Chapter 2: Atomic Structure and Interatomic Bonding

Goals
- Define basic concepts (reinforce your chemistry):
  - Filling of Atomic Energy Levels: Pauli Exclusion Principle
  - Atomic Orbitals (s-, p-, d-, and f-type electrons)
  - Types of Bonding between Atoms
  - The Periodic Table (and solid state structures)
  - Bond Energy Curves
- Describe how types of bonding affect Bond-Energy Curves.
- Describe how the Bond-Energy Curve describes macroscale properties.

Learning Objective
- Know, and be able to use, filling of atomic levels to get ionic electron configurations of atoms.
- Use the Bond-Energy Curve to describe qualitatively the difference types of materials and their macroscale properties.
- Know the origins of stress and strain, melting temperature, and thermal expansion.

How are Macroscopic Properties related to Bonding?

The Bond-Energy Curve
A. Dependence of potential energy on atomic spacing
   1. Long-range attraction versus short-range repulsion
   2. Superposition of attractive and repulsive potentials
B. The bond-energy curve and engineering properties
   1. Melting temperature
   2. Elastic modulus
   3. Thermal expansion coefficient

- How are macroscopic properties (mechanical, structural, thermal, electrical, optical, ...) most simply related to bonding?
- Are there directionality dependencies in materials response?
- Can point defects (i.e., vacancies or impurities) change such bonding related properties?

Atomic Structure and Periodic Table

Electrons
The behavior of electrons can be correctly described only by the theory of quantum mechanics, which for most of you have or will be covered in physics/ECE course.

For this class, we will simply borrow some of the major results of the theory so that we can adequately understand the behavior of electrons.

Notably, the Bohr model of the atom is incorrect as it does not describe the dual particle (e.g., photo-electric effect) and wave (e.g., electron diffraction) features of electron scattering.
Major Results from Quantum Mechanics

- Electrons sometimes behave like particles.
  - They can scatter off objects and have momentum, $p = \hbar k / 2\pi$.

- But sometimes they behave like waves.
  - They don’t exist uniquely at any given location, but are spread out in space.
  - They can interfere with each other, and even form standing waves in a cavity.
  - Their energy and momentum depend on their wavelength.

- When orbiting an atomic nucleus, electrons are best described by energy waves with a specific amplitude and wavelength, and these specific values may be found by solving Schrödinger’s equation.

- Solutions of Schrödinger’s Equation are catalogued in terms of quantum numbers (three integers, plus a fourth that is either 1/2 or -1/2).

- These quantum numbers are $n$, $l$, and $m$, and spin ($1/2$ or $-1/2$).

- They can be collected as a set of integers and the electron spin, e.g., (1012).

Electron Quantum Numbers

**Principle, $n$:** Allowed values of $n$ are 1, 2, 3...
- Roughly associated with electron’s energy – higher values of $n$ mean larger (less favorable) energies.
- The value of $n$ also tells how “fat” from the nucleus the electron is.
- $n$ is also called the electron shell ($n=1$ is the first shell, etc.)

**Angular momentum, $l$:** Allowed values of $l$ are 0 to $(n-1)$
- Related to angular momentum of the electron in its orbit
- $l$ is also called the electron orbital within a given shell
- Each value of $l$ is assigned a letter of the alphabet:

<table>
<thead>
<tr>
<th>Value</th>
<th>Letter</th>
<th>Why?</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>s</td>
<td>sharp</td>
</tr>
<tr>
<td>1</td>
<td>p</td>
<td>principal</td>
</tr>
<tr>
<td>2</td>
<td>d</td>
<td>diffuse</td>
</tr>
<tr>
<td>3</td>
<td>f</td>
<td>fundamental</td>
</tr>
</tbody>
</table>

**Spin, $m$:** Allowed values of $m$ are $-l$ to $+l$ ($2l + 1$ distinct values)

**Pauli Exclusion Principle:** No two electrons in the same system can share the same four $(n, l, m, s)$ quantum numbers!

Electron States

See, e.g., Table 2.1: The Pauli exclusion principle forces there to be only a certain number of electrons in each shell and orbital.

<table>
<thead>
<tr>
<th>shell $n$</th>
<th>orbital ((0 \text{ to } n-1))</th>
<th>$m$ values ((m = l \text{ to } l))</th>
<th>spin ((m_s = \pm 1/2))</th>
<th>$\theta$ electrons in shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 (1s)</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>0 (2s)</td>
<td>1</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1 (2p)</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2 (2p)</td>
<td>3</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>0 (3s)</td>
<td>1</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>1 (3p)</td>
<td>3</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>2 (3p)</td>
<td>3</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>3 (3p)</td>
<td>3</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>4 (3p)</td>
<td>3</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>0 (4s)</td>
<td>1</td>
<td>2</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>1 (4p)</td>
<td>3</td>
<td>2</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>2 (4p)</td>
<td>3</td>
<td>2</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>3 (4p)</td>
<td>3</td>
<td>2</td>
<td>32</td>
</tr>
</tbody>
</table>
Electrons have sharp energy states with diffuse orbits
Unlike Bohr model orbits are given probabilistically.
• For each \((n, l, m, m_s)\) radial distribution is given by \(R_{\ell m}(r)\), and electrons inhabit much more space around the nuclei.
• e.g., \(n = 1\) tells \(\theta\) of nodes.
• The angular distribution is given by the shapes of the \(Y_{\ell m}\) dictated by the \(l\) and \(m\).

\[
\begin{align*}
Y_{00} &\sim 1, \\
Y_{10} &\sim z = \cos \theta, \\
Y_{11} &\sim y = \sin \phi \sin \theta, \\
Y_{1-1} &\sim x = \sin \phi \cos \theta.
\end{align*}
\]

Energy Shell Diagrams
Note: \(4s\) state fills before \(3d\) state, i.e. \((n+1)s\) state fills before \(n-d\) state, otherwise states fill according to increasing quantum numbers \((n,l)\).

Note: a similar thing happens for \(f\) state also. It fills before some of the \(d\)-states.

Periodic Table: Orbital Filling
\(\sim\) Example of Pauli Exclusion Principle
no 2 electrons share the same quantum numbers for the same \((n,l)\) at same E.

Electron-Level Filling
• \(4s\) is slightly lower in energy and fills first, but is removed first as it is less tightly bound (remove electron in higher lowest quantum levels first).
• Electrons in higher states, which resides farther from nuclei, come off first.

Consider Mn \((1s^22s^22p^63s^23p^63d^54s^2)\), what is Mn\(^{2+}\) state?
(Image of the periodic table showing close-packed structures with a note that bcc Mn is metastable and Alpha-Mn has many atoms per cell.

Summary of Periodic Table Trends:
- Metallic properties decrease
- Atomic radius decreases
- Atomic number increases
- Ionization energy increases

Periodic Table Information:
- Avogadro's Number: 1 mole has $6.023 \times 10^{23}$ atoms (or molecules).
- 1 amu/atom (or molecule) = 1 g/mol (e.g., at. wt. of Fe is 55.85 amu/atom or g/mol).

Primary Bonding Types: Ionic Bonding
- Occurs for electronegative (positive) elements that can form close-shell configurations. Requires work to remove (add) e⁻ from Na⁺ to Cl⁻.
- Electronegativity plays a role here, e.g., H-F.
**Primary Bonding Types: IONIC**

Structure is determined by electrostatic attraction $E_A = -\frac{A}{r}$ (Coulomb’s Law) and collapse is prevented by electronic and nuclear repulsion $E_R = +\frac{B}{r}$. 

For closed-shell gases (Ar, Kr, …) $n \approx 12$. Generally need quantum mechanics.

**Primary Bonding Types: METALLIC**

Metals share so-called *itinerant* electrons, or a “sea of electron” (electron-glue). 

*Itinerant* electrons move (or "hop") about spending more time at an atom if they are more tightly bound, as with d-state, and less time if they are less bound, as with s-state.

**Primary Bonding Types: COVALENT**

Covalent bonds share electrons amongst adjacent atoms.

For Si, the electronic filling is $3s^23p^2$.
- To fill up all the remaining p-states in bulk Si, 4 electrons are required.
- One way to do this is promote one of the 3s electrons into a p-state, creating a $sp^3$ hybrid state, which has tetrahedral symmetry due to bond.
Primary Bonding Types: COVALENT

- Materials with pi bonds have less electrons (not as many shared) between the atoms compared to sigma bonds, and therefore are weaker bonds.
- Hence, the electrons are more mobile (i.e., delocalized), giving rise to the conduction in carbon-graphite, for example.
- Benzene (C$_6$H$_6$) has sigma sp$^2$ 120° bonds in plane and sigma $p_z$ orbitals out of plane.
- Acetylene (C$_2$H$_2$) has sp$^1$ 180° bonds.

Of course, not all atoms with only s and p states form hybrids to get covalent bonds. Hydrogen-Sulfide, H$_2$S, does not need to promote hybrid orbitals to form a strong covalent bond.

Lower energy bond configuration as there is no need to promote to hybrid.
**Self-Assessment Questions**

Types of Bonding Lead to Specific Charge Distributions and Polar Molecules

Consider the "Simple Molecules" H with C, N, O, and F:

Configurations are 1s^2 2s^2 plus 2p^3 for C; 2p^3 for N; 2p^4 for O; 2p^5 for F.

- If the 2s and 2p states form four sp^3 hybrids, what shape can be anticipated for the molecules? (You must consider how many H are needed for each case.)
- Can you identify the polar character of the molecule?
- How does this roughly explain that H_2O is bent at ~109.3\(^\circ\)?
- What is the effect of the increasing nuclear charge from C to F?
- Why is H-F different than others in shape?

**Primary Bonding Types: Secondary (van der Waals)**

Two types of Secondary: induced dipolar and permanent dipole.

- Induced dipolar interactions are weak and depend on molecular environment.
- They are typically caused by vibrational effects within the particular molecule and lead to interactions between molecules.
- Hence, they are weak secondary bonds to the stronger molecular bonds.

**Example of Induced Dipole: Argon Gas**

The positive nuclei repel one another and the electron cloud deforms in the neighboring atoms such that the two dipoles align and there is a weak attraction via dipolar forces, 1/r^4.

**Primary Bonding Types: Secondary (van der Waals)**

Example of Permanent Dipole: H-Cl Gas

The Cl has a large electronegativity (3.0) compared to H (2.1); hence, Cl grabs the electron away from H. H-F and H_2O are other examples of this.

Notably, such "Hydrogen bonds" with permanent dipoles lead to higher melting points and boiling temperatures, more than can be expected from their low molecular weights. Such bonds are crucial for polymer chemistry.

**Primary Bonding Types: Secondary (van der Waals)**

van der Waals Bonds lead to induced dipole interactions between, e.g., graphite layers, or polymer chains.

Hence, to strengthen bonds between such layered and chain molecules additional interactions must be made, as done in Vulcanization of rubber where sulfur atoms are bonded between rubber molecules (later).

**Example: C_8H_18 (Octane)**

A molecular mass of 114, larger than most (e.g., Acetylene), has weaker van der Waals bonds, hence lower melting temperature.

In fact, Octane bonds are easy to break and form more stable bonds, giving off lots of energy; that's why it is used in gasoline.
Primary Bonding Types: Secondary (van der Waals)

Example of Permanent Dipole: $\text{H}_2\text{O}$
Water is a Polar Molecule with a Permanent Dipole Moment.

Again, such "Hydrogen bonds" with permanent dipoles lead to higher melting points and boiling temperatures, more than can be expected from their low molecular weights. Such bonds are crucial for polymer chemistry.

Percent Ionicity: Ionic to metallic

Nature of the Bonds: Percent ionicity
(see text, where $X$ is the electronegativity)

$$\%\text{IC} = 1 - e^{\frac{(X_A - X_B)^2}{4}}$$

Macroscopic Properties: Force vs Extension

Issues to be addressed:

How are macroscopic properties (mechanical, structural, thermal, electrical, ...) most simply related to bonding?

Are there directionality dependencies?

Can point defects (i.e., vacancies or impurities) change such bonding related properties?

For linear-elastic strain, not plastic!
Slope is Young’s Modulus.

Macroscopic Properties: Stress-Strain Curves

linear-elastic strain only – not plastic!

Normalized forces ($\frac{F}{A_0}$) versus normalized strain ($\frac{\Delta l}{l_0}$)

Hooke’s Law

$$\sigma = \frac{F}{A_0}$$

Units: $\sigma$: [GPa] or [psi]

$E$: [GPa] or [psi]

Slope is Young’s (Elastic) Modulus, $E$
Macroscopic Properties Inferred from Bonding

- Bond Length, \( r_0 \)
- Binding Energy, \( U_b \)
- Melting Temperature, \( T_m \) (really \( T_{sub} \))

Stored energy goes ↑ as \( U_b \) goes ↓

\[ \text{Equil. bond } r_0 : F = -\frac{dU}{dr} |_{r_0} = 0 \]

\[ \text{Min. energy } E_0 : U(r_0) \]

Linear Thermal Strain

\[ \Delta L(L)/L_0 = \alpha \epsilon (T - T_0) \]

\( \alpha \) is asymmetry at \( r_0 \)
No asymmetry at \( r_a \)
No affect on \( r(T) \) or \( V(T) \)

\( \alpha \) ↑ as \( E \) ↑ (less negative)

Volume Thermal Strain

\[ \Delta V(V)/V_0 = \beta \epsilon (T - T_0) \]

Parabolic \( E \) vs. \( r \) shape

Symmetric well \( r(T) \) : No expansion possible
Atoms just vibrate back and forth!

Coefficient of Thermal Expansion, \( \alpha \), or \( dL/dT \)

Elastic Moduli, \( E \) (Young's Modulus)

\[ E \propto \text{curvature at } r_0 \]
\[ \propto \text{U/dr}(r_0) \]
liking “spring constant” \( F = k(r-r_a) \)
and linear near equilibrium.

Negative \( F \) - compression
Positive \( F \) - tension

\( E \) modulus ↑ as \( E \) ↓ (deeper)

Origin of Bonding Curve

arises from attractive plus repulsive interactions between atoms(ions)

Particular forms if \( E_a \) and \( E_r \) depend upon atoms and quantum mechanics,
but often described by simple forms.

\[ E_a = \frac{A}{r} \text{ and } E_r = \frac{B}{r^3} \]

\( \text{R.E. Coulomb, } A = \frac{Z_e^2 e^4}{4}\epsilon_0 \)
For \( \text{NaCl}, Z_e^2 = +2 \text{ and } Z_p Z_a = -2 \)

Macrosopic consequences of generic \( E_{\text{total}} \) shown in previous slides

\[ \text{Force: } F = -\frac{dE}{dr} = -\frac{dE_a}{dr} - \frac{dE_r}{dr} \]

Repulsive force

Attractive force

Minus sign in force makes sure that,
by definition, repulsive force is “+”
What is relationship between Bonding Energy and $T_{\text{melt}}$?

### Summary: Bonding, Structure, Properties

- **Ceramics**
  - Large bond energies: large $T_m$, $E$, small $\alpha$
- **Ionic and Covalent bonds**
- **Metals**
  - Varying bond energy: intermediate $T_m$, $E$, $\alpha$
- **Metallic bonding**
- **Polymers**
  - Directional properties: small $T_m$, $E$, large $\alpha$
- **Covalent and Secondary**

### Energy vs Volume: Bulk Modulus

- **Elastic Bulk modulus, $K$**
  
  \[ P = -K \frac{\Delta V}{V_0} \]

  Units: $E$: [GPa] or [psi]

  \[ V_0 \text{ Pressure test: } \]
  \[ \text{Init. vol} = V_0 \]
  \[ \text{Vol chg.} = \Delta V \]

  \[ K \]

### Bond Energy and Melting Temperature

**Table 2.3** Bonding Energies and Melting Temperatures for Various Substances

<table>
<thead>
<tr>
<th>Bonding Type</th>
<th>Substance</th>
<th>$E_{\text{bond}}$</th>
<th>$\Delta H_{\text{melt}}$</th>
<th>$T_{\text{melt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>NaCl</td>
<td>0.1 (152)</td>
<td>0.3</td>
<td>1001</td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td>0.2 (106)</td>
<td>0.5</td>
<td>2100</td>
</tr>
<tr>
<td>Covalent</td>
<td>C (diamond)</td>
<td>7.4 (170)</td>
<td>7.4</td>
<td>&gt;1550</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>1.6 (108)</td>
<td>6.7</td>
<td>1400</td>
</tr>
<tr>
<td>Metallic</td>
<td>Al</td>
<td>5.4 (179)</td>
<td>5.4</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>6.6 (190)</td>
<td>6.6</td>
<td>830</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>10.9 (220)</td>
<td>10.9</td>
<td>2,400</td>
</tr>
<tr>
<td>Van der Waals</td>
<td>Ar</td>
<td>7.7 (140)</td>
<td>12.0</td>
<td>-149</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>71 (4)</td>
<td>71</td>
<td>-101</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>NH$_3$</td>
<td>5 (2.0)</td>
<td>5.0</td>
<td>-70</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>51 (2.8)</td>
<td>51.0</td>
<td>0</td>
</tr>
</tbody>
</table>

- What is $T_{\text{melt}}$ of ceramic, metal, polymer? Why?
- What is $E$ of ceramic, metal, polymer? Why?
- What do force-extension or stress-strain curves look like?
Energy vs Volume : Bulk Modulus

Total Force: equilibrium $r_0$ when $F=0$

$F = F_A + F_R = - \frac{d}{dr}(U_A + U_R) \sim r^{-2}$

Bulk Modulus: volume deformation under hydrostatic pressure

$K = -\frac{dP}{dV} \Bigg|_{V_0} = \frac{V_0^2}{V_0^2} \frac{dU}{dV} \sim V_0^{-4/3}$

since $V_0 \sim r_0^3$

Surprisingly this represents alkal, covalent and compounds having diamond cubic structures (but not TiC, TaC, etc.)

Simple analysis gives trends in simple systems!

Example Test Question

Why are covalently bonded materials generally less dense than ionically bonded or metallically bonded ones?

Hint: Consider what is distinctive about covalent bonds. What does this tell you about the density of bonds (bonds per unit volume)?

If I suddenly changes Na$^+$ to Ca$^{2+}$ and Cl$^-$ to S$^2-$ what would happen to the equilibrium bond distance, the melting temperature, etc?

Hint: There are multiple effects due to change in charge.

Synopsis

- Bonding between atoms dictates macroscale properties in solids, e.g. mechanical and electrical, as well as molecules.
  - Binding energies related to sublimation (loosely melting) temperature.
  - In molecules, it determines also the solid/liquid/gas behavior (relative evaporation temperatures), dependent on type of bonds (metallic, ionic, covalent, and secondary).
  - Thermal expansion related to curvature of binding curve.
  - Initial stress-strain behavior (elastic moduli) dictated by binding curve.
    (NOT TRUE for plasticity, which is controlled by line defects - later!)

- Point defects do not affect mechanical properties to a large extent, but could affect electrical properties (resistivity).