

Lecture 36 — Heteronuclear Diatomics & Valence Bond Theory

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

Learning Objectives

- 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

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: $E(2p_{\text{F}}) < E(1s_{\text{H}})$

Bonding MO: More F character ($|c_{\text{F}}| > |c_{\text{H}}|$) — electron density shifted toward F

Antibonding MO: More H character ($|c_{\text{H}}| > |c_{\text{F}}|$)

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

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.

3. MO Diagrams for Common Heteronuclear Diatomics

CO (isoelectronic with N_2)

CO has 14 electrons, same as N_2 . 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 $2p_z$ 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

4. Valence Bond (VB) Theory

Heitler-London Approach (1927)

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

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

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

Comparison: MO vs. VB at Dissociation

MO (σ_g doubly occupied):

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

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?

5. Hybridization in VB Theory

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 ₂ , CO ₂ , C ₂ H ₂
<i>sp</i> ²	Trigonal planar	120°	BF ₃ , C ₂ H ₄ , graphene
<i>sp</i> ³	Tetrahedral	109.5°	CH ₄ , NH ₃ , H ₂ O
<i>sp</i> ³ <i>d</i>	Trigonal bipyramidal	90°/120°	PCl ₅
<i>sp</i> ³ <i>d</i> ²	Octahedral	90°	SF ₆

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.

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 ₂)	Fails for O ₂
Symmetry	Uses full molecular symmetry	Uses hybrid orbitals
Aromatic systems	Natural (delocalized π)	Needs resonance
Computational use	Dominant (HF, DFT)	GVB methods

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.

Practice Problems

- HF MO diagram.** Draw the MO diagram for HF. Identify the HOMO and LUMO. Which orbitals are nonbonding? What is the bond order?
- 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.
- 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?

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