ECE 4070: Physics of Semiconductor and Nanostructures

Spring 2014

Homework 4   `   **Due on March 04, 2014 at 5:00 PM**

Suggested Readings and Exam Reminder:
a) Read lecture notes.
b) First prelim exam is on Thursday March 13, 2013 at 7:00 PM in the evening. Room (TBD).

Problem 4.1 (Energy bands for a hexagonal lattice in 2D and Graphene)

Consider the following 2D hexagonal lattice from your last homework along with the primitive lattice vectors:
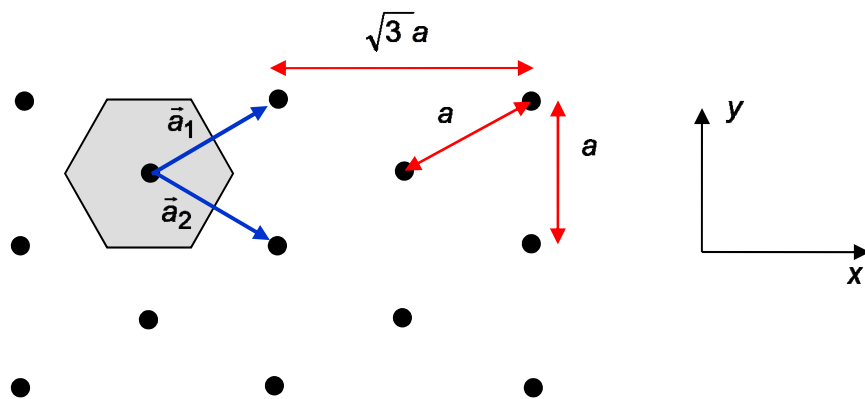
The corresponding reciprocal lattice is shown below.
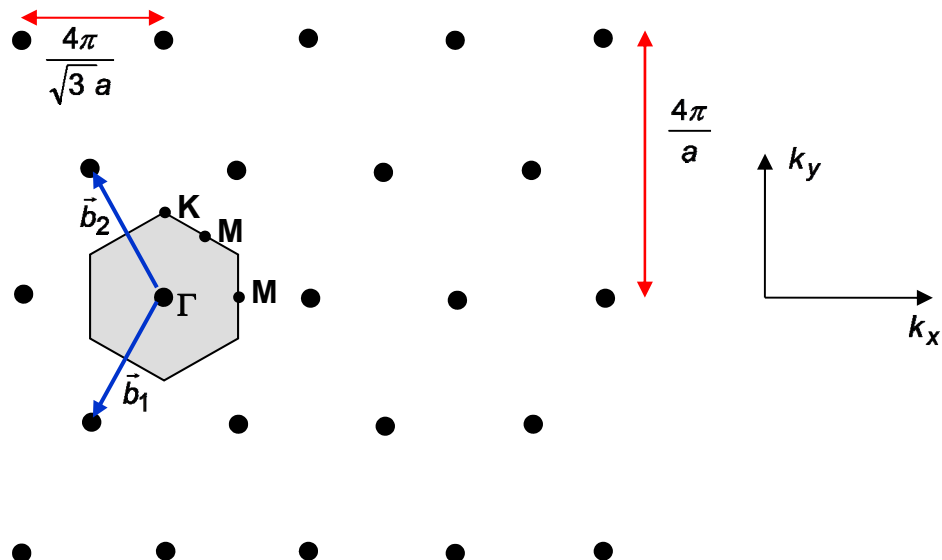
Suppose the potential is:

$$V(\vec{r}) = V_1 \cos(\vec{b}_1 \cdot \vec{r}) + V_1 \cos(\vec{b}_2 \cdot \vec{r}) + V_1 \cos((\vec{b}_1 + \vec{b}_2) \cdot \vec{r}) + V_2 \cos((\vec{b}_1 - \vec{b}_2) \cdot \vec{r})$$

where in 2D:

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

The goal of this problem is to figure out the bandgaps at the K and M pointw in FBZ using a perturbative approach.

a) As a result of the periodic potential, the free-electron state with k-vector equal to $(0, 4\pi/3a)$, which is the K-point in the first BZ, is coupled very strongly to 2 other degenerate free electron states. What are the k-vectors of these other free-electron states? Note that the K-point is located at the intersection of 2 different Bragg lines and therefore the free electron state here becomes strongly coupled to 2 other free electron states.

b) Write the solution for the actual electron wavefunction at the K-point $(0, 4\pi/3a)$ as a superposition of three degenerate free electron states, obtain a 3x3 matrix energy eigenvalue equation, and then solve it to obtain:

    i) the energies of the 3 energy bands at the K-point $(0, 4\pi/3a)$ and,

    ii) the actual wavefunctions of the electron at the K-point $(0, 4\pi/3a)$ corresponding to the 3 energy bands

c) As a result of the periodic potential, the free-electron state with k-vector equal to $(2\pi/\sqrt{3}\,a, 0)$, which is the M-point in the first BZ, is coupled very strongly to one other degenerate free electron state. What is the k-vector of this other free-electron state?

d) Write the solution for the actual electron wavefunction at the M-point $(2\pi/\sqrt{3}\,a, 0)$ as a superposition of two degenerate free electron states, obtain a 2x2 matrix energy eigenvalue equation, and then solve it to obtain:

    i) the energies of the 2 energy bands at the M-point $(2\pi/\sqrt{3}\,a, 0)$ and,

    ii) the actual wavefunctions of the electron at the M-point $(2\pi/\sqrt{3}\,a, 0)$ corresponding to the 2 energy bands

e) Starting from the following free-electron band diagram (from your previous homework set), sketch (on top of it, if you want to) the actual energy bands based on your calculations in parts (a), (b), (c) and (d).
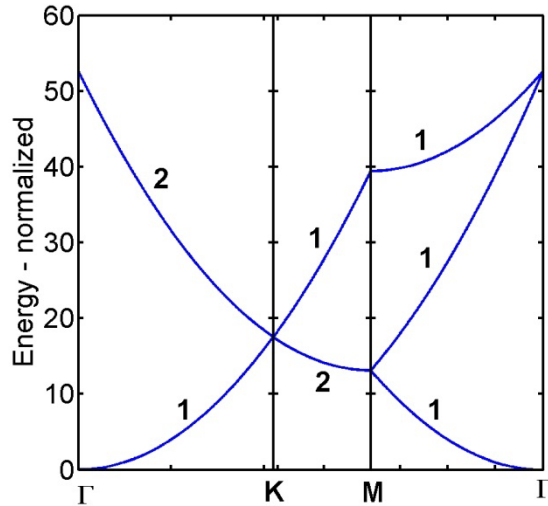
If you did part (b) correctly you would have noticed that the 3-fold degeneracy of the lowest 3 free-electron bands at the K-point (as found in problem 3.2(d) in homework 3) is only partially lifted when the periodic potential is turned on; two bands remain degenerate at the K-point but the third one has a higher energy. The hexagonal Bravais lattice under discussion describes graphene which is a single atomic layer of carbon atoms with two carbon atoms per unit cell, as shown below. The underlying hexagonal Bravais lattice is shown by the small black dots. The two carbon atoms per primitive cell are shown by the blue and red filled circles.
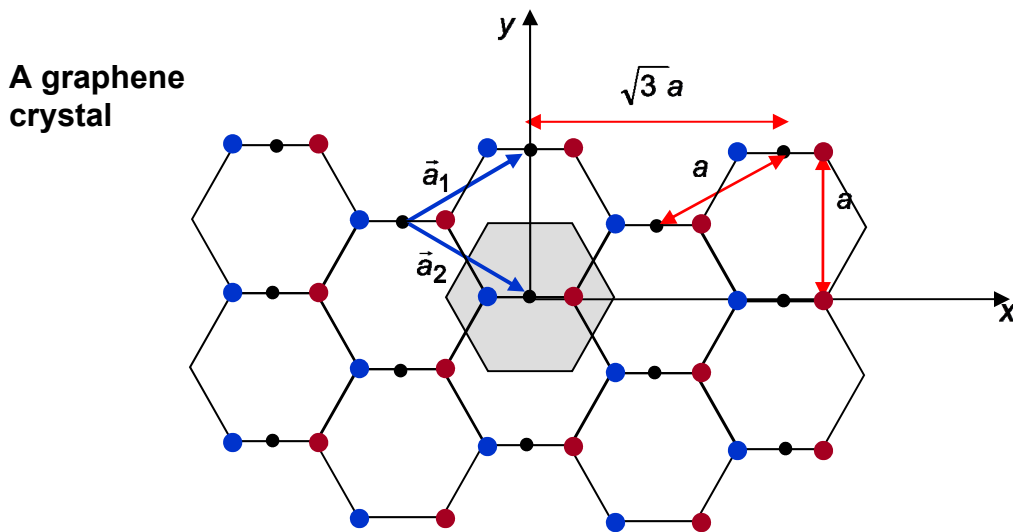
In part (b) you showed that two bands at the K-point remain degenerate even in the presence of the periodic atomic potential. **This degeneracy has something to do with inversion symmetry of the graphene crystal.** So we look at that next.

Inversion Symmetry: a 2D crystal will have inversion symmetry with respect to y-axis if, $V(-x, y) = V(x, y)$. Similarly, a 2D crystal will have inversion symmetry with respect to the x-axis if, $V(x, -y) = V(x, y)$.

f) Verify that the potential:

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$$V(\vec{r}) = V_1 \cos(\vec{b}_1 . \vec{r}) + V_1 \cos(\vec{b}_2 . \vec{r}) + V_1 \cos((\vec{b}_1 + \vec{b}_2) . \vec{r}) + V_2 \cos((\vec{b}_1 - \vec{b}_2) . \vec{r})$$
has inversion symmetry with respect to the y-axis.

g) Verify that the potential:
$$V(\vec{r}) = V_1 \cos(\vec{b}_1 . \vec{r}) + V_1 \cos(\vec{b}_2 . \vec{r}) + V_1 \cos((\vec{b}_1 + \vec{b}_2) . \vec{r}) + V_2 \cos((\vec{b}_1 - \vec{b}_2) . \vec{r})$$
has inversion symmetry with respect to the x-axis.

We will now break the inversion symmetry of the crystal and see what happens. In graphene, the blue and the red carbon atoms are exactly the same and therefore the atomic potential in graphene has inversion symmetry with respect to the y-axis. However, if the blue and the red atoms were not the same, say one was carbon and the other was silicon, then the inversion symmetry could be broken. In our model, we can break the inversion symmetry by assuming the following form of the potential:

$$V(\vec{r}) = V_1 \cos(\vec{b}_1 . \vec{r}) + V_1 \cos(\vec{b}_2 . \vec{r}) + V_1 \sin((\vec{b}_1 + \vec{b}_2) . \vec{r}) + V_2 \cos((\vec{b}_1 - \vec{b}_2) . \vec{r})$$

h) Verify that the above potential does not have inversion symmetry with respect to the y-axis.

i) For the above potential without inversion symmetry, write the solution for the actual electron wavefunction at the X-point $(0, \; 4\pi/3a)$ as a superposition of three degenerate free electron states, obtain a 3x3 matrix energy eigenvalue equation, and then solve it to obtain:

   i) the energies of the 3 energy bands at the X-point $(0, \; 4\pi/3a)$ and,

   ii) the actual wavefunctions of the electron at the X-point $(0, \; 4\pi/3a)$ corresponding to the 3 energy bands

If you did part (i) correctly, you would have seen that the 3-fold degeneracy at the K-point has been completely lifted. The systematic study of crystal symmetries, and their effect on the energy bands and electron wavefunctions, falls under group theory (a topic which is well beyond the scope of this course).

Problem 4.2 (Free electron energy bands for a FCC lattice in 3D)

Consider the following FCC lattice, and the corresponding reciprocal lattice:
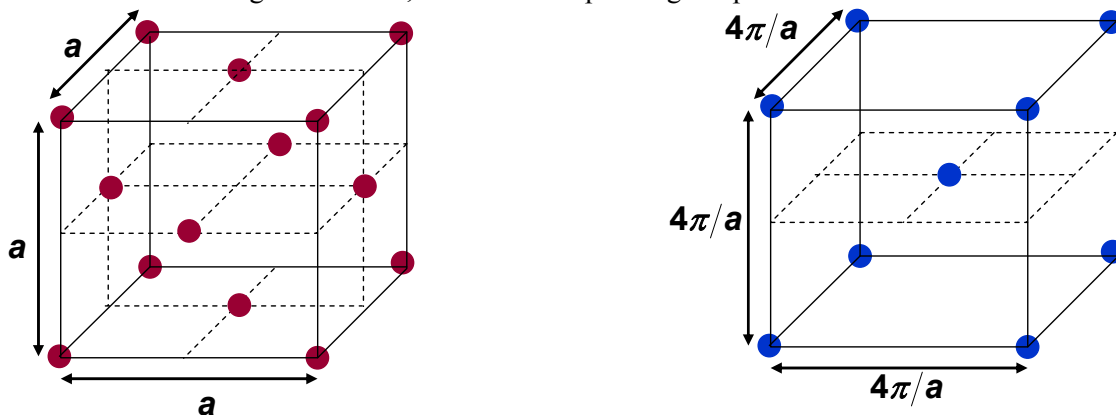
The FBZ of the reciprocal lattice is shown below, along with some important points.
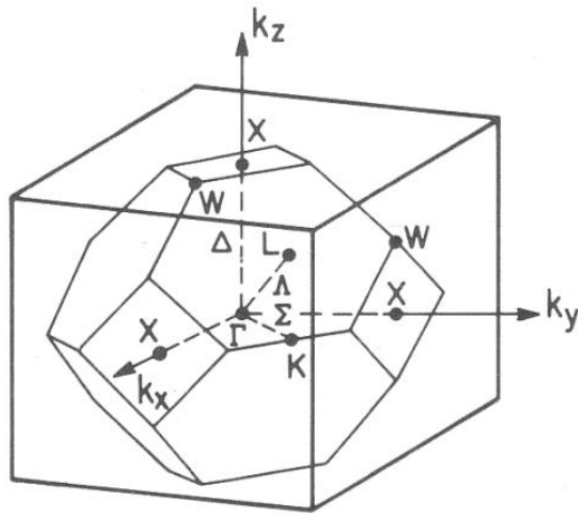
The are 6 equivalent X-points, 8 equivalent L-points, one Γ-point, and 24 equivalent W-points, as shown above. The labeling schemes using alphabets are mostly conventions so you need not worry too much about them.

a) Draw the first 3 free-electron energy bands in the first BZ from the Γ-point (0,0,0) to the X-point ($2\pi/a$,0,0) in k-space, indicate the degeneracy of each band. In drawing your bands you should use a scientific plotting program like matlab or mathematica and choose energy units such that $\hbar^2/2m\,a^2 = 1$ for simplicity.

b) Draw the first 3 free-electron energy bands in the first BZ from the Γ-point (0,0,0) to the L-point (π/a, π/a, π/a) in k-space, indicate the degeneracy of each band. In drawing your bands you should use a scientific plotting program like matlab or mathematica and choose energy units such that $\hbar^2/2m\,a^2 = 1$ for simplicity.

Problem 4.3 (Ethene (or Ethylene) molecule: LCAO)

Two carbon atoms and four hydrogen atoms form an ethene molecule with the chemical formula C_2H_4. It is the most manufactured hydrocarbon in the world. The structure of the ethene molecule is shown below:
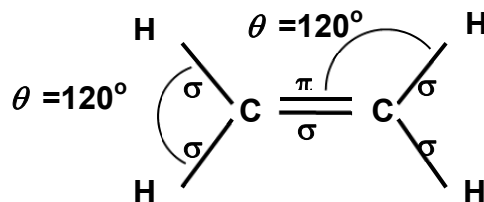
a) Convince yourself that the 2p-orbitals on C atoms oriented out of the plane of the paper do not have a non-zero energy matrix element with any of the 1s-orbitals, or 2s-orbitals, or any of the 2p-orbitals that are in the plane of the paper. Explain why this is so.

For parts (b) and (c) you can ignore the 2p-orbitals on C atoms that are oriented out of the plane of the paper. You are then left with 4 1s orbitals – one on each H atom, 2 2s-orbitals – one on each C-atom, and 4 2p-orbitals – two on each C atom that are in the plane of the paper.

b) What is the hybridization scheme (sp3 or sp2) for each C atom?

c) Write an appropriate trial solution for the wavefunction of the electron using LCAO (remember to ignore the 2p-orbitals on C atoms that are oriented out of the plane of the paper). Use the result from part (b) to guide you.

d) Using your solution in part (b), solve for the eigenenergies. Show all the eigenenergies and the corresponding degeneracies going from the atomic orbitals to the molecular orbitals in an energy level diagram. Use values of energy matrix elements given in the handouts (e.g. $V_{ss\sigma}$, $V_{sp\sigma}$, etc).

Now we will consider what the 2p-orbitals on C atoms oriented out of the plane of the paper do. They are going to form molecular orbitals of their own.

e) Write an appropriate trial solution for the wavefunction of the electron using LCAO using only the 2p-orbitals on C atoms oriented out of the plane of the paper.

f) Using your solution in part (e), solve for the eigenenergies. Show all the eigenenergies and the corresponding degeneracies going from the atomic orbitals to the molecular orbitals in an energy level diagram. Use values of energy matrix elements given in the handouts (e.g. $V_{ss\sigma}$, $V_{sp\sigma}$, etc). What type of bond is made by the 2p-orbitals on C atoms oriented out of the plane of the paper (sigma or pi)?

g) Combine your results from part (d) and part (f) and draw an energy level diagram that shows all the energies and the corresponding degeneracies going from the atomic orbitals to the molecular orbitals (and remember this time ALL atomic orbitals are being included). On the energy level diagram indicate (by black dots) the electron occupation of each molecular orbital (you have a total of 12 electrons participating in bonding).