

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).
- To consider solids, let's first consider an infinite chain of hydrogen atoms.
 - This should separate into H_2 molecules (**Peierl's instability**).
 - 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.
 - The appropriate SALC ψ is
$$\psi_k = \sum_n e^{ikna} \phi_n$$
 - 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. *picture*
 - 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 $E(k) = E(-k)$.
- The energy is proportional to the electron momentum.
- 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:

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

- 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 ? where all atomic orbitals are in phase (all bonding σ). *Also known as Γ .*
- **Zone border:** The ? 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**.*

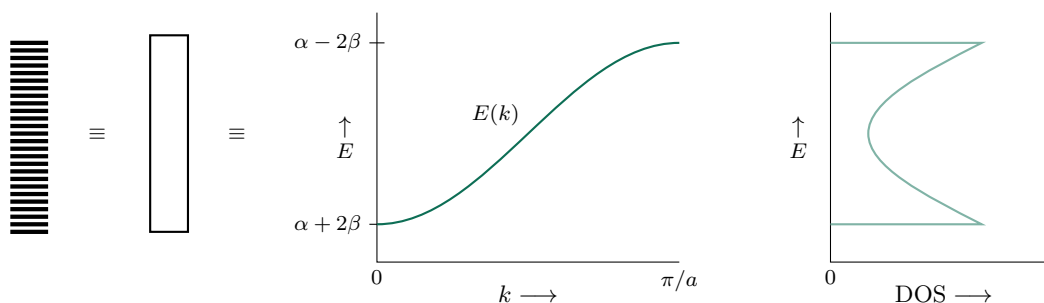


Figure VII.3: Density of states.

- 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**).

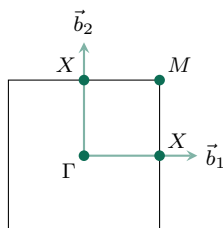
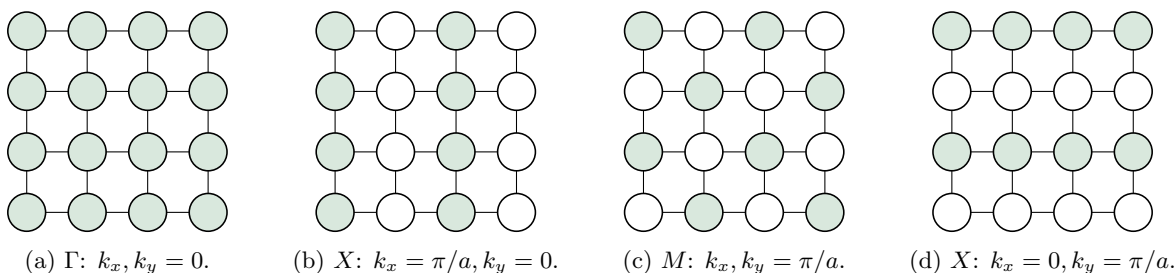


Figure VII.4: 2D Brillouin zone.

Figure VII.5: Special k points.

- The center is the Γ point ($k_x = k_y = 0$). The midpoint of the lines are called X points ($k_x = \frac{\pi}{a}, k_y = 0$, and vice versa). The maximum point is the M point ($k_x = k_y = \frac{\pi}{a}$).
- Calculating $E(k)$ in two dimensions.

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

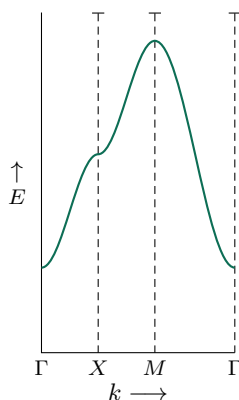


Figure VII.6: Schematic band structure (2D).

- Our schematic band structure (Figure VII.6) traces a 2D path $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$.