

Topic VII

Band Theory in Solids

VII.1 Module 21: Electronic Structure of Solids (1D Solids)

2/5:

- Solid silicon's symmetry space group would be $Fd\bar{3}m$.
- Suggested reading: Hoffmann (1987).
 - A rare less mathematical article on band theory that has taught generations of chemists; comes at it from a physics perspective.
- To consider solids, let's first consider an infinite chain of hydrogen atoms.
 - This should separate into H_2 molecules (**Peierl's instability**); considering it to exist is a consequence of looking at chemistry through a physics perspective, where this is a simple model.
 - However, other substances can have chains of p_z orbitals, such as platinum atoms.
- An imaginary zoo of hydrogen molecules (we use the limit of a cycle of hydrogen atoms to approximate an infinitely long chain):
 - H_2 has a bonding and antibonding MO.
 - Cyclic H_3^+ is the most abundant ion in the universe (recently discovered by UChicago). One bonding and two antibonding orbitals.
 - We can keep adding hydrogen atoms to our rings.
 - For an infinitely long cycle of hydrogen atoms, we will have an infinite number of states close together that resembles a band in solids.
- Back to the chain of H atoms:
 - The basis function on each lattice point is a H_{1s} orbital; there are countably many.
 - The appropriate SALCs ψ_k are based in translating every orbital by a finite number of units:

$$\psi_k = \sum_n e^{ikna} \phi_n$$

- a is the distance between neighboring hydrogen atoms.
- Since there are infinitely many translations, there should be infinitely many translational symmetry elements, so infinitely many irreducible representations, too.
- The coefficients e^{ikna} come from **Bloch's theorem**.
- In this formalism, k is an index labeling irreducible representations of the translation group. ψ transforms just like a , e_1 , and e_2 (e.g., in the C_5 point symmetry group).
- This process of symmetry adaptation is called “forming Bloch functions.”

- Elementary band theory for extended solids:
 - Energy bands in solids arise from overlapping atomic orbitals, which become the **crystal orbitals** that make up the bands.
 - Recipe: Use LCAO (tight binding) approach.
 - A crystal is a regular periodic array with translational symmetry.
 - Periodic boundary conditions require $\psi(x+Na) = \psi(x)$, i.e., each wavefunction must be symmetry equivalent to the one in the neighboring cells.
 - For a 1D solid with lattice constant a and atom index n , Bloch's theorem tells us that the above SALC ψ_k is a solution to the Schrödinger equation.
- If we calculate ψ_0 and $\psi_{\pi/a}$, we get the most and least bonding states possible, respectively (the least bonding state is the most antibonding state and has the highest energy).

Figure VII.1: s orbital bonding states.

$$\begin{aligned}\psi_0 &= \phi_0 + \phi_1 + \phi_2 + \phi_3 + \cdots \\ \psi_{\pi/a} &= \phi_0 - \phi_1 + \phi_2 - \phi_3 + \cdots\end{aligned}$$

- At this point, we can construct a band between these two states.
 - The band is *almost* infinite; it's on the order of Avogadro's number.
 - We have as many k values as translations in the crystal or as many unit cells in a crystal.
- **First Brillouin zone:** The region that covers all possible energy states that the crystal can have.
 - It is $-\frac{\pi}{a} < k < \frac{\pi}{a}$; which is the range of all possible values that the sine function will give.
- There is one energy level for each value of k , but $E(k) = E(-k)$.
- k is proportional to the electron momentum, or electron velocity.
- Calculation of 1D band structure:
 - We have N atoms such that $\psi_k = \sum_{n=0}^N e^{inka} \phi_n$.
 - The crystal Schrödinger equation is $\hat{H}\Psi(k) = E(k)\Psi(k)$.
 - Thus, the electron energies are given by

$$E(k) = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

- Recall that in Dirac's bra-ket notation, $\langle \psi | \hat{H} | \psi \rangle \equiv \int \psi^* \hat{H} \psi \, d\tau$; for normalized atomic orbitals and ignoring overlap integrals:

$$\langle \phi_m | \phi_n \rangle = \begin{cases} 1 & m = n \\ 0 & m \neq n \end{cases}$$

- Also recall that

$$\langle \psi | \psi \rangle = \sum_{m,n} e^{i(n-m)ka} \langle \phi_m | \phi_n \rangle = N$$

- Thus, we can calculate for on-site ($m = n$):

$$\langle \psi(k) | \hat{H} | \psi(k) \rangle = \sum_n \langle \phi_n | \hat{H} | \phi_n \rangle = N\alpha$$

And for resonance ($m \neq n$), where we need only consider the two nearest neighbors:

$$\langle e^{-inka} \phi_n | \hat{H} | e^{i(n\pm 1)ka} \phi_{n\pm 1} \rangle = \beta e^{\pm ika}$$

- Putting everything together, we have

$$E(k) = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{N\alpha + N\beta(e^{ika} + e^{-ika})}{N} = \alpha + 2\beta \cos(ka)$$

- **Zone center:** The state where all atomic orbitals are in phase (all bonding σ). *Also known as Γ .*
- **Zone border:** The state where all atomic orbitals are out of phase (all antibonding σ^*). *Also known as X .*
- Large numbers of MOs form bands of states.
- **Band structure:** The plot of E as a function of k .
 - The one we've derived so far is an s-shape curve.
- The p -orbitals are opposite — they form a bonding state with inverted phases.



Figure VII.2: p orbital bonding states.

- The analysis of Figures VII.1 and VII.2 can be done for many more types of orbitals, including p_z , d_{z^2} , and d_{xz} .
- Bonding orbital bands run uphill (concave upwards $E(k)$) at $k = 0$ and antibonding orbital bands run downhill (concave downwards $E(k)$) at $k = 0$.
- Energy bands run from $\alpha + 2\beta$ to $\alpha - 2\beta$ since β is negative for s orbitals.
- **Density of states:** The number of energy levels in the energy interval ΔE . *Also known as **DOS**.*

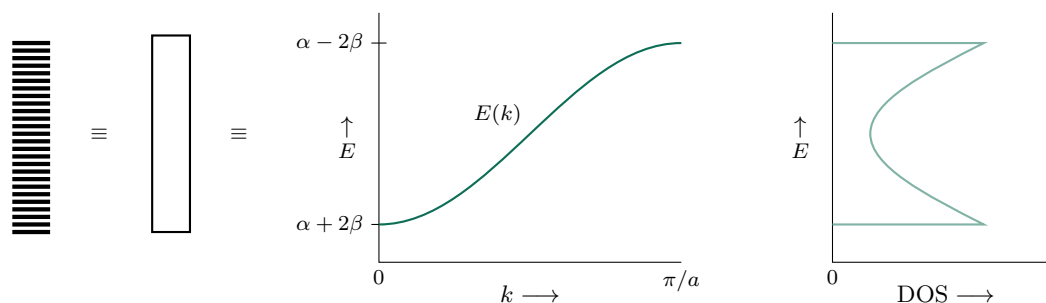


Figure VII.3: Density of states.

- Proportional to the inverse slope of the band; steep bands with large overlap yield a small DOS, and vice versa for flat bands.
- Reality check: PES for a long-chain alkane ($C_{36}H_{74}$) shows this inverse DOS relationship for a little while.

VII.2 Module 22: Electronic Structure of Solids (2D and 3D solids)

- 2D band structure:

- Simple Hückel: A two-dimensional square net (s orbitals only (or p_z)).

$$\psi(k) = \sum_{m,n} e^{ik_x m a + i k_y n a} \cdot \phi_{m,n}$$

- Consider the **crystal orbitals** at special k points (high symmetry).
- The **Brillouin zone** is 2D here (we have a **wave vector**).

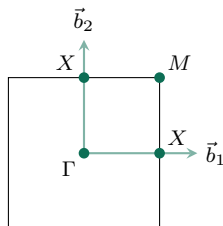


Figure VII.4: 2D Brillouin zone.

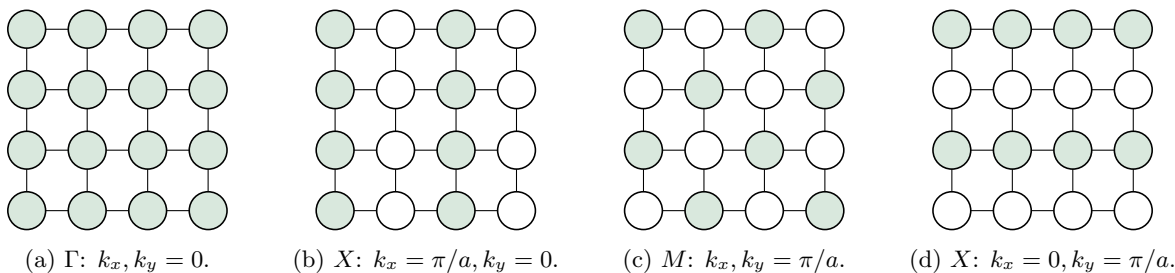


Figure VII.5: Special k points.

- The center is the Γ point ($k_x = k_y = 0$; every orbital is surrounded by 4 orbitals of matching phase). The midpoint of the lines are called X points ($k_x = \frac{\pi}{a}, k_y = 0$, and vice versa; every orbital is surrounded by 2 orbitals of matching phase and 2 orbitals of unlike phase). The maximum point is the M point ($k_x = k_y = \frac{\pi}{a}$; every orbital is surrounded by 4 orbitals of unlike phase).
- Calculating $E(k)$ in two dimensions.

$$E(k) = \alpha + 2\beta(\cos(k_x a) + \cos(k_y a))$$

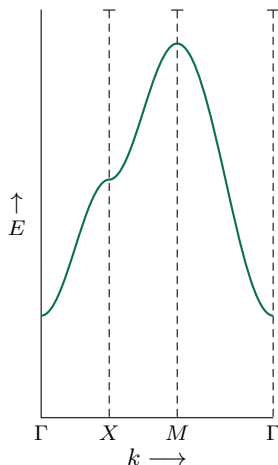


Figure VII.6: Schematic band structure (2D).

- Our schematic band structure (Figure VII.6) traces values along a 1D path in two-space from $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$.

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- The bandwidth $4|\beta|$ is proportional to the degree of interaction between neighboring orbitals.
 - Since β is the interaction integral and $E(k)$ varies from $\alpha - 2\beta$ to $\alpha + 2\beta$.
- For p_σ orbitals, $\beta > 0$.
- Deriving the density of states formula:
 - We often simplify $E(k)$ with the first term of the Taylor series expansion; this gives us

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

- This implies that $E \propto k^2$ and, hence, $k \propto \sqrt{E}$.
- Thus, the one-dimensional density $D_{1d}(k)$ of states as a function of k is $dN(k)/dk = 1$ since the number of states is evenly distributed along the k axis (i.e., in Figure VII.3).
- It follows that the one-dimensional density $D_{1d}(E)$ of states as a function of E is

$$D_{1d}(E) = \frac{dN(E)}{dE} = \frac{dN(k)}{dk} \frac{dk}{dE} \propto 1 \cdot \frac{1}{\sqrt{E}} = \frac{1}{\sqrt{E}}$$

- For each orbital, there is a unique path akin to Figure VII.6. The combination of all of these **bands** in one graph characterizes a material.
- **Wigner-Seitz cell** (of the reciprocal lattice): The first Brillouin zone, or FBZ.
 - A primitive cell with a lattice point at its center.
 - A 3D discrete Fourier transform of the lattice.
 - Has $k_{x,y,z}$.
 - What is “d.I.” and “r.I.”?
 - We once again can find high symmetry points and directions akin to those in Figure VII.4.
- Electronic band structure is calculated within the first Brillouin zone to give us the electronic band structure of a solid.

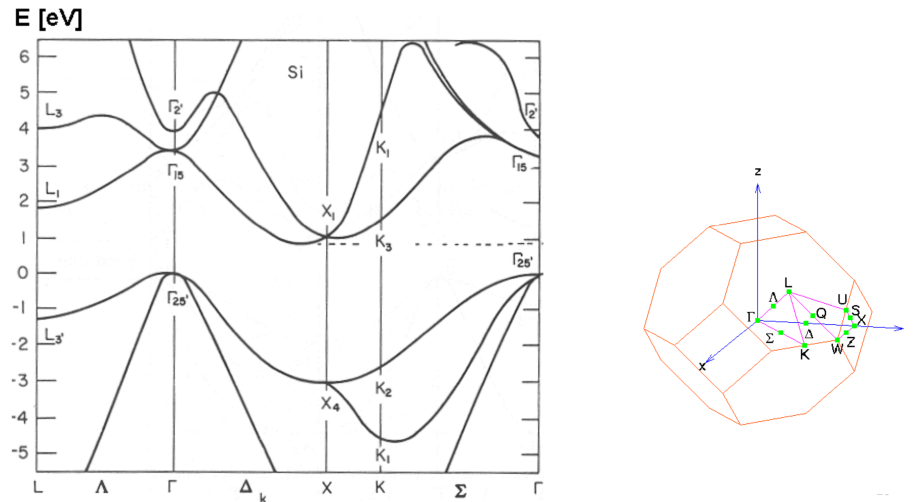


Figure VII.7: Electronic band structure of Si.

- **Angle-resolved photoemission spectroscopy**^[1]: If the incoming photon's energy is greater than the electron's binding energy, the electron will eventually be emitted with a characteristic kinetic energy and angle relative to the surface normal. This angle is related to the electron's crystal momentum. The Bloch wave vector is linked to the measured electron's momentum. *Also known as ARPES.*

– Indeed, ARPES can be used to reconstruct the band structure of a solid. The bands are real!

VII.3 Module 23: Filling Bands With Electrons

- The Fermi-Dirac statistics and Fermi Energy:
 - At $T = 0$, we expect all of the atoms in a solid to be in the ground state. The distribution of electrons (fermions) at the various energy levels is governed by the Fermi-Dirac distribution:

$$F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

where E_F is the Fermi energy.

■ $F(E)$ is the probability to fill the states with a given energy E .

- When $T = 0$ K, the Fermi energy is the energy of the last occupied state. Moreover,
- The Fermi energy is the energy of the last occupied state at $T = 0$ K; it is proportional to the square of the Fermi state k_F , i.e., $E_F \propto k_F^2$.
- If $T > 0$, then:
 - We fill the states from bottom to top.
 - Instead of having a sharp shift from occupied to unoccupied states, we have a sort-of washed-out step function.
 - Far below E_F , $F(E) = 1$; far above E_F , $F(E) = 0$. In the small **Fermi window** (aka. **Fermi level**) at the border (where the washed-out step function is), $0 < F(E) < 1$.
 - The Fermi window is $4kbt$.
 - It is in the Fermi level that all of the important stuff happens (i.e., electrons flowing in metals).

¹Figure 7.20 in Labalme (2020) actually refers to this kind of photoelectron spectroscopy!

- If the gap (range where $\text{DOS}(E) = 0$) in the density of states at the Fermi level is smaller than 3 eV, then we have a semiconductor. If larger, we have an insulator. If 0, we have a conductor. Magnitude of DOS at Fermi level correlates with conductivity (e.g., Al has a higher DOS at the Fermi level than Ag, and we observe that Al is more conductive than Ag).
 - In metals and insulators, the Fermi level is within bands.
 - In semiconductors, it is between bands.
 - In physics, everything is a metal or insulator; semiconductors are a constructed perspective.
- Fermi sphere:
 - The surface of the Fermi sphere separates occupied and unoccupied states in k -space.
 - Bounded by Fermi surface.
 - Radius is Fermi wave vector $k_F = \sqrt[3]{3\pi^2 n}$ where n is a parameter related to the density of electrons.
 - Fermi energy: $E_F = \hbar^2 k_F^2 / 2m$.
 - Fermi momentum: $p_F = \hbar k_F$.
 - Fermi velocity: $v_F = \hbar k_F / m$.
 - Fermi temperature: $T_F = E_F / k_B$.
- Electrons at $T = 0$ K still move very quickly (approximately 0.06 the speed of light) since they're quantum particles (not classical ones).
- 3D density of states:
 - The density of states $g(E)$ is the number of one-electron states (including spin multiplicity) per unit energy and volume:

$$g(E)_{3D} \equiv \frac{1}{V} \frac{dN}{dE}$$

■ N is twice the product of the Fermi sphere volume and the number of levels per unit volume.
 - Thus,

$$N = 2 \times \frac{4}{3} \pi k^3 \times \frac{V}{8\pi^3} = \frac{V}{3\pi^2 \hbar^3} (2m^* E)^{3/2}$$

so

$$g(E)_{3D} = \frac{1}{V} \frac{dN}{dE} = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E}$$
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