

Quantum Transport:

ATOM TO TRANSISTOR

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Lecture 18: Bandstructure: 3D Solids

Ref. Chapter 5.3



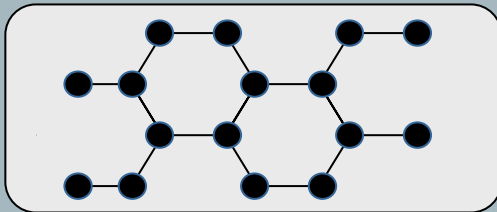
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Bandstructure

00:00

- Last lecture we analyzed the band structure of Graphite (which is 2D)



2D
Plane

- In this lecture we will look at the band structure of common semiconductors (e.g. GaAs). Remarkably, most common semiconductors possess a diamond lattice structure.
- As you may know both graphite and diamond are composed of carbon, yet their electronic properties are different. So what are these different properties?

- Naturally, diamond also forms a diamond lattice.

Graphite:

- Structure: Parallel 2D Planes. **Loose** coupling between planes. Atoms on each plane are closely spaced.
- In-plane conducts ≈ 100 times better than perpendicular direction
- sp^2 bonding

Diamond:

- Poor Conductor
- 3D structure, no weakly coupled separate planes
- sp^3 bonding

Graphite

04:00

- Why do graphite and diamond have such different properties? The answer to this question lies in the interaction of the carbon valence orbitals $2s^2p^2$

Carbon Valence Orbitals

2 Atoms in a unit cell



- In graphite the p_z orbitals are completely decoupled from s, p_x and p_y orbitals.

- Hence the Hamiltonian matrix looks like

$$H = \begin{matrix} & s & p_x & p_y & p_z \\ \begin{matrix} s \\ p_x \\ p_y \\ p_z \end{matrix} & \left[\begin{array}{ccc|c} \hline & & & \bigcirc \\ \hline & & & \\ \hline & & & \\ \hline & \bigcirc & & \\ \hline \end{array} \right] & \text{Block Diagonal} \end{matrix}$$

meaning $\int d\vec{r} u_{s,p_x,p_y} \hat{H} u_{p_z} = 0$

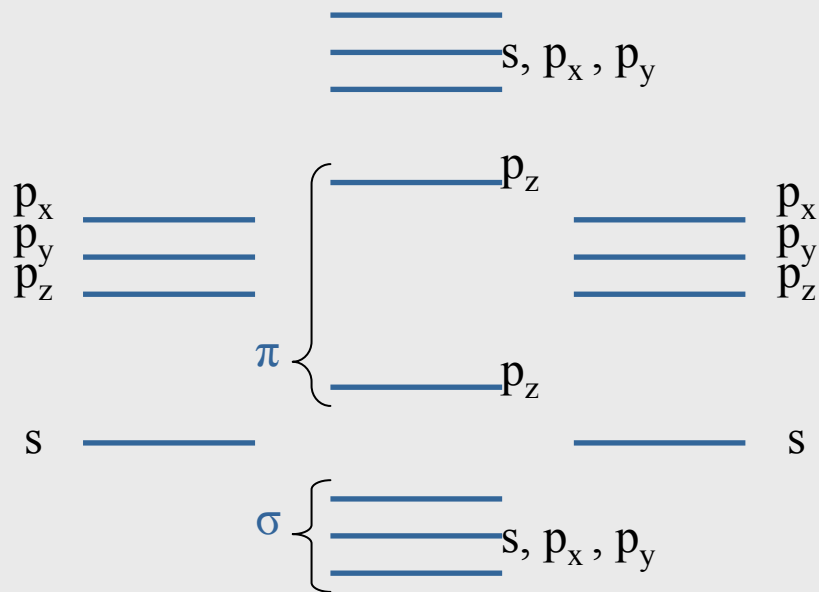
- In the case of diamond, the p_z orbitals are not decoupled such that

$$\int d\vec{r} u_{s,p_x,p_y} \hat{H} u_{p_z} \neq 0$$

Graphite and Diamond

04:00

- So, the bonding levels of graphite are



- The s, p_x, p_y bonds are called “ σ -bonds” and the p_z bonds are called “ π bonds.”

- One might ask, why are the s, p_x, p_y bonds lower than the p_z bond? Essentially, it is because the s, p_x, p_y levels overlap more:

$$\left| \int d\vec{r} u_{s, p_x, p_y} \hat{H} u_{s, p_x, p_y} \right| < \left| \int d\vec{r} u_{p_z} \hat{H} u_{p_z} \right|$$

Giving rise to bigger overlap matrix elements M :

$$\begin{bmatrix} \varepsilon & M \\ M & \varepsilon \end{bmatrix}$$

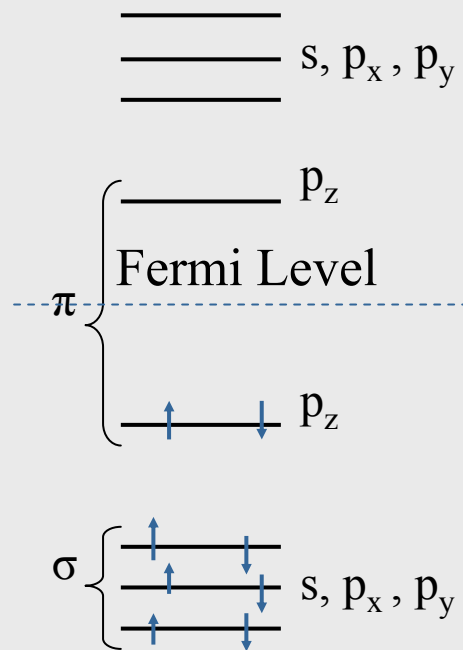
that lead to bigger splitting in the eigenvalues

$$\begin{array}{l} \text{—————} \varepsilon + M \\ \text{—————} 2M \\ \text{—————} \varepsilon - M \end{array}$$

Properties of Graphite

15:00

- Based on the states that get filled during C-C bonding in graphite Fermi energy lies between the pi levels.



- Since conduction depends on the states right around Fermi energy, the optical and electrical properties of graphite are largely determined by the p_z π levels!

- This is why we use only one orbital (2 per unit cell) when simulating graphite! When are the σ levels needed? Usually when determining structural properties such as the melting point.

- However, in the case of diamond and other common semiconductors the p_x, p_y, p_z and s levels are mixed up. Because the p_z orbitals are not decoupled, there is no sharp separation between bonding levels and we must use all 4 $2s^2 2p$ orbitals when studying them.

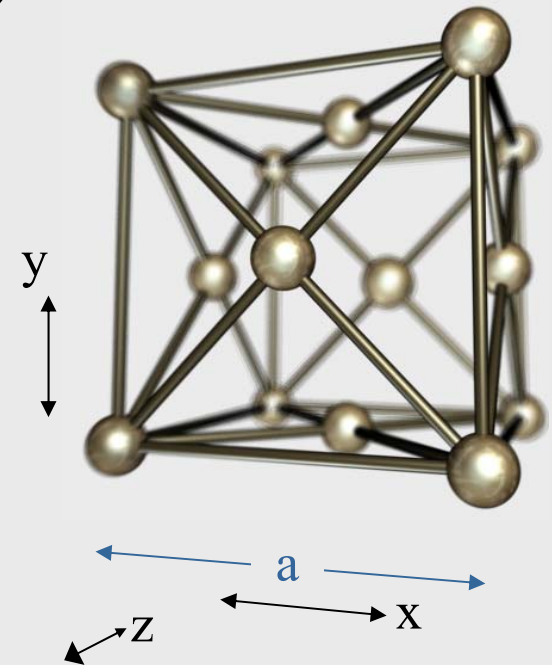
Diamond and Common Semiconductors

15:00

- So, it is the mixing of orbitals during bonding which results such different properties for diamond and graphite
- This mixing of orbitals is common to all diamond lattice structures including common semiconductors
- Now, let's look deeper at the lattice structure of semiconductors...

- In common semiconductors, if one considers the corresponding atoms form each unit cell, together they form a structure called FCC →
- In common semiconductors like GaAs we have two overlapping (interlocked) FCC lattices (since there are two atoms per unit cell). For instance to get the structure of GaAs, 1) Take an FCC lattice. 2) Duplicate it. 3) Finally move the Duplicate by $\frac{1}{4}$ the length of body diagonal along the body diagonal.

FCC Lattice



Semiconductors: Spacing Within a Unit Cell

19:00

- The unit vectors of an FCC lattice can be defined as

$$\vec{a}_1 = (\hat{x} + \hat{y})a/2$$

$$\vec{a}_2 = (\hat{y} + \hat{z})a/2$$

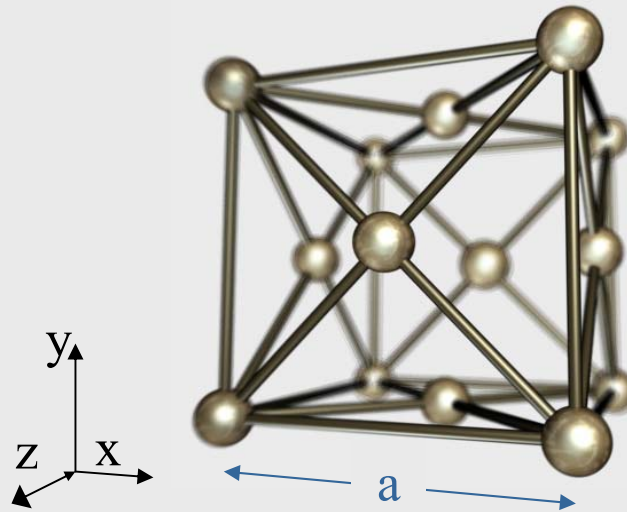
$$\vec{a}_3 = (\hat{x} + \hat{z})a/2$$

such that the position of any unit cell is given by

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

(m, n and p are integers)

FCC Lattice



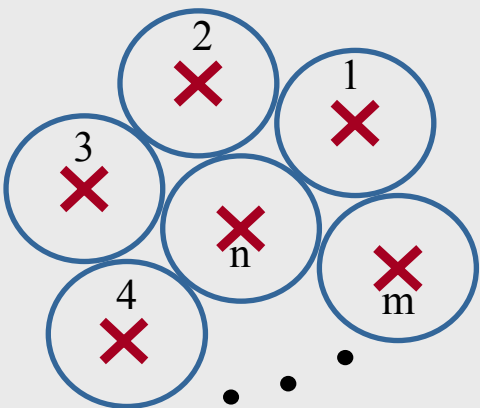
- The separation of two atoms in a unit cell, or offset between the two FCC lattices, may be defined as $(a/4, a/4, a/4)$. This gives a nearest neighbor distance of $\sqrt{3}a/4$

- We now have everything required to calculate the overlap matrix

$$[h(\vec{k})] = \sum_m H_{nm} e^{i\vec{k} \cdot (\vec{d}_m - \vec{d}_n)}$$

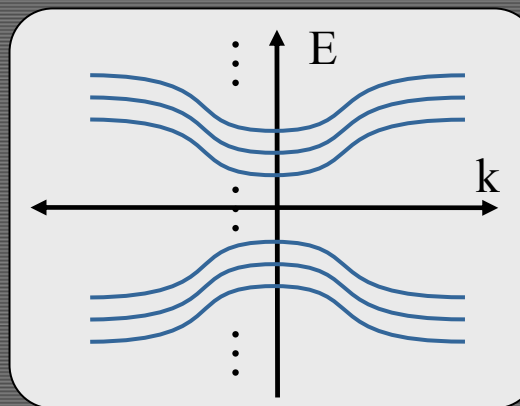
Bandstructure and $[h(\vec{k})]$

- Recall, in $[h(\vec{k})]$, n is the unit cell under consideration and m is a nearest neighbor of n .



- From $[h(\vec{k})]$ we obtain the eigen-energies of our periodic lattice structure. These eigen-energies form the levels commonly defined as band structure.

Eigen-energies and bandstructure

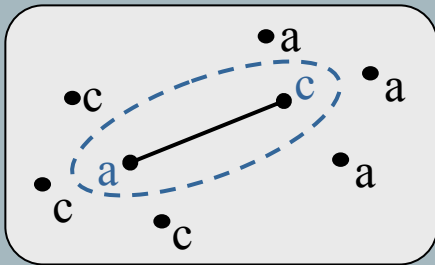


- Solving $[h(\vec{k})]$ is slightly more difficult in semiconductors because we must consider multiple orbitals in 3-dimensions
- Let's start simple and only consider the s orbitals.

Semiconductor "s" Orbitals

25:15

- First, however, distinguish the two atoms in a unit cell as a "cation" (c) and an "anion" (a)



Such that an anion has only 4 cations as nearest neighbors and a cation has only 4 anions as nearest neighbors

- So, the first s-orbital matrix is

$$\begin{matrix}
 S_c & S_a \\
 S_c \begin{bmatrix} E_{Sc} & E_{SS} \\ E_{SS} & E_{Sa} \end{bmatrix} ; (m = n) \\
 S_a
 \end{matrix}$$

- The first cation to anion s overlap matrix is

$$\begin{matrix}
 S_c & S_a \\
 S_c \begin{bmatrix} 0 & E_{SS} \\ 0 & 0 \end{bmatrix} e^{i\vec{k}\cdot\vec{a}_1} ; (m \neq n) \\
 S_a
 \end{matrix}$$

- Adding all other cation to anion matrices we get

$$\begin{matrix}
 S_c & S_a \\
 S_c \begin{bmatrix} 0 & E_{SS} \\ 0 & 0 \end{bmatrix} (e^{i\vec{k}\cdot\vec{a}_1} + e^{i\vec{k}\cdot\vec{a}_2} + e^{i\vec{k}\cdot\vec{a}_3}) \\
 S_a
 \end{matrix}$$

- Similarly, all anion to cation s overlap matrices give

$$\begin{matrix}
 S_c & S_a \\
 S_c \begin{bmatrix} 0 & 0 \\ E_{SS} & 0 \end{bmatrix} (e^{-i\vec{k}\cdot\vec{a}_1} + e^{-i\vec{k}\cdot\vec{a}_2} + e^{-i\vec{k}\cdot\vec{a}_3}) \\
 S_a
 \end{matrix}$$

Full $[h(k)]$ Matrix

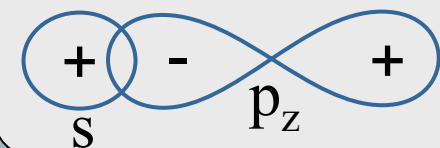
- The total s overlap matrix is $\begin{bmatrix} E_{Sc} & E_{SS}g_0 \\ E_{SS}g_0^* & E_{Sa} \end{bmatrix}$ where:
 $g_0 = 1 + e^{i\vec{k}\cdot\vec{a}_1} + e^{i\vec{k}\cdot\vec{a}_2} + e^{i\vec{k}\cdot\vec{a}_3}$
- Altogether the full matrix looks something like:

$$\begin{array}{c}
 S_c \quad S_a \quad p_{x^c} \quad p_{y^c} \quad p_{z^c} \quad p_{x^a} \quad p_{y^a} \quad p_{z^a} \\
 \left[\begin{array}{cccccccc}
 E_{Sc} & E_{SS}g_0 & 0 & 0 & 0 & E_{scpa}g_1 & E_{scpa}g_2 & E_{scpa}g_3 \\
 E_{SS}g_0^* & E_{Sa} & & & & & \vdots & \\
 0 & & E_{p_{x^c}} & & & & & \\
 0 & & & \dots & & & & \\
 0 & & & & & & & \\
 \vdots & & & & & & & \\
 p_{x^a} & & & & & & & \\
 p_{y^a} & & & & & & & \\
 p_{z^a} & & & & & & &
 \end{array} \right]
 \end{array}$$

- Note: the g_1, g_2, g_3 terms differ only from the g_0 term by a +ve or -ve sign. For example,

$$g_1 = 1 + e^{i\vec{k}\cdot\vec{a}_1} - e^{i\vec{k}\cdot\vec{a}_2} - e^{i\vec{k}\cdot\vec{a}_3}$$

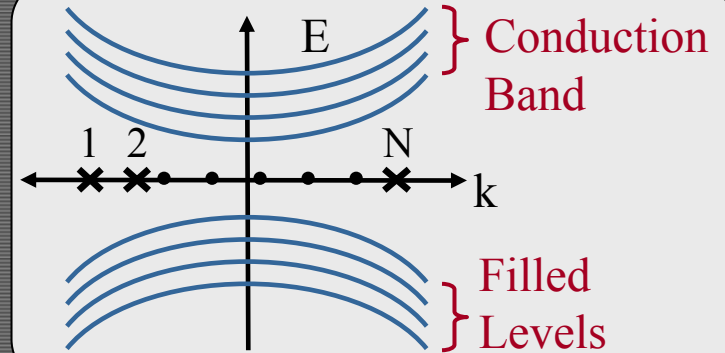
These changes in sign are due to positive negative overlap such as with the s and p_x levels :



- The s, p_x, p_y, p_z orbitals provide the minimum basis set needed to describe semiconductor behavior. Often, though, 4 orbitals insufficiently describe conduction so in practice a fifth “s” orbital is usually incorporated. This is known as the sp^3s^* model, it produces a 10×10 rather than 8×8 matrix $[h(\vec{k})]$
- Moving on, how do we relate the band diagram by $[h(\vec{k})]$ to the electrons in a lattice

- If we are modeling a lattice with 4 basis per atom (8 per unit cell) and N unit cells then our k axis will have N points with 8 eigen-energies per point

Band Diagram with Electrons

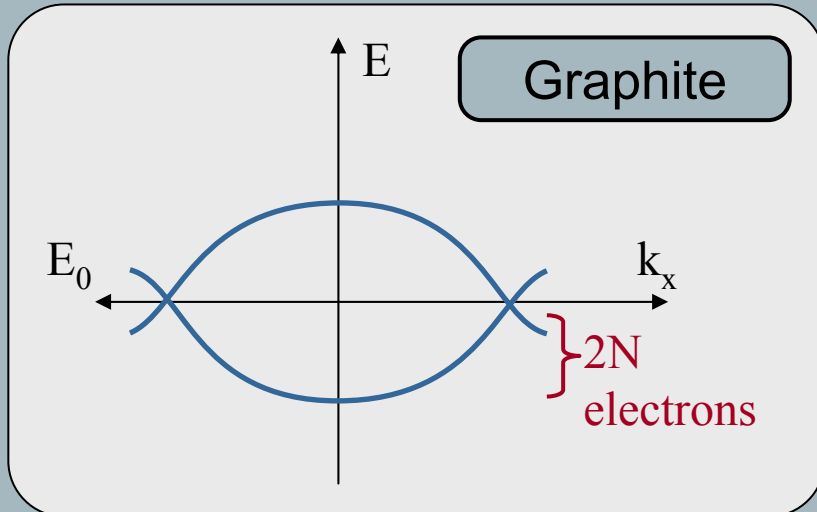


- For silicon, with 4 basis orbitals per atom and a total of 8 per unit cell, there will be a total of $8N$ electrons. Including spin degeneracy $8N$ electrons occupy $4N$ states or the 1st 4 levels in the band diagram

Graphite Band Structure

45:54

- One last point on electron occupation in band diagrams. Recall, for graphite a band diagram of the form

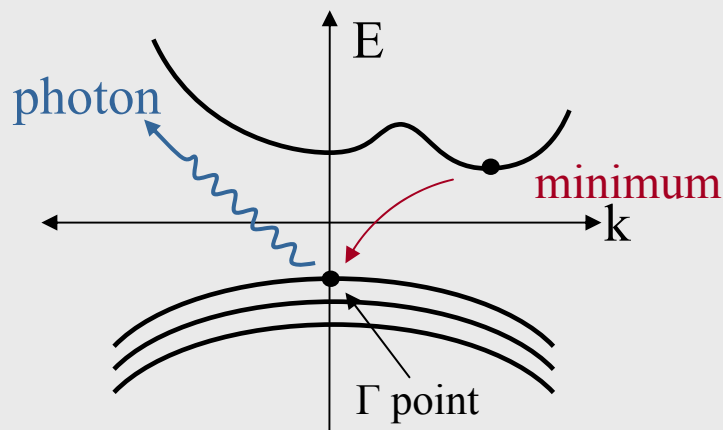


with eigenvalues of $E_0 \pm |h_0|$. Given 2 electrons per unit cell, we have $2N$ electrons which fill the bottom half of the band diagram up to E_0

- Thus graphite is completely filled up to the Fermi energy, E_0 . As we can see there are states available right around Fermi energy giving rise to conduction (the conduction band touches the Fermi energy)! The Fermi energy in diamond does not lie so close to the conduction bands, hence its well known insulating properties.

- Band diagrams can shed light on the optical properties of materials
- For instance, in many semiconductors such as Si and Ge the lowest point in the conduction band can occur not at $k = 0$ but offset somewhat (these are known as indirect semiconductors).

Offset CB Minimum



- Note: The " Γ " gamma point is the location of greatest energy in the valence band
- This offset minimum, where excited electrons prefer to settle makes Si less than ideal for lasers and other electro-optical devices. GaAs, on the other hand, does *not* have an offset minimum and therefore has a wide range of applications in electro-optical devices.

• **Next Lecture: Further Discussion of Band Diagrams**