Chapter 1: Orbitals And Bonding
Chapter 1 Topics: Bonding Concepts

Look back at your General Chemistry Textbook!!!

Ionization Potential
Ionic Bonds
Hund’s Rule
Aufbau Principle
Lewis Structures
Electronegativity
Octet Rule
Bond Dissociation Energy
Covalent Bonds
Wave Functions

Quantum Numbers
Electronic Configuration
Pauli Exclusion Principle
Atomic Orbitals
Dipole Moment
Valence Electrons
Resonance Structures
Formal Charge
Nodes
Molecular Orbitals
Organic Chemists usually don't use quantum numbers – but we have to remember the correlations:

**Orbital Nomenclature**

- **principle quantum number** \( (n) \)
- **azimuthal quantum number** \( (l) \)
- **magnetic quantum number** \( (m) \)

Shell 1: **One S orbital** \( (1s) \)

Shell 2: **One S, three P** \( (2s, 2p) \)

Shell 3: **One S, three P, five D** \( (3s, 3p, 3d) \)

Shell 4: **One S, three P, five D, seven F** \( (4s, 4p, 4d, 4f) \)

The three P orbitals are designated \( P_x, P_y, P_z \) (different spacial orientations).
Ionic Bonding

**Ionic bonds:** One atom transfers electrons to another. Molecules are held together by electostatic (coulombic) forces. Ionic bonds are formed between two atoms of very different electonegativities (>2.0 electronegativity difference)

\[ \text{Li} \cdot \rightarrow \text{Li}^+ : \text{F}^- \]

Loss of one electron will lead to a completely empty valence shell  
Addition of one electron will lead to a completely filled valence shell (full octet)

Atoms are especially stable when all of the valence orbitals are either completely filled or completely empty (the "noble gas" configuration). This has been adapted to the **octet rule:** (most) atoms are stable when there are 8 electrons in their outermost (valence) shell. For this course: 1st & 2nd row atoms can never have more than 8 valence electrons and/or 4 valence orbitals!!!
Covalent Bonding

**Covalent bonds:** Two atoms share electrons. Both atoms can count the shared electrons toward their octet. This type of bond is formed between two atoms of similar electronegativities (<2.0 electronegativity difference)

\[ \text{H} \cdot + \cdot \text{H} \rightarrow \text{H}:\text{H} \quad \text{or} \quad \text{H} \equiv \text{H} \quad \text{or} \quad \text{H}_2 \]

- **Sharing one additional electron will lead to a completely filled valence shell**
- **Sharing one additional electron will lead to a completely filled valence shell**
- **A line (bond) signifies 2 shared electrons**

Both hydrogens have a filled valence shell (shared electrons count for both atoms)
Electronegativity and Percent Covalency
Fluorine has a higher electronegativity, and will "pull" electrons toward itself causing bond **polarization**. This creates a **dipole** along the bond axis.

Identical atoms will share electrons equally: a **nonpolar covalent bond**.

Nonidentical atoms will not share electrons equally: a **polar covalent bond**.
Writing Lewis Structures

Lewis Structures: Represent connectivity of a chemical species. Dots reach represent one electron; lines represent a shared electron pair; atomic symbols represent the nucleus and all non-valence electrons. *Nonbonding electron pairs are frequently omitted!*
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NH$_3$ ammonia

\[
\begin{align*}
\text{NH}_3 & \quad \rightarrow \quad \cdot \cdot \cdot \cdot \cdot \\
\text{ammonia} & \quad \rightarrow \quad \text{or}
\end{align*}
\]
Writing Lewis Structures

Lewis Structures: Represent connectivity of a chemical species. Dots reach represent one electron; lines represent a shared electron pair; atomic symbols represent the nucleus and all non-valence electrons. *Nonbonding electron pairs are frequently omitted!*

H₂CCH₂ → H··C··C··H (ethylene) → H·C:C·:H

or

```
H C ≡ C
H H
```
Writing Lewis Structures

Lewis Structures: Represent connectivity of a chemical species. Dots reach represent one electron; lines represent a shared electron pair; atomic symbols represent the nucleus and all non-valence electrons. *Nonbonding electron pairs are frequently omitted!*

\[
\text{H}_3\text{CS(O)CH}_3 \quad \xrightarrow[\text{dimethylsulfoxide}]{\text{H}} \quad \text{H} \cdot \text{C} \cdot \text{S} \cdot \text{C} \cdot \text{H} \quad \xrightarrow[\text{H}]{} \quad \text{H} \cdot \text{C} \cdot \text{S} \cdot \text{C} \cdot \text{H} \cdot \text{O}
\]

\[
\begin{align*}
\text{Formal Charge} & = \text{Valence e}^- - \text{Nonbonding e}^- - \frac{1}{2} \text{Bonding e}^- \\
\end{align*}
\]
Atomic Orbitals: A Brief Review

A 1s orbital

node (nodal plane)

A 2p orbital
Atomic Orbitals: A Brief Review

In General, electrons are lower in energy if:

1. They are closer to a positive charge (nucleus or multiple nucleii)
2. They are in an orbital with fewer nodes
Molecular Orbitals: A Brief Review

Mixing orbitals of opposite phase: leads to an antibonding interaction that is destabilizing (higher in energy than the atomic orbitals)

Mixing orbitals with same phase: leads to a bonding interaction that is stabilizing (lower in energy than the atomic orbitals)
Molecular Orbitals: A Brief Review

a σ*-orbital (antibonding)

σ* H–H

a σ-orbital (bonding)

σ H–H
Electrons are 52 kcal/mol (per electron) more stable in a $\sigma$ H–H orbital (larger orbital space) than in a hydrogen 1s orbital.
Molecular Orbitals: A Brief Review

\[
\text{bond formation} \quad \begin{array}{c}
\text{H} \\ \text{•} \\
\text{+} \\
\text{H} \\ \text{•}
\end{array} \quad \text{→} \quad \begin{array}{c}
\text{H} \\
\text{—H}
\end{array} \quad \text{exothermic by 104 Kcal/mol} \quad (\Delta H = -104 \text{ Kcal/mol})
\]

\[
\text{bond cleavage (BDE)} \quad \begin{array}{c}
\text{H—H}
\end{array} \quad \text{→} \quad \begin{array}{c}
\text{H} \\ \text{•}
\end{array} \quad + \quad \begin{array}{c}
\text{H} \\ \text{•}
\end{array} \quad \text{endothermic by 104 Kcal/mol} \quad (\Delta H = +104 \text{ Kcal/mol})
\]

*The bond dissociation energy (BDE) is the energy required to break a bond homolytically (into a diradical). BDE \((H_2) = 104 \text{ Kcal/mol})*
Molecular Orbitals: A Brief Review

Mixing orbitals of opposite phase: leads to an **antibonding** interaction that is **destabilizing** (higher in energy than the atomic orbitals)

Mixing orbitals with same phase: leads to a **bonding** interaction that is **stabilizing** (lower in energy than the atomic orbitals)
Molecular Orbitals: A Brief Review

\[ \pi^* \text{C–C} \]

\[ \text{a } \pi^* \text{-orbital (antibonding)} \]

\[ \pi \text{C–C} \]

\[ \text{a } \pi \text{-orbital (bonding)} \]

\[ \text{All multiple bonds that we will encounter will be } \pi \text{-type} \]
**Curved Arrow Notation**

*Curved arrows* are used to designate the movement or flow of electrons.

![Diagram of curved arrows]

- The electrons start here (a filled orbital).
- This atom has the empty orbital to receive the electrons.
- Incorrect flow of electrons.
- Correct flow of electrons.
Resonance Structures allow Lewis Structures to describe multicenter bonding (more than 2 atoms sharing electrons). There are also situations where resonance structures are used to show bond polarization.

A more accurate single representation: