

Solution by Kevin Lee

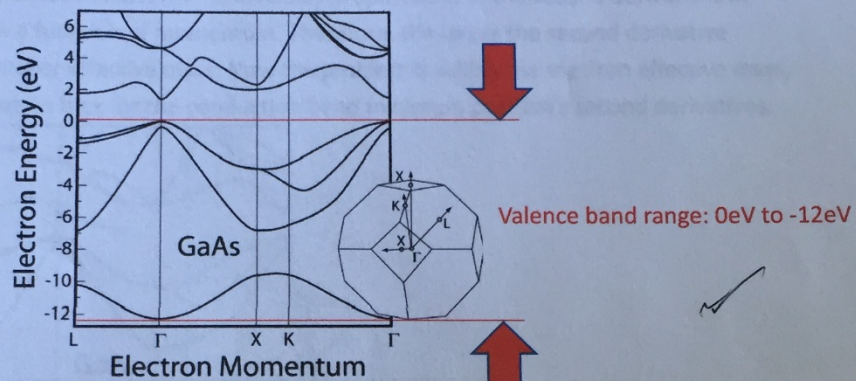
Problem 1.1)

MSS (Rockett) Problem 2.6.1

Consider the energy vs. momentum relationships (band diagrams) shown in Figure 2.7.

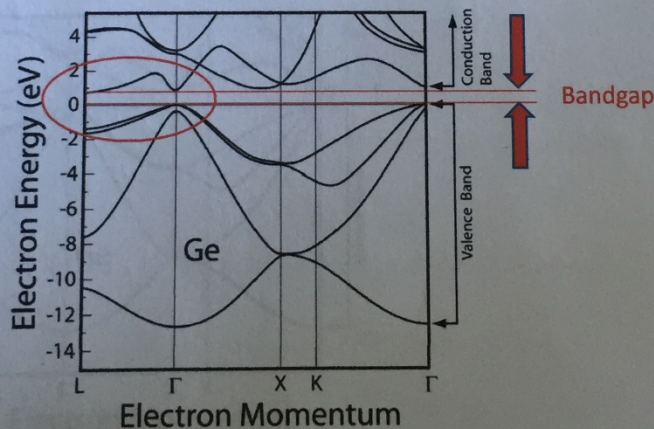
a) What range of energies does the valence band of GaAs span based on Figure 2.7.?

Ans:



b) Sketch the most important features of the E(k) diagram for Ge and indicate the minimum energy gap.

Ans:



Although it is not very obvious, Ge has indirect bandgap. The valence band maximum is at Γ point. The conduction band minimum is at the L point.

c) Which semiconductor (GaAs or Ge) has the indirect energy gap? How do you know?

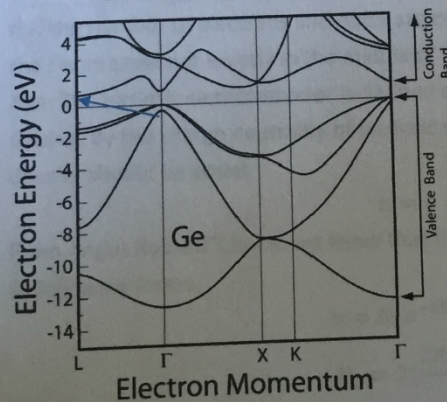
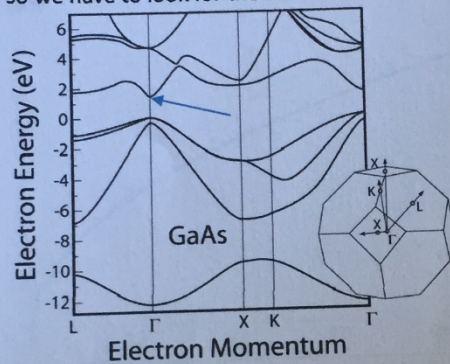
Ans: The definition of indirect bandgap is that the conduction band minimum and

valence band maximum have the same momentum. From the above figures, we can easily see that **Ge is an indirect bandgap semiconductor**. The valence band maximum of Ge is at Γ point. The conduction band minimum is at the L point.

d) The effective masses of the carriers are given by: $\frac{1}{m^*} = \frac{\partial^2 E}{\partial^2 k}$. Which semiconductor,

Ge or GaAs has the higher electron effective mass?

Ans: The effective mass m^* is inversely proportional to the second derivatives of energy as a function of momentum. Therefore, the larger the second derivative means smaller effective mass. Now the problem is asking the electron effective mass, so we have to look for the conduction band minimum position's second derivatives.



The blue arrows are pointing at the conduction band minimum for each materials. It is obvious that Ge has a smaller second derivative at the conduction band minimum in comparison with GaAs. So **Ge has larger electron effective mass**.

e) Sketch the density of states near the top of the valence band. What is the functional form of this curve?

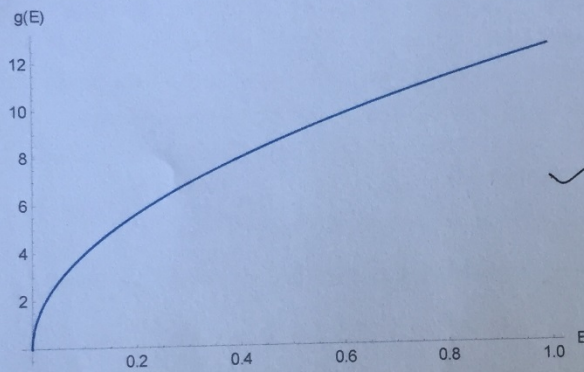
Ans: At the top of valence band, we can approximate the energy momentum relation as parabola. The function is of the form of equation 2.16.

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

And we can calculate the density of states in the 3D case.

$$g(E) = \frac{\pi}{2} \left(\frac{8m^*}{h^2} \right) E^{1/2}$$

If I set all the parameters to 1, we will get the following plot.



f) If the number of electrons and holes are equal in an intrinsic semiconductor, why is the Fermi Level not exactly in the middle of the energy gap? (Eq. 2.31)

Ans: The intrinsic semiconductor is defined as the semiconductor is free of significant doping. By the charge neutrality of intrinsic semiconductor, electron density and hole density should be equal.

$$n = p = n_i$$

From Angus Rockett's book, we know that the carrier concentrations can be obtained as following forms.

$$n = N_C e^{-(E_C - E_F)/k_B T}$$

$$N_C = 2 \left(\frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2}$$

$$p = N_V e^{-(E_F - E_V)/k_B T}$$

$$N_V = 2 \left(\frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2}$$

$$n_i = \sqrt{N_V N_C} e^{-E_{gap}/2k_B T}$$

$$\sqrt{N_V N_C} e^{-E_{gap}/2k_B T} = N_V e^{-(E_F - E_V)/k_B T}$$

$$E_F = \frac{E_C + E_V}{2} + \frac{3}{4k_B T} \ln\left(\frac{m_h^*}{m_e^*}\right)$$

The " $\frac{E_C + E_V}{2}$ " is the mid-energy of the bandgap. If the effective mass of holes and electrons are different, the natural log will contribute to the Fermi energy. Therefore, the Fermi level deviates from the middle of the bandgap.

15 ✓

MSS (Rockett) Problem 2.6.3

Consider phosphorous as an impurity in silicon.

- a) Would you expect it to be an electron donor or an acceptor? Explain why.

Ans: Since phosphorous is group V element, it has one more electron in comparison with silicon. So the extra electron will dope silicon into n-type. And the phosphorous will act as a donor because it contributes additional electrons to silicon.

- b) If the ionization energy (the difference in energy between the phosphorous state and the band edge) is 35 meV, calculate the fraction of the phosphorous atoms ionized at (i) 80 K, (ii) 300 K, (iii) 400 K? You may assume that the Fermi energy is at the phosphorous state energy and that electrons escaping into the band need only reach the band edge rather than integrating the product of the Fermi function and the density of states throughout the conduction band.

Ans: Use equation 2.32 in Rockett's book.

$$n \approx N_D e^{-(E_C - E_D)/k_B T}$$

N_D : Concentration of donors

Therefore, the fraction of ionized phosphorous is $\frac{n}{N_D} = e^{-(E_C - E_D)/k_B T}$. $E_C - E_D$

is given 35 meV and $k_B = 8.617 \times 10^{-5} \text{ eV/K}$.

- i. $80\text{K} \quad \frac{n}{N_D} = e^{-(E_C - E_D)/k_B T} = 0.00624 = 0.624\%$
 ii. $300\text{K} \quad \frac{n}{N_D} = e^{-(E_C - E_D)/k_B T} = 0.2582 = 25.82\%$
 iii. $400\text{K} \quad \frac{n}{N_D} = e^{-(E_C - E_D)/k_B T} = 0.362 = 36.2\%$

- c) If there are 10^{17} cm^{-3} phosphorous atoms in a sample of Si, calculate the minority carrier concentration at 300K. You may need the following: $N_C = 2.8 \times 10^{19} \text{ cm}^{-3}$, $N_V = 1.04 \times 10^{19} \text{ cm}^{-3}$, and $E_{\text{gap}}(300\text{K}) = 1.12 \text{ eV}$ for Si.

Ans: We can use the same equation as above to calculate the carrier concentration.

$$n \approx N_D e^{\frac{E_C - E_D}{k_B T}} = 2.582 \times 10^{16} \text{ cm}^{-3}$$

And from Rockett's equation 2.34, we can calculate the minority carrier concentration.

$$np = n_i^2$$

From equation 2.29, we have $n_i^2 = N_C N_V e^{-E_{\text{gap}}/k_B T} = 4.449 \times 10^{19} \text{ cm}^{-6}$

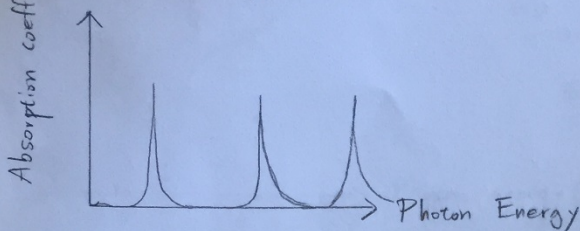
The minority carrier concentration is $p = \frac{n_i^2}{n} = 1723 \text{ cm}^{-3}$.

Problem 1.2) Optical Absorption Coefficients

Solution by Kevin Lee

a) Atoms.

Take Hydrogen atom for example. Its energy levels are discrete.



$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

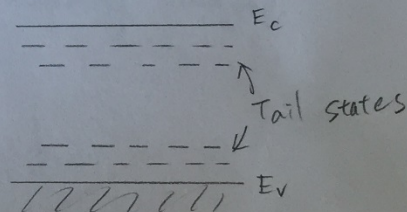
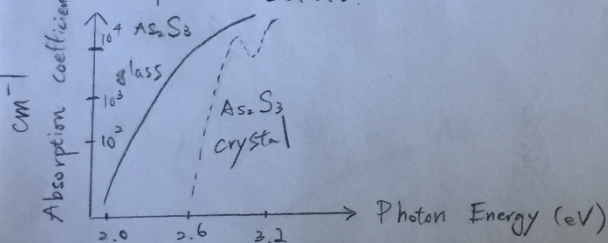
Only when the photon energy matches the difference between two levels, the atom would absorb this photon.

$$n=2 \rightarrow n=1$$

$$\Delta E = -13.6 \left(\frac{1}{4} - 1 \right) = 13.6 \text{ eV} \cdot \frac{3}{4}$$

$= 10.2 \text{ eV} \Rightarrow$ When injecting a photon of 10.2 eV , we will see a dramatic absorption from the H atom.

b) Amorphous solids.



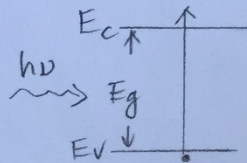
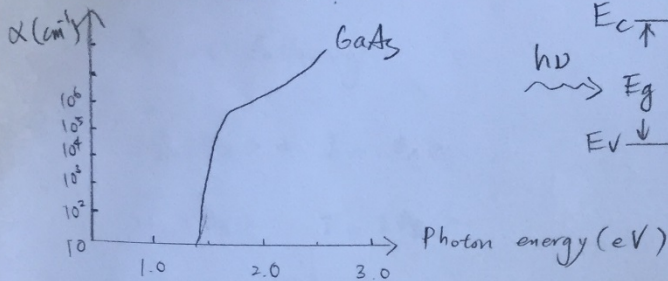
Amorphous solid means the material is partially crystalline.

Sometimes the grain size is about a few 10 nm .

Since the solid itself is not a good crystal. It will not form a smooth band. So there might be many states in between crystal bandgap. Therefore, amorphous solid can absorb smaller energy photons in comparison with its crystal form.

Problem 1.2)

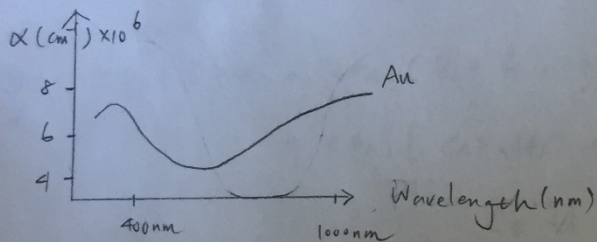
c) Semiconductors



$$\alpha \sim (h\nu - E_g)^{\frac{1}{2}}$$

Semiconductor is crystalline. For crystal, it forms band structure. When injected photon's energy is larger than the bandgap of semiconductor. Electrons in the valence band will jump to conduction band. That is the reason that there is a abrupt turn-on at the photon energy exceeding bandgap.

d) Metals



15

Metals are partially filled band. When injecting photon on metals, it has large density of electrons on the surface. They can response fast enough to photon and re-radiate photon back. In this sense, metals are highly reflective. When there is an exceptionally large density of states at certain energies, it would cause absorption. That's the reason why gold has color.

Problem 1.3)

Solution by Kevin Lee

a) We can write down the Schrödinger's equations for atom A and B as following -

$$\hat{H}_0 |\phi_A\rangle = E_A |\phi_A\rangle$$

$$\hat{H}_0 |\phi_B\rangle = E_B |\phi_B\rangle$$

\hat{H}_0 is the Hamiltonian for individual atom system.

The total solution of two interacting system can be written as.

$$\hat{H} |\psi\rangle = E |\psi\rangle$$

$$|\psi\rangle = C_A |\phi_A\rangle + C_B |\phi_B\rangle$$

$$\hat{H} = \hat{H}_0 + \hat{H}' \text{ (hopping between A and B)}$$

$$\begin{aligned} \textcircled{1} \quad \langle \phi_A | \hat{H} |\psi\rangle &= \langle \phi_A | (\hat{H}_0 + \hat{H}') |\psi\rangle \\ &= \langle \phi_A | [C_A E_A |\phi_A\rangle + C_B E_B |\phi_B\rangle - C_A U |\phi_B\rangle - C_B U |\phi_A\rangle] \\ &= C_A E_A - C_B U \end{aligned}$$

Note: $\langle \phi_A | \phi_B \rangle = 0$ for tight binding approximation.

$$\hat{H} |\psi\rangle = E |\psi\rangle$$

$$\langle \phi_A | \hat{H} |\psi\rangle = E \cdot C_A$$

$$\textcircled{2} \quad \langle \phi_B | \hat{H} |\psi\rangle = -C_A U + C_B E_B$$

$$\langle \phi_B | \hat{H} |\psi\rangle = E \cdot C_B$$

Problem 1.3)

Continued.

From ① and ②, we have the matrix form of the system.

$$\Rightarrow \begin{pmatrix} E_A & -U \\ -U & E_B \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = E \begin{pmatrix} C_A \\ C_B \end{pmatrix}$$

Now the problem is simplified to find the eigenvalue of the matrix.

$$\Rightarrow \det \begin{pmatrix} E_A - E & -U \\ -U & E_B - E \end{pmatrix} = 0$$

$$\Rightarrow (E_A - E)(E_B - E) - U^2 = 0$$

$$\Rightarrow E_A E_B - (E_A + E_B)E + E^2 - U^2 = 0$$

$$E^2 - (E_A + E_B)E + E_A E_B - U^2 = 0$$

$$E = \frac{E_A + E_B}{2} \pm \sqrt{\left(\frac{E_A + E_B}{2}\right)^2 - 4(E_A E_B - U^2)}$$

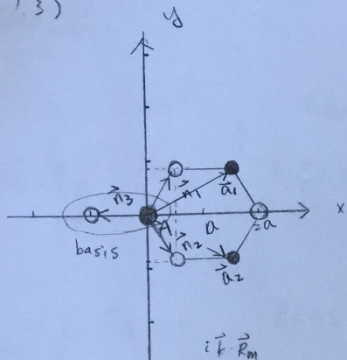
$$= \frac{(E_A + E_B)}{2} \pm \frac{1}{2} \left(E_A^2 + E_B^2 + 2E_A E_B - 4E_A E_B + 4U^2 \right)^{\frac{1}{2}}$$

$$= \frac{(E_A + E_B)}{2} \pm \sqrt{\frac{(E_A - E_B)^2}{2} + U^2}$$

#

Problem 1.3)

b)



$$\vec{a}_1 = \vec{n}_1 - \vec{n}_3$$

$$\vec{a}_2 = \vec{n}_2 - \vec{n}_3$$

$$\vec{R}_m = \vec{a}_1 \text{ or } \vec{a}_2$$

$$\vec{a}_1 = a \left(\frac{3}{2}, \frac{\sqrt{3}}{2} \right)$$

$$\vec{a}_2 = a \left(\frac{3}{2}, -\frac{\sqrt{3}}{2} \right)$$

$$|\psi(\vec{k})\rangle = \sum_m \frac{e^{i\vec{k} \cdot \vec{R}_m}}{\sqrt{N}} \left[C_{PZA} |\phi_{PZA}(\vec{r} - \vec{R}_m)\rangle + C_{PZB} e^{i\vec{k} \cdot \vec{n}_3} |\phi_{PZB}(\vec{r} - \vec{R}_m - \vec{n}_3)\rangle \right]$$

$$\langle \phi_{PZA}(\vec{r}) | \hat{H} | \psi(\vec{k}) \rangle = E C_{PZA}$$

$$= C_{PZA} E_A + C_{PZB} e^{i\vec{k} \cdot \vec{n}_3} \sum_m \langle \phi_{PZA}(\vec{r}) | \hat{H} | \phi_{PZB}(\vec{r} - \vec{R}_m - \vec{n}_3) \rangle e^{i\vec{k} \cdot \vec{R}_m}$$

$$= C_{PZA} E_A + C_{PZB} e^{i\vec{k} \cdot \vec{n}_3} \langle \phi_{PZA}(\vec{r}) | \hat{H} | \phi_{PZB}(\vec{r} - \vec{n}_3) \rangle [1 + e^{i\vec{k} \cdot \vec{a}_1} + e^{i\vec{k} \cdot \vec{a}_2}]$$

$$= C_{PZA} E_A + C_{PZB} e^{i\vec{k} \cdot \vec{n}_3} \langle \phi_{PZA}(\vec{r}) | \hat{H} | \phi_{PZB}(\vec{r} - \vec{n}_3) \rangle (1 + e^{i\vec{k} \cdot (\vec{n}_1 - \vec{n}_3)} + e^{i\vec{k} \cdot (\vec{n}_2 - \vec{n}_3)})$$

$$= C_{PZA} E_A - t C_{PZB} (e^{i\vec{k} \cdot \vec{n}_1} + e^{i\vec{k} \cdot \vec{n}_2} + e^{i\vec{k} \cdot \vec{n}_3})$$

$$\uparrow \\ h(\vec{k})$$

$$\langle \phi_{PZB}(\vec{r} - \vec{n}_3) | \hat{H} | \psi(\vec{k}) \rangle = E C_{PZB} e^{i\vec{k} \cdot \vec{n}_3}$$

$$= e^{i\vec{k} \cdot \vec{n}_3} C_{PZB} E_B + C_{PZA} \sum_m e^{i\vec{k} \cdot \vec{R}_m} \langle \phi_{PZB}(\vec{r} - \vec{n}_3) | \hat{H} | \phi_{PZA}(\vec{r} - \vec{R}_m) \rangle$$

$$= e^{i\vec{k} \cdot \vec{n}_3} C_{PZB} E_B + C_{PZA} (-t) [e^{-i\vec{k} \cdot \vec{a}_1} + e^{-i\vec{k} \cdot \vec{a}_2} + 1]$$

$$\Rightarrow C_{PZB} E_B - t C_{PZA} (e^{-i\vec{k} \cdot \vec{n}_1} + e^{-i\vec{k} \cdot \vec{n}_2} + e^{-i\vec{k} \cdot \vec{n}_3}) = E C_{PZB}$$

$$\uparrow \\ h(\vec{k})^*$$

Problem 1.3)

b) Continued

$$\begin{pmatrix} E_A - t h(\vec{k}) & \\ t h(\vec{k})^* & E_B \end{pmatrix} \begin{pmatrix} C_{P2A} \\ C_{P2B} \end{pmatrix} = E \begin{pmatrix} C_{P2A} \\ C_{P2B} \end{pmatrix}$$

$$\det \begin{pmatrix} E_A - E & -t h(\vec{k}) \\ -t h(\vec{k})^* & E_B - E \end{pmatrix} = 0$$

$$\vec{n}_1 = \frac{a}{2} (1, \sqrt{3})$$

$$\vec{n}_2 = \frac{a}{2} (1, -\sqrt{3})$$

$$\vec{n}_3 = -a (1, 0)$$

$$(E_A - E)(E_B - E) - t^2 (e^{i\vec{k} \cdot \vec{n}_1} + e^{i\vec{k} \cdot \vec{n}_2} + e^{i\vec{k} \cdot \vec{n}_3}) (e^{-i\vec{k} \cdot \vec{n}_1} + e^{-i\vec{k} \cdot \vec{n}_2} + e^{-i\vec{k} \cdot \vec{n}_3}) = 0$$

$$h^*(\vec{k}) h(\vec{k}) = 3 + 2 \cos(a k_y \sqrt{3}) + 2 \cos\left(\frac{3}{2} k_x a + \frac{\sqrt{3}}{2} k_y a\right) + 2 \cos\left(\frac{3}{2} k_x a - \frac{\sqrt{3}}{2} k_y a\right)$$

$$= 3 + 2 \cos(\sqrt{3} k_y a) + 2 \left(2 \cos\left(\frac{3}{2} k_x a\right) \cos\left(\frac{\sqrt{3}}{2} k_y a\right) \right)$$

$$= 3 + 2 \left(2 \cos^2\left(\frac{\sqrt{3}}{2} k_y a\right) - 1 \right) + 4 \cos\left(\frac{3}{2} k_x a\right) \cos\left(\frac{\sqrt{3}}{2} k_y a\right)$$

$$= 3 + 4 \cos^2\left(\frac{\sqrt{3}}{2} k_y a\right) - 2 + 4 \cos\left(\frac{3}{2} k_x a\right) \cos\left(\frac{\sqrt{3}}{2} k_y a\right)$$

$$= 4 \cos^2\left(\frac{\sqrt{3}}{2} k_y a\right) + 4 \cos\left(\frac{3}{2} k_x a\right) \cos\left(\frac{\sqrt{3}}{2} k_y a\right) + 1$$

$$A = \frac{E_A + E_B}{2}, \quad B = \frac{E_A - E_B}{2}$$

$$E_A E_B - (E_A + E_B) E + E^2 - t^2 \left(4 \cos^2\left(\frac{\sqrt{3}}{2} k_y a\right) + 4 \cos\left(\frac{3}{2} k_x a\right) \cos\left(\frac{\sqrt{3}}{2} k_y a\right) + 1 \right) = 0$$

$$E^2 - 2 A E + E_A E_B - t^2 \left(1 + 4 \cos\left(\frac{3}{2} k_x a\right) \cos\left(\frac{\sqrt{3}}{2} k_y a\right) + 4 \cos^2\left(\frac{\sqrt{3}}{2} k_y a\right) \right) = 0$$

$$4 A^2 = E_A^2 + E_B^2 + 2 E_A E_B$$

$$4 B^2 = E_A^2 + E_B^2 - 2 E_A E_B$$

$$4(A^2 - B^2) = 4 E_A E_B \Rightarrow E_A E_B = A^2 - B^2$$

Problem 1.3)

$$\Rightarrow E^2 - 2AE + (A^2 - B^2) - t^2 \left(1 + 4 \cos\left(\frac{3}{2} k_x a\right) \cos\left(\frac{\sqrt{3}}{2} k_y a\right) + 4 \cos^2\left(\frac{\sqrt{3}}{2} k_y a\right) \right) = 0$$

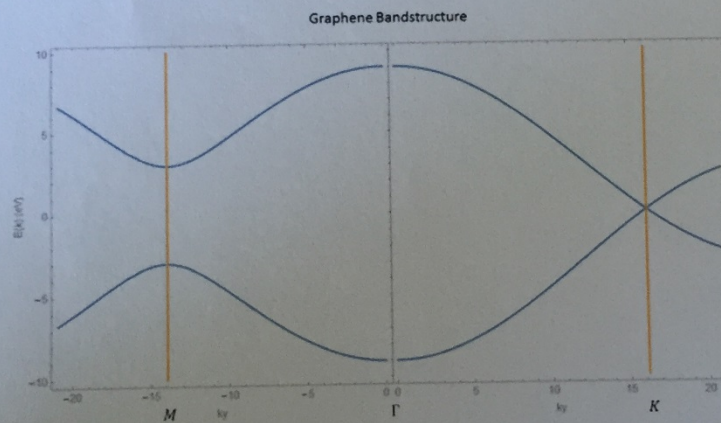
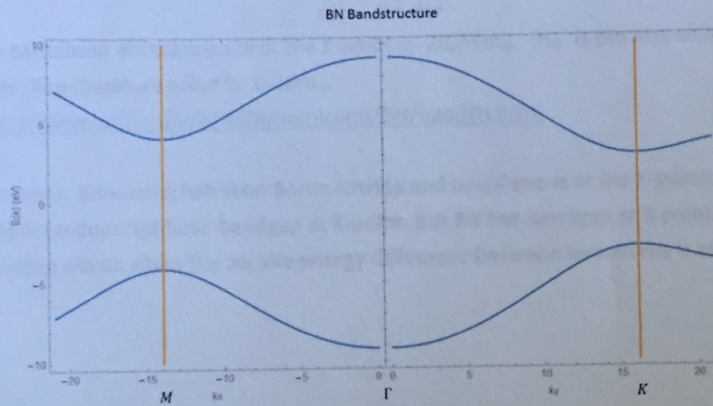
$$E = \left(\frac{1}{2}\right) \left\{ 2A \pm \left[4A^2 - 4(A^2 - B^2) + 4t^2 \left(1 + 4 \cos\left(\frac{3}{2} k_x a\right) \cos\left(\frac{\sqrt{3}}{2} k_y a\right) + 4 \cos^2\left(\frac{\sqrt{3}}{2} k_y a\right) \right) \right]^{\frac{1}{2}} \right\}$$

$$= A \pm \sqrt{B^2 + t^2 \left(1 + 4 \cos\left(\frac{3}{2} k_x a\right) \cos\left(\frac{\sqrt{3}}{2} k_y a\right) + 4 \cos^2\left(\frac{\sqrt{3}}{2} k_y a\right) \right)}$$

#

Problem 1.3)

c) Plot with Mathematica. Codes are included in the following pages.



For graphene, the bandgap closes at the K-point. We can calculate the Fermi velocity at the K-point of bandstructure. Since the bandstructure at K-point experiences a singularity, I choose a k value that is very close to K-point to determine the Fermi velocity.

$$E = \hbar v_F \sqrt{k_x^2 + k_y^2}$$

After substituting the values into above equation, the Fermi velocity is 164473 m/s, which is very similar to literature value in the class note.

For Boron Nitride, the effective mass can be determined by the following equations.

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$$

The calculated effective mass at the K-point is $20.54m_0$. m_0 is the rest electron mass. The literature value is $0.26m_0$.

<http://www.ioffe.ru/SVA/NSM/Semicond/BN/bandstr.html>

The major difference between Boron Nitride and Graphene is at the K-point. Graphene does not have bandgap at K-point. But BN has bandgap at K-point. The bandgap closes when the on-site energy difference between two atoms is zero.

1.3

a. The system of 2 atoms can be described by a Hamiltonian with diagonal entries that correspond to the individual energies and off diagonal elements that correspond to the lowering of energy via interaction. In the basis of the atomic orbitals,

$$\begin{pmatrix} E_A & U \\ U & E_B \end{pmatrix} \psi = E \psi \quad (H - \lambda E) \psi = 0 \quad \text{so the new eigenstates are the } E \text{ values that allow to have non-trivial solutions.}$$

$$\det \begin{pmatrix} E_A - E & U \\ U & E_B - E \end{pmatrix} = 0 \Rightarrow E_A E_B - E(E_A + E_B) + E^2 - U^2 = 0$$

$$E = \frac{E_A + E_B}{2} \pm \sqrt{\left(\frac{E_A - E_B}{2}\right)^2 + U^2}$$

$$E = \frac{E_A + E_B}{2} \pm \sqrt{\frac{E_A^2 + E_B^2 + 2E_A E_B - E_A E_B + U^2}{4}}$$

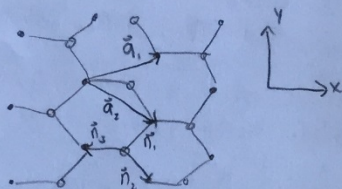
$$E = \frac{E_A + E_B}{2} \pm \sqrt{\frac{E_A^2 + E_B^2 - E_A E_B + U^2}{4}}$$

After the formation of the bond, both electrons will rest in the lower energy state, so the total lowering of energy is $E_A - E_- + E_B - E_-$.

$$= \sqrt{(E_A - E_B)^2 + 4U^2}$$

1.3 (cont.)

b. The lattice looks like:



To find $\vec{n}_1, \vec{n}_2, \vec{n}_3$:

A geometric diagram showing a vector \vec{a} of length a at an angle 60° to the horizontal. It is decomposed into a horizontal component b and a vertical component c . The relationships are given as $a \cos(60^\circ) = b = \frac{a}{2}$ and $a \sin(60^\circ) = c = \frac{\sqrt{3}}{2}a$.

$$\text{so } \vec{n}_1 = (b, c) = \frac{a}{2}(1, \sqrt{3})$$

$$\vec{n}_2 = (b, -c) = \frac{a}{2}(1, -\sqrt{3})$$

$$\vec{n}_3 = (-a, 0) = -a(1, 0)$$

The off diagonal term in H will be a phase factor that determines effectively how in phase is an electron relative to the lattice, where if it is in phase it interacts more strongly to lower the energy.

Because all the electrons we are considering are in the p_z orbital, each nearest neighbor looks the same, so the total phase factor is just the sum.

For example, here, all the orbital overlap looks the same towards each neighbor, and is all parametrized by the energy t .

The lowering of energy due to an atom's neighbors, therefore, is

$$-(t e^{i\vec{k} \cdot \vec{n}_1} + t e^{i\vec{k} \cdot \vec{n}_2} + t e^{i\vec{k} \cdot \vec{n}_3})$$

with each exponential picking up the phase information from 1 neighbor.

Now we have:

$$\begin{bmatrix} E_A & -(t e^{i\vec{k} \cdot \vec{n}_1} + t e^{i\vec{k} \cdot \vec{n}_2} + t e^{i\vec{k} \cdot \vec{n}_3}) \\ -(t e^{-i\vec{k} \cdot \vec{n}_1} + t e^{-i\vec{k} \cdot \vec{n}_2} + t e^{-i\vec{k} \cdot \vec{n}_3}) & E_B \end{bmatrix} \psi = E \psi$$

and so like before, diagonalizing will give:

$$E = \frac{E_A + E_B}{2} \pm \sqrt{\left(\frac{E_A - E_B}{2}\right)^2 + |h(k)|^2}$$

$$h(k) = -t \left(e^{i\frac{a}{2}k_x} e^{i\frac{\sqrt{3}}{2}ak_y} + e^{i\frac{a}{2}k_x} e^{-i\frac{\sqrt{3}}{2}ak_y} + e^{-iak_x} \right)$$

$$= -t \left(2 \cos\left(\frac{\sqrt{3}}{2}ak_y\right) e^{i\frac{a}{2}k_x} + e^{-iak_x} \right)$$

$$|h(k)|^2 = +t^2 \left(2 \cos\left(\frac{\sqrt{3}}{2}ak_y\right) e^{i\frac{a}{2}k_x} + e^{-iak_x} \right) \left(2 \cos\left(\frac{\sqrt{3}}{2}ak_y\right) e^{-i\frac{a}{2}k_x} + e^{iak_x} \right)$$

$$= +t^2 \left(4 \cos^2\left(\frac{\sqrt{3}}{2}ak_y\right) + 1 + 2 \cos\left(\frac{\sqrt{3}}{2}ak_y\right) \left(e^{i\left(\frac{3}{2}ak_x\right)} + e^{-i\frac{3}{2}ak_x} \right) \right)$$

$$= +t^2 \left(1 + 4 \cos\left(\frac{3}{2}ak_x\right) \cos\left(\frac{\sqrt{3}}{2}ak_y\right) + 4 \cos^2\left(\frac{\sqrt{3}}{2}ak_y\right) \right)$$

and finally:

$$E = \frac{E_A + E_B}{2} \pm \sqrt{\left(\frac{E_A - E_B}{2}\right)^2 + t^2 \left[1 + 4 \cos\left(\frac{3}{2}ak_x\right) \cos\left(\frac{\sqrt{3}}{2}ak_y\right) + 4 \cos^2\left(\frac{\sqrt{3}}{2}ak_y\right) \right]}$$

c. The plots of the h-BN and graphene band structures are attached at the back.

At most points they are very similar, for example at M and Γ both bands for both crystals have similar energies, but they differ significantly at the K point. While BN's bands curve to create a band gap, graphene's meet exactly at $E=0$, with both bands being linear.

For BN: the effective mass is defined by $E \approx E_0 + \frac{\hbar^2 k^2}{2m^*}$ so we will need to expand E about the high symmetry points

at K . $\vec{K} = \frac{\pi}{a}(\frac{2}{3}, \frac{2}{3\sqrt{3}})$, so for small $\Delta\vec{K}$, to second order,

$$\cos(\frac{3}{2}aK_x) \approx -1 + \frac{9}{8}a^2\Delta K_x^2$$

$$\cos(\frac{\sqrt{3}}{2}aK_y) \approx \frac{1}{2} - \frac{3}{4}a\Delta K_y - \frac{3}{16}a^2\Delta K_y^2$$

$$\cos^2(\frac{\sqrt{3}}{2}aK_y) \approx \frac{1}{4} - \frac{3}{4}a\Delta K_y + \frac{3}{8}a^2\Delta K_y^2$$

Putting this into E , and simplifying (omitting some algebra)

$$E \approx \frac{E_A + E_B}{2} \pm \sqrt{\left(\frac{E_A - E_B}{2}\right)^2 + \frac{9}{4}a^2(\Delta K_x^2 + \Delta K_y^2)} = \frac{E_A + E_B}{2} \pm \sqrt{\left(\frac{E_A - E_B}{2}\right)^2 + \frac{9}{4}a^2\Delta K^2}$$

Then again we can use the expansion $f(x) = c + \sqrt{g^2 + dx^2} \approx c + g + \frac{dx^2}{2g}$

$$\Rightarrow E \approx \frac{E_A + E_B}{2} \pm \frac{E_A - E_B}{2} + \frac{9a^2\Delta K^2}{4(E_A - E_B)} = E_0 \pm \frac{\hbar^2 k^2}{2m^*} \Rightarrow \boxed{m_e^* = \frac{2\hbar^2 E_g}{9a^2 + 2}}$$

This is the electron effective mass, and because the valence band has the same magnitude of curvature the hole effective mass will just be $\boxed{m_h^* = \frac{-2\hbar^2 E_g}{9a^2 + 2}}$

This comes out to be $\boxed{m_e^* = 0.518 m_e}$
 $\boxed{m_h^* = -0.518 m_e}$

Here we have implicitly used that $E_g = E_A - E_B$, which comes from, at $\vec{K} = \frac{\pi}{a}(\frac{2}{3}, \frac{2}{3\sqrt{3}})$,

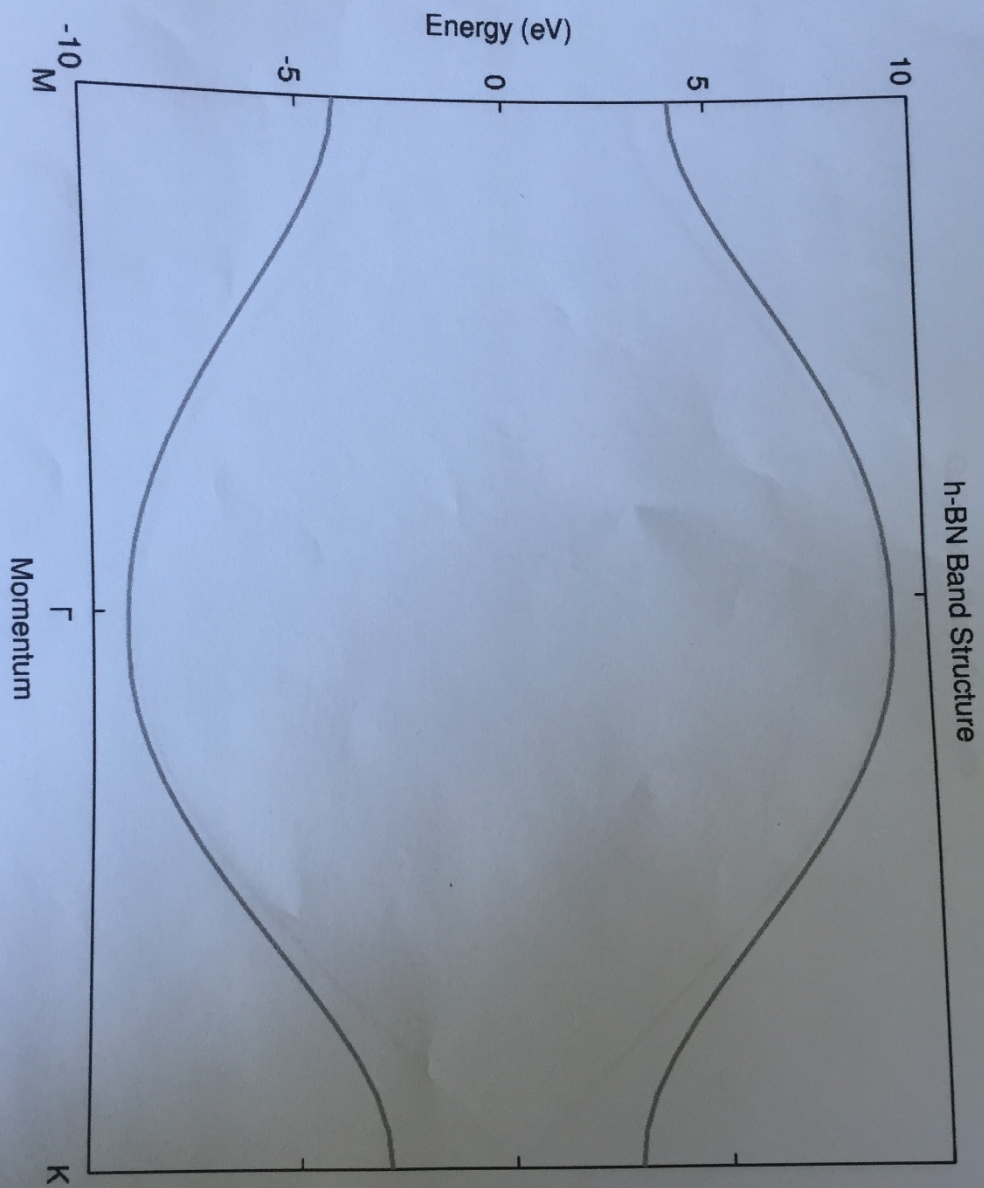
$$h(\vec{K}) = 0 \Rightarrow |h(\vec{K})|^2 = 0 \Rightarrow E^+ = \frac{E_A + E_B}{2} + \frac{E_A - E_B}{2} = E_A, \quad E^- = \frac{E_A + E_B}{2} - \frac{E_A - E_B}{2} = E_B,$$

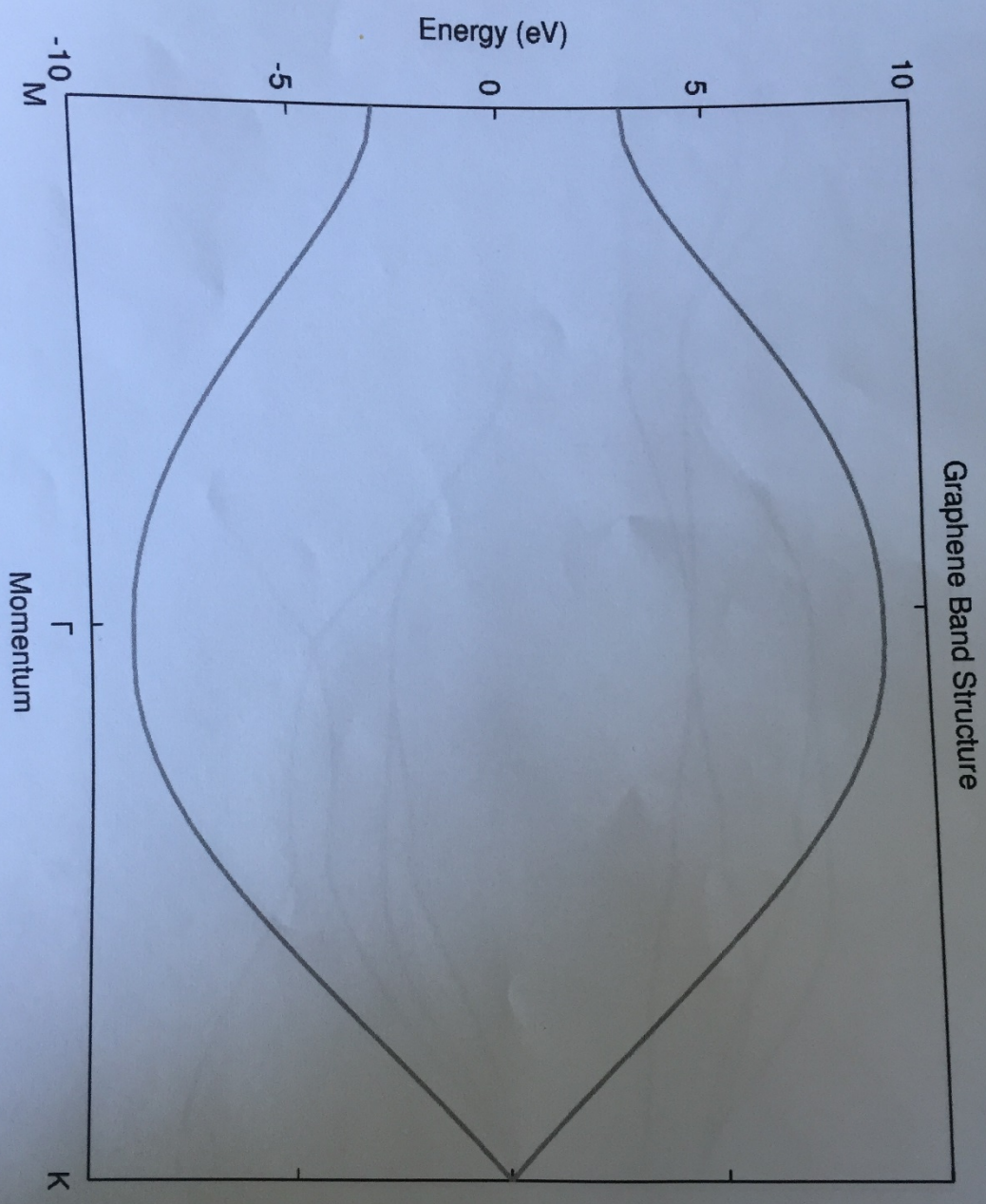
$$\text{so } \Delta E = E_g = E_A - E_B = 5.8 \text{ eV}$$

For graphene: Using the same expansion as before, we get the same E , but now

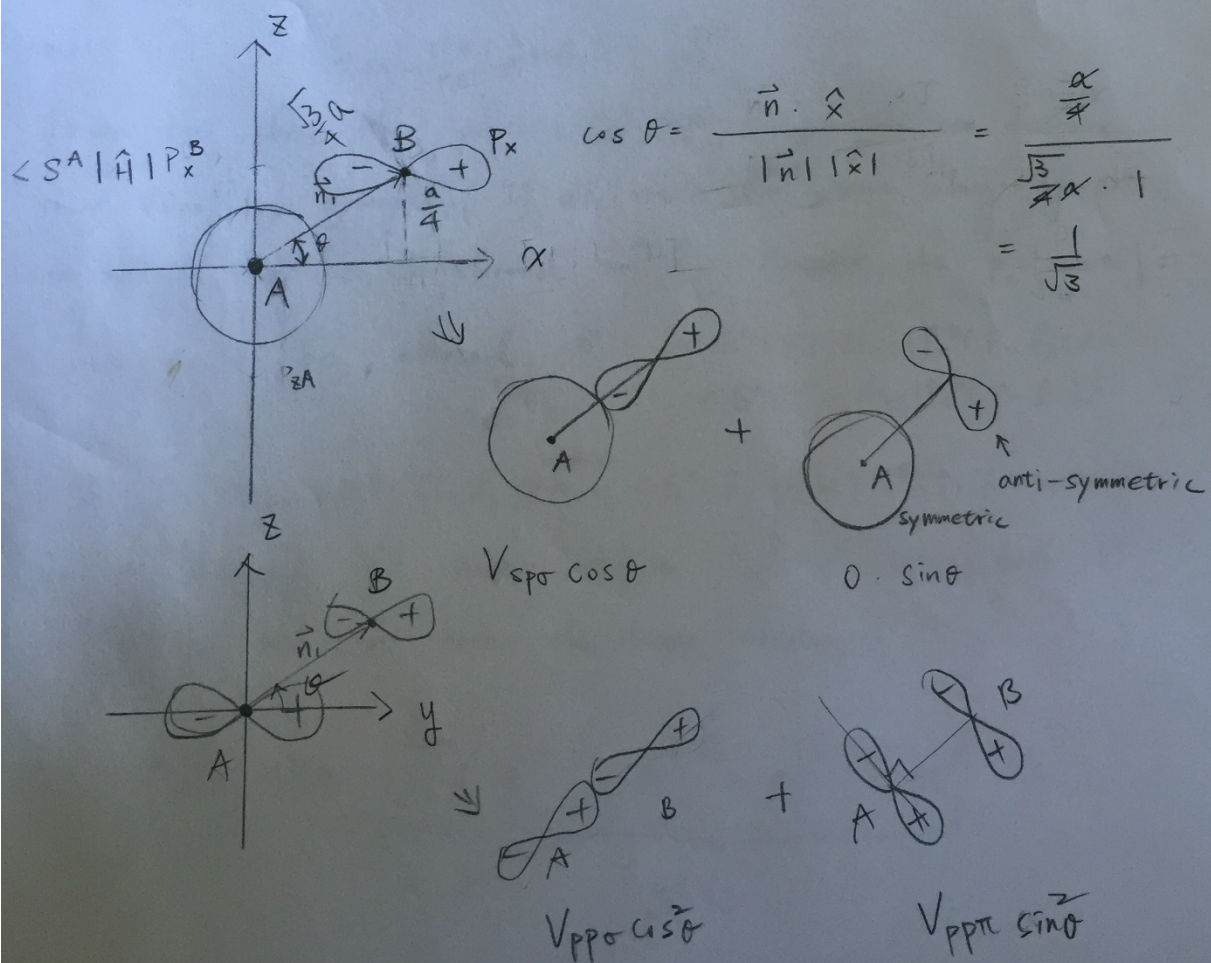
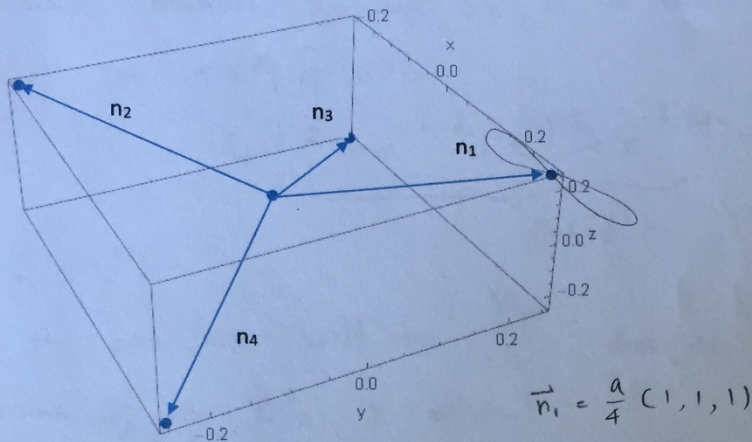
$$E_A + E_B = E_A - E_B = 0, \text{ so } E \approx \sqrt{\frac{9}{4}a^2(\Delta K_x^2 + \Delta K_y^2)} = \frac{3}{2}a\Delta K^2$$

The Fermi velocity is defined as $E = \hbar v_F |\vec{K}|^2$, so $\boxed{v_F = \frac{3a}{2\hbar} = 1.026 \times 10^6 \text{ m/s}}$





Problem 1.4) Energy Bandstructure of Silicon and GaAs
a)



Problem 1.4)

b) orbitals

For the ^v overlap between S_A and S_B , it is trivial. Since S -orbital

is spherical $\Rightarrow \langle S^A | \hat{H} | S^B \rangle$

$$= \underbrace{(e^{i\vec{k}\cdot\vec{n}_1} + e^{i\vec{k}\cdot\vec{n}_2} + e^{i\vec{k}\cdot\vec{n}_3} + e^{i\vec{k}\cdot\vec{n}_4})}_{g_0(\vec{k})} \underbrace{\langle S^A | \hat{H}_{int} | S^B \rangle}_{V_0 = V_{SS\sigma}}$$

$$\langle S^A | \hat{H} | P_x^B \rangle = ?$$

First, the pre-factor will be $\frac{V_{sp\sigma}}{\sqrt{3}}$ due to Problem 1.4)(a) decomposition of the B's p -orbital.

$$\Rightarrow \langle S^A(\vec{r}) | \hat{H}_{int} | P_x^B(\vec{r}-\vec{n}_1) \rangle = \frac{V_{sp\sigma}}{\sqrt{3}}$$

There are three other positions of P_x^B orbitals. We can determine their value by symmetry. If we rotate the system along y -axis, vector \vec{n}_1 can be transformed to \vec{n}_3 . However, the P_x -orbital's

$$\text{sign would be inverted. } \Rightarrow \langle S^A(\vec{r}) | \hat{H}_{int} | P_x^B(\vec{r}-\vec{n}_3) \rangle = -\langle S^A(\vec{r}) | \hat{H}_{int} | P_x^B(\vec{r}-\vec{n}_1) \rangle$$

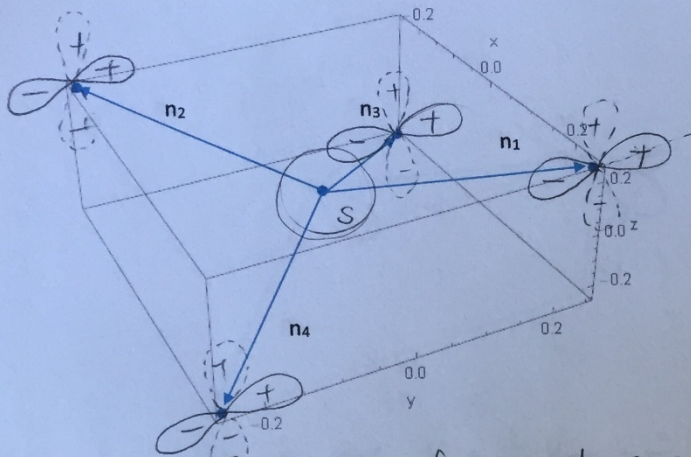
$$\langle S^A(\vec{r}) | \hat{H}_{int} | P_x^B(\vec{r}-\vec{n}_2) \rangle = -\langle S^A(\vec{r}) | \hat{H}_{int} | P_x^B(\vec{r}-\vec{n}_1) \rangle$$

Since \vec{n}_2 and \vec{n}_1 have opposite P_x sign overlap with S^A .

While \vec{n}_4 and \vec{n}_1 have the same overlapping sign.

$$\Rightarrow \langle S^A | \hat{H} | P_x^B \rangle = \underbrace{\frac{V_{sp\sigma}}{\sqrt{3}}}_{V_1} \underbrace{(e^{i\vec{k}\cdot\vec{n}_1} - e^{i\vec{k}\cdot\vec{n}_2} - e^{i\vec{k}\cdot\vec{n}_3} + e^{i\vec{k}\cdot\vec{n}_4})}_{g_1(\vec{k})}$$

Problem 1.4)



$\langle S^A | \hat{H} | P_y^B \rangle = ?$ The pre-factor is the same as before

$$\langle S^A(\vec{r}) | \hat{H}_{int} | P_y^B(\vec{r} - \vec{n}_1) \rangle = \langle S^A(\vec{r}) | \hat{H}_{int} | P_y^B(\vec{r} - \vec{n}_3) \rangle$$

$$\begin{aligned} \langle S^A(\vec{r}) | \hat{H}_{int} | P_y^B(\vec{r} - \vec{n}_1) \rangle &= - \langle S^A(\vec{r}) | \hat{H}_{int} | P_y^B(\vec{r} - \vec{n}_4) \rangle \\ &= - \langle S^A(\vec{r}) | \hat{H}_{int} | P_y^B(\vec{r} - \vec{n}_2) \rangle \end{aligned}$$

$$\Rightarrow \langle S^A | \hat{H} | P_y^B \rangle = \frac{V_{sp\sigma}}{\sqrt{3}} \underbrace{\left[e^{i\vec{k} \cdot \vec{n}_1} - e^{i\vec{k} \cdot \vec{n}_2} + e^{i\vec{k} \cdot \vec{n}_3} - e^{i\vec{k} \cdot \vec{n}_4} \right]}_{g_2(\vec{k})}$$

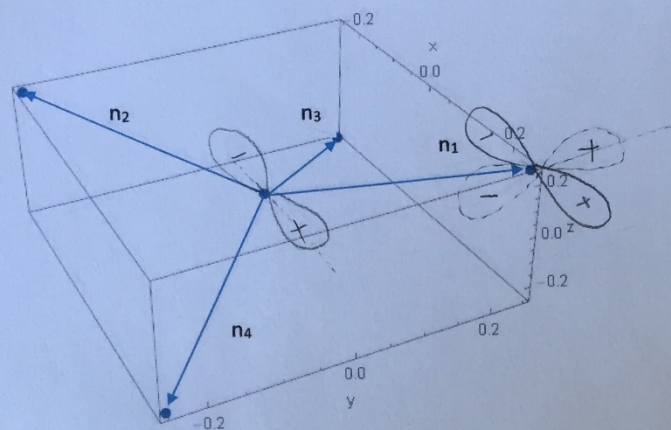
$$\langle S^A | \hat{H} | P_z^B \rangle = ?$$

$$\begin{aligned} \langle S^A(\vec{r}) | \hat{H}_{int} | P_z^B(\vec{r} - \vec{n}_1) \rangle &= \langle S^A(\vec{r}) | \hat{H}_{int} | P_z^B(\vec{r} - \vec{n}_2) \rangle \\ &= - \langle S^A(\vec{r}) | \hat{H}_{int} | P_z^B(\vec{r} - \vec{n}_3) \rangle \\ &= - \langle S^A(\vec{r}) | \hat{H}_{int} | P_z^B(\vec{r} - \vec{n}_4) \rangle \end{aligned}$$

$$\Rightarrow \langle S^A | \hat{H} | P_z^B \rangle = \frac{V_{sp\sigma}}{\sqrt{3}} \underbrace{\left[e^{i\vec{k} \cdot \vec{n}_1} + e^{i\vec{k} \cdot \vec{n}_2} - e^{i\vec{k} \cdot \vec{n}_3} - e^{i\vec{k} \cdot \vec{n}_4} \right]}_{g_3(\vec{k})}$$

So we check the four cases of phase factor.

Problem 1.4)

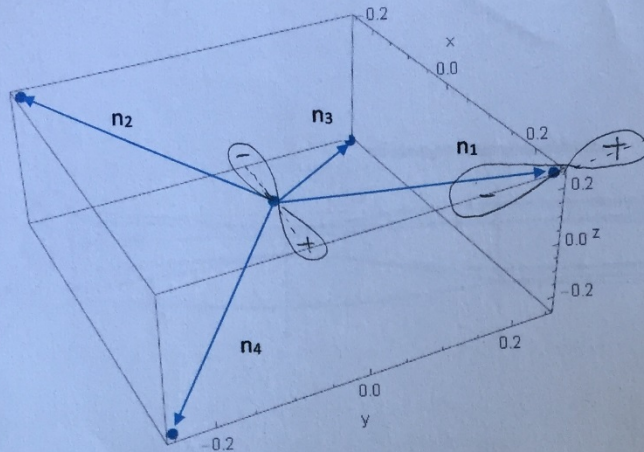


Now check how to get $V_2 = \frac{1}{3} V_{pp\sigma} - \frac{2}{3} V_{pp\pi}$. From (a), we know that two P orbitals should be decomposed. And we know $\cos \theta = \frac{1}{\sqrt{3}}$. Hence, $\langle P_x^A | \hat{H} | P_x^B \rangle = [V_{pp\sigma} \cos^2 \theta + V_{pp\pi} \sin^2 \theta] g_0(\vec{r})$
 \Downarrow
 $\sin \theta = \frac{\sqrt{2}}{\sqrt{3}}$ $= \left(\frac{1}{3} V_{pp\sigma} + \frac{2}{3} V_{pp\pi} \right) g_0(\vec{r})$

For $\langle P_x^A | \hat{H} | P_y^B \rangle = ?$

For the zero parts, it is easy to show. For example, consider $\langle S^A | \hat{H} | P_x^A \rangle = 0$, Since S^A is symmetric around the origin. However, P_x^A is anti-symmetric around origin. The overlapping between S^A and P_x^A will cancel out. Hence, it's zero.

Problem 1.4)



$$\langle P_x^A | \hat{H} | \hat{P}_y^B \rangle = V_3 g_3(\vec{k})$$

Projection to $[111] \Rightarrow \text{A} \otimes \text{B} \Rightarrow V_{PP\sigma} \frac{1}{\sqrt{3}} \cdot \frac{1}{\sqrt{3}} = \frac{V_{PP\sigma}}{3}$

Another component projected on to $[-1 \ 1 \ -2]$, which is perpendicular to $[111]$.

$$V_{PP\pi} \cdot \frac{\sqrt{2}}{3} \cdot \cos \theta' = \frac{1}{3} V_{PP\pi} \Rightarrow V_3 = \frac{1}{3} V_{PP\sigma} + \frac{1}{3} V_{PP\pi}$$

$$\cos \theta' = \frac{1}{|[0 \ 1 \ 0]||[-1 \ 1 \ -2]|} = \frac{1}{\sqrt{6}}$$

Solution by Zachary Ziegler

