{k})=\sum_{\vec{k}'}W(\vec{k}'\rightarrow\vec{k})\,f(\vec{k}',t)\left[1-f(\vec{k},t)\right]$$

Boltzmann Equation: Beyond the Relaxation Time Approximation



$$\frac{\partial f(\vec{k},t)}{\partial t}+\nabla_{\vec{k}}f(\vec{k},t).\frac{d\vec{k}(t)}{dt}=\{\text{changes due to scattering}\}$$

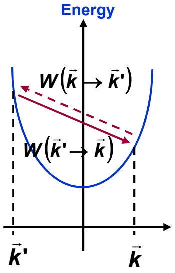
The term that represents the changes in the distribution due to scattering can be written as:

$$\frac{\partial f(\vec{k},t)}{\partial t}+\nabla_{\vec{k}}f(\vec{k},t).\frac{d\vec{k}(t)}{dt}=\sum_{\vec{k}'}W(\vec{k}'\rightarrow\vec{k})\,f(\vec{k}',t)\left[1-f(\vec{k},t)\right]$$
$$-\sum_{\vec{k}'}W(\vec{k}\rightarrow\vec{k}')\,f(\vec{k},t)\left[1-f(\vec{k}',t)\right]\approx\boxed{-\frac{\left[f(\vec{k},t)-f_o(\vec{k})\right]}{\tau}}$$

$W(\vec{k}\rightarrow\vec{k}')$ is the rate of scattering of an electron from momentum state $\vec{k}$ to $\vec{k}'$ due to impurities, defects, phonons, etc. The RHS can be shown to reduce to the relaxation time approximation expression in many cases of practical interest.

Boltzmann Equation: Beyond the Relaxation Time Approximation

$$\frac{\partial f(\vec{k},t)}{\partial t}+\nabla_{\vec{k}} f(\vec{k},t).\frac{d\vec{k}(t)}{dt}=\sum_{\vec{k}'} W(\vec{k}'\rightarrow\vec{k})\,f(\vec{k}',t)\left[1-f(\vec{k},t)\right]$$
$$-\sum_{\vec{k}'} W(\vec{k}\rightarrow\vec{k}')\,f(\vec{k},t)\left[1-f(\vec{k}',t)\right]$$



Assume thermal equilibrium:

$$f(\vec{k},t)=f_o(\vec{k}) \qquad \frac{d\vec{k}(t)}{dt}=0$$

Therefore:

$$0=\sum_{\vec{k}'} W(\vec{k}'\rightarrow\vec{k})\,f_o(\vec{k}')\left[1-f_o(\vec{k})\right]-\sum_{\vec{k}'} W(\vec{k}\rightarrow\vec{k}')\,f_o(\vec{k})\left[1-f_o(\vec{k}')\right]$$

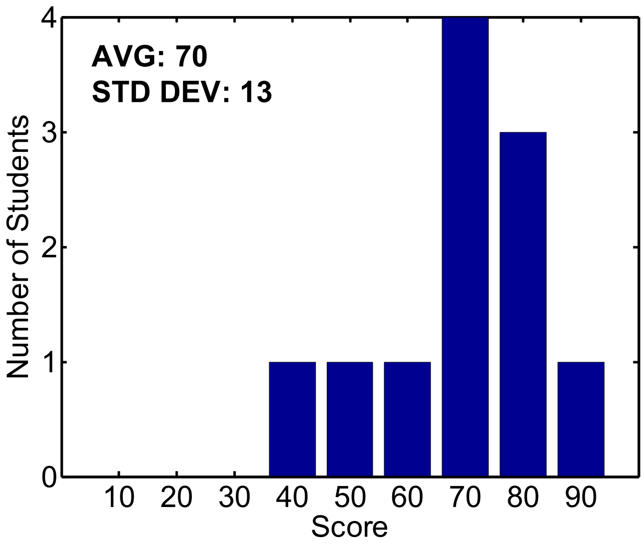
$$\Rightarrow\quad 0=\sum_{\vec{k}'}\; W(\vec{k}'\rightarrow\vec{k})\,f_o(\vec{k}')\left[1-f_o(\vec{k})\right]-W(\vec{k}\rightarrow\vec{k}')\,f_o(\vec{k})\left[1-f_o(\vec{k}')\right]$$

$$\Rightarrow\quad 0=W(\vec{k}'\rightarrow\vec{k})\,f_o(\vec{k}')\left[1-f_o(\vec{k})\right]-W(\vec{k}\rightarrow\vec{k}')\,f_o(\vec{k})\left[1-f_o(\vec{k}')\right]$$

$$\Rightarrow\quad \frac{W(\vec{k}\rightarrow\vec{k}')}{W(\vec{k}'\rightarrow\vec{k})}=\frac{f_o(\vec{k}')}{1-f_o(\vec{k}')}\,\frac{1-f_o(\vec{k})}{f_o(\vec{k})}=\frac{e^{E(\vec{k})/KT}}{e^{E(\vec{k}')/KT}}\quad\longrightarrow$$

Scattering rate to lower energy states is larger than scattering to higher energy states

Exam 1: Results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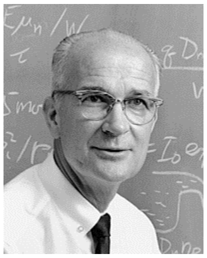
Handout 23

Electron Transport Equations

In this lecture you will learn:

- Position dependent non-equilibrium distribution functions
- The Liouville equation
- The Boltzmann equation
- Relaxation time approximation
- Transport equations



William Schockley (1910-1989)

Note on Notation

In this handout, unless states otherwise, we will assume a conduction band with a dispersion given by:

$$E(\vec{k}) = E_c + \frac{\hbar^2}{2}\vec{k}^T \,.\, M^{-1} \,.\, \vec{k}$$

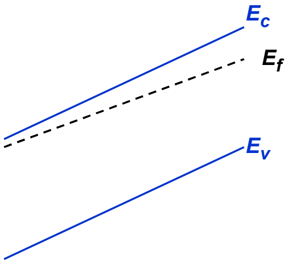
$$\Rightarrow \quad \vec{v}(\vec{k}) = M^{-1} \,.\, \hbar\,\vec{k}$$

In the presence of an electric field:

$$E(\vec{k},\vec{r}) = E_c(\vec{r}) + \frac{\hbar^2}{2}\vec{k}^T \,.\, M^{-1} \,.\, \vec{k}$$

where:

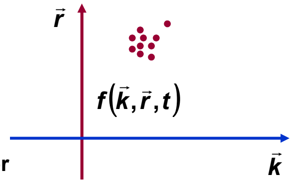
$$\nabla E_c(\vec{r}) = e\vec{E}$$



Position Dependent Non-Equilibrium Distribution Function

We generalize the concept of non-equilibrium distribution functions to situations where electron distributions could also be a function of position (as is the case in almost all electronic/optoelectronic devices):

$$f\left(\vec{k},\vec{r},t\right)$$



The local electron density is obtained upon integration over k-space:

$$n(\vec{r},t)=2\times\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\,f\left(\vec{k},\vec{r},t\right)$$

Local Equilibrium Distribution Function:

Electrons at a given location are likely to reach thermal equilibrium among themselves much faster than with electrons in other locations. The local equilibrium distribution function is defined by a local Fermi-level in the following way:

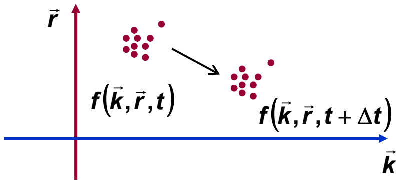
$$f_o\left(\vec{k},\vec{r},t\right)=\frac{1}{1+e^{\left(E\left(\vec{k},\vec{r}\right)-E_f(\vec{r},t)\right)/KT}}$$

with the condition that the local Fermi level must be chosen such that:

$$n(\vec{r},t)=2\times\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\,f_o\left(\vec{k},\vec{r},t\right)=2\times\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\,f\left(\vec{k},\vec{r},t\right)$$

Case of No Scattering: Liouville Equation

Question: How does the non-equilibrium distribution function behave in time in the absence of scattering?



Consider an initial non-equilibrium distribution 2*d* dimensions at time "*t* ", as shown

There is also an applied electric field, as shown

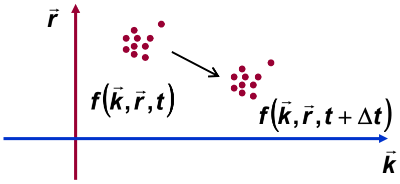
In time interval "Δ*t* " each electron would have moved in k-space according to the dynamical equation:

$$\frac{d\,\hbar\vec{k}(t)}{dt}=-e\,\vec{E}\qquad\begin{cases}\vec{k}(t)=\text{initial momentum value}\\ \vec{k}(t+\Delta t)=\text{final momentum value}\end{cases}$$

But in the same time interval "Δ*t* " each electron would have moved in real-space according to the equation:

$$\frac{d\,\vec{r}(t)}{dt}=\vec{v}\left(\vec{k}(t)\right)\qquad\begin{cases}\vec{r}(t)=\text{initial position value}\\ \vec{r}(t+\Delta t)=\text{final position value}\end{cases}$$

Case of No Scattering: Liouville Equation



$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}$$

$$\frac{d\,\vec{r}(t)}{dt} = \vec{v}\left(\vec{k}(t)\right)$$

The distribution at time "$t+\Delta t$" must obey the equation:

$$f\left(\vec{k}(t+\Delta t),\vec{r}(t+\Delta t),t+\Delta t\right) = f\left(\vec{k}(t),\vec{r}(t),t\right)$$

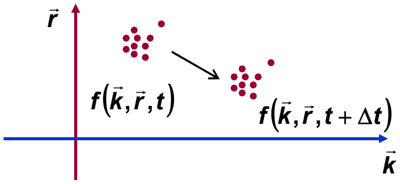
This is because in time "Δt" the electron with initial momentum $\vec{k}(t)$ and position $\vec{r}(t)$ would have gone over to the state with momentum $\vec{k}(t+\Delta t)$ and position $\vec{r}(t+\Delta t)$

$$f\left(\vec{k}(t+\Delta t),\vec{r}(t+\Delta t),t+\Delta t\right) = f\left(\vec{k}(t),\vec{r}(t),t\right)$$

$$\Rightarrow \quad f\left(\vec{k}+\frac{d\vec{k}(t)}{dt}\Delta t,\vec{r}+\frac{d\vec{r}(t)}{dt}\Delta t,t+\Delta t\right) = f\left(\vec{k},\vec{r},t+\Delta t\right)$$

$$\Rightarrow \quad f\left(\vec{k},\vec{r},t\right)+\nabla_{\vec{k}}f\left(\vec{k},\vec{r},t\right).\frac{d\vec{k}(t)}{dt}\Delta t+\nabla_{\vec{r}}f\left(\vec{k},\vec{r},t\right).\frac{d\vec{r}(t)}{dt}\Delta t+\frac{\partial f\left(\vec{k},\vec{r},t\right)}{\partial t}\Delta t = f\left(\vec{k},\vec{r},t\right)$$

Case of No Scattering: Liouville Equation



$$\frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E}$$

$$\frac{d\,\vec{r}(t)}{dt} = \vec{v}\left(\vec{k}(t)\right)$$

We have:

$$f\left(\vec{k},\vec{r},t\right)+\underline{\nabla_{\vec{k}}f\left(\vec{k},\vec{r},t\right).\frac{d\vec{k}(t)}{dt}\Delta t+\nabla_{\vec{r}}f\left(\vec{k},\vec{r},t\right).\frac{d\vec{r}(t)}{dt}\Delta t+\frac{\partial f\left(\vec{k},\vec{r},t\right)}{\partial t}\Delta t} = f\left(\vec{k},\vec{r},t\right)$$

The above equation implies that the underlined term must be zero:

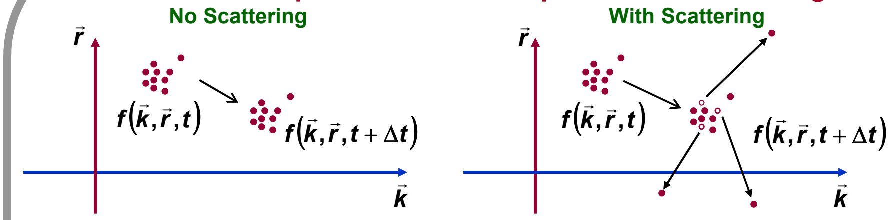
$$\boxed{\frac{\partial f\left(\vec{k},\vec{r},t\right)}{\partial t}+\nabla_{\vec{k}}f\left(\vec{k},\vec{r},t\right).\frac{d\vec{k}(t)}{dt}+\nabla_{\vec{r}}f\left(\vec{k},\vec{r},t\right).\frac{d\vec{r}(t)}{dt}=0} \longrightarrow$$

$$\boxed{\frac{\partial f\left(\vec{k},\vec{r},t\right)}{\partial t}+\nabla_{\vec{k}}f\left(\vec{k},\vec{r},t\right).\frac{d\vec{k}(t)}{dt}+\nabla_{\vec{r}}f\left(\vec{k},\vec{r},t\right).\vec{v}\left(\vec{k}\right)=0} \nearrow$$

Liouville equation

Describes the deterministic evolution of electron distribution in k-space and real-space

Boltzmann Equation: Liouville Equation with Scattering



Now we have:

$$f(\vec{k}(t+\Delta t),\vec{r}(t+\Delta t),t+\Delta t) = f(\vec{k}(t),\vec{r}(t),t) + \{\text{ changes due to scattering }\}\Delta t$$

$$\Rightarrow \boxed{\underbrace{\frac{\partial f(\vec{k},\vec{r},t)}{\partial t} + \nabla_{\vec{k}} f(\vec{k},\vec{r},t) . \frac{d\vec{k}(t)}{dt} + \nabla_{\vec{r}} f(\vec{k},\vec{r},t) . \vec{v}(\vec{k})}_{\text{Deterministic evolution}} = \underbrace{\{\text{ changes due to scattering}\}}_{\text{Non-deterministic evolution}}}$$

Boltzmann's equation

Boltzmann Equation: Relaxation Time Approximation

$$\frac{\partial f(\vec{k},\vec{r},t)}{\partial t} + \nabla_{\vec{k}} f(\vec{k},\vec{r},t) . \frac{d\vec{k}(t)}{dt} + \nabla_{\vec{r}} f(\vec{k},\vec{r},t) . \vec{v}(\vec{k}) = \{\text{ changes due to scattering}\}$$

Local Equilibrium:

- Scattering is local in space – i.e. electrons at one location do not scatter from impurities, defects, phonons, and other electrons that are present at another location
- Scattering restores local equilibrium – i.e. it drives the distribution function at any location to the local equilibrium distribution function at that location

$$\{\text{changes due to scattering}\} = -\frac{\left[f(\vec{k},\vec{r},t) - f_o(\vec{k},\vec{r},t) \right]}{\tau}$$

Note that: $n(\vec{r},t) = 2 \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} f(\vec{k},\vec{r},t) = 2 \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} f_o(\vec{k},\vec{r},t)$

$$\Rightarrow \boxed{\frac{\partial f(\vec{k},\vec{r},t)}{\partial t} + \nabla_{\vec{k}} f(\vec{k},\vec{r},t) . \frac{d\vec{k}(t)}{dt} + \nabla_{\vec{r}} f(\vec{k},\vec{r},t) . \vec{v}(\vec{k}) = -\frac{\left[f(\vec{k},\vec{r},t) - f_o(\vec{k},\vec{r},t) \right]}{\tau}}$$

Boltzmann equation in the relaxation time approximation

Transport Equations: Continuity Equation

Boltzmann equation can be manipulated to give simpler transport equations

$$\frac{\partial f(\vec{k},\vec{r},t)}{\partial t} + \nabla_{\vec{k}} f(\vec{k},\vec{r},t) \cdot \frac{d\vec{k}(t)}{dt} + \nabla_{\vec{r}} f(\vec{k},\vec{r},t) \cdot \vec{v}(\vec{k}) = -\frac{\left[f(\vec{k},\vec{r},t) - f_o(\vec{k},\vec{r},t) \right]}{\tau}$$

Integrate LHS and RHS over k-space, multiply by two, and use:

$$n(\vec{r},t) = 2 \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} f(\vec{k},\vec{r},t) = 2 \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} f_o(\vec{k},\vec{r},t)$$

$$\vec{J}(\vec{r},t) = 2\,(-e) \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} f(\vec{k},\vec{r},t)\, \vec{v}(\vec{k})$$

$$2 \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} \nabla_{\vec{k}} f(\vec{k},\vec{r},t) \cdot \frac{d\vec{k}(t)}{dt} = 0 \qquad \left\{ \frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E} \right.$$

to get:

$$\boxed{\frac{\partial n(\vec{r},t)}{\partial t} - \frac{1}{e} \nabla \cdot \vec{J}(\vec{r},t) = 0} \longrightarrow \text{Continuity equation}$$

Transport Equations: Current Density Equation

Assume DC applied electric field and steady state: $\left\{ \frac{d\,\hbar\vec{k}(t)}{dt} = -e\,\vec{E} \right.$

$$\cancelto{0}{\frac{\partial f(\vec{k},\vec{r},t)}{\partial t}} + \nabla_{\vec{k}} f(\vec{k},\vec{r},t) \cdot \frac{d\vec{k}(t)}{dt} + \nabla_{\vec{r}} f(\vec{k},\vec{r},t) \cdot \vec{v}(\vec{k}) = -\frac{\left[f(\vec{k},\vec{r},t) - f_o(\vec{k},\vec{r},t) \right]}{\tau}$$

$$\Rightarrow -e\, \nabla_{\vec{k}} f(\vec{k},\vec{r}) \cdot \frac{\vec{E}}{\hbar} + \nabla_{\vec{r}} f(\vec{k},\vec{r}) \cdot \vec{v}(\vec{k}) = -\frac{\left[f(\vec{k},\vec{r}) - f_o(\vec{k},\vec{r}) \right]}{\tau}$$

$$\Rightarrow e\tau\, \nabla_{\vec{k}} f(\vec{k},\vec{r}) \cdot \frac{\vec{E}}{\hbar} - \tau\, \nabla_{\vec{r}} f(\vec{k},\vec{r}) \cdot \vec{v}(\vec{k}) = f(\vec{k},\vec{r}) - f_o(\vec{k},\vec{r})$$

$$\Rightarrow f(\vec{k},\vec{r}) = f_o(\vec{k},\vec{r}) + e\frac{\tau}{\hbar} \nabla_{\vec{k}} f(\vec{k},\vec{r}) \cdot \vec{E} - \tau\, \nabla_{\vec{r}} f(\vec{k},\vec{r}) \cdot \vec{v}(\vec{k})$$

Assumption:

Since the difference between $f(\vec{k},\vec{r})$ and $f_o(\vec{k},\vec{r})$ will be of the order of the applied field, it is safe replace $f(\vec{k},\vec{r})$ by $f_o(\vec{k},\vec{r})$ on the RHS in the above equation:

$$\Rightarrow f(\vec{k},\vec{r}) \approx f_o(\vec{k},\vec{r}) + e\frac{\tau}{\hbar} \nabla_{\vec{k}} f_o(\vec{k},\vec{r}) \cdot \vec{E} - \tau\, \nabla_{\vec{r}} f_o(\vec{k},\vec{r}) \cdot \vec{v}(\vec{k})$$

Transport Equations: Current Density Equation

$$\Rightarrow f(\vec{k},\vec{r}) \approx f_o(\vec{k},\vec{r}) + e\frac{\tau}{\hbar}\nabla_{\vec{k}} f_o(\vec{k},\vec{r}).\vec{E} - \tau\,\nabla_{\vec{r}} f_o(\vec{k},\vec{r}).\vec{v}(\vec{k})$$

Multiply both sides by $2\,(-e)\,\vec{v}(\vec{k})$ and integrate over k-space to get:

LHS:

$$2\,(-e)\times\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\,f(\vec{k},\vec{r})\,\vec{v}(\vec{k})$$

$$=\vec{J}(\vec{r})$$

RHS:

First note that: $f_o(\vec{k},\vec{r}) = \dfrac{1}{1+e^{(E(\vec{k},\vec{r})-E_f(\vec{r}))/KT}}$

$$\Rightarrow \nabla_{\vec{r}}\, f_o(\vec{k},\vec{r}).\vec{v}(\vec{k}) = \frac{\partial f_o(\vec{k},\vec{r})}{\partial E}\nabla_{\vec{r}}\,[E_c(\vec{r})-E_f(\vec{r})].\frac{1}{\hbar}\nabla_{\vec{k}}E(\vec{k})$$

$$=\frac{1}{\hbar}\nabla_{\vec{k}} f_o(\vec{k},\vec{r}).\nabla_{\vec{r}}\,[E_c(\vec{r})-E_f(\vec{r})]$$

Therefore the RHS can be written compactly as:

$$2(-e)\times\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\left\{f_o(\vec{k},\vec{r})+\nabla_{\vec{k}} f(\vec{k},\vec{r}).\left[\frac{e\tau}{\hbar}\vec{E}-\frac{\tau}{\hbar}\nabla_{\vec{r}}\,[E_c(\vec{r})-E_f(\vec{r})]\right]\right\}\vec{v}(\vec{k})$$

$$\approx 2(-e)\times\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\,f_o\left(\vec{k}+\frac{e\tau}{\hbar}\vec{E}-\frac{\tau}{\hbar}\nabla_{\vec{r}}\,[E_c(\vec{r})-E_f(\vec{r})],\vec{r}\right)\vec{v}(\vec{k})$$

Transport Equations: Current Density Equation

$$\approx 2(-e)\times\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\,f_o\left(\vec{k}+\frac{e\tau}{\hbar}\vec{E}-\frac{\tau}{\hbar}\nabla_{\vec{r}}[E_c(\vec{r})-E_f(\vec{r})],\vec{r}\right)\vec{v}(\vec{k})$$

$$=2(-e)\times\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\,f_o(\vec{k},\vec{r})\,\vec{v}\left(\vec{k}-\frac{e\tau}{\hbar}\vec{E}+\frac{\tau}{\hbar}\nabla_{\vec{r}}[E_c(\vec{r})-E_f(\vec{r})]\right)$$

For the conduction band of a semiconductor with parabolic dispersion:

$$\vec{v}(\vec{k}) = M^{-1}.\hbar\,\vec{k}$$

The RHS becomes:

$$2(-e)\times\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\,f_o(\vec{k},\vec{r})\,M^{-1}.\hbar\left(\cancelto{0}{\vec{k}}-\frac{e\tau}{\hbar}\vec{E}+\frac{\tau}{\hbar}\nabla_{\vec{r}}[E_c(\vec{r})-E_f(\vec{r})]\right)$$

$$=n(\vec{r})e^2\tau\,M^{-1}.\left[\vec{E}-\frac{1}{e}\nabla_{r}[E_c(\vec{r})-E_f(\vec{r})]\right]=\bar{\bar{\sigma}}.\vec{E}-\frac{1}{e}\bar{\bar{\sigma}}.\nabla_{\vec{r}}[E_c(\vec{r})-E_f(\vec{r})]$$

Finally putting together the LHS and the RHS we get:

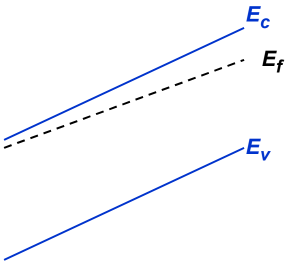
$$\boxed{\vec{J}(\vec{r})=\bar{\bar{\sigma}}.\left(\vec{E}-\frac{1}{e}\nabla_{\vec{r}}[E_c(\vec{r})-E_f(\vec{r})]\right)} \longrightarrow \text{Current density equation}$$

Current Density and the Fermi Level (Chemical Potential)

The expression for the current density is:

$$\vec{J}(\vec{r}) = \bar{\bar{\sigma}} \, . \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} \left[E_c(\vec{r}) - E_f(\vec{r}) \right] \right)$$

Therefore, currents can flow as a result of both potential gradients and Fermi-level (or chemical potential) gradients



Since:

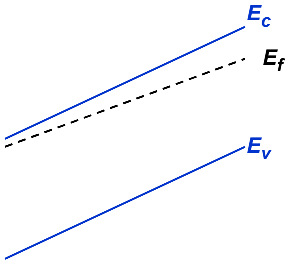
$$\nabla E_c(\vec{r}) = e\vec{E}$$

We get:

$$\vec{J}(\vec{r}) = \bar{\bar{\sigma}} \, . \frac{1}{e} \nabla_{\vec{r}} E_f(\vec{r})$$

Therefore, currents flow ONLY as a result of gradients in the Fermi level (or the chemical potential)

Transport Equations: Drift and Diffusion



The current density equation:

$$\vec{J}(\vec{r}) = \bar{\bar{\sigma}} \, . \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} \left[E_c(\vec{r}) - E_f(\vec{r}) \right] \right)$$

can be cast in one more form that is more common

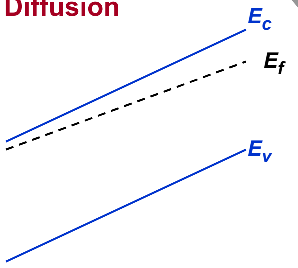
We start by relating the gradient in the Fermi level to the gradient in the carrier density:

$$n(\vec{r}) = 2 \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} f_o(\vec{k},\vec{r})$$

$$\Rightarrow \nabla_{\vec{r}} n(\vec{r}) = 2 \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} \nabla_{\vec{r}} f_o(\vec{k},\vec{r}) = 2 \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} \frac{\partial f_o(\vec{k},\vec{r})}{\partial E} \nabla_{\vec{r}} \left[E_c(\vec{r}) - E_f(\vec{r}) \right]$$

$$= -\left(2 \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} \; - \frac{\partial f_o(\vec{k},\vec{r})}{\partial E} \right) \nabla_{\vec{r}} \left[E_c(\vec{r}) - E_f(\vec{r}) \right]$$

Transport Equations: Drift and Diffusion



The expression for the current density becomes:

$$\vec{J}(\vec{r}) = \bar{\bar{\sigma}}\,.\,\vec{E} - \frac{1}{e}\bar{\bar{\sigma}}\,.\,\nabla_{\vec{r}}\left[E_c(\vec{r}) - E_f(\vec{r})\right]$$

$$= \bar{\bar{\sigma}}\,.\,\vec{E} + \frac{1}{e}\frac{\bar{\bar{\sigma}}}{2\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\left(-\frac{\partial f_o(\vec{k},\vec{r})}{\partial E}\right)}\,.\,\nabla_{\vec{r}}\,n(\vec{r})$$

$$\boxed{\vec{J}(\vec{r}) = \bar{\bar{\sigma}}\,.\,\vec{E} + e\,\bar{\bar{D}}\,.\,\nabla_{\vec{r}}\,n(\vec{r})} \longrightarrow \text{Current density equation}$$

Where we have the defined the diffusivity tensor as:

$$\bar{\bar{D}} = \frac{1}{e^2}\frac{\bar{\bar{\sigma}}}{2\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\left(-\frac{\partial f_o(\vec{k},\vec{r})}{\partial E}\right)}$$

$$\left\{\;\bar{\bar{\sigma}} = n(\vec{r})e^2\tau\,M^{-1}\right.$$

The current density equation shows that current can result from drift when there is an electric field (the first term on the RHS) and also by diffusion if there is a carrier density gradient (the second term on the RHS)

Diffusivity, Conductivity, and Mobility - I

We define the mobility tensor as:

$$\bar{\bar{\mu}} = e\tau\,M^{-1}$$

$$\left\{\;\bar{\bar{\sigma}}(\vec{r}) = n(\vec{r})\,e\,\bar{\bar{\mu}}\right.$$

Einstein Relation:

Conductivity and diffusivity are related by the Einstein relation:

$$\bar{\bar{D}} = \frac{1}{e^2}\frac{\bar{\bar{\sigma}}}{2\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\left(-\frac{\partial f_o(\vec{k},\vec{r})}{\partial E}\right)}$$

Example - Semiconductors:

Consider a semiconductor at high temperatures and assume that Maxwell-Boltzmann statistics apply:

$$f_o(\vec{k},\vec{r}) = \frac{1}{1+e^{\left(E(\vec{k})-E_f\right)/KT}} \approx e^{-\left(E(\vec{k})-E_f(\vec{r})\right)/KT}$$

$$\left\{\;E_c - E_f >> KT\right.$$

Then:

$$2\int_{\text{FBZ}}\frac{d^d\vec{k}}{(2\pi)^d}\left(-\frac{\partial f_o(\vec{k},\vec{r})}{\partial E}\right) = \frac{n(\vec{r})}{KT}$$

and the Einstein relation can be expressed as:

$$\bar{\bar{D}} = \frac{1}{e^2}\frac{\bar{\bar{\sigma}}}{n(\vec{r})/KT} = \frac{KT}{e}\left[e\tau\,M^{-1}\right] = \frac{KT}{e}\bar{\bar{\mu}}$$

Diffusivity, Conductivity, and Mobility - II

Example - Metals:

Consider a metal or a highly doped semiconductor at low temperatures. Then:

$$-\frac{\partial f_o(\vec{k},\vec{r})}{\partial E} \approx \delta\left(E(\vec{k}) - E_f\right)$$

And:

$$2\int_{FBZ} \frac{d^d\vec{k}}{(2\pi)^d}\left(-\frac{\partial f_o(\vec{k},\vec{r})}{\partial E}\right) = g_{dD}(E_f)$$

and the Einstein relation becomes:

$$\overline{\overline{D}} = \frac{1}{e^2}\frac{\overline{\overline{\sigma}}}{g_{dD}(E_f)}$$

Handout 32

Electronic Energy Transport and Thermoelectric Effects

In this lecture you will learn:

- Thermal energy transport by electrons
- Thermoelectric effects
    - Seebeck Effect
    - Peltier Effect
- Thermoelectric coolers
- Thermoelectric power converters

Lars Onsager
(1903-1976)

Note on Notation

In this handout, unless states otherwise, we will assume a conduction band with a dispersion given by:

$$E(\vec{k}) = E_c + \frac{\hbar^2}{2} \vec{k}^T \,.\, M^{-1} \,.\, \vec{k}$$

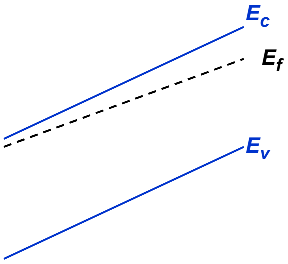
$$\Rightarrow \quad \vec{v}(\vec{k}) = M^{-1} \,.\, \hbar\, \vec{k}$$

In the presence of an electric field:

$$E(\vec{k},\vec{r}) = E_c(\vec{r}) + \frac{\hbar^2}{2} \vec{k}^T \,.\, M^{-1} \,.\, \vec{k}$$

where:

$$\nabla E_c(\vec{r}) = e\vec{E}$$



Thermoelectric Effects

There are two important effects in materials that relate electrical currents, heat flow (or thermal currents), voltage gradients (or electric fields), and temperature gradients:

1) Seebeck Effect

2) Peltier Effect

The Seebeck effect is important technologically since it expresses how temperature differences can be used to generate voltage differences

The Peltier effect expresses how current flow can be used to generate temperature differences.

Electrical Currents and Thermal Currents of Electrons

$$\boxed{\nabla_{\vec{r}} T(\vec{r}) \neq 0 \qquad \vec{E} \neq 0 \qquad \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \neq 0 \; (\text{or } \nabla_{\vec{r}} n(\vec{r}) \neq 0)}$$

In the most general case, when electric field, density gradient, and/or a temperature gradients are all present, the electrical and thermal currents can be written as,

$$\vec{J}(\vec{r}) = \overline{\overline{\sigma}}.\left(\vec{E} - \frac{1}{e}\nabla_{\vec{r}}[E_c(\vec{r}) - E_f(\vec{r})]\right) - \overline{\overline{\kappa}}.\nabla_{\vec{r}} T(\vec{r})$$

$$\vec{J}_{th}(\vec{r}) = T(\vec{r})\,\overline{\overline{\kappa}}.\left(\vec{E} - \frac{1}{e}\nabla_{\vec{r}}[E_c(\vec{r}) - E_f(\vec{r})]\right) - \overline{\overline{\kappa}}_{th}.\nabla_{\vec{r}} T(\vec{r})$$

Or in matrix form as:

$$\begin{bmatrix} \vec{J}(\vec{r}) \\ \vec{J}_{th}(\vec{r}) \end{bmatrix} = \begin{bmatrix} \overline{\overline{\sigma}} & -\overline{\overline{\kappa}} \\ T(\vec{r})\,\overline{\overline{\kappa}} & -\overline{\overline{\kappa}}_{th} \end{bmatrix} . \begin{bmatrix} \vec{E} - \frac{1}{e}\nabla_{\vec{r}}[E_c(\vec{r}) - E_f(\vec{r})] \\ \nabla_{\vec{r}} T(\vec{r}) \end{bmatrix}$$

- The above equations show that a temperature gradient can generate an electrical current and an electric field (or a carrier density gradient) can generate a thermal current

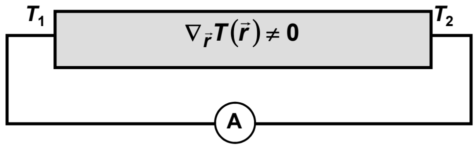
- The above equations can be used to evaluate the material responses in different situations of practical interest

- NOTE: The contribution of phonons (or the lattice) to the thermal current will be ignored here

Electrical Current from Temperature Gradient

A temperature gradient in conductive material can cause an electric current

- Consider electrons in the conduction band of a n-doped semiconductor or a metal
- There is no applied field
- There is a temperature gradient



$$\nabla_{\vec{r}} T(\vec{r}) \neq 0 \qquad \vec{E} = 0 \qquad \nabla_{\vec{r}}\left[E_c(\vec{r}) - E_f(\vec{r})\right] = 0$$

Assume for the electron density:

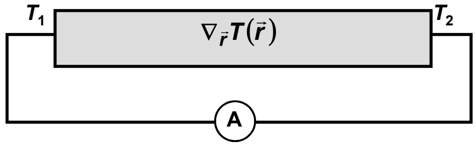
$$n(\vec{r}) = 2 \times \int_{\mathrm{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} f(\vec{k},\vec{r})$$

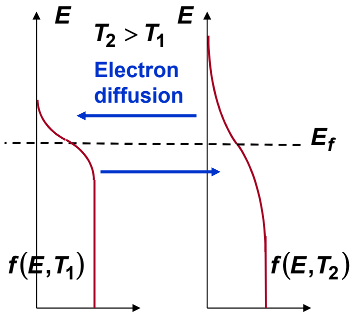
The local equilibrium distribution function is:

$$f_o(\vec{k},\vec{r}) = \frac{1}{1 + e^{\left(E(\vec{k}) - E_f\right)/KT(\vec{r})}}$$

→ Temperature is position dependent

A Physical Explanation





- Electrons with energies higher than the Fermi level diffuse from the region of higher temperature to the region of lower temperature

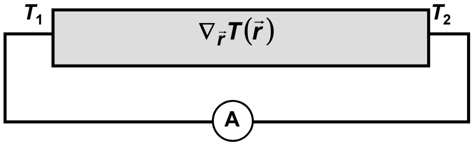
- Electrons with energies lower than the Fermi level diffuse from the region of lower temperature to region of higher temperature

- The higher energy electrons of course win and the current is in the direction of the temperature gradient

(Q:What will happen in a p-doped semiconductor?)

- Fermi level can also change with temperature but we will assume that it does not

Electrical Current from Temperature Gradient: Boltzmann Equation



Start from the Boltzmann equation assuming no applied field:

$$\Rightarrow -e\,\nabla_{\vec k} f(\vec k,\vec r)\,.\,\cancelto{0}{\frac{\vec E}{\hbar}} + \nabla_{\vec r} f(\vec k,\vec r)\,.\,\vec v(\vec k) = -\frac{\left[f(\vec k,\vec r)-f_o(\vec k,\vec r)\right]}{\tau}$$

$$\Rightarrow -\tau\,\nabla_{\vec r} f(\vec k,\vec r)\,.\,\vec v(\vec k) = f(\vec k,\vec r)-f_o(\vec k,\vec r)$$

$$\Rightarrow f(\vec k,\vec r) = f_o(\vec k,\vec r) - \tau\,\nabla_{\vec r} f(\vec k,\vec r)\,.\,\vec v(\vec k)$$

$$\Rightarrow f(\vec k,\vec r) \approx f_o(\vec k,\vec r) - \tau\,\nabla_{\vec r} f_o(\vec k,\vec r)\,.\,\vec v(\vec k)$$

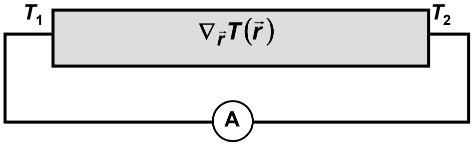
Multiply both sides by $2\,(-e)\,\vec v(\vec k)$ and integrate over k-space to get:

LHS:

$$2\,(-e)\times \int_{\text{FBZ}} \frac{d^d\vec k}{(2\pi)^d}\, f(\vec k,\vec r)\,\vec v(\vec k)$$

$$=\vec J(\vec r)$$

Electrical Current from Temperature Gradient: Boltzmann Equation



RHS:

$$-\;2(-e)\times \int_{\text{FBZ}} \frac{d^d\vec k}{(2\pi)^d}\;\tau\,\nabla_{\vec r} f_o(\vec k,\vec r)\,.\,\vec v(\vec k)\,\vec v(\vec k)$$

Note that:

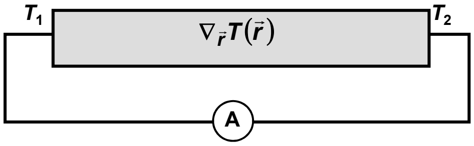
$$f_o(\vec k,\vec r) = \frac{1}{1+e^{\left(E(\vec k)-E_f\right)/KT(\vec r)}} \quad\Rightarrow\quad \nabla_{\vec r}\, f_o(\vec k,\vec r) = -\frac{\partial\, f_o(\vec k,\vec r)}{\partial E}\left(E(\vec k)-E_f\right)\frac{\nabla_{\vec r}\, T(\vec r)}{T(\vec r)}$$

Therefore, RHS becomes:

$$= 2e\,\tau\times \int_{\text{FBZ}} \frac{d^d\vec k}{(2\pi)^d}\;\nabla_{\vec r} f_o(\vec k,\vec r)\,.\,\vec v(\vec k)\;\vec v(\vec k)$$

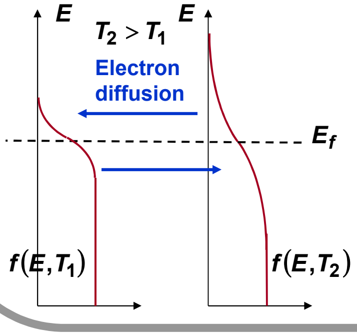
$$= 2e\,\tau\times \int_{\text{FBZ}} \frac{d^d\vec k}{(2\pi)^d}\;-\frac{\partial f_o(\vec k,\vec r)}{\partial E}\frac{\left(E(\vec k)-E_f\right)}{T(\vec r)}\left[\vec v(\vec k).\nabla_{\vec r} T(\vec r)\right]\vec v(\vec k)$$

Electrical Current from Temperature Gradient: Boltzmann Equation



Finally, putting LHS and RHS together we have:

$$\vec J(\vec r) = 2e\,\tau \times \int_{FBZ} \frac{d^d\vec k}{(2\pi)^d}\, -\frac{\partial f_o(\vec k,\vec r)}{\partial E}\frac{\left(E(\vec k)-E_f\right)}{T(\vec r)}\left[\vec v(\vec k).\nabla_{\vec r}T(\vec r)\right]\vec v(\vec k) = -\bar{\bar\kappa}\,.\,\nabla_{\vec r}T(\vec r)$$

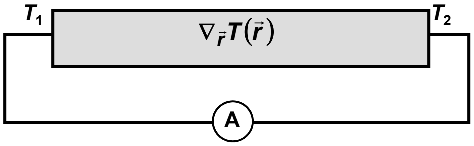


- Electrons with energies higher than the Fermi level diffuse from the region of higher temperature to the region of lower temperature

- Electrons with energies lower than the Fermi level diffuse from the region of lower temperature to region of higher temperature

- For n-doped semiconductor: $\kappa < 0$
- For p-doped semiconductor: $\kappa > 0$

Electrical Current from Temperature Gradient: Semiconductors



$$\vec J(\vec r) = 2e\,\tau \times \int_{FBZ} \frac{d^d\vec k}{(2\pi)^d}\, -\frac{\partial f_o(\vec k,\vec r)}{\partial E}\frac{\left(E(\vec k)-E_f\right)}{T(\vec r)}\left[\vec v(\vec k).\nabla_{\vec r}T(\vec r)\right]\vec v(\vec k) = -\bar{\bar\kappa}\,.\,\nabla_{\vec r}T(\vec r)$$

Example – n-doped semiconductor at high temperatures:

Consider a semiconductor at high temperatures and assume that Maxwell-Boltzmann statistics apply:

$$f_o(\vec k,\vec r) = \frac{1}{1+e^{\left(E(\vec k)-E_f\right)/KT}} \approx e^{-\left(E(\vec k)-E_f(\vec r)\right)/KT} \qquad \left\{ E_c - E_f >> KT \right.$$

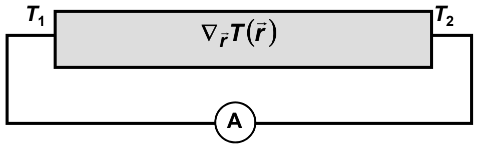
For the conduction band of a semiconductor with the following dispersion:

$$E(\vec k) = E_c + \frac{\hbar^2}{2}\vec k^T\,.\,M^{-1}\,.\,\vec k \qquad\qquad \vec v(\vec k) = M^{-1}\,.\,\hbar\,\vec k$$

We get:

$$\bar{\bar\kappa} = -\left(\frac{K}{e}\right)\left(\frac{E_c-E_f+2.5KT}{KT}\right)ne^2\tau\,M^{-1} = -\left(\frac{K}{e}\right)\left(\frac{E_c-E_f+2.5KT}{KT}\right)\bar{\bar\sigma}$$

Electrical Current from Temperature Gradient: Metals



$$\vec J(\vec r) = 2e\,\tau \times \int_{FBZ} \frac{d^d\vec k}{(2\pi)^d} \; -\frac{\partial f_o(\vec k,\vec r)}{\partial E}\frac{\left(E(\vec k)-E_f\right)}{T(\vec r)}\left[\vec v(\vec k).\nabla_{\vec r}T(\vec r)\right]\vec v(\vec k) = -\overline{\overline{\kappa}}\,.\,\nabla_{\vec r}T(\vec r)$$

Example – metal or a n-doped semiconductor at low temperatures:

In this case:

$$-\frac{\partial f_o(\vec k,\vec r)}{\partial E} \approx \delta\left(E(\vec k)-E_f\right)$$

However, using the above approximation will give a zero for $\overline{\overline{\kappa}}$ so one has to be more careful. For the conduction band with the following isotropic dispersion:

$$E(\vec k) = E_c + \frac{\hbar^2 k^2}{2m_{eff}}$$

One obtains after a more careful computation of the above integral:

$$\overline{\overline{\kappa}} = -\frac{\pi^2}{3}\left(\frac{K}{e}\right)KT\, g_{dD}(E_f)\frac{e^2\tau}{m_{eff}} = -\frac{\pi^2}{2}\left(\frac{K}{e}\right)\left(\frac{KT}{E_f}\right)\frac{ne^2\tau}{m_{eff}} = -\frac{\pi^2}{2}\left(\frac{K}{e}\right)\left(\frac{KT}{E_f}\right)\overline{\overline{\sigma}}$$

Thermopower: The Seebeck Effect and the Seebeck Tensor

- Consider a piece of metal (or semiconductor) with its two ends kept at different temperatures by some external means
- Since no current can flow in the external circuit, an electric field will build up inside the material in response to the temperature gradient resulting in a voltage difference between the two output terminals (this is the "Seebeck Effect")

The total current density in the material can be written as:

$$\vec J(\vec r) = \overline{\overline{\sigma}}\,.\,\vec E + e\,\cancelto{0}{\overline{\overline{D}}\,.\,\nabla_{\vec r}}\,n(\vec r) - \overline{\overline{\kappa}}\,.\,\nabla_{\vec r}T(\vec r) = 0$$

$$\Rightarrow\ \overline{\overline{\sigma}}\,.\,\vec E = \overline{\overline{\kappa}}\,.\,\nabla_{\vec r}T(\vec r)$$

$$\Rightarrow \vec E = \overline{\overline{\sigma}}^{-1}\,.\,\overline{\overline{\kappa}}\,.\,\nabla_{\vec r}T(\vec r) = \overline{\overline{S}}\,.\,\nabla_{\vec r}T(\vec r)$$

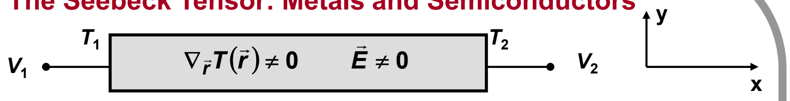
The **Thermopower tensor** or the **Seebeck tensor** is defined as:

$$\overline{\overline{S}} = \overline{\overline{\sigma}}^{-1}\,.\,\overline{\overline{\kappa}}$$

For the diagram above:

$$\vec E = \overline{\overline{S}}\,.\,\nabla_{\vec r}T(\vec r) \quad\Rightarrow\quad -\frac{dV}{dx} = S_{xx}\frac{dT}{dx} \quad\Rightarrow\quad (V_2 - V_1) = -S_{xx}\,(T_2 - T_1)$$

The Seebeck Tensor: Metals and Semiconductors



CASE I - If the slab was a n-doped semiconductor (and Maxwell Boltzmann statistics applied):

$$n = N_c e^{(E_f - E_c)/KT} \quad \Rightarrow \quad E_f - E_c = KT \log\left(\frac{n}{N_c}\right)$$

$$\overline{\overline{S}} = \overline{\overline{\sigma}}^{-1} . \overline{\overline{\kappa}} \quad \Rightarrow \quad S_{xx} = -\frac{K}{e}\left(2.5 + \log\left(\frac{N_c}{n}\right)\right)$$

$$(V_2 - V_1) = -S_{xx}\,(T_2 - T_1) = \frac{K}{e}\left(2.5 + \log\left(\frac{N_c}{n}\right)\right)(T_2 - T_1)$$

CASE II - If the slab was a heavily n-doped semiconductor (or a metal):

$$\overline{\overline{S}} = \overline{\overline{\sigma}}^{-1} . \overline{\overline{\kappa}} \quad \Rightarrow \quad S_{xx} = \frac{\pi^2}{3}\frac{K}{e}\left(\frac{KT}{E_f}\right)$$

$$(V_2 - V_1) = -S_{xx}\,(T_2 - T_1) = \frac{\pi^2}{3}\frac{K}{e}\left(\frac{KT}{E_f}\right)(T_2 - T_1)$$

$$\left\{ T = \frac{(T_2 + T_1)}{2} \right.$$

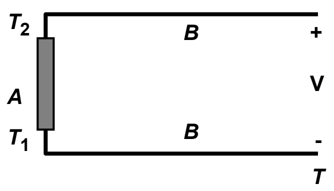
Lesson: compared to metals (in which $E_f >> KT$), doped semiconductors will produce a larger potential difference for a given temperature difference

---

Measurement of the Seebeck Tensor and Thermocouple

Some care is needed in the measurement of the Seebeck Effect

Consider a setup to measure the Seebeck Effect of material *A* by contacting it with leads made of material *B*, as shown:



The temperature of the two ends of material *A* are kept at T_2 and T_1

It is not difficult to show that in the absence of current flow, the potential *V* measured in the external circuit is:

$$V = (S_A - S_B)(T_2 - T_1)$$

Therefore, the Seebeck tensors of the materials *A* and *B* need to be significantly different in order to obtain a large potential difference. If $S_A \approx S_B$, then the voltages generated in each material cancel when going around the loop.

The Seebeck Effect is the principle behind the operation of the temperature sensor called the thermocouple

Thermodynamics and Thermal Currents in Materials

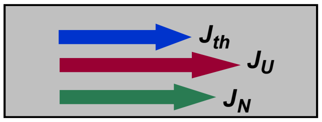
The first law of thermodynamics relates the change *dU* in the internal energy of a system to the heat energy intake *dQ*, the mechanical work done by the system *PdV*, and the particle number change *dN*:

$$dU = dQ - PdV + \mu dN$$

For electrons in semiconductors or metals, the mechanical work term can be neglected and the chemical potential μ equals the Fermi level E_f:

$$dQ = dU - E_f dN$$

Consider a slab of material in which heat energy, carried by the electrons, is flowing from left to right, as shown:



Suppose each carrier has energy *E*
$\Rightarrow J_U = E\, J_N$

Suppose the heat energy flux (units: Watts/cm^2) is J_{th}, the internal energy flux is J_U (units: Watts/cm^2) , and the carrier number flux is J_N (units: #/cm^2) , then:

$$J_{th} = J_U - E_f J_N = (E - E_f) J_N$$

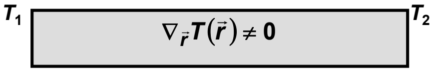
The above relation is used to compute the thermal energy flow due to electrons in materials

---

Thermal Current from Temperature Gradient

A temperature gradient in a conductive material results in heat flow (thermal current) because of electron flow

- **Consider electrons in the conduction band of a n-doped semiconductor or a metal**
- **There is no applied field but there is a temperature gradient**
- **As the electrons move from the hot side to the cold side, they also transfer thermal energy**



We have already solved for the distribution function:

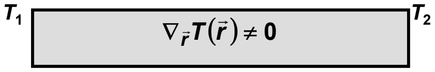
$$f(\vec k,\vec r) \approx f_o(\vec k,\vec r) - \tau\, \nabla_{\vec r} f_o(\vec k,\vec r) . \vec v(\vec k)$$
$$\approx f_o(\vec k,\vec r) + \tau \frac{\partial f_o(\vec k,\vec r)}{\partial E}\left(\frac{E(\vec k) - E_f}{T(\vec r)}\right) \nabla_{\vec r} T(\vec r) . v(\vec k)$$

The contribution to heat flow by the electrons can be obtained by multiplying the distribution function by $(E(\vec k) - E_f) v(\vec k)$ and summing over all states:

$$\vec J_{th}(\vec r) = 2 \times \int_{\text{FBZ}} \frac{d^d \vec k}{(2\pi)^d}\, \tau \frac{\partial f_o(\vec k,\vec r)}{\partial E} \frac{(E(\vec k) - E_f)^2}{T(\vec r)} \left[\vec v(\vec k) . \nabla_{\vec r} T(\vec r)\right] \vec v(\vec k) = -\overline{\overline{\kappa}}_{th} . \nabla_{\vec r} T(\vec r)$$

Here, $\overline{\overline{\kappa}}_{th}$ is the Thermal Conductivity tensor of the electrons

Thermal Current from Temperature Gradient: Semiconductors



$$\vec{J}_{th}(\vec{r}) = 2\times\int_{FBZ}\frac{d^d\vec{k}}{(2\pi)^d}\,\tau\,\frac{\partial f_o(\vec{k},\vec{r})}{\partial E}\frac{\left(E(\vec{k})-E_f\right)^2}{T(\vec{r})}\left[\vec{v}(\vec{k}).\nabla_{\vec{r}}T(\vec{r})\right]\vec{v}(\vec{k}) = -\overline{\overline{\kappa}}_{th}\,.\,\nabla_{\vec{r}}T(\vec{r})$$

Example – n-doped semiconductor at high temperatures:

Consider a semiconductor at high temperatures and assume that Maxwell-Boltzmann statistics apply:

$$f_o(\vec{k},\vec{r}) = \frac{1}{1+e^{\left(E(\vec{k})-E_f\right)/KT}} \approx e^{-\left(E(\vec{k})-E_f(\vec{r})\right)/KT} \qquad \left\{\ E_c - E_f \gg KT\right.$$

For the conduction band of a semiconductor with the following dispersion:

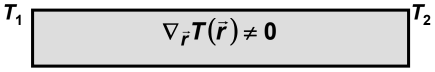
$$E(\vec{k}) = E_c + \frac{\hbar^2}{2}\vec{k}^T\,.\,M^{-1}\,.\,\vec{k} \qquad\qquad \vec{v}(\vec{k}) = M^{-1}\,.\,\hbar\,\vec{k}$$

The thermal conductivity of the electrons comes out to be:

$$\overline{\overline{\kappa}}_{th} = \left(\frac{K}{e^2}\right)\left(\frac{(E_c-E_f)^2 + 5(E_c-E_f)KT + (35/4)(KT)^2}{KT}\right)ne^2\tau\,M^{-1}$$

$$= \left(\frac{K}{e^2}\right)\left(\frac{(E_c-E_f)^2 + 5(E_c-E_f)KT + (35/4)(KT)^2}{KT}\right)\overline{\overline{\sigma}}$$

Thermal Current from Temperature Gradient: Metals



$$\vec{J}_{th}(\vec{r}) = 2\times\int_{FBZ}\frac{d^d\vec{k}}{(2\pi)^d}\,\tau\,\frac{\partial f_o(\vec{k},\vec{r})}{\partial E}\frac{\left(E(\vec{k})-E_f\right)^2}{T(\vec{r})}\left[\vec{v}(\vec{k}).\nabla_{\vec{r}}T(\vec{r})\right]\vec{v}(\vec{k}) = -\overline{\overline{\kappa}}_{th}\,.\,\nabla_{\vec{r}}T(\vec{r})$$

Example – metal or a n-doped semiconductor at low temperatures:

In this case:

$$-\frac{\partial f_o(\vec{k},\vec{r})}{\partial E} \approx \delta\left(E(\vec{k})-E_f\right)$$

However, using the above approximation expression will give a zero for $\overline{\overline{\kappa}}_{th}$ so one has to be more careful. For the conduction band with the following isotropic dispersion:

$$E(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_{eff}}$$

The thermal conductivity of the electrons comes out to be:

$$\overline{\overline{\kappa}}_{th} = \frac{\pi^2}{3}\left(\frac{K}{e^2}\right)\left(\frac{2}{3}E_f KT\right)g_{dD}(E_f)\frac{e^2\tau}{m_{eff}} = \frac{\pi^2}{3}\left(\frac{K^2T}{e^2}\right)\frac{ne^2\tau}{m_{eff}} = \frac{\pi^2}{3}\left(\frac{K^2T}{e^2}\right)\overline{\overline{\sigma}}$$

$$\Rightarrow \frac{\kappa_{th}}{T\sigma} = \frac{\pi^2}{3}\left(\frac{K}{e}\right)^2 \xrightarrow{\qquad} \text{Wiedemann–Franz Law for metals}$$

Thermal Currents from Electric Fields and Density Gradients

$$\boxed{\nabla_{\vec{r}} T(\vec{r}) = 0 \quad \vec{E} \neq 0 \quad \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \neq 0}$$

- Consider electrons in the conduction band of a n-doped semiconductor or a metal
- There is no temperature gradient but there is an applied field and possibly a carrier density gradient as well
- As the electrons move they also transfer thermal energy

We have already solved for the relevant distribution function:

$$f(\vec{k},\vec{r}) \approx f_o(\vec{k},\vec{r}) + e\tau \frac{f_o(\vec{k},\vec{r})}{\partial E} \vec{v}(\vec{k}) . \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right)$$

The contribution to heat flow by electrons can be obtained by multiplying the distribution function by $\left(E(\vec{k}) - Ef\right) v(\vec{k})$ and summing over all states:

$$\vec{J}_{th}(\vec{r}) = 2e\tau \times \int_{\text{FBZ}} \frac{d^d\vec{k}}{(2\pi)^d} \frac{\partial f_o(\vec{k},\vec{r})}{\partial E} \left(E(\vec{k}) - E_f\right) \left[\vec{v}(\vec{k}) . \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right) \right] \vec{v}(\vec{k})$$

$$= T\, \bar{\bar{\kappa}} . \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right)$$

Here, $\bar{\bar{\kappa}}$ is the same tensor found earlier which related electrical current to a temperature gradient

Electrical Currents and Thermal Currents

$$\boxed{\nabla_{\vec{r}} T(\vec{r}) \neq 0 \quad \vec{E} \neq 0 \quad \nabla_{\vec{r}} E_f(\vec{r}) \neq 0}$$

In the most general case, when electric field, density gradient, and/or a temperature gradients are all present, the electrical and thermal currents can be written as,

$$\vec{J}(\vec{r}) = \bar{\bar{\sigma}} . \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right) - \bar{\bar{\kappa}} . \nabla_{\vec{r}} T(\vec{r})$$

$$\vec{J}_{th}(\vec{r}) = T(\vec{r})\, \bar{\bar{\kappa}} . \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right) - \bar{\bar{\kappa}}_{th} . \nabla_{\vec{r}} T(\vec{r})$$

Or in matrix form as:

$$\begin{bmatrix} \vec{J}(\vec{r}) \\ \vec{J}_{th}(\vec{r}) \end{bmatrix} = \begin{bmatrix} \bar{\bar{\sigma}} & -\bar{\bar{\kappa}} \\ T(\vec{r})\, \bar{\bar{\kappa}} & -\bar{\bar{\kappa}}_{th} \end{bmatrix} . \begin{bmatrix} \vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \\ \nabla_{\vec{r}} T(\vec{r}) \end{bmatrix}$$

The above equations can be used to evaluate the material responses in different situations of practical interest

The Peltier Effect and the Peltier Tensor

Consider a material in which thermal (or density) gradients are not present. We have:

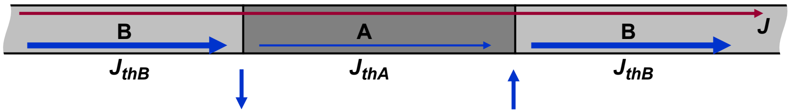
$$\left.\begin{aligned}\vec{J}(\vec{r}) &= \overline{\overline{\sigma}}.\vec{E}(\vec{r})\\ \vec{J}_{th}(\vec{r}) &= T(\vec{r})\,\overline{\overline{\kappa}}.\vec{E}(\vec{r})\end{aligned}\right\} \Longrightarrow \vec{J}_{th}(\vec{r}) = T(\vec{r})\,\overline{\overline{\kappa}}.\overline{\overline{\sigma}}^{-1}\,\vec{J}(\vec{r}) = \overline{\overline{\Pi}}.\vec{J}(\vec{r})$$

$\overline{\overline{\Pi}}$ **is called the Peltier tensor and is related to the Seebeck tensor. The relation,**

$$\vec{J}_{th}(\vec{r}) = \overline{\overline{\Pi}}.\vec{J}(\vec{r}) \qquad \Big\{ \text{For an isotropic material: } \Pi = T\,S$$

implies that a thermal current accompanies an electrical current

Now consider current flow in a double junction of materials A and B, as shown below, and suppose that $\Pi_A < \Pi_B$. The electrical current J is constant everywhere.

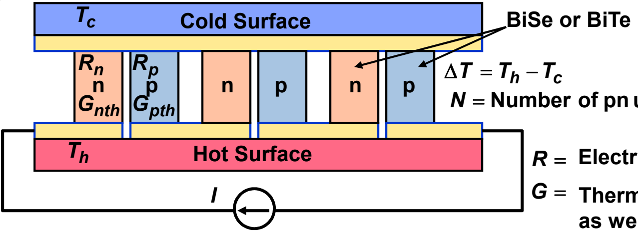


$$J_{thB} - J_{thA} = (\Pi_B - \Pi_A)\,J \qquad\qquad J_{thB} - J_{thA} = (\Pi_B - \Pi_A)\,J$$

Since material B carries more thermal current than material A for the same electrical current, the extra thermal current needs to be extracted out from the left junction otherwise thermal energy will pile up at that junction and make it hot. Similarly, heat must be provided to the right junction otherwise it will loose heat and become cold

This principle is used in electronic thermoelectric coolers (or Peltier coolers)

Thermoelectric Coolers for Refrigeration



$\Delta T = T_h - T_c$

N = Number of pn units in series

R = Electrical resistance

G = Thermal conductance (electronic as well as lattice contributions)

Thermal energy absorbed from the n-semiconductor and top metal junction: $(\Pi_m - \Pi_n)\,I$

Thermal energy absorbed from the p-semiconductor and top metal junction: $(\Pi_p - \Pi_m)\,I$

Total thermal energy absorbed from the top metal in single cell: $(\Pi_p - \Pi_n)\,I = T_c(S_p - S_n)I$

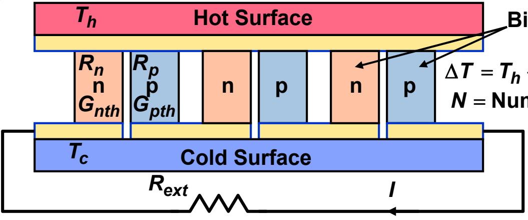
Note that the Seebeck and the Peltier coefficients are negative for n-semiconductors

After taking into account Joule losses, and heat conductance, the coefficient of performance (COP) for cooling is:

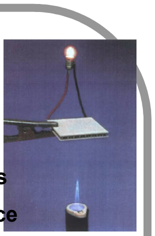
$$\text{COP} = \frac{\text{Heat removed from cold body}}{\text{Work done by the current source}} = \frac{T_c(S_p - S_n)I - (G_{nth} + G_{pth})\Delta T - I^2(R_n + R_p)/2}{\Delta T(S_p - S_n)I + I^2(R_n + R_p)}$$

$$\text{COP} \rightarrow \frac{T_c}{T_h - T_c}\ (\text{Carnot limit for refrigerators}) \qquad \text{when} \qquad R\,,G \rightarrow 0$$

Thermoelectrics for Power Generation



BiSe or BiTe



$\Delta T = T_h - T_c$

$N =$ Number of pn units in series

$R =$ Electrical resistance

$G =$ Thermal conductance (electronic as well as lattice contributions)

A thermoelectric cooler operated in reverse acts like a heat engine

The power conversion efficiency is given by:

$$\eta = \frac{\text{Power delivered to the external load}}{\text{Heat lost to the cold body}} = \frac{\dfrac{R_{ex}}{\left(N\left(R_n + R_p\right) + R_{ex}\right)}\Delta T\left(S_p - S_n\right)I}{T_h\left(S_p - S_n\right)I + \left(G_{nth} + G_{pth}\right)\Delta T + I^2\left(R_n + R_p\right)/2}$$

where: $I = \dfrac{\left(S_p - S_n\right)}{\left(N\left(R_n + R_p\right) + R_{ex}\right)}\Delta T$

$\eta \rightarrow \dfrac{T_h - T_c}{T_h}$ (Carnot limit for heat engines) when $R, G \rightarrow 0$

A commonly used figure of merit for a pn thermoelectric is: $Z = \dfrac{\left(S_p - S_n\right)^2}{\left(R_n + R_p\right)\left(G_{nth} + G_{pth}\right)}$

Both COP and η approach the Carnot values as $Z \rightarrow \infty$

Thermoelectric Figure of Merit and 3D Parabolic Band Limit

The FOM is usually expressed as the dimensionless product *ZT*: $Z\,T = \dfrac{S^2 \sigma\, T}{\kappa_{th}}$

In the ideal scenario where lattice contribution to the thermal conductivity is much smaller compared to the electronic contribution, and the semiconductor is reasonably well doped (E_c-E_f ~ 0.5*KT*), then:

$$Z\,T = \frac{S^2 \sigma\, T}{\kappa_{th}} \rightarrow \frac{\left(0.5 + 5/2\right)^2}{\left(0.5 * 0.5 + 5 * 0.5 + 35/4\right)} = 0.78 \longrightarrow$$

Independent of most material parameters!

In experiments, electronic κ_{th} is measured under conditions of zero current, which gives:

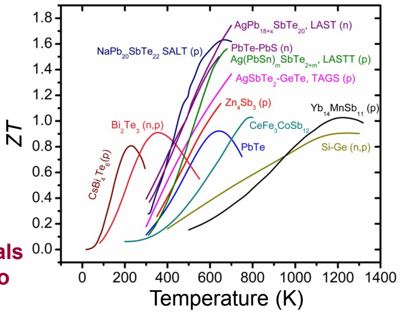
$$\kappa_{th}^{\text{measured}} = \kappa_{th}\left(1 - ZT\right)$$

⇒ The best measured value of *ZT* to be expected is,

$$\left(Z\,T\right)^{\text{measured}} = \frac{ZT}{1 - ZT} \rightarrow 3.55$$

⇒ a value of ~3-4 is the maximum upper limit for *ZT* for 3D parabolic band materials and typically it is 2-4 times smaller due to mostly lattice thermal conductivity

Values of ZT for Various Materials



Handout 28

Ballistic Quantum Transport in Semiconductor Nanostructures

In this lecture you will learn:

- Electron transport without scattering (ballistic transport)
- The quantum of conductance and the quantum of resistance
- Quantized conductance

Rolf Landauer (IBM)
(1927-1999)

Lester F. Eastman (Cornell)
(1928-)

Electron Transport Physics in Nanoscale Systems

Hydrodynamic and ballistic transport

Quantized conductance

Coulomb blockage of tunneling and single electron transistors

Coherent carrier transport

Universal conductance fluctuations

Integer and fractional quantum Hall effects

Charge density wave and spin density wave transport

Anderson localization and weak localization

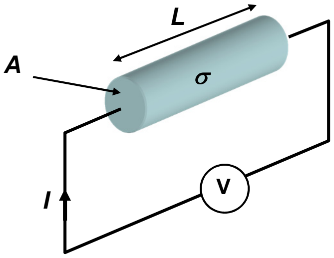
Metal-insulator transitions and Mott insulators

Molecular electronics and polarons

Strongly correlated electrons: Ferromagnets, aniterromagnets, and high-Tc superconductors, spin liquids, topological insulators

Conductors and Dissipation

Traditional View of Conductors:



$$E = \frac{V}{L}$$

$$J = \sigma E$$

$$I = AJ = A\sigma E = \frac{\sigma A}{L} V = GV = \frac{V}{R}$$

$$\Rightarrow G = \frac{\sigma A}{L} = \frac{1}{R}$$

Power Dissipation in Conductors:

E&M (energy continuity equation) tells us that the power dissipation per unit volume of a resistor is:

$$= J\,E = \sigma\,E^2 = \frac{J^2}{\sigma}$$

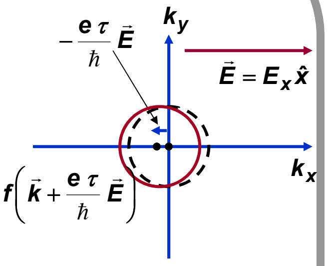
Power dissipation in the entire resistor is:

$$P = J\,E\,(AL) = J^2\frac{AL}{\sigma} = J^2A^2\frac{L}{\sigma A} = I^2R = \frac{I^2}{G}$$

Characteristic Velocity for Conduction

Consider a 3D solid in which the energy dispersion for conduction band near a band minimum is given by:

$$E_c(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_e} \quad \Rightarrow \quad \vec{v}_c(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}} E_c(\vec{k}) = \frac{\hbar \vec{k}}{m_e}$$



Current Density:

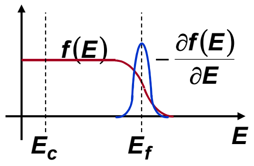
$$\vec{J} = -2\,e \times \int \frac{d^3\vec{k}}{(2\pi)^3}\, f\left(\vec{k} + \frac{e\tau}{\hbar}\vec{E}\right)\vec{v}_c(\vec{k})$$

$$= -2\,e \times \int \frac{d^3\vec{k}}{(2\pi)^3}\left[\cancelto{0}{f(\vec{k})} + \frac{e\tau}{\hbar}\vec{E}\,.\,\nabla_{\vec{k}} f(\vec{k})\right]\vec{v}_c(\vec{k})$$

$$= -2\,e \times \int \frac{d^3\vec{k}}{(2\pi)^3}\left[\frac{e\tau}{\hbar}\vec{E}\,.\,\nabla_{\vec{k}} E_c(\vec{k})\frac{\partial f(E)}{\partial E}\right]\vec{v}_c(\vec{k})$$

$$= 2\,e^2\tau \times \int \frac{d^3\vec{k}}{(2\pi)^3}\left(-\frac{\partial f(E)}{\partial E}\right)\left[\vec{E}\,.\,\vec{v}_c(\vec{k})\right]\vec{v}_c(\vec{k})$$

$$= \frac{ne^2\tau}{m_e}\vec{E}$$



Only electrons close to the Fermi energy contribute to the conductivity in metals or heavily doped semiconductors at low temperatures

Characteristic Velocity for Conduction and Mean Free Path

Characteristic Velocity:

The characteristic velocity is the average velocity of those electrons that contribute to the conductivity:

$$\left\langle v^2 \right\rangle = \frac{\int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} \left(-\frac{\partial f(E)}{\partial E}\right) \vec{v}(\vec{k}) . \vec{v}(\vec{k})}{\int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} \left(-\frac{\partial f(E)}{\partial E}\right)}$$

For metals and heavily doped semiconductors at low temperatures: $\sqrt{\left\langle v^2 \right\rangle} \approx v_F$

For low doped semiconductors at high temperatures: $\sqrt{\left\langle v^2 \right\rangle} \approx \sqrt{\frac{d\, KT}{m_e}}$

Mean Free Path:

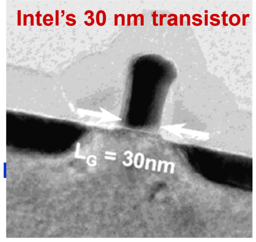
The mean free path ℓ is defined as the average distance an electron travels before it scatters. It is given by:

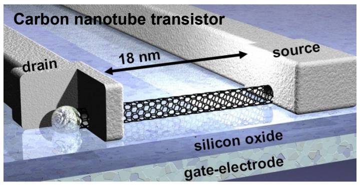
$$\ell = \sqrt{\left\langle v^2 \right\rangle}\, \tau$$

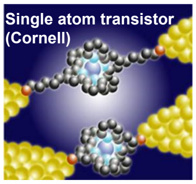
where τ is the scattering time.

Ballistic Electron Transport

The length scales involved in the smallest transistors and nanoscale devices, such as carbon nanotubes and molecular conductors, can be small enough so that the electrons do not scatter during the time it takes to travel through the device







When the length L of the conductor becomes much smaller than the mean free path ℓ the transport is termed “ballistic” meaning that the electrons do not scatter during the time it takes to travel through the conductor

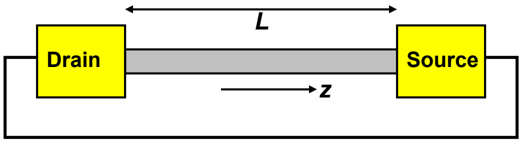
Ballistic transport condition: $L \ll \ell$

Questions:

- What happens when $L \ll \ell$?
- The formulas for conductivity that have the scattering time τ in them are clearly no longer valid since there is no scattering: $\sigma = \frac{ne^2\tau}{m_e} \quad \{\tau \to \infty$
- What about dissipation?

Ballistic Electron Transport in a 1D Conductor

Consider a 1D conductor (example, a quantum nanowire) that is contacted at both ends by an external circuit.

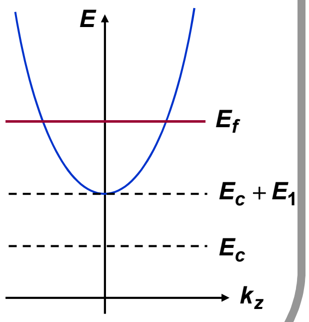


The dispersion relation for the electrons inside the quantum wire is:

$$E_c(k_z) = E_c + E_1 + \frac{\hbar^2 k_z^2}{2m_e}$$

$$v(k_z) = \frac{1}{\hbar}\frac{\partial E_c(k_z)}{\partial z} = \frac{\hbar k_z}{m_e}$$

Assume only one subband



The electron density (number per unit length) is:

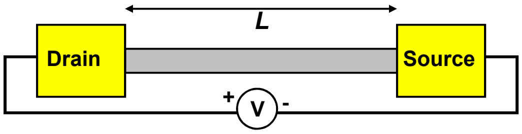
$$n = 2 \times \int_{-\infty}^{\infty} \frac{dk_z}{(2\pi)} f(E_c(k_z) - E_f)$$

The length *L* of the wire is short enough such that:

$$L \ll \ell$$

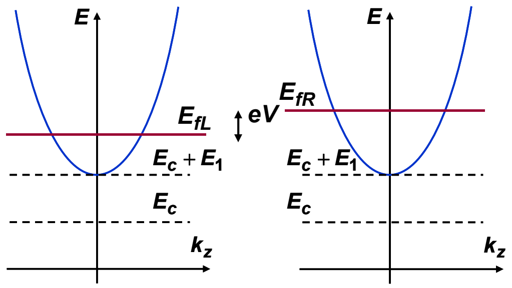
Electric Fields, Chemical Potentials, and Voltage Sources

Now suppose a voltage source is applied from outside:



In electronics, one never applies "electric fields" nor even "electrostatic potential differences" to circuits but only "chemical potential differences" by using voltage sources

The voltage source will raise the chemical potential (or the Fermi level) on one side of the conductor with respect to the other by an amount *eV*



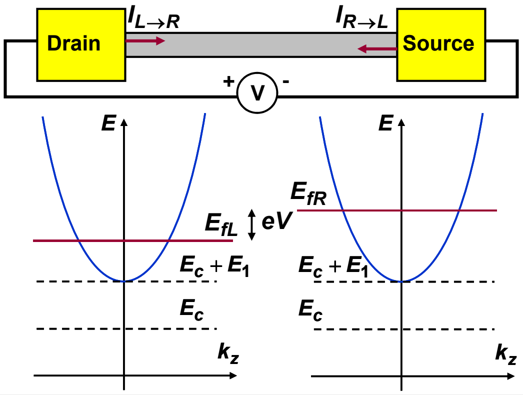
Electron Currents

At the left contact, the current due to electrons moving in the right direction is:

$$I_{L\to R} = (-e)2\times\int_{0}^{\infty}\frac{dk_z}{2\pi}\, v_c(k_z)\; f(E_c(k_z)-E_{fL})$$

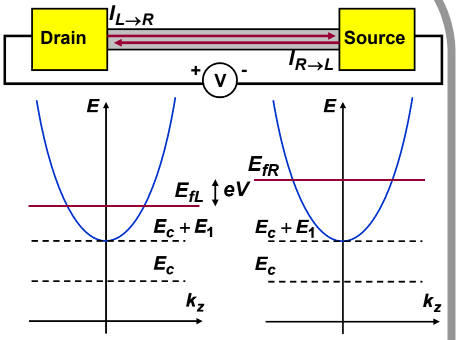
At the right contact, the current due to electrons moving in the left direction is:

$$I_{R\to L} = (-e)2\times\int_{-\infty}^{0}\frac{dk_z}{2\pi}\, v_c(k_z)\; f(E_c(k_z)-E_{fR})$$



Arrows indicate the direction of electron flow (not the direction of current, which is opposite)

Ballistic Transport



Electrons do not scatter in the quantum wire. Therefore:

- All electrons that enter the wire from the left contact make it to the right contact
- All electrons that enter the wire from the right contact make it to the left contact

Total Current:

The net current is the sum of the currents due to the right-moving and left-moving electrons:

$$I = I_{L\to R} + I_{R\to L}$$

$$= (-e)2\times\int_{0}^{\infty}\frac{dk_z}{2\pi}\, v_c(k_z)\; f(E_c(k_z)-E_{fL}) + (-e)2\times\int_{-\infty}^{0}\frac{dk_z}{2\pi}\, v_c(k_z)\; f(E_c(k_z)-E_{fR})$$

$$= e\,2\times\int_{0}^{\infty}\frac{dk_z}{2\pi}\, v_c(k_z)\; \left[f(E_c(k_z)-E_{fR}) - f(E_c(k_z)-E_{fL})\right]$$

Ballistic Transport Conductance

Total Current:

$$I = e\,2\times\int_0^\infty \frac{dk_z}{2\pi}\, v_c(k_z)\,\left[f\left(E_c(k_z)-E_{fR}\right)-f\left(E_c(k_z)-E_{fL}\right)\right]$$

$$= 2\times\frac{e}{2\pi}\int_{E_c+E_1}^{\infty}\left|\frac{dk_z}{dE}\right| dE\; v_c(k_z)\,\left[f\left(E-E_{fR}\right)-f\left(E-E_{fL}\right)\right]$$

$$= 2\times\frac{e}{2\pi\hbar}\int_{E_c+E_1}^{\infty} dE\,\left[f\left(E-E_{fR}\right)-f\left(E-E_{fL}\right)\right] \longrightarrow \text{Very simple}$$

Assume T ≈ 0K:

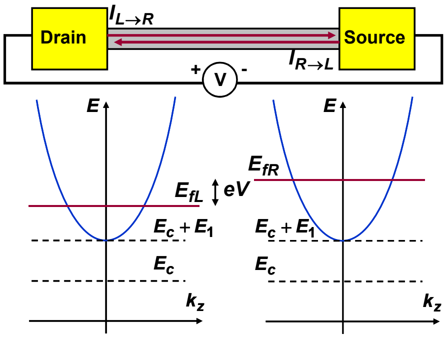
$$I = \frac{e}{\pi\hbar}(eV)$$

$$= \frac{e^2}{\pi\hbar}V$$

Conductance:

$$I = GV$$

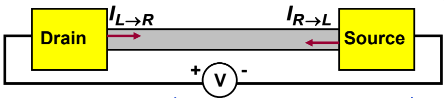
$$\Rightarrow G = \frac{e^2}{\pi\hbar}$$



Quantum of Conductance

The relation:

$$I = GV \quad\Rightarrow\quad G = \frac{e^2}{\pi\hbar}$$



defines the quantum of conductance as:

$$G_Q = \frac{e^2}{\pi\hbar} = 7.72\times10^{-5}\ \text{S}$$

The quantum of resistance is therefore: $R_Q = \frac{1}{G_Q} = \frac{\pi\hbar}{e^2} = 12.95\ \text{k}\Omega$

The Quantum of Conductance:

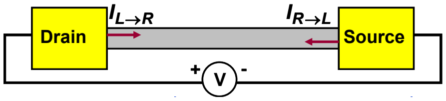
- The quantum of conductance is the smallest possible non-zero conductance of a completely ballistic conductor. Equivalently, the quantum of resistance is the highest possible resistance of a completely ballistic conductor.

- All completely ballistic conductors (whether in 1D, 2D, or 3D) will have conductance that is in multiples of the quantum conductance value (one can think of ballistic conductance in 2D and 3D as a number of 1D conductors in parallel)

The Question of Energy Dissipation

The relation:

$$I = G_Q V = \frac{V}{R_Q}$$



suggests that there should be power dissipation in the conductor given by:

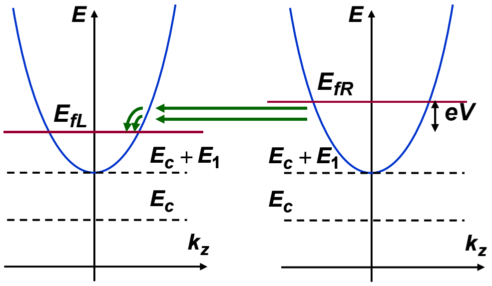
$$P = I^2 R_Q = \frac{V^2}{R_Q}$$

But, as we have seen, electrons do not loose any energy in the conductor – they do not scatter – they go ballistic. So where is the energy being dissipated?

Answer:

The energy is dissipated in the contact not in the conductor!

Electrons loose energy and thermalize when they reach the contact



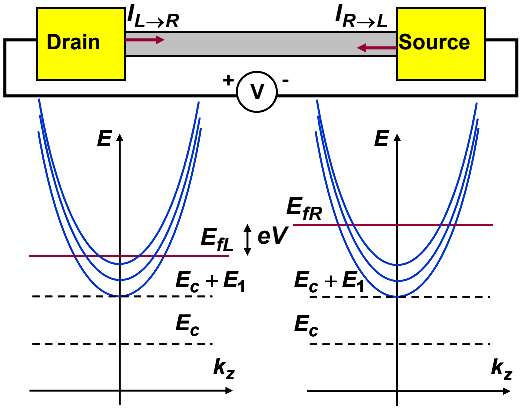
Multiple Subbands: Quantized Conductance

3 Subbands ⇒ $E_c(p,k_z) = E_c + E_p + \dfrac{\hbar^2 k_z^2}{2m_e} \qquad \{\, p = 1,2,3$

$$\Rightarrow I = \sum_{p=1}^{3} 2 \times \frac{e}{2\pi\,\hbar} \int_{E_c+E_p}^{\infty} dE \;\; \left[f(E - E_{fR}) - f(E - E_{fL}) \right]$$

$$= 3\, G_Q\, V$$

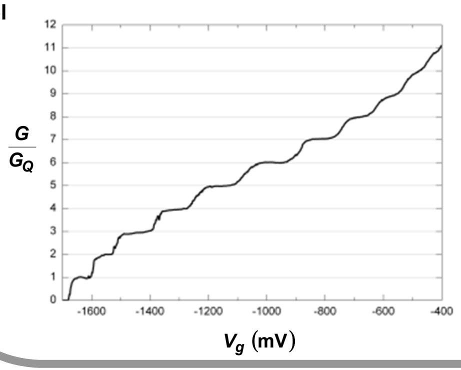
Conductance increases in multiples of G_Q (quantized conductance!)

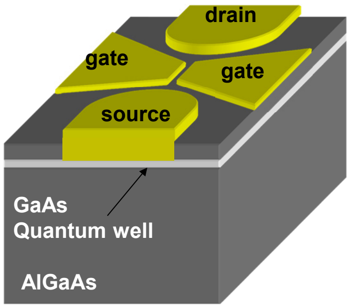


Quantized Conductance: Experiments with 1D Quantum Wires

Semiconductor Quantum Point Contacts:

- Electrons are confined in 2D in the quantum well
- Negative bias on metal gates repel electrons from underneath the gates creating a narrow 1D channel for electrons in the spacing between the gates
- The gate voltage can also control how many subbands of the 1D channel are below the Fermi level



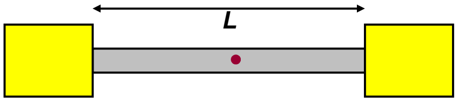


Phys. Rev. Lett., 60, 848 (1988)

The conductance (and resistance) is quantized so effectively in Quantum Hall Effect that it can give a value of the Plank’s constant to one part in 10^8

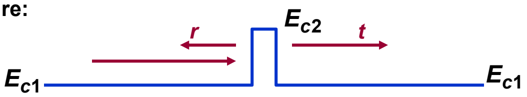
Scattering and Conductance in 1D

What if there is one scatterer (like an impurity atom) in the 1D channel?



Quantum Mechanical Reflection and Transmission from a Potential Barrier:

Consider what happens when there is a potential barrier in the path of an electron in a 1D quantum wire:



$$E_{c1}(k_z) = E_{c1} + E_1 + \frac{\hbar^2 k_z^2}{2m_e} \qquad E_{c2}(k_z) = E_{c2} + E_1 + \frac{\hbar^2 k_z^2}{2m_e}$$

Left Side Solution:

$$\phi_1(\bar{r}) = f(x,y)\, e^{ik_z z} + r\, f(x,y)\, e^{-ik_z z}$$

Right Side Solution:

$$\phi_1(\bar{r}) = t\, f(x,y)\, e^{ik_z z}$$

Transmission probability: $T_c = |t|^2$

Reflection probability: $R_c = |r|^2 = 1 - T$

$\Big\}$ Assume they are energy independent

Conductance as Transmission: Landauer's Formula

$$I = (-e)2\times\int_0^{\infty}\frac{dk_z}{2\pi}\,v_c(k_z)\;T_c\;f(E_c(k_z)-E_{fL}) + (-e)2\times\int_{-\infty}^{0}\frac{dk_z}{2\pi}\,v_c(k_z)\;f(E_c(k_z)-E_{fR})$$

$$+(-e)2\times\int_0^{\infty}\frac{dk_z}{2\pi}\,v_c(k_z)\;R_c\;f(E_c(k_z)-E_{fR})$$

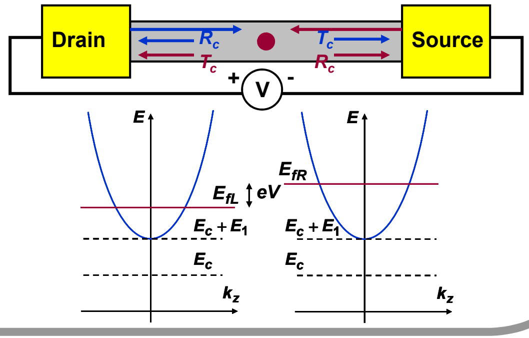
Use: $R_c+T_c = 1$

$$= e\,2\times\int_0^{\infty}\frac{dk_z}{2\pi}\,v_c(k_z)\,T_c\,[f(E_c(k_z)-E_{fR})-f(E_c(k_z)-E_{fL})]$$

$$= 2\times\frac{e\,T_c}{2\pi\,\hbar}\int_{E_c+E_1}^{\infty} dE\;\;[f(E-E_{fR})-f(E-E_{fL})]$$

$$= \left(\frac{e^2}{\pi\,\hbar}T_c\right)V$$

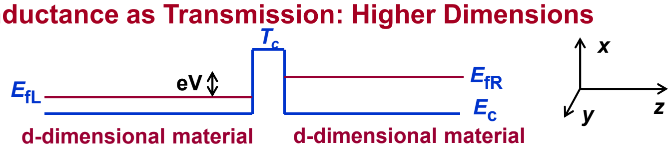
$$\Rightarrow G = \frac{e^2}{\pi\,\hbar}T_c \;<\; G_Q$$



Landauer's formula

$$\boxed{G = \frac{e^2}{\pi\,\hbar}T_c}$$

Conductance as Transmission: Higher Dimensions



$$E_c(\vec{k}) = E_c + \frac{\hbar^2\left(k_x^2+k_y^2\right)}{2m_e} + \frac{\hbar^2 k_z^2}{2m_e} = E_c + E_{xy} + E_z$$

$$J = J_{L\rightarrow R} + J_{R\rightarrow L}$$

$$= (-e)2\times\int\frac{dk_x dk_y}{(2\pi)^2}\int_0^{\infty}\frac{dk_z}{2\pi}\,v_{cz}(k_z)\;T_c\;f\left(E_c(\vec{k})-E_{fL}\right)\left[1-f\left(E_c(\vec{k})-E_{fR}\right)\right]$$

$$+(-e)2\times\int\frac{dk_x dk_y}{(2\pi)^2}\int_{-\infty}^{0}\frac{dk_z}{2\pi}\,v_{cz}(k_z)\;T_c\;f\left(E_c(\vec{k})-E_{fR}\right)\left[1-f\left(E_c(\vec{k})-E_{fL}\right)\right]$$

$$= (-e)2\times\int\frac{dk_x dk_y}{(2\pi)^2}\int_0^{\infty}\frac{dk_z}{2\pi}\,v_{cz}(k_z)\;T_c\;\left[f\left(E_c(\vec{k})-E_{fL}\right)-f\left(E_c(\vec{k})-E_{fR}\right)\right]$$

$$= -e\,\frac{m_e T_c}{2\pi^2\hbar^3}\int_0^{\infty}dE_{xy}\int_0^{\infty}dE_z\left[f\left(E_c+E_{xy}+E_z-E_{fL}\right)-f\left(E_c+E_{xy}+E_z-E_{fR}\right)\right]$$

$$= e^2\,\frac{m_e T_c}{2\pi^2\hbar^3}\left(\frac{E_{fL}+E_{fR}}{2}-E_c\right)V = GV$$

{ at *T*~0K