CHEM 103 Valence Bond and Molecular Orbital Theories

Lecture Notes May 4, 2006 Prof. Sevian





Agenda

- Valence bond theory
 - Bonds are formed by overlap of atomic orbitals
 - Before atoms bond, their atomic orbitals can hybridize to prepare for bonding
 - Molecular geometry arises from hybridization of atomic orbitals
 - σ and π bonding orbitals
- Molecular orbital theory
 - Energy level diagrams for simple diatomic molecules
 - Bonding vs. antibonding orbitals → bond order predictions
 - Other predictive features: excited states, paramagnetism

Two competing theories that predict various properties of molecules

Valence bond theory

- Theory of quantum mechanical wave functions that would satisfy Schrodinger equation for the molecule (if it could be solved)
- Lewis structure's electron pairs translated into quantum mechanics
- Electrons in a particular bond are localized to specific valence bond orbitals

Molecular orbital theory

- Theory of quantum mechanical wave functions that would satisfy Schrodinger equation for the molecule (if it could be solved)
- Wave functions (molecular orbitals) are formed from all bonding electrons in molecule
- Electrons in all bonds are spread out (delocalized) over all molecular bonding orbitals in molecule

Mathematically, the approaches are different. Results (predictions) are often the same.

Molecular Orbital Theory

Central ideas:

- Atomic orbitals on all atoms mathematically combine to form molecular orbitals.
- Electrons then populate the molecular orbitals and are delocalized across entire molecule.
 Resulting



Molecular Orbital Theory Principles



- 1. Orbitals are conserved. The total number of molecular orbitals equals the total number of atomic orbitals that contributed.
- 2. Conservation of energy is obeyed. Bonding molecular orbitals have lower energy than the average of the contributing atomic orbitals. Antibonding molecular orbitals have higher energy.
- 3. When assigning electrons to molecular orbitals, the Pauli exclusion principle and Hund's rule still apply.
 - Bond order can be predicted by comparing how many bonding orbitals are filled vs. how many antibonding orbitals are filled.
 - Paramagnetism can be predicted as with electronic configurations of atoms.
- 4. The more similar the atoms are, the more effective the bonding can be. (Molecular orbitals form most effectively when the atoms that contribute the atomic orbitals are most similar.)

Compare and Learn



Molecular orbital theory prediction for H₂ molecule forming from two isolated H atoms

Net 1 bond because 1 pair of electrons in a bonding orbital

Molecular orbital theory prediction for He₂ molecule forming from two isolated He atoms

Net 0 bonds because equal pairs of electrons in bonding and antibonding orbitals



Diatomics Formed from Elements in Second Period of Periodic Table





Note: only the valence level (*n*=2) is shown here





Compare and Learn

	Large	Large 2s-2p interaction				Small 2s-2p interaction			
		B ₂	C ₂	N ₂		O ₂	F ₂	Ne ₂	
	σ_{2v}^*				σ_{2p}^*			11	
	π_{2p}^*				π_{2p}^*	1 1	11 11	11 11	
)	σ_{2p}			11	π_{2p}	11 11	11 11	11 11	
	π_{2p}	1 1	11 11	11 11	σ_{2p}	11	11	11	
	σ_{2s}^*	11	11	11	σ_{2s}^*	11	11	11	
Ĩ	σ_{2s}	11	11	11	σ_{2s}	11	11	11	
Bond order		1	2	3		2	1	0	
Bond enthalpy (kJ/mol) Bond length (Å) Magnetic behavior		290	620	941		495	155	-	
		1.59 Paramagnetic	1.31 Diamagnetic	1.10 Diamagnetic		1.21 Paramagnetic	1.43 Diamagnetic	_	

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Valence Bond Theory vs. Molecular Orbital Theory for O₂



- 1. Molecular shape predicted to be flat
- 2. Correct bond order 2 predicted
- 3. All orbitals are occupied by pairs of electrons – not paramagnetic



- 1. No prediction about molecular shape
- 2. Correct bond order predicted (net pairs of electrons in bonding orbitals)
- 3. Some unpaired electrons paramagnetic