

General Chemistry I

Tutorial 07

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Outline

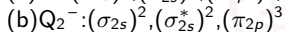
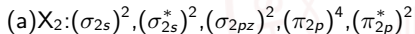
1 Quiz

2 Molecular Orbital Theory



Quiz 7.1

For each of the following valence electron configurations of a homonuclear diatomic molecule or molecular ion, identify the element X or Q, and determine the total bond order.



Quiz 7.2

Compare NO with NO^+ :

- (a) What are their bond orders?
- (b) Which one has shorter bond length?
- (c) Why do higher bond orders correspond to shorter bond lengths in general?

LCAO

- LCAO

If $\psi_1, \psi_2, \psi_3, \dots$ are probable states of a microscopic system, linear combination of atomic orbitals(LCAO) is also a probable configuration:

$$\Psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \dots$$

where c_1, c_2, c_3, \dots are adjustable coefficients that quantify the contribution of each atomic orbital to the molecular orbital.

- Wavefunctions v.s. vectors:

Three-dimensional space: 3 bases span overall space / Every vector can be expressed as a linear combination of 3 bases, e.g.

$$[1, 2, 3]^T = 1[1, 0, 0]^T + 2[0, 1, 0]^T + 3[0, 0, 1]^T$$

Molecular Orbital Theory

Remark 2.1

Three requirements for effective bonding:

- *Compatible orbital symmetries(The most important)*
- *Approximate atomic orbital energies(Lower energy AOs contributes more to lower energy MOs)*
- *Maximum orbital overlap(AOs of adjacent atoms contribute to MOs)*

Types of bonds:

In this course, we mainly consider two types of bonds: σ bond and π bond.

- σ bond: orbitals that are symmetric to rotation about the line connecting the nuclei(bond axis, we often define z axis to be bond axis).
- π bond: There's a nodal plane containing bond axis. (Whether or not there are nodal planes perpendicular to bond axis doesn't determine if bond is π bond)

Molecular Orbital Theory

Notation of orbitals: (σ_g , σ_u^* , π_u , π_g^*)

- Bonding, nonbonding, antibonding(, *)
- Centrosymmetric, antisymmetric (g, u)

Remark 2.2

$$\text{Bond order (B.O.)} = \frac{1}{2}(\# \text{ bonding electrons} - \# \text{ antibonding electrons})$$

- *Bond length decreases with increasing B.O.*
- *Bond energy increases with increasing B.O.*
- *Force constant increases with increasing B.O. (Harmonic oscillator)*

Correlation diagram of homonuclear diatomic molecules

- Valence orbitals(Energy, symmetry)
- Linear combination of AOs to make MOs (Energy, symmetry, bonding/antibonding)
- Fill in electrons
- (Calculate bond order)

Correlation Diagram of Homonuclear Diatomic Molecules

Without considering s-p mixing: $\sigma_{2s} < \sigma_{2s}^* < \sigma_{2pz} < \pi_{2px} = \pi_{2py} < \pi_{2px}^* = \pi_{2py}^* < \sigma_{2pz}^*$

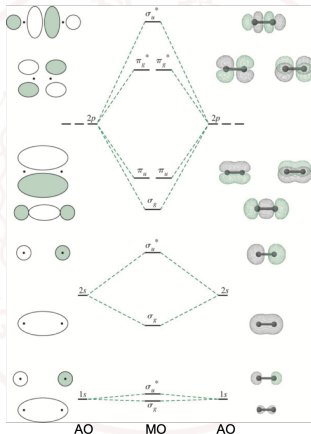


Figure 1: Molecular Orbitals for the First 10 Elements, Assuming Significant Interactions Only between the Valence Atomic Orbitals of Identical Energy.

S-p Mixing

Rev.: AOs have large contribution to MOs only when their energy are fairly close.
For the main group elements within the same period, $\Delta E = E_{np} - E_{ns}$ increases with increasing atomic numbers.[Can be estimated through Slater rules]

$$\Psi = c_1\psi(2s_a) \pm c_2\psi(2s_b) \pm c_3\psi(2p_a) \pm c_4\psi(2p_b)$$

Another way to consider: When two molecular orbitals of the same symmetry mix, the one with higher energy moves still higher in energy, and the one with lower energy moves lower.

Valence Atomic Orbital Energies

Element	1s	2s	2p	3s	3p	4s	4p
H	-13.6						
He	-24.5						
Li		-5.4					
Be		-9.0					
B		-8.4	-8.3				
C		-11.4	-10.7				
N		-13.6	-13.1				
O		-13.6	-15.8				
F		-18.0	-18.7				
Ne		-21.6					
Na			-5.2				
Mg			-7.4				
Al			-5.8	-6			
Si			-8.5	-7.8			
P			-10.5	-10			
S			-10.7	-12			
Cl			-13.1	-13.7			
Ar			-15.9				
K				-4.3			
Ca				-6.1			
Zn				-9.6			
Ga				-12.6	-6		
Ge				-15.8	-7.6		
As				-15.6	-9.1		
Se				-16.8	-10		
Br				-14.1	-12.8		
Kr				-15.5	-14.3		

$E_p - E_s < 15\text{eV}$
 $E_p - E_s > 15\text{eV}$

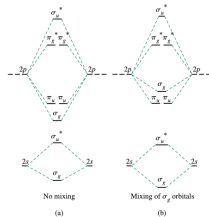


Figure 2: Energy of valence orbitals

Figure 3: S-p mixing

S-p mixing

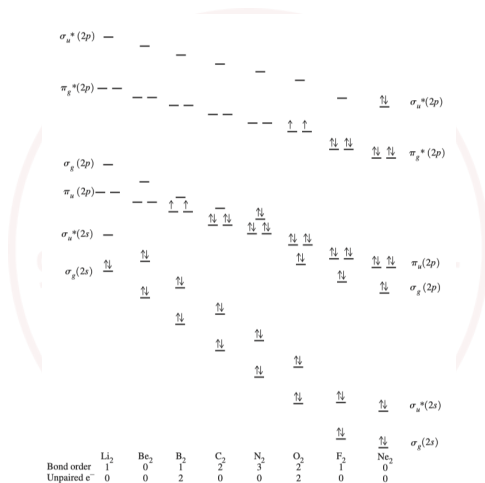


Figure 4: Energy diagram for 2nd period diatomic molecules