

# Lecture 36 — Heteronuclear Diatomics & Valence Bond Theory

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**Reading:** Engel 4th ed., Chapter 12 (Sections 12.7–12.9)

## Learning Objectives

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- Construct MO diagrams for heteronuclear diatomic molecules
  - Relate orbital energy asymmetry to bond polarity and electronegativity
  - Explain valence bond (VB) theory and how it differs from MO theory
  - Define hybridization and its role in VB theory
  - Compare the strengths and weaknesses of MO and VB approaches
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## 1. Heteronuclear Diatomics: Asymmetric MOs

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When two different atoms form a bond, the AO energies are no longer equal. The more electronegative atom has **lower-energy** AOs.

### LCAO-MO for HF

$$\psi_{\text{MO}} = c_{\text{H}}\phi_{1s}^{\text{H}} + c_{\text{F}}\phi_{2p_z}^{\text{F}}$$

Since F is more electronegative:  $E(2p_F) < E(1s_H)$

**Bonding MO:** More F character ( $|c_F| > |c_H|$ ) — electron density shifted toward F

**Antibonding MO:** More H character ( $|c_H| > |c_F|$ )

### General Rule

In the bonding MO, the coefficient on the more electronegative atom is larger. In the antibonding MO, the coefficient on the less electronegative atom is larger.

[!NOTE] **Concept Check 36.1** In a heteronuclear diatomic molecule like *HF*, which atom's atomic orbital contributes more to the bonding Molecular Orbital? How does this relate to the concept of electronegativity?

## Bond Polarity

The **polarity** is determined by the asymmetry:

$$|c_A|^2 - |c_B|^2 \propto \text{charge separation} \propto \text{dipole moment}$$

If both coefficients were equal  $\rightarrow$  nonpolar (homonuclear) If one dominates  $\rightarrow$  ionic

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## 2. Electronegativity from MO Theory

The Mulliken definition of electronegativity:

$$\chi_M = \frac{IE + EA}{2}$$

This directly connects to the orbital energies: a more electronegative atom has both higher *IE* and higher *EA*, meaning its *AOs* are at lower energy.

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## 3. MO Diagrams for Common Heteronuclear Diatomics

### CO (isoelectronic with N<sub>2</sub>)

CO has 14 electrons, same as N<sub>2</sub>. The MO diagram is similar but asymmetric:

- C contributes 2s and 2p (higher energy)
- O contributes 2s and 2p (lower energy)
- The HOMO (5σ) is a lone pair on C — explains why CO is a good ligand through C
- Bond order = 3 (triple bond)

### HF

- H: 1s orbital
- F: 2p orbital (only 2p<sub>z</sub> has the right symmetry to bond with H 1s)

- The  $2p_x$  and  $2p_y$  orbitals on F are **nonbonding** lone pairs
  - Bond order = 1
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## 4. Valence Bond (VB) Theory

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### Heitler-London Approach (1927)

For  $H_2$ , VB theory starts from atomic states and allows electrons to exchange:

$$\Psi_{\text{VB}} = N[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] \cdot [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

This is a **covalent** wavefunction — each atom contributes one electron.

### Comparison: MO vs. VB at Dissociation

#### MO ( $\sigma_g$ doubly occupied):

$$\begin{aligned}\Psi_{\text{MO}} &= [\phi_A(1) + \phi_B(1)][\phi_A(2) + \phi_B(2)] \\ &= \phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2) + \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)\end{aligned}$$

This contains **ionic terms** ( $\phi_A(1)\phi_A(2)$  = both electrons on A) that are unphysical at large  $R$ .

**VB:** Contains only covalent terms — correct dissociation behavior.

**MO is better for most molecular properties; VB dissociates correctly.**

Modern computational chemistry: CI (configuration interaction) fixes MO's dissociation problem.

[!NOTE] **Concept Check 36.2** What is the primary failing of the basic Molecular Orbital (MO) theory when describing a diatomic molecule at large internuclear distances? How does Valence Bond (VB) theory handle this differently?

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## 5. Hybridization in VB Theory

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### The Concept

In VB theory, atoms form hybrids of their *s* and *p* orbitals before bonding:

$$|sp^3\rangle = \frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)$$

Hybridization	Geometry	Bond angle	Examples
<i>sp</i>	Linear	180°	BeCl <sub>2</sub> , CO <sub>2</sub> , C <sub>2</sub> H <sub>2</sub>
<i>sp</i> <sup>2</sup>	Trigonal planar	120°	BF <sub>3</sub> , C <sub>2</sub> H <sub>4</sub> , graphene
<i>sp</i> <sup>3</sup>	Tetrahedral	109.5°	CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O
<i>sp</i> <sup>3</sup> <i>d</i>	Trigonal bipyramidal	90°/120°	PCl <sub>5</sub>
<i>sp</i> <sup>3</sup> <i>d</i> <sup>2</sup>	Octahedral	90°	SF <sub>6</sub>

### Important Caveat

Hybridization is a mathematical tool in VB theory, **not** a physical process. In MO theory, the same molecular structure emerges naturally from symmetry-adapted combinations without invoking hybridization.

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## 6. MO vs. VB: Summary Comparison

Feature	MO Theory	VB Theory
Starting point	AOs → delocalized MOs	AOs → localized bonds
Electron delocalization	Natural	Requires resonance structures
Dissociation	Incorrect (ionic terms)	Correct
Magnetic properties	Predicts correctly (O <sub>2</sub> )	Fails for O <sub>2</sub>
Symmetry	Uses full molecular symmetry	Uses hybrid orbitals
Aromatic systems	Natural (delocalized π)	Needs resonance
Computational use	Dominant (HF, DFT)	GVB methods

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## Key Equations Summary

Equation	Expression
Heteronuclear LCAO	$\psi = c_A\phi_A + c_B\phi_B \ (c_A \neq c_B)$
Mulliken electronegativity	$\chi_M = (IE + EA)/2$
VB wavefunction ( $H_2$ )	$\Psi = N[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)]$
$sp^3$ hybrid	$\frac{1}{2}(\ s\rangle + \ p_x\rangle + \ p_y\rangle + \ p_z\rangle)$
Bond polarity	$\propto \ c_A\ ^2 - \ c_B\ ^2$

## Recent Literature Spotlight

**"On the Nature of the Chemical Bond in Valence Bond Theory"** S. Shaik, D. Danovich, P. C. Hiberty, Journal of Chemical Physics, 2022, 157, 090901. [DOI](#)

This perspective by the founders of modern valence bond theory provides a comprehensive overview of how VB theory describes covalent bonds, ionic bonds, and the newly identified "charge-shift" bonds. The authors compare VB and MO descriptions of molecules like  $F_2$  and  $C_2$ , showing how both approaches converge when done properly — reinforcing the complementary views of bonding introduced in this lecture.

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## Practice Problems

- 1. HF MO diagram.** Draw the MO diagram for HF. Identify the HOMO and LUMO. Which orbitals are nonbonding? What is the bond order?
- 2. CO.** CO is isoelectronic with  $N_2$ . Draw its MO diagram and explain why the HOMO has more carbon character. Relate this to CO acting as a ligand through C in transition metal complexes.
- 3. MO vs. VB.** Write both the MO and VB wavefunctions for  $H_2$  at equilibrium. Expand the MO wavefunction and identify the ionic and covalent terms. What happens to the MO wavefunction at large internuclear separation?

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Next week: Polyatomic Molecules, Molecular Orbital Theory & Electronic Spectroscopy