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).

(a) $k = 0$.   (b) $k = \frac{\pi}{a}$.

Figure VII.1: s orbital bonding states.

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

- 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:

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

- 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 state where all atomic orbitals are in phase (all bonding σ). *Also known as* $\mathbf{\Gamma}$.

- **Zone border**: The state where all atomic orbitals are out of phase (all antibonding σ^*). *Also known as* $\mathbf{X}$.

- 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.

(a) $k = 0$.   (b) $k = \frac{\pi}{a}$.

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**.
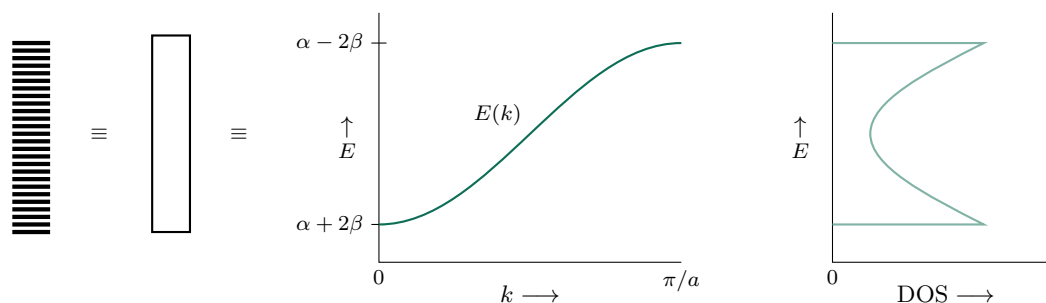

Figure VII.3: Density of states.

  - 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)).

  $$\psi(k) = \sum_{m,n} e^{ik_x ma + ik_y na} \cdot \phi_{m,n}$$

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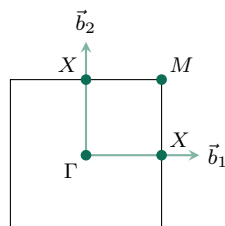 - The **Brillouin zone** is 2D here (we have a **wave vector**).
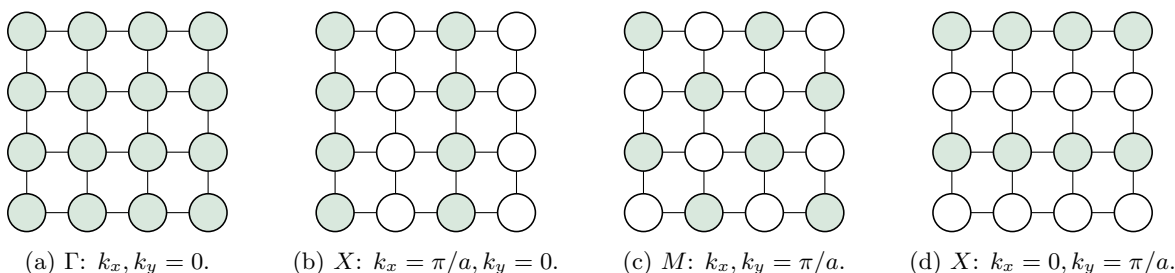

Figure VII.4: 2D Brillouin zone.

(a) Γ: $k_x, k_y = 0$. (b) X: $k_x = \pi/a, k_y = 0$. (c) M: $k_x, k_y = \pi/a$. (d) X: $k_x = 0, k_y = \pi/a$.

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.

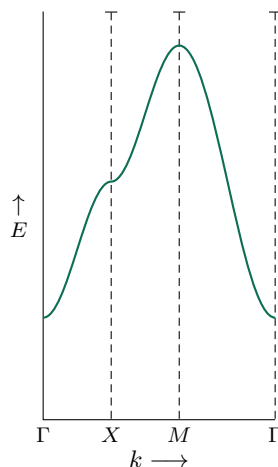 $$E(k) = \alpha + 2\beta(\cos(k_x a) + \cos(k_y a))$$

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

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

2/8:
- 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

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

    – 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 $\mathrm{d}N(k)/\mathrm{d}k = 1$ 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

$$D_{1d}(E) = \frac{\mathrm{d}N(E)}{\mathrm{d}E} = \frac{\mathrm{d}N(k)}{\mathrm{d}k}\frac{\mathrm{d}k}{\mathrm{d}E} \propto 1 \cdot \frac{1}{\sqrt{E}} = \frac{1}{\sqrt{E}}$$

- 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 Brilluoin zone to give us the electronic band structure of a solid.
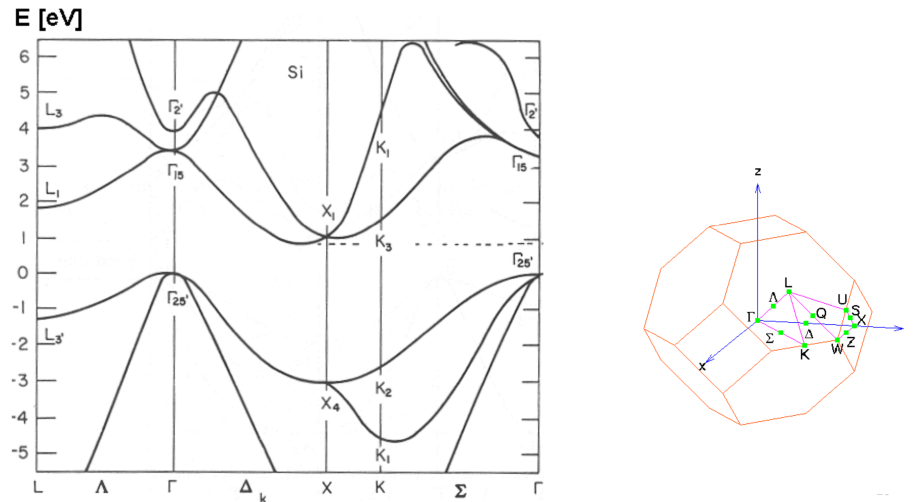
Figure VII.7: Electronic band structure of Si.

- **Angle-resolved photoemission spectroscopy**[1]: If the incoming photon's energy is greater than the electron's ginding 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 $T = 0\,\mathrm{K}$, the Fermi energy is the energy of the last occupied state. Moreover,

    - The Fermi energy is the energy of the last occupied state at $T = 0\,\mathrm{K}$; 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).

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[1]Figure 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 $3\,\text{eV}$, 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 $T = 0\,\text{K}$ 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:

  $$g(E)_{3D} \equiv \frac{1}{V}\frac{\mathrm{d}N}{\mathrm{d}E}$$

  ■ 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

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

  – Take CHEM 39000 Solids, Materials, and Surfaces to learn more.

VII.4 Hoffmann's Band Theory

From Hoffmann (1987).

3/8:
- Lists and attempts to resolve some minor problems at the intersection of solid-state chemistry and physics/the rest of chemistry.

- An understanding of the electromagnetic properties of solids hinges on an understanding of modern solid-state physics, or band theory.

  – Yet while physicists can better *describe* (i.e., mathematically) a solid-state system, chemists better *understand* them (i.e., intuitively).

- Solid state chemists must consider not just ionic packing and electrostatic properties, but covalency and other more "molecular" notions.

- **Zintl concept**: "In some compounds $A_x B_y$, where A is very electropositive relative to a main-group element B, one could just think, that's all, think that the A atoms transfer their electrons to the B atoms, which they then use to form bonds" (Hoffmann, 1987, p. 847).

- Three big problems (in Hoffmann's opinion; in some others' opinions, these may not be issues at all):

  1. Some lack of knowledge (therefore fear) of solid-state physics language on the part of chemists.
  2. Insufficient appreciation of the chemists' intuitive feeling for bonding on the part of physicists.
  3. Not enough reaching out for connections with molecular chemistry on the part of solid-state chemists.

- This paper will largely focus on problem 1, taking a simple (indeed, oversimplified) approach that utilizes the extended Hückel model or the **tight-binding method** (with overlap).

- **Tight-binding method** (with overlap): The solid-state analogue of the extended Hückel model.

- **Peierls distortion**: The instability of the band for an equally spaced one-dimensional polymer of H atoms. *Also known as* **strong electron-phonon coupling**, **pairing distortion**, **$2k_F$ instability**.

  - This will lead to a one-dimensional H-atom polymer to form a chain of hydrogen molecules at ambient pressure.

- **Applying cyclic boundary conditions**: Thinking of a long chain as an imperceptibly bent segment of a large ring.
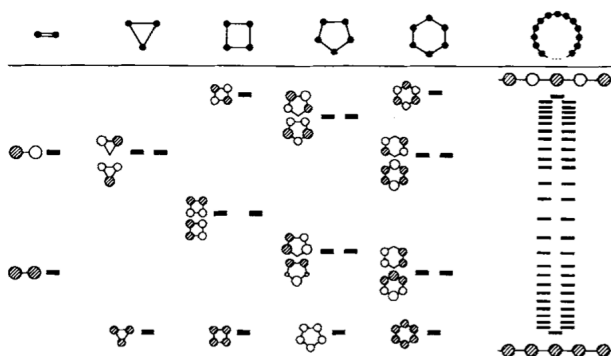

Figure VII.8: Orbitals in H-atom rings.

  - We apply cyclic boundary conditions to the 1D H-atom chain.

- In a cyclic structure, "except for the lowest (and occasionally the highest) level, the orbitals come in degenerate pairs" (Hoffmann, 1987, p. 848).

  - The number of nodes also increases as one rises in energy: The lowest level is nodeless, the highest has the maximum number of nodes, and a growing number of nodes are present in between.

- Introduces Bloch's theorem.

- The larger the absolute value of k (within the FBZ), the more nodes in the wave function.

- The number of values of k is equal to the number of translations in the crystal, or the number of microscopic unit cells in the macroscopic crystal.

  - And this will be on the order of Avogadro's number N_A.
  - Keep in mind that although the $E(k)$ curve in Figure VII.3 appears continuous, there are only a finite (albeit very large) number of points in k-space.

- "There is an energy level for each value of k (actually a degenerate pair of levels for each pair of positive and negative k values)" (Hoffmann, 1987, p. 848).

  - Since $E(k) = E(-k)$ (as can be proved in an easy but unreferenced theorem), most graphical representations of the function depict $E(|k|)$ and label it $E(k)$.

- **Reciprocal space**: The space of k, in which the allowed values of k are equally spaced. *Also known as* **momentum space**, **k-space**.

  - k is related to momentum because $k = 1/\lambda$, and from de Brogelie, $\lambda = h/p$.
  - This means that k is not only a symmetry label and a node counter, but also a wave vector (thus a measure of momentum).

- **Band width**: The difference in energy between the highest and lowest levels of the band. *Also known as* **dispersion**.

  - Determined by the overlap between the interacting orbitals of neighboring unit cells.

- Bands extend unsymmetrically around their origin (which is the energy of a free H atom at $-13.6\,\mathrm{eV}$) because of the inclusion of overlap in calculations.

  - Note that bands with greater band width are *more* symmetric about the origin, i.e., as $4|\beta|$ increases in Figure VII.3, the $E(k)$ band centers itself more around the origin.

- To recap band width and the import of bands running up or down, "band width is set by inter-unit-cell overlap, and the way bands run is determined by the topology of that overlap" (Hoffmann, 1987, p. 849).

- Discusses stacking of platinum square-planar complexes, incorporating CFT and MO theory to build its band structure[2].

- **Fermi level**: The HOMO of a solid.

  - The alternate thermodynamic definition (appropriate to both metals and semiconductors) is what was discussed in lecture.

- Determining the Fermi level of $[\mathrm{PtH_4}]^{2-}$:
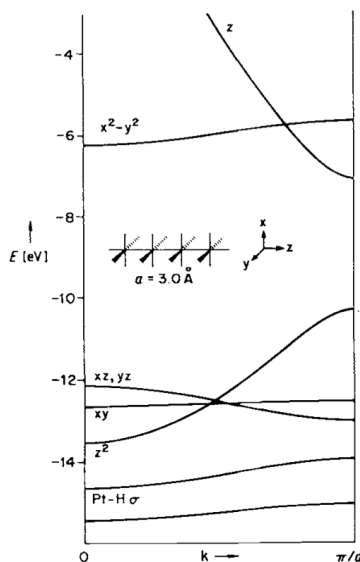
Figure VII.9: Electronic band structure of $[\mathrm{PtH_4}]^{2-}$.

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[2]If I have time to come back and digest this, it would be fascinating and educational.

- Each platinum atom is d^8.
- From the band structure, the $\frac{8 \text{ electrons}}{2 \text{ electrons per level}} = 4$ lowest energy bands are the z^2, xy, xz, and yz bands (with the latter two degenerate).
- Thus, these will be completely filled, making the Fermi level the top of the band that protrudes the highest (the z^2 band).

- Although this is not formal, we can tell from Figures VII.1 and VII.2 that the bottom of each band is bonding and the top, antibonding.

  - Thus, filling a band entirely provides no net bonding (and, in fact, net antibonding).

- Returning to our $[\text{PtH}_4]^{2-}$ example:

  - The stack likely forms due to a combination of van der Waals attractions and a combination of orbital interactions involving the mixing of the d_{z^2} and p_z bands.
  - Additionally, Pt–Pt separation likely decreases on oxidation because losing electrons takes them away from the higher energy antibonding portions of the bands, enhancing bonding character.
    - A typical oxidation of 0.3 electrons per Pt atom empties the top 15% of the d_{z^2} band, which had been strongly σ^* antibonding.
  - Importantly, "the oxidized material... has its Fermi level in a band; i.e., there is a zero band gap between filled and empty levels. The unoxidized cyanoplatinates have a substantial gap — they are semiconductors or insulators. The oxidized materials are good low dimensional conductors" (Hoffmann, 1987, pp. 851–52).

- For good conductivity, the Fermi level must cut one or more bands. However, we must also beware distortions which open up gaps at the Fermi level and exceedingly narrow bands that are cut by the Fermi level.

- Density of states resolves the following conundrum:

  - In a discrete molecule, we can single out one or a few orbitals (HOMO, LUMO) as being the frontier orbitals responsible for geometry, reactivity, etc.
  - There is no way that a few orbitals determine the properties of a solid.
  - How, then, can we determine such properties?
  - We can do so by looking at bunches of levels (all those in a given energy interval between E and $E + \mathrm{d}E$).

- The shapes of DOS curves are predictable from the band structures.

- "The integral of DOS up to the Fermi level is the total number of occupied MOs. Multiplied by two, it's the total number of electrons" (Hoffmann, 1987, p. 852).

  - Thus, the DOS curves plot the distribution of electrons in energy.

- DOS curves represent a return from reciprocal space to real space since it's an average over the Brillouin zone, i.e., over all k that might give molecular orbitals at the specified energy.

  - One benefit to this is that it facilitates intuitively sketching the DOS from the MO diagram using our knowledge of orbital interactions in space, as we did when rationalizing the $[\text{PtH}_4]^{2-}$ band structure.

- Continues into some higher level 1D topics, from which there are a couple of relevant points:

  - "The Jahn-Teller theorem says that such a situation necessitates a large interaction of vibrational and electronic motion. It states that there must be at least one normal mode of vibration which will break the degeneracy and lower the energy of the system (and, of course, lower its symmetry). It even specifies which vibrations would accomplish this" (Hoffmann, 1987, p. 862).

– The Peierls distortion is the solid-state counterpart of the Jahn-Teller distortion, a phenomenon where electrons in a partially filled band can distort the system (á la Jahn-Teller) to lower its energy and open up a gap at the Fermi level.

- In higher dimensions, $\vec{k}$ must be treated as a vector with components in reciprocal space.
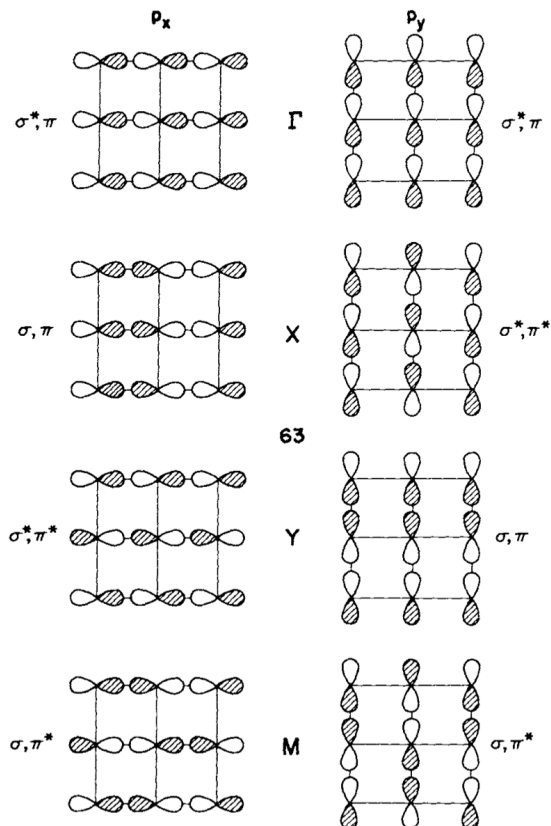
Figure VII.10: 2D $p_{x,y}$ orbital bonding states.

- When we include p orbitals in our 2D lattice, the Γ, X, and M configurations have varying σ / σ^* character and π / π^* character (see Figure VII.10).