Crystal Structure: XRD

**Bragg’s Law**

\[ n\lambda = 2d \sin \theta \]
Centering Allowed Peaks

- **I-centered** → \( h+k+l \) is an even number
- **F-centered** → \( hkl \) either all even or all odd
- **C-centered** → \( h+k \) is an even number
- **B-centered** → \( h+l \) is an even number
- **A-centered** → \( k+l \) is an even number
- **R-centered** → \(-h+k+l\) is a multiple of 3

\[ hkl = 100 \]
\[
\frac{1}{d^2} = \frac{(1^2 + 0^2 + 0^2)}{(3.90 \, \text{Å})^2} \quad \rightarrow \quad d = 3.90 \, \text{Å}
\]
\[
\sin \theta_{100} = \frac{1.54 \, \text{Å}}{2(3.90 \, \text{Å})} \quad \rightarrow \quad \theta = 11.4^\circ \quad (2\theta = 22.8^\circ)
\]

\[ hkl = 110 \]
\[
\frac{1}{d^2} = \frac{(1^2 + 1^2 + 0^2)}{(3.90 \, \text{Å})^2} \quad \rightarrow \quad d = 2.76 \, \text{Å}
\]
\[
\sin \theta_{100} = \frac{1.54 \, \text{Å}}{2(2.76 \, \text{Å})} \quad \rightarrow \quad \theta = 16.2^\circ \quad (2\theta = 32.4^\circ)
\]

\[ hkl = 111 \]
\[
\frac{1}{d^2} = \frac{(1^2 + 1^2 + 1^2)}{(3.90 \, \text{Å})^2} \quad \rightarrow \quad d = 2.25 \, \text{Å}
\]
\[
\sin \theta_{100} = \frac{1.54 \, \text{Å}}{2(2.25 \, \text{Å})} \quad \rightarrow \quad \theta = 20.0^\circ \quad (2\theta = 40.0^\circ)
\]
**XRD: Diffraction Peak Intensities**

\[ I(hkl) = |S(hkl)|^2 \times M_{hkl} \times LP(\theta) \times TF(\theta) \]

- \( S(hkl) = \text{Structure Factor} \)
- \( M_{hkl} = \text{Multiplicity} \)
- \( LP(\theta) = \text{Lorentz & Polarization Factors} \)
- \( TF(\theta) = \text{Temperature factor} \) (more correctly referred to as the displacement parameter)
XRD: Diffraction Peak Widths

Scherrer Equation

\[ B(2\theta) = \frac{K\lambda}{L \cos \theta} \]

- Peak width (B) is inversely proportional to crystallite size (L)

Molecular Orbital Theory to Band Theory

Schrödinger equation

\[ i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi \]

\[ E\Psi = \hat{H}\Psi \]

Four quantum numbers define the properties of each atomic orbital

- Principle quantum number, \( n = 1, 2, 3, \ldots \)
- Azimuthal quantum number, \( l = 0(\text{s}), 1(\text{p}), 2(\text{d}), 3(\text{f}), n-1 \)
- Magnetic quantum number, \( m_l = -l, \ldots, l \) (i.e. px, py, pz)
- Spin quantum number, \( m_s = +1/2 \) or \(-1/2\)

Pauli Exclusion Principle

No two electrons can have the same set of quantum numbers (each orbital can hold 2 e\(^-\))

Hund’s Rule

For degenerate orbitals the lowest energy configuration maximizes the electron spin (no pairing of electrons if avoidable)
Molecular Orbital Theory to Band Theory

Schrödinger equation

Four quantum numbers define the properties of each atomic orbital

Pauli Exclusion Principle

Hund’s Rule
Molecular Orbital Theory to Band Theory

Orbital Overlap:
Molecular Orbital (MO) Theory

- **Bonding Orbital, $\sigma$**
  - $1s$ orbitals of $H$ atoms combine to form a bonding orbital.
  - Symbol: $\sigma_{1s}$

- **Antibonding Orbital, $\sigma^*$**
  - $1s$ orbitals of $H$ atoms combine to form an antibonding orbital.
  - Symbol: $\sigma^*_{1s}$

- **Node**
  - The location where the wave function is zero.
Molecular Orbital Theory to Band Theory

Orbital Overlap:
Molecular Orbital (MO) Theory
Molecular Orbital Theory to Band Theory

Orbital Overlap: Molecular Orbital (MO) Theory

The overlap of two atomic orbitals is dependent upon:
- Symmetry of the orbitals
- Distance between the orbitals
- Spatial extent of the orbitals
- The energy difference between orbitals

Increasing the overlap (spatial and energetic) leads to the following:
- Stabilization of the bonding MO
- Destabilization of the antibonding MO
- The antibonding MO is destabilized to a greater extent than the bonding MO is stabilized

The spatial overlap in a bond depends upon symmetry
- It decreases as the number of nodal planes increases, $\sigma > \pi$
- $\pi$ bonds are more sensitive to changes in bond angle
Molecular Orbital Theory to Band Theory

MO Diagram for H₂

The number of MO’s is equal to the number of atomic orbitals.

Each MO can hold 2 electrons (with opposite spins).

The antibonding MO has a nodal plane between atoms and ⊥ to the bond.

As the spatial overlap increases $\psi_1$ (bonding MO) is stabilized and $\psi_2$ (antibonding MO) is destabilized.

The destabilization of the antibonding MO is always greater than the stabilization of the bonding MO.
Band Theory

Review – Wavefunction

The wave function does not represent any physical quantities. It should be understood merely as a mathematical description of an electron which enables us to calculate its actual behavior in a convenient way. This thought probably sounds unfamiliar to a beginner in quantum physics. However, by repeated exposure, one can become accustomed to this kind of thought.

\[ \Psi = \sin(kx - wt) \]

\[ \Psi_1 + \Psi_2 = \Psi = 2 \cos\left(\frac{\Delta \omega}{2} t - \frac{\Delta k}{2} x\right) \cdot \sin\left[\left(\frac{k+\Delta k}{2}\right)x - \left(\omega + \frac{\Delta \omega}{2}\right)t\right]. \]
Band Theory

Review – Wave function

The simplest waveforms is mathematically expressed by a sine (or a cosine) function. This simple disturbance is "harmonic wave." (Fourier transformation can substitute any odd type of waveform by a series of harmonic waves, each having a different frequency.) The properties of electrons will be described by a harmonic wave.

\[ \Psi = \sin(kx - wt) \]

\[ \Psi_1 + \Psi_2 = \Psi = 2 \cos \left( \frac{\Delta \omega}{2} t - \frac{\Delta k}{2} x \right) \cdot \sin \left[ \left( k + \frac{\Delta k}{2} \right) x - \left( \omega + \frac{\Delta \omega}{2} \right) t \right]. \]
The 2s orbitals have a lower energy than the 2p orbitals.

The σ-bonds have a greater spatial overlap than the π-bonds. This leads to a larger splitting of the bonding and antibonding orbitals.

The 2p_x and 2p_y π-interaction produces two sets of degenerate orbitals.

In O_2 there are 12 valence electrons and each of the 2pπ* orbitals (π_g) are singly occupied. Thus the bond order = 2, and O_2 is paramagnetic.
A more accurate depiction of the bonding takes into account mixing of MOs with the same symmetry ($\sigma_g^+ & \sigma_u^+$). The consequences of this 2nd order effect are:

- The lower energy orbital is stabilized while the higher energy orbital is destabilized.
- The s and p character of the $\sigma$ MOs becomes mixed.
Heteronuclear Case & Electronegativity

The atomic orbitals of the more electronegative atom are lowered. The splitting between bonding and antibonding MO’s now has an ionic (Ei) and a covalent (Ec) component. The ionic component of the splitting (Ei) increases as the electronegativity difference increases. The covalency and the covalent stabilization / destabilization decrease as the electronegativity difference increases. The orbital character of the more electronegative atom is enhanced in the bonding MO and diminished in the antibonding MO.

AX₂ Linear & Bent

In bent H₂O the O 2s σ* orbital and the O 2px orbital are allowed to mix by symmetry, lowering the energy of the O 2px orbital. Now there is only one non-bonding orbital (O 2py).
Molecular Orbital Theory to Band Theory

Walsh’s Rule
A molecule adopts the structure that best stabilizes the HOMO. If the HOMO is unperturbed the occupied MO lying closest to it governs the geometrical preference.

2\textsuperscript{nd} Order Jahn-Teller Distortion
A molecule with a small energy gap between the occupied and unoccupied MOs is susceptible to a structural distortion that allows intermixing between them.
As you go proceed down the group the tendency for the s-orbitals to become involved in bonding diminishes. This destabilizes tetrahedral coordination and semiconducting/insulating behavior.
The diagram to the left shows a MO diagram for a transition metal octahedrally coordinated by σ-bonding ligands. (π-bonding has been neglected)

Note that in an octahedron there is no mixing between s, p and d-orbitals.

For a main group metal the same diagram applies, but we neglect the d-orbitals.
**Band Theory**

**Band Structure ReO$_3$**

Band Structure
(aka Spaghetti diagram): MO diagram with translational symmetry taken into account.

Density of States (DOS)
Integration of the band structure. Shows the # of available levels between $E$ and $E+dE$ as $dE \to 0$. 

Band Theory

Important Points of Band Structures

• What is being plotted?
  Energy vs. k, where k is the wavevector that gives the phase of the AOs as well as the wavelength of the electron wavefunction (crystal momentum).

• How many lines are there in a band structure diagram?
  As many as there are orbitals in the unit cell.

• How do we determine whether a band runs uphill or downhill?
  By comparing the orbital overlap at k=0 and k=π/a.

• How do we distinguish metals from semiconductors and insulators?
  The Fermi level cuts a band in a metal, whereas there is a gap between the filled and empty states in a semiconductor.

• Why are some bands flat and others steep?
  This depends on the degree of orbital overlap between building units.
  Wide bands → Large intermolecular overlap → delocalized e⁻
  Narrow bands → Weak intermolecular overlap → localized e⁻
Band Theory

Constructing a DOS Diagram: TiO$_2$

It is possible to construct a reasonable approximation of the DOS diagram from the MO diagram of the building block.

The energy levels of each block of bands (BOB) comes from the MO diagram (based on electronegativity and bonding interactions)

The area of each BOB is proportional to the number of MOs at that approximate energy.
Band Theory

Chain of Atoms

2 H atoms

Antibonding

Nonbonding

Bonding

Chain of 5 H atoms
**Band Theory**

**Infinite 1D Chain of atoms**

The wavefunction for each electronic State (MOs) is:

\[
\Psi_k = \sum e^{ikna} \chi_n
\]

(Euler’s formula: mathematical formula for converting relationship between the trigonometric functions and the complex exponential function.)

- **a** is the lattice constant (spacing between H atoms).
- **n** identifies the individual atoms within the chain.
- **\( \chi_n \)** represents the atomic orbitals
- **k** is a quantum # that identifies the wavefunction and tells us the phase of the orbitals.
Band Theory

Infinite 1D Chain of atoms

$k = \pi/a$

$\Psi_{\pi/a} = \chi_0 + (\exp\{i\pi\})\chi_1 + (\exp\{i2\pi\})\chi_2 + (\exp\{i3\pi\})\chi_3 + (\exp\{i4\pi\})\chi_4 + \ldots$

$k = \pi/2a$

$\Psi_{\pi/2a} = \chi_0 + (\exp\{i\pi/2\})\chi_1 + (\exp\{i\pi\})\chi_2 + (\exp\{i3\pi/2\})\chi_3 + (\exp\{i2\pi\})\chi_4 + \ldots$

$k = 0$

$\Psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \chi_4 + \ldots$
Band Theory

Band Structure of 1D Chain of atoms

\[ k = \pi/a \]

\[ \Psi_{\pi/a} = \chi_0 + (\exp\{i\pi\})\chi_1 + (\exp\{i2\pi\})\chi_2 + (\exp\{i3\pi\})\chi_3 + (\exp\{i4\pi\})\chi_4 + \ldots \]

\[ k = \pi/2a \]

\[ \Psi_{\pi/2a} = \chi_0^\dagger(\exp\{i\pi/2\})\chi_1 + (\exp\{i\pi\})\chi_2 + (\exp\{i3\pi/2\})\chi_3 + (\exp\{i2\pi\})\chi_4 + \ldots \]

\[ k = 0 \]

\[ \Psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \chi_4 + \ldots \]

- The band runs "uphill" (from 0 to \( \pi/a \)) because the in phase (at \( k=0 \)) combination of orbitals is bonding and the out of phase (at \( k=\pi/a \)) is antibonding.

- The Fermi energy separates the filled states from the empty states (\( T = 0 \) K).
Band Theory

Band Structure of 1D Chain of atoms

Band Structure: Linear Chain of F

Which is the correct band structure for a linear chain of F atoms?
Band Theory

Band Structure of 1D Chain of atoms

Band Structure: Linear Chain of F

Antibonding $2p_z \sigma^*$

Doubly degenerate

Bonding $2p_x/2p_y \pi$

Bonding $2s \sigma$

Doubly degenerate

Antibonding $2p_x/2p_y \pi^*$

Antibonding $2s \sigma^*$

Bonding $2p_z \sigma$
Band Theory

Band Structure of 1D Chain of atoms

Effect of Orbital Overlap

If we reduce the lattice parameter $a$ it has the following effects:

- The band becomes more bonding at $k=0$
- The band becomes more antibonding $k=\pi/a$. The increased antibonding is larger than the increased bonding.
- The bandwidth increases.
- The electron mobility increases.

Wide bands $\rightarrow$ Good orbital overlap $\rightarrow$ High carrier mobility

Wide bands $\rightarrow$ Large intermolecular overlap $\rightarrow$ delocalized e-
Narrow bands $\rightarrow$ Weak intermolecular overlap $\rightarrow$ localized e-
Band Theory

Band Structure of 3D Chain of atoms

\[ \Gamma = (k_x=0, k_y=0, k_z=0) \]
\[ M = (\pi/a, \pi/a, 0) \]
\[ R = (\pi/a, \pi/a, \pi/a) \]
\[ X = (\pi/a, 0, 0) \]
\[ Y = (0, \pi/a, 0) \]
\[ Z = (0, 0, \pi/a) \]
Band Theory

Three Dimensions - Band Structure of $\text{Ba}_2\text{SnO}_4$
Band Theory

Three Dimensions - Band Structure of $\text{Ba}_2\text{SnO}_4$