**Big Idea:** Bonding can be described using two theories which take into account quantum mechanics. In the Local Electron Model, bonds are formed from the overlap of atomic orbitals. In Molecular Orbital Theory, electrons are redistributed throughout the molecules and placed into new orbitals called molecular orbitals.

- Local Electron Model (Valence-Band Theory)
- Molecular Orbital Theory
Local Electron Model (Valence-Bond Theory)

- **Lewis Model (VSEPR):** Did not take into account quantum mechanic’s effects. Assumes bonds located directly between atoms, therefore, electrons did not have wavelike properties.
- **Local Electron Model (Valence-Bond Theory):** Uses a quantum mechanical description of the distribution of electrons in bonds that provides a way of calculating the numerical values of bond angles and bond lengths.
Local Electron Model (Valence-Bond Theory)

**σ-bonds**

- **Overlap:** The merging of orbitals belonging to different atoms of a molecule.

  - **Note:** The greater the extent of orbital overlap, the stronger the bond.

- **σ-bond:** Two electrons in a cylindrically symmetrical cloud between two atoms.

  - **Note:** σ-bonds contain no nodal planes along the internuclear axis.

- **Nodal Plane:** A plane on which electrons will not be found.
A σ–bond is formed in HF when electrons in 1s- and 2p<sub>Z</sub>-orbitals pair (where z is the direction along the internuclear axis). Notice that there is cylindrical symmetry and no nodal plane on the internuclear axis.
Local Electron Model (Valence-Bond Theory)

- **π-bond**: A bond formed by the side-to-side overlap of two \( p \)-orbitals.
- A σ-bond is formed by the pairing of electron spins in the two \( 2p_z \)-orbitals.
- **π-bonds** are formed when electrons in two other \( 2p \)-orbitals pair and overlap side by side.

Note: **π-bonds** contain a single nodal plane along the internuclear axis.
Student Question

How many $\sigma$ bond and $\pi$ bonds are there in $\text{CO}_2$?

Hint: Draw the Lewis structure.

a) 1 $\sigma$ bond and 1 $\pi$ bonds
b) 0 $\sigma$ bond and 2 $\pi$ bonds
c) 2 $\sigma$ bond and 2 $\pi$ bonds
d) None of the Above
Promotion of an electron is possible if:

- There are empty \( p \)-orbitals
- The energy gained by forming additional bonds is greater than the energy needed to promote the electron to the \( p \) orbital

Promotion Can Occur For Carbon

Promotion Cannot Occur For Nitrogen
These are the bonding orbitals of C, therefore, what angles should be between each H in CH₄?
These hybrid orbitals can be mathematically represented by linear combinations of the atomic orbitals (within one atom).

- \( h_1 = \frac{1}{2}(s + p_x + p_y + p_z) \)
- \( h_2 = \frac{1}{2}(s - p_x - p_y + p_z) \)
- \( h_3 = \frac{1}{2}(s - p_x + p_y - p_z) \)
- \( h_4 = \frac{1}{2}(s + p_x - p_y - p_z) \)

Note: Since one s orbital and three p orbitals went into forming the new hybrid orbitals, these hybrid orbitals are referred to as sp\(^3\) hybridized orbitals.
The new molecular orbitals have energies that are at the same level.

The hydride orbitals show that CH$_4$ should be in a tetrahedral bonding configuration.

**Note:** The number of atomic orbitals that go into the linear combinations are the same number of hybrid orbitals that form.

### $sp^3$ hybridized carbon

- C$_2$sp$^3$
- $sp^3$ hybridized carbon

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Hybrid orbitals can be formed from other combinations of atomic orbitals.

- \( h_1 = s + \sqrt{2}p_y \)
- \( h_2 = s + \sqrt{\frac{3}{2}}p_x - \sqrt{\frac{1}{2}}p_y \)
- \( h_3 = s - \sqrt{\frac{3}{2}}p_x - \sqrt{\frac{1}{2}}p_y \)
Local Electron Model (Valence-Bond Theory)
Assigning Hybridization

- **Step 1:** Draw Lewis structure.
- **Step 2:** Count the number of bonds and lone pairs on the atom of interest.

**Note:** All types of bonds (single, double, and triple) between two atoms count as 1 bond.

- **Step 3:** Assign hybridization $s^{\text{up to 1}} p^{\text{up to 3}} d^{\text{up to 5}}$

Describe Bonding using the local electron (LE) model

- **Step 1:** Draw Lewis structure (if possible obey the octet rule).
- **Step 2:** Determine hybridization.
- **Step 3:** Describe bonding.
The bonding model that we looked at before for $N_2$ was a little oversimplified. The sigma bonding should be looked at as taking place between two sp hybridized orbitals instead of between two $p_z$ orbitals. However, sp hybridized orbitals are very similar in shape to $p_z$ orbitals.
LE Description of Bonding

- Sulfur forms one \( \sigma \) bond to each oxygen atom. The bonds are formed from the overlap of a sp\(^3\) hybridized orbitals on both the sulfur and oxygen atoms. All the lone pair electrons on both sulfur and oxygen atoms are located in sp\(^3\) hybridized orbitals.
Local Electron Model (Valence-Bond Theory)

\[ \text{CO}_3^{2-} \]

**LE Description of Bonding**

- The carbon atom forms one \( \sigma \) bond to each of the single bonded oxygen atoms. This bond is formed from the overlap of a \( \text{sp}^2 \) hybridized orbital on the carbon atom and a \( \text{sp}^3 \) hybridized orbital on the single bonded oxygen atoms. A third \( \sigma \) bond is formed from the overlap of an \( \text{sp}^2 \) hybridized orbital on the carbon atom and a \( \text{sp}^2 \) hybridized orbital on the double bonded oxygen atom. The \( \pi \) bond between the double bonded oxygen atom and the carbon atom is formed from the overlap of the unhybridized \( p \) orbitals on both the carbon and oxygen atoms. The loan pair electrons on the double bonded carbon sit in \( \text{sp}^2 \) hybridized orbitals and the loan pair electron on the single bonded oxygen atoms sit in \( \text{sp}^3 \) hybridized orbitals.
Identify the hybrid orbitals used by the underlined atom in acetone, CH$_3$COCH$_3$. The O atom is double bonded to the central carbon atom.

a) sp$^3$d  
b) sp$^2$  
c) None; pure p$_z$-orbitals are used in bonding.  
d) sp$^3$  
e) sp

If you have extra time tell the person next to you the LE description of the molecule.
What atoms can form double and triple bonds?

- Atoms in period 2 (especially C, N, O) readily form double bonds with themselves and other period 2 atoms.

- However, atoms in period 3 and later have trouble forming multiple bonds with other large atoms due to the fact that the atoms are so large and bond lengths so great that it is difficult for their p-orbitals to take part in effective side-by-side bonding.
Limits of Lewis Theory/LE Theory

1. Cannot draw some structures that are known to exist.
   
   Ex: B$_2$H$_6$ (12 valence e$^-$) Not enough electrons to make all of the bonds

2. Does not explain resonance structures

3. Paramagnetic/Diamagnetic Problems
Local Electron Model (Valence-Bond Theory)

- **Paramagnetic**: Having the tendency to be pulled into a magnetic field; a paramagnetic substance is composed of atoms or molecules with unpaired spin.

  **Note**: Laymen would call these materials magnetic.

- **Diamagnetic**: A substance that tends to be pushed out of a magnetic field; a diamagnetic substance is composed of atoms or molecules with no unpaired electrons.

  **Note**: Very weak response and is not observable in every day life.
Local Electron Model (Valence-Bond Theory)
Molecular Orbital Theory

- Molecular orbitals are formed by superimposing atomic orbitals of all the atoms in the molecule.

  **Note:** Superimposing just means adding together.

  **Note:** This is similar to Local Electron Model (valence band theory), however, the Local Electron Model only formed hybrid orbitals from $\sigma$ bonds and lone pair electrons within one atom. Molecular Orbital Theory is going to use all of the atomic orbitals on all of the atoms. Not just $\sigma$ orbitals and lone pair electrons.

- The molecular orbitals that are formed are a linear combination of atomic orbitals (LCAO).
Molecular Orbital Theory

H₂

Notes:
1. + and – are the signs of the wavefunction
2. No electron density in bonding plane
3. Electron density in bonding plane

Note: The number of atomic orbitals that go into making the molecular orbitals is the number of molecular orbitals generated.
Bonding Orbitals: A molecular orbital with no nodes between neighboring atoms.

Note: These orbitals contribute to holding all the atoms together.

Antibonding Orbitals: A molecular orbital with a node between all neighboring pairs of atoms.

Note: These orbitals contribute to pushing all the atoms apart.

Note: These type of orbitals are denoted with a * next to them.
Student Question

Which molecular orbital is a $\sigma$?
Which molecular orbital is a $\sigma^*$?
Which molecular orbital is a $\pi$?
Which molecular orbital is a $\pi^*$?

a) 

b) 

c) 

d)
How do Electrons Fill Molecular Orbitals?

- Electrons are first accommodated in the lowest-energy molecular orbitals, followed by orbitals of increasingly higher energy.

- According to the Pauli Exclusion Principle, each molecular orbital can accommodate up to two electrons. If two electrons are present in one orbital they must be paired.

- If more than one molecular orbital of the same energy is available the electrons enter them singly and adopt parallel spins (Hund’s Rule).
MO diagram for homonuclear diatomic molecules Li$_2$ through N$_2$

MO diagram for homonuclear diatomic molecules O$_2$ and F$_2$
Molecular Orbital Theory

Comparisons Between the VSEPR/LE/MO Theory

- **VSEPR \((N_2)\):** \(\equiv N \equiv N\): \(N_2\) has a triple bond
- **LE \((N_2)\):** \(N_2\) has 1 \(\sigma\) bond that is formed from the overlap of \(sp\) hybridized orbitals on the nitrogen atoms and 2 \(\pi\) bonds that are formed from the overlap of \(p\) orbitals on the nitrogen atoms
- **MO \((N_2)\)**
  - **Bond Order \((b)\):** The number of electron pairs (bonds) that link a specific pair of atoms
  - \(b = \frac{1}{2} \ (N-N^*)\)
  - \(N = \#\) of e\(^-\) in bonding orbitals
  - \(N^* = \#\) of e\(^-\) in antibonding orbitals

- **All three predict that \(N_2\) bonds with a triple bond**
**Student Question**

What is the bond order of \( \text{O}_2 \)?

a) 2.5  
b) 2  
c) 1.5  
d) 1  
e) None of the above
Molecular Orbital Theory

Heteronuclear Diatomic Molecules

- Note: The energy level of atomic orbitals decreases as electronegativity increases.
Note: The molecular orbitals for CO fill in the same order as C₂.
Similar to diatomic molecules, the number of molecular orbitals in a polyatomic species equals the number of atomic orbitals that are available.

MO Diagram CH₄

Energy

Carbon
4 atomic orbitals (2s, 2pₓ, 2pᵧ, 2pₗ)

Hydrogens
4 [1 atomic orbit each (1s)]

8 molecular orbitals total
We already know that when $N$ atomic orbitals merge together in a molecule, they form $N$ molecular orbitals. The same is true of a metal; but for a metal $N$ is enormous (about $10^{23}$ for 10 g of copper). This results in the energy levels being so close together that they form a continuous band.
Molecular Orbital Theory

- **Highest Occupied Molecular Orbital (HOMO):** The highest-energy molecular orbital in the ground state of a molecule occupied by at least one electron.

- **Lowest Unoccupied Molecular Orbital (LUMO):** The lowest-energy molecular orbital that is unoccupied in the ground state.
**Molecular Orbital Theory**

- **Valence Band**: In the theory of solids, a band of energy-levels fully occupied by electrons.
- **Conduction Band**: An incompletely occupied band of energy-levels in a solid.

**Note**: In order to conduct electricity electrons must be promoted from the valence band into the conduction band.
Semiconductors can be doped to enhance electrical properties

- **Doping**: The addition of a known, small amount of a second substance, to an otherwise pure solid substance.

- **n-type Semiconductor**: Dopants are added to the material that provide extra electrons.
  
  **Example**: As added to Si

- **p-type Semiconductor**: Dopants are added to the material that provide extra holes (less electrons).
  
  **Example**: In added to Si
Molecular Orbital Theory

- **MOSFET Devices**

  ![Diagram of MOSFET devices under different biases](image)

  - When you apply a positive bias to the gate you end up generating an $e^-$ channel at the oxide semiconductor interface which allows electrons to flow between the source and the drain.
Take Away From Chapter 14

- **Big Idea:** Bonding can be described using two theories which take into account quantum mechanics. In the Local Electron Model, bonds are formed from the overlap of atomic orbitals. In Molecular Orbital Theory, electrons are redistributed throughout the molecules and placed into new orbitals called molecular orbitals.

- **Local Electron Model (Valence Band-Theory)**
  - Know that bonding occurs from the overlap of atomic orbitals on neighboring atoms (12)
    - \(\sigma\) Bonds: Cylindrical symmetry no nodal plane on internuclear axis
    - \(\pi\) Bonds: One nodal plane on internuclear axis
  - Be able to determine the number and type (\(\sigma\) or \(\pi\)) of bonds in a molecule (25, 26, 27)

Numbers correspond to end of chapter questions.
Take Away From Chapter 14

- **Local Electron Model (Valence Band-Theory) (Continued)**
  - Know that in order to describe the experimentally seen shape of molecules, a linear combination of atomic orbitals is needed (hybridization)
    - Be able to determine the hybridization of atoms (21,22,28,79)
  - Be able to write out the local electron (LE) description of bonding (14)
  - Be able to determine which atoms are in the same bonding plane. (23,24)
  - Know the limitations of the Local Electron Model/Lewis Model
    - Not all molecules can be explained \( \text{(B}_2\text{H}_6\text{)} \)
    - Does not account for resonance
    - Incorrect magnetic properties \( \text{(O}_2\text{)} \)

Numbers correspond to end of chapter questions.
Take Away From Chapter 14

Molecular Orbital Theory

- Know that atomic orbitals, from all atoms in the molecule, are mixed together to form molecular orbitals.
  - The new molecular orbitals are delocalized over the entire molecule (accounts for resonance structures). (51)
- Be able to visually identify bonding/antibonding orbitals and $\sigma$ and $\pi$ molecular orbitals. (32,33)
- Memorize molecular orbital energy levels for homonuclear diatomic atoms in periods one and two.
  - Be able to write out molecular electron configuration
- Be able to determine the bonding order (40,41,44,53)
  - $BO = \frac{\#\text{bonding } e^- - \#\text{antibonding } e^-}{2}$
    - If bonding order is positive - stable species.
    - If bonding order is 0 - not a stable species.

Numbers correspond to end of chapter questions.
Molecular Orbital Theory (Continued)

- The greater the number of atoms in the molecule the greater the number of molecular orbitals
- Be able to determine if a structure paramagnetic (unpaired e\(^-\)) or diamagnetic (paired e\(^-\))