Electronic Structure of Solid

Macromolecules extended in one, two, and three dimensions, of biological/natural or synthetic origin, fill the world around us. Metals, alloys, and composites, be they copper or bronze or ceramic, have played a pivotal and a shaping role in our culture. Mineral structures form the base of the paint that colors our walls and the glass through which we look at the outside world.

References:
Organic polymers, natural or synthetic, clothe us. New materials— inorganic superconductors, conducting organic polymers— exhibiting unusual electric and magnetic properties, promise to shape the technology of the future. Solid state chemistry is important, alive, and growing.
Clasification of solids

**Metal**: partly filled valence band

**Semiconductor**: completely filled valence band, small energy gap ($E_g$) between valence and conduction band

**Insulator**: completely filled valence band, large energy gap ($E_g$) between valence and conduction band

**Semi-metal**: partly filled valence band due to overlapping of conduction and valence band
Schrödinger wave equation

Electrons are waves. The functions that describe their propagation in an arbitrary medium are solutions of the Schrödinger wave equation:

\[
(1) \quad -\frac{\hbar^2}{2m} \frac{\partial^2 \Phi(x,t)}{\partial^2 x} + V(x) \cdot \Phi(x,t) = \frac{\hbar i \partial \Phi(x,t)}{\partial t}
\]

The solutions \( \Phi(x,t) \) can be considered as:

\[
(2) \quad \Phi(x,t) = \Psi(x) \cdot e^{\frac{Et i}{\hbar}}
\]
Substituting (1) in (2), we obtain the time independent Schrödinger equation:

\[
\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{d^2 x} + V(x) \cdot \Psi(x) = E \cdot \Psi(x)
\]  

(3)

If we define a Hamiltonian operator:

\[
H \Psi(x) = E \Psi(x)
\]  

(4)

The probability of finding the electron in a region of the space between \( x \) and \( x + dx \) is given by:

\[
P(x < e^- < x + dx) = |\Psi(x)|^2 dx
\]  

(5)
Electron in a hydrogen atom

\[ V(r) = -\frac{e^2}{r} \rightarrow -\frac{\hbar^2}{2\mu} \nabla^2 \Psi(r, \theta, \phi) - \frac{e^2}{r} \cdot \Psi(r, \theta, \phi) = E \cdot \Psi(r, \theta, \phi) \]
Free Electron Model
Free particle: Electron in vacuum

Electrons are waves. The functions that describe their propagation in free space are solutions of the Schrödinger wave equation:

\[ H\Psi(x) = E\Psi(x) \quad \text{with} \quad V = 0 \]

\[ -\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} = E \cdot \Psi(x) \]

Main features of the equation:

1) Solutions: plane waves.

\[ \Psi(x) = e^{ik \cdot x} \]

\[ k = \frac{\sqrt{2mE}}{\hbar} \]

\[ k \text{ is the wavevector: } |\vec{k}| = \frac{2\pi}{\lambda} \]
2) Relation between energy and wavevector: energy dispersion relation

\[ k = \frac{\sqrt{2mE}}{\hbar} \]

3) Relation between wave and particle parameters

\[ E = \frac{|\vec{k}|^2 \hbar^2}{2m} \quad \rightarrow \quad \vec{p} = \vec{k} \hbar \quad \rightarrow \quad E = \frac{|\vec{p}|^2}{2m} \]

Electron momentum
Bloch Description of Electrons in Solids

In a solid, electrons interact with the periodic potential created by the ion cores (1D model).

Now, their motion will be described by the solutions of the Schrödinger wave equation:

\[- \frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + V(x) \cdot \Psi(x) = E \cdot \Psi(x)\]

where the electronic potential is periodic:

\[V(x) = V(x + a)\]
**Bloch theorem.** The solutions (electron waves) in a periodic lattice are of the form:

\[ \Psi_k(x) = u_k(x) \cdot e^{ikx} \]

\( u_k(x) \) is a periodic function with the same periodicity than the lattice:

\[ u(x) = u(x + a) \]

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*C. Kittel, Introduction to Solid State Physics, John Wiley (1996). : Ch7*
Origin of electronic bands in solids
Two center molecular orbital

\[ \Psi = c_1 \chi_1 + c_2 \chi_2 \]

\[ 1 = \int |\psi|^2 d\tau = \int |c_1 \chi_1 + c_2 \chi_2|^2 d\tau = c_1^2 + c_2^2 + 2c_1 c_2 S_{12} \]

\( S_{12} = \) overlap integral between \( \chi_1 \) and \( \chi_2 \).
\[ e_j = \langle \psi_j | H_{\text{eff}} | \psi_j \rangle \]

\[ = \alpha + \beta \sum_p \left[ c_{pj}^* c_{(p+1)j} + c_{pj}^* c_{(p-1)j} \right] \]

\[ e_j = \alpha + \beta \sum_p \left( \frac{1}{\sqrt{N}} \exp \frac{-2\pi ij(p-1)}{N} \cdot \frac{1}{\sqrt{N}} \exp \frac{2\pi ij(p-1)}{N} \right) \left[ \exp \frac{2\pi ij}{N} + \exp \frac{-2\pi ij}{N} \right] \]

\[ e_j = \alpha + \beta \sum_{p=1}^{N} \frac{1}{N} \cdot 2 \cos \frac{2\pi j}{N}, \quad j = 0, \pm 1, \pm 2 \ldots \]

\[ e_j = \alpha + 2\beta \cos \frac{2\pi j}{N}, \quad j = 0, \pm 1, \pm 2 \ldots \]
\[ e_j = \alpha + 2\beta \cos \frac{2j\pi}{N} \]

\[ \psi_j = \sum_{p=1}^{N} c_{pj} \chi_p = \frac{1}{\sqrt{N}} \sum_{p=1}^{N} \left[ \exp \left( \frac{2\pi ij(p-1)}{N} \right) \right] \chi_p \]

\[ k = \frac{2\pi j}{N} \]

\[ (p-1) = x \]

\[ e_j = \alpha + 2\beta \cos \frac{2\pi j}{5} \quad e_j = \alpha + 2\beta \cos \frac{2\pi j}{15} \quad e = \alpha + 2\beta \cos \frac{2\pi j}{N} \]

\[ N = 5 \quad N = 15 \quad N = \infty \]
\[ e_j = \alpha + 2\beta \cos \frac{2\pi j}{N}, \quad j = 0, \pm 1, \pm 2 \ldots \]

\[ e = \alpha + 2\beta \cos ka \]
\[ e = \alpha + 2\beta \cos \frac{2\pi j}{N} \]

\( N \) is very large

13.11

or \(-\frac{N-1}{2}\) \quad or \(\frac{N-1}{2}\)
\[
\phi_j = \sum_{p=1}^{N} c_{pj} \chi(r - R_p) = \frac{1}{\sqrt{N}} \sum_{p=1}^{N} \left\{ \exp \left[ \frac{2\pi ij (p - 1)}{N} \right] \right\} \chi(r - R_p)
\]

\[
\phi(k) = \frac{1}{\sqrt{N}} \sum_{p=1}^{N} \left\{ \exp \left[ ik(p - 1) a \right] \right\} \chi(r - R_p)
\]

\[
\phi(k) = \frac{1}{\sqrt{N}} \sum_{p=1}^{N} \left[ \exp (ikR_p) \right] \chi(r - R_p)
\]

\[
k = \frac{2\pi j}{Na} \quad (p-1)a = R_p
\]

\[
R_p = \text{real space} \quad k = \text{reciprocal space}
\]
• The unique value of $k$ are in the interval $-\pi/a \leq k \leq \pi/a \rightarrow \text{First Brillouin zone}$

• The number of $k$ is in the order of $N$.

• Each $k$ represent an unique electronic state (or energy level). All possible electronic states are located within the first Brillouin zone.

• $E(k) = E(-k)$. (Only half of the band is shown).
Reciprocal Space and Brillouin Zone
The 12 planes $d_{12}$ indicated

12 plane

13 planes

(b)

(c)
First Brillouin Zone

One-Dimensional

\[-\frac{\pi}{a}\]
\[-\frac{1}{2} K\]
\[-0.5a^*\]

0

\[-\frac{\pi}{a}\]
\[\frac{1}{2} K\]
\[0.5a^*\]

Linear lattice

Two-Dimensional

Square lattice

Hexagonal lattice

Three-Dimensional

Face-centered cubic

Simple cubic
LCAO: Linear Combination of Atomic Orbitals

Unit cell = $a$

Each unit cell contains one atom and one orbital.
\[ \psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots \]

\[ \psi_{\pi/a} = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots \]

![Diagram](image)
Orbital Interactions in Solids
Band Width

\[ E_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}} \]

- \[ a = 3 \text{Å} \]
- \[ a = 2 \text{Å} \]
- \[ a = 1 \text{Å} \]
Density of States (DOS)

\[ \text{DOS}(E)dE = \text{number of levels between } E \text{ and } E + dE \]
Where are the Bonds?

$\text{N}_2$

$\text{COOP}(E) \propto S_{a-b}^2$
Crystal Orbital Overlap Population
COOP in Varies Bands
Fermi energy (or Fermi level): highest occupied energy level in the ground state (T=0 K) of the N electron system. At T=0 K, the N electron system is in the ground state: The electrons occupied all the energy states up to the Fermi level.
Band theory

1. Electrons in crystals are arranged in energy bands.

2. These bands are separated by regions in which no electron states exist. These regions are called energy gaps or band gaps.

3. The lowest empty band is the conduction band. The highest band with occupied electron levels is the valence band.
4. The highest occupied band can be completely or partly filled depending on the ratio between the number of electron levels available in the band and the number of valence electrons given by each atom in the crystal.

5. **Fermi level**: highest occupied energy level in the ground state (T=0 K) of the N electron system.

6. The **occupancy** of the valence band and the size of the gap between the valence and the conduction band will determine the conductive, semiconductive or insulator character of a crystal.
Band formation in solids

- The electronic band structure of a solid will determine its electrical, magnetic, and optical properties. Everything can be described in terms of bands!!
• Bands result from the overlapping of the orbitals of the atoms that form the solid. This overlapping depends on:

1. The *geometric arrangement* of the lattice (fcc, bcc, hcp, ...)
2. The *difference of energy* between the atomic orbitals in the atoms.
3. The *number of valence electrons* in the atoms.
$K_2Pt(CN)_4$
MO derivation
Qualitative approach
1D Band Structure
$[\text{PtCN}_4^{2-}]_{\infty}^1$
$[\text{PtH}_4^{2-}]^1_{\infty}$
Where are the electrons?

$[\text{PtH}_4^{2-}]_\infty$: Partial Density of States (PDOS)
Under $C_{2v}$, $\pi_1$, $\pi_2$, $\pi_3$, $\pi_4$.

(a) $b_1$, $a_2$.

(b) $\pi_1$, $\pi_2$, $\pi_3$, $\pi_4$.

All interactions are bonding.

Antibonding between $B_1-B_2$.

Bonding between $B_2-B_3$.

Antibonding between $B_2-B_3$.

All interactions antibonding.

(c) $\pi_1$, $\pi_2$, $\pi_3$, $\pi_4$. 
Band Structure
What happen when $[\text{PtH}_4^{2-}]_\infty$ is oxidized?
Band folding
$K_2Pt(CN)_4(Cl)_{0.3}$ or $K_2Pt(CN)_4(FHF)_{0.25}$
TiO$_2$

Ti-O

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Peierls Distortion
3D Peierls distortion
Two Dimension System
GRAPHITE

Clinographic Views

Atom Positions

\[ a = b = c \]
\[ \alpha = \beta = 90^\circ \]
\[ \gamma = 120^\circ \]

(0,0,0)  (2/3,1/3,0)

(0,0,1/2)  (1/3,2/3,1/2)

Plan View

\[ 0,1/2 \]
\[ 0,1/2 \]

\[ a \]
\[ b \]
\[ c \]

\[ \Gamma \]

\[ M \]

\[ K \]
3D band structure

Extended Huckel

LMTO method
Graphite vs. BN
Cubic system
TiO$_2$, Rutile

Qualitative DOS curve
Band structure, DOS of TiO$_2$
DOS, COOP

Ti-O
PDOS of TiO$_2$

PDOS can isolate specific group of orbitals.
ThCr$_2$Si$_2$ Structure Type Cpds

- More than 200 compounds of AB$_2$X$_2$ stoichiometry adopt the ThCr$_2$Si$_2$ type structure.
  
  A: rare earth, alkaline earth or alkali element
  B: transition metal or main group element
  X: Group 13 (rare), 14, or 15 element
Structure Features

$B_2X_2^{2-}$ layer

d(M-M) $\sim 2.7-2.9\text{Å}$
$B_2X_2^{2-}$ network
Tunable X···X Contact

Table 1 X–X Distance in Some Phosphide Compounds of AB₂X₂ Type

<table>
<thead>
<tr>
<th>AB₂X₂</th>
<th>dₓₓ (Å)</th>
<th>AB₂X₂</th>
<th>dₓₓ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCu₁.₇₅P₂</td>
<td>2.25</td>
<td>SrCu₁.₇₅P₂</td>
<td>2.30</td>
</tr>
<tr>
<td>CaNi₂P₂</td>
<td>2.30</td>
<td>SrCo₂P₂</td>
<td>3.42</td>
</tr>
<tr>
<td>CaCo₂P₂</td>
<td>2.45</td>
<td>SrFe₂P₂</td>
<td>3.43</td>
</tr>
<tr>
<td>CaFe₂P₂</td>
<td>2.71</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

P–P 2.21Å (P₄), 2.192(Me₂PPMe₂)
P=P 2.03Å
P≡P 1.87Å
• For $\text{AB}_2\text{X}_2$ cpds, the $d(\text{P-P})$ distances varies from 2.25 Å (single bond) to 3.43Å (nearly nonbonding) depending on the transition metals.

• As one moves left to right in the transition series, the P-P contact shortens.
  → There is a electronic effect on the P-P bond.

• Zintl’s Idea:
  Long $\bullet\bullet\bullet\text{P}$ → $\text{P}^{3-}$
  P-P single bond → P-$\text{P}^{4-}$
• For $A^{2+} \rightarrow P\cdot\cdot\cdot P$ nonbonding
• For $A^{+} \rightarrow P-P$ single bond
• But how does one describe a P-P contact with distance of 2.72Å?
  $\rightarrow$ A delocalized approach
• Zeng & Hoffmann: Used the BaMn$_2$P$_2$ as a model compound to rationalize the trend of P-P contact.

Mn$_2$P$_2^{2-}$:  
Mn-P = 2.455
Mn-Mn = 2.855 (M-M bonding)
MO of Mn(\text{PR}_3)_4
Expand to 3D

Mn-Mn interactions
Band and DOS of Mn$_2$P$_2^{2-}$

Mn, $d$ band
P, $p$ band
P, $s$ band)
DOS, PDOS and COOP

Dashed: Total; Slid: Mn
Bonding Characters
A Different Approach

- 4s, 4p
- 3d
- Wide Mn-Mn Interaction
- Narrow Nonbonding
The localized $p_z$ band

- The $p_z$ is localized on the P atom and it can be treated as a lone pair electrons.
- The localization in energy space implies localization in real space.
Interaction of two Mn$_2$P$_2$$^{2-}$ layer

- P-P = 2.4 Å
- The P-P $\sigma$ and $\sigma^*$ band splitting decrease with increasing P···P separation.
The Effect of Transition Metal

• The increased nuclear charge will be more incompletely screened and the d electrons more tightly bond.

• As s results, the d band comes down in energy and becomes narrower.

• At the same time, the band filling increases as one moves to the right in the transition series.
$e_f$ vs. d band filling
P-P and d bands
Metal carbides \((\text{RE})_2\text{X}_2\text{C}_2\)

**Figure 2.** Projection of the monoclinic unit cell of the (1s)-layered structure of \((\text{RE})_2\text{X}_2\text{C}_2\) in the direction of the \(b\) axis (a horizontal). The atoms, \(\text{X}, \text{RE},\) and \(\text{C}\) are shown with decreasing size.

**Figure 3.** Schematic MO diagram of the \((\text{C}_2)_2^{2-}\) and \((\text{C}_2)_2^{+}\) ions as found in \(\text{CaC}_2\) and (to a first approximation) in \((\text{RE})_2\text{X}_2\text{C}_2\), respectively. The degeneracy of the \(\pi^*\) levels is removed through the monoclinic crystal symmetry.
$Y_2I_2C_2$

Figure 4. Transition to superconductivity in a $Y_2I_2C_2$ crystal. Top: The disappearance of the electrical resistance $\rho$ (m$\Omega$cm); bottom: magnetization results (measured at 10 G; field cooled curve (←) shows Meissner effect; zero field cooled curve (→) displays shielding)[40]. Mass susceptibility $\chi_s$ in $10^{-2}$ emu g$^{-1}$.)
Chemical bonding

Figure 12. Schematic representation (from left to right) of the MO sequence for the π-like interaction in a polyene, the density of states $N(E)$, the dispersion $k$ of the electronic band, and the chemical characterization of the band states with regard to the interaction between nearest neighbors ("crystal orbital overlap population", COOP). The bottom of the band corresponds to all-bonding, the top to all-antibonding combinations of the AOs[68].

Figure 13. Band structure calculation for $Y_2Br_2C_2$ in the Extended Hückel approximation. On the left the total density of states $N(E)$ (also known as DOS) is given; right is the COOP analysis for the C–C (solid line), Y–C (dotted line), and Y–Y (dashed line) exchange interaction between nearest neighbors. The dotted horizontal line corresponds to $E_g$.

$Y_2Br_2C_2$
Band structure of $\text{Y}_2\text{Br}_2\text{C}_2$

Fat band:
$\text{C}_2^- \pi_{xz}^*$

$\text{Y} - d_{xz}$

$\text{Y} - d_{x^2-y^2}$

Figure 14. Representation of the dispersion of the bands for $\text{Y}_2\text{Br}_2\text{C}_2$ in the energy range close to the Fermi level, calculated self-consistently according to the TB-LMTO-ASA method ($E_F = 0$ eV). The prominent orbital contributions to the band structure are indicated in the form of “fat bands” (from top to bottom: $\text{C}_2^- \pi_{xz}^*$, $\text{Y} - d_{xz}$, $\text{Y} - d_{x^2-y^2}$) [36].
$\text{Ce}_9\text{Br}_5(\text{CBC})_3$
Band structure of Ce$_9$Br$_5$(CBC)$_3$

Fat band:
CBC- $\pi^*_xz$

La – $d_{xz}, d_{yz}$

La – $d_{x^2-y^2}$

Figure 19. Self-consistently calculated band structure of La$_9$Br$_5$(CBC)$_3$ for the bands lying around the Fermi level at $E_f = 0$ eV. From top to bottom the contributions of the BC$_2$-MOs (approximate $\pi^*$), the La-$d_{xz}$, and La-$d_{x^2-y^2}$ orbitals are emphasized in the fat band representation [95].
Nb$_3$Sn

Figure 22. Band structure of tetragonal Nb$_3$Sn with an extended flat band at the Fermi level [112].

$T_{cr} = 18.1$ K
Mo$_2$SbS$_2$
BaSn_5

Fig. 1 Crystal structure of BaSn_5. Emphasizing hexagonal prisms of Sn2 atoms centered with Sn1. Ba atoms are shown as cross-hatched ellipsoids. All thermal ellipsoids are shown at 90% probability level.

M / (emu/g) vs. T / K for BaSn_5 in a magnetic field of 10 G.
The ‘filled’ scutterudite: \( \text{LaFe}_4\text{Sb}_{12} \)

\[ \text{LaFe}_4\text{Sb}_{12} \text{: metallic} \]

\[ \text{LaFe}_3\text{CoSb}_{12} \text{: maximal ZT value of 1.4} \]