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**MSE 5460/ECE 5570, Spring Semester 2016**  
**Compound Semiconductors Materials Science**

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**Assignment 1**

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**Policy on assignments:** Please turn them in by 5pm, Thursday, February 18th, 2016.

**General notes:** Present your solutions *neatly*. Do not turn in rough unreadable worksheets - learn to **take pride in your presentation**. Show the relevant steps, so that partial points can be awarded. BOX your final answers where applicable. Draw figures wherever necessary. Please print out this question sheet and staple to the top of your homework. Write your name and email address on the cover.

### Problem 1.1) Warmup: Silicon and Compound Semiconductors

MSS (Rockett) Problems **2.6.1** and **2.6.3**.

### Problem 1.2) Warmup: Optical Absorption Coefficients

Sketch and explain the microscopic physics behind the optical absorption coefficient spectra of typical **a)** atoms, **b)** amorphous solids, **c)** semiconductors, and **d)** metals. State the typical quantitative absorption coefficients.

### Problem 1.3) Energy Bandstructure of 2D Graphene and BN

In this problem, we will quantitatively calculate the electronic bandstructure for 2D graphene and 2D Boron Nitride as our first ‘elemental’ and ‘compound’ semiconductors respectively.

**a)** Show that if the energies allowed for the electron in individual atoms A and B are  $E_A$  and  $E_B$ , and the lowering of energy because of hopping of the electron between the atoms between the atoms is  $U$ , the energies allowed for the electron after the formation of a chemical bond are  $E_{\pm} = \frac{E_A + E_B}{2} \pm \sqrt{\left(\frac{E_A - E_B}{2}\right)^2 + U^2}$ . Because each allowed electron state can hold *two* electrons of opposite spins, what is the *lowering* of energy due to the formation of the bond?

**b)** Now consider 2D Boron Nitride (or graphene), whose atomic basis has *two* atoms: B & N for BN (and C & C for graphene). We saw in class that the whole 2D crystal may be generated by repeating this two-atom basis, by translating by the two primitive lattice vectors  $\mathbf{a}_1 = a\left(\frac{3}{2}, \frac{\sqrt{3}}{2}\right)$  and  $\mathbf{a}_2 = a\left(\frac{3}{2}, -\frac{\sqrt{3}}{2}\right)$ , where  $a$  is the distance between the A and B atoms. Sketch the basis, the lattice, and these vectors, and show that the three vectors from any atom to the three nearest neighbors are  $\mathbf{n}_1 = \frac{a}{2}(1, \sqrt{3})$ ,  $\mathbf{n}_2 = \frac{a}{2}(1, -\sqrt{3})$ , and  $\mathbf{n}_3 = -a(1, 0)$ . We will look at only the  $p_z$  orbital bands. For on-site orbital energies  $E_A$  and  $E_B$  and a hopping energy  $t$ , show that the off-diagonal (hopping) term is  $h(\mathbf{k}) = -t(e^{i\mathbf{k}\cdot\mathbf{n}_1} + e^{i\mathbf{k}\cdot\mathbf{n}_2} + e^{i\mathbf{k}\cdot\mathbf{n}_3})$ , and

the resulting bandstructure is  $E_{\pm} = A \pm \sqrt{B^2 + t^2[1 + 4\cos\left(\frac{3}{2}k_x a\right)\cos\left(\frac{\sqrt{3}}{2}k_y a\right) + 4\cos^2\left(\frac{\sqrt{3}}{2}k_y a\right)]}$ , where  $A = \frac{E_A + E_B}{2}$  and  $B = \frac{E_A - E_B}{2}$ .

**c)** Using the following parameters, make 2D plots of the bandstructures of BN and graphene similar to shown in class. For BN:  $E_A = +2.9$  eV,  $E_B = -2.9$  eV,  $t = -2.9$  eV, and  $a = 0.15$  nm. For graphene,  $E_A = E_B = 0$  eV,  $t = 3.0$  eV,  $a = 0.15$  nm. Describe the differences and similarities between them. Specifically, find the band-edge *effective masses* and *bandgap* for BN, and the *Fermi velocity* characterizing the slope of the  $E - k$  Dirac cone of Graphene. Relate these analytically to the known parameters.

## Problem 1.4) Energy Bandstructure of Silicon and GaAs

In this problem we extend the ideas of problem 1.3 to calculate the tight-binding bandstructure of Silicon and GaAs, which are 3D semiconductors. The procedure is the same, just the matrices are larger. Do not be turned off by the forbidding looking matrix below-it is simpler than you think, and understanding it will put you in a select league! Because for graphene and BN we looked at a single  $|p_z\rangle$  orbital and a 2-atom basis, the matrix was  $2 \times 2$ . For Silicon and GaAs, the basis has two atoms too, but attached to each atom will be 4 orbitals:  $|s\rangle, |p_x\rangle, |p_y\rangle, |p_z\rangle$ , and the chemical bonding is  $sp^3$ . Thus, to get the energy bandstructure we have to solve a  $8 \times 8$  matrix numerically.

**a)** Sketch the crystal structure, the atomic basis, and the nearest neighbor vectors  $\mathbf{n}_1 = \frac{a}{4}(1, 1, 1)$ ,  $\mathbf{n}_2 = \frac{a}{4}(-1, -1, 1)$ ,  $\mathbf{n}_3 = \frac{a}{4}(-1, 1, -1)$ ,  $\mathbf{n}_4 = \frac{a}{4}(1, -1, -1)$ , where  $a$  is the lattice constant ( $\neq$  nearest neighbor distance!). Sketch the orbitals centered at each site and identify the overlaps, and the angles between them.

**b)** Because of various orbital overlaps  $ss$ ,  $sp\sigma$ ,  $pp\sigma$  and  $pp\pi$ , there are multiple hopping terms. Examine the matrix carefully and explain its structure. Specifically, explain all the diagonal terms, and the zeroes. Then explain the non-zero off-diagonal terms by invoking symmetries, geometries, and orbital overlaps.

$$\begin{array}{c} \langle s^A | \\ \langle p_x^A | \\ \langle p_y^A | \\ \langle p_z^A | \\ \langle s^B | \\ \langle p_x^B | \\ \langle p_y^B | \\ \langle p_z^B | \end{array} \begin{array}{c} |s^A\rangle \\ |p_x^A\rangle \\ |p_y^A\rangle \\ |p_z^A\rangle \\ |s^B\rangle \\ |p_x^B\rangle \\ |p_y^B\rangle \\ |p_z^B\rangle \end{array} \begin{pmatrix} E_s^A & 0 & 0 & 0 & -V_0 g_0(\mathbf{k}) & V_1 g_1(\mathbf{k}) & V_1 g_2(\mathbf{k}) & V_1 g_3(\mathbf{k}) \\ 0 & E_p^A & 0 & 0 & -V_1 g_1(\mathbf{k}) & V_2 g_0(\mathbf{k}) & V_3 g_3(\mathbf{k}) & V_3 g_2(\mathbf{k}) \\ 0 & 0 & E_p^A & 0 & -V_1 g_2(\mathbf{k}) & V_3 g_3(\mathbf{k}) & V_2 g_0(\mathbf{k}) & V_3 g_1(\mathbf{k}) \\ 0 & 0 & 0 & E_p^A & -V_1 g_3(\mathbf{k}) & V_3 g_2(\mathbf{k}) & V_3 g_1(\mathbf{k}) & V_2 g_0(\mathbf{k}) \\ \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & E_s^B & 0 & 0 & 0 \\ \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & 0 & E_p^B & 0 & 0 \\ \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & 0 & 0 & E_p^B & 0 \\ \text{c.c.} & \text{c.c.} & \text{c.c.} & \text{c.c.} & 0 & 0 & 0 & E_p^B \end{pmatrix}, \quad (1)$$

where c.c. stands for the complex conjugate (e.g.  $H_{51} = H_{15}^*$ ). The constants in this matrix are

$$\begin{aligned} V_0 &= V_{ss\sigma}, \\ V_1 &= \frac{1}{\sqrt{3}} V_{sp\sigma}, \\ V_2 &= \frac{1}{3} V_{pp\sigma} - \frac{2}{3} V_{pp\pi}, \text{ and} \\ V_3 &= \frac{1}{3} V_{pp\sigma} + \frac{1}{3} V_{pp\pi}, \end{aligned}$$

and the nearest neighbor ‘hopping’ phases are

$$\begin{aligned} g_0(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{n}_1} + e^{i\mathbf{k}\cdot\mathbf{n}_2} + e^{i\mathbf{k}\cdot\mathbf{n}_3} + e^{i\mathbf{k}\cdot\mathbf{n}_4}, \\ g_1(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{n}_1} - e^{i\mathbf{k}\cdot\mathbf{n}_2} - e^{i\mathbf{k}\cdot\mathbf{n}_3} + e^{i\mathbf{k}\cdot\mathbf{n}_4}, \\ g_2(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{n}_1} - e^{i\mathbf{k}\cdot\mathbf{n}_2} + e^{i\mathbf{k}\cdot\mathbf{n}_3} - e^{i\mathbf{k}\cdot\mathbf{n}_4}, \text{ and} \\ g_3(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{n}_1} + e^{i\mathbf{k}\cdot\mathbf{n}_2} - e^{i\mathbf{k}\cdot\mathbf{n}_3} - e^{i\mathbf{k}\cdot\mathbf{n}_4} \end{aligned}$$

for the 4 nearest neighbors. The eigenvalue spectrum of the  $8 \times 8$  matrix above yields the bandstructure  $E(\mathbf{k})$  of Silicon, GaAs, and all 3D semiconductors of the diamond-cubic or zinc-blende families. The electron wavevector  $\mathbf{k} = (k_x, k_y, k_z)$  is three dimensional: the electron energy depends on the direction it moves.

**c)** Set up the matrix above in Mathematica, Matlab, Python (or any tool you love!) to plot the energy bandstructure  $E(k)$  for  $k$  from  $\mathbf{L} \leftrightarrow \mathbf{\Gamma} \leftrightarrow \mathbf{X} \leftrightarrow \mathbf{K} \leftrightarrow \mathbf{\Gamma}$ . For Silicon,  $E_s^A = E_s^B = -13.55$  eV,  $E_p^A = E_p^B = -6.52$  eV,  $V_{ss\sigma} = +2.03$  eV,  $V_{sp\sigma} = +2.55$  eV,  $V_{pp\sigma} = +4.55$  eV,  $V_{pp\pi} = +1.09$  eV, and  $a = 0.543$  nm.

**d)** Repeat the bandstructure plot for our first 3D compound semiconductor: GaAs! Use  $E_s^{Ga} = -11.37$  eV,  $E_s^{As} = -17.33$  eV,  $E_p^{Ga} = -4.9$  eV,  $E_p^{As} = -7.91$  eV,  $V_{ss\sigma} = +1.70$  eV,  $V_{sp\sigma} = +2.15$  eV,  $V_{pp\sigma} = +3.44$  eV,  $V_{pp\pi} = +0.89$  eV, and  $a = 0.565$  nm. If you have worked your way to this stage, congratulations, your early hard work will pay off handsomely in the course.