

Physical Chemistry

Lecture 23
Diatomic Molecular Orbitals

Molecular orbitals

- ◆ Electronic wave functions for the molecule
- ◆ Various ways to approximate molecular orbitals
 - Linear combination of atomic orbitals (LCAO)
 - Hückel orbitals
 - SCF Hartree-Fock orbitals
 - Valence-bond orbitals
- ◆ Determine approximate energy as an integral of the Hamiltonian operator over the function

$$E = \int_{\text{all space}} \Psi_{MO}^* H \Psi_{MO} d^3\mathbf{r}$$

H₂⁺ molecular orbitals

- ◆ Use LCAO-MO approach
- ◆ Linear combinations of orbitals centered on each atom
- ◆ Normalization constant expressed in terms of overlap integral, S_{AB}
- ◆ Energy determined by integrals over the one-electron orbitals
 - Can be evaluated for 1s orbitals

$$\Psi_{MO,\pm} = \frac{1}{\sqrt{2(1 \pm S_{AB})}} (\Psi_{1sA} \pm \Psi_{1sB})$$

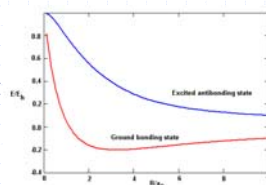
$$E_{MO,\pm} = \frac{1}{1 \pm S_{AB}} \{H_{AA} \pm H_{AB}\}$$

$$H_{AA} = \frac{1}{4\pi\epsilon_0 a_0} \left\{ \left(1 + \frac{a_0}{R} \right) e^{-2R/a_0} - \frac{1}{2} \right\}$$

$$H_{AB} = \frac{1}{4\pi\epsilon_0 a_0} \left\{ S_{AB} \left(\frac{a_0}{R} - \frac{1}{2} \right) - e^{-R/a_0} \left(1 + \frac{R}{a_0} \right) \right\}$$

Energetics of H₂⁺ orbitals

- ◆ Calculation for 1s orbitals
- ◆ One **bonding orbital** has a stable state at a finite nuclear distance
- ◆ One **antibonding orbital** shows no stability, except at the dissociated state



Comparison of MO theory with Lewis theory

- | | |
|---|---|
| <ul style="list-style-type: none"> ◆ MO theory <ul style="list-style-type: none"> ■ Less "ad hoc" ■ Does not give description in terms of atom-centered bonds ■ Difficult to find expressions exactly because of difficulty in solving Schrodinger's equation | <ul style="list-style-type: none"> ◆ Lewis theory <ul style="list-style-type: none"> ■ Ad hoc postulate ■ Focuses on bonding between atomic centers ■ Rules are rather arbitrary ■ Predicts certain bonding motifs and stabilities |
|---|---|

Molecular-orbital symmetry

- ◆ Use eigenvalues to describe properties of wave function
- ◆ Invariance of symmetry properties of the square of the wave function defines wave functions
 - Inversion through origin
 - Reflection through a plane
 - Rotation about an axis
 - Related to angular momentum about axis
- ◆ Symmetry under inversion

$$i \Psi(x, y, z) = \Psi(-x, -y, -z) = \pm \Psi(x, y, z)$$
- ◆ Symmetry under reflection through x-y plane

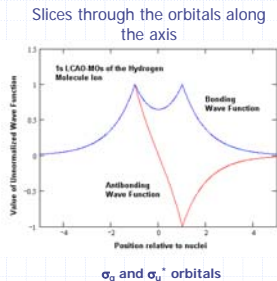
$$\sigma \Psi(x, y, z) = \Psi(x, y, -z) = \pm \Psi(x, y, z)$$
- ◆ Symmetry under rotation by θ

$$R_{z,\theta} \Psi(x, y, z) = \Psi(x \cos \theta + y \sin \theta, y \cos \theta - x \sin \theta, -z) = \pm \Psi(x, y, z)$$

Molecular-orbital nomenclature

◆ Symmetry under inversion

- Eigenvalue of +1
 - Gerade wave function
 - Subscript g
- Eigenvalue of -1
 - Ungerade wave function
 - Subscript u



Excited one-electron LCAO molecular orbitals

◆ Form LCAO-MOs from combinations of higher-energy atomic orbitals

$$\Psi_{\sigma,2s} = N\{\Psi_{2s,A} + \Psi_{2s,B}\}$$

$$\Psi_{\sigma',2s} = N\{\Psi_{2s,A} - \Psi_{2s,B}\}$$

- Must be symmetry-connected
- Estimate energy by integral of Hamiltonian

$$\Psi_{\sigma,2p} = N\{\Psi_{2p,A} + \Psi_{2p,B}\}$$

$$\Psi_{\sigma',2p} = N\{\Psi_{2p,A} - \Psi_{2p,B}\}$$

◆ One-electron MOs used for creating configurations

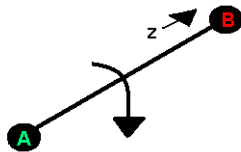
$$\Psi_{\sigma,2p} = N\{\Psi_{2p,A} + \Psi_{2p,B}\} \text{ and } N\{\Psi_{2p,A} - \Psi_{2p,B}\}$$

$$\Psi_{\sigma',2p} = N\{\Psi_{2p,A} + \Psi_{2p,B}\} \text{ and } N\{\Psi_{2p,A} - \Psi_{2p,B}\}$$

Molecular orbital nomenclature

◆ Angular momentum about z (internuclear) axis

- 0, σ state
- ±1, π state
- ±2, δ state
- ±3, φ state
- Et cetera



Molecular aufbau principle

◆ Like aufbau for atoms

◆ Fill one-electron states according to energy

- Have to be aware of Pauli's principle
- Have to be aware of degeneracy of π, δ, φ, etc

◆ Filling order (energy order) for homonuclear diatomic molecules of the first rows

$$\sigma_g(1s), \sigma_u^*(1s), \sigma_g(2s), \sigma_u^*(2s), \pi_u(2p), \sigma_g(2p), \pi_g^*(2p), \sigma_u^*(2p)$$

Hydrogen configurations

◆ Ground configuration

- (1σ_g)²
- L_z(σ_g)² = L_{z1}σ_g + L_{z2}σ_g = 0 (σ_g)²
- i(σ_g)² = (iσ_g)(iσ_g) = (+1σ_g)(+1σ_g) = (+1)²(σ_g)²
- Has to be a singlet because of pairing of electrons

◆ First excited configuration, probably unstable

- (1σ_g)¹(1σ_u^{*})¹
- L_z(σ_g)¹(σ_u^{*})¹ = 0 (σ_g)¹(σ_u^{*})¹
- i(σ_g)¹(σ_u^{*})¹ = (iσ_g)(iσ_u^{*}) = (+1σ_g)(-1σ_u^{*}) = (-1)(σ_g)¹(σ_u^{*})¹
- Can be either a "singlet" or a "triplet" without violating Pauli's principle
- Leads to two terms

Further excited configurations of hydrogen

◆ (1σ_g)¹(2σ_g)¹ or (1σ_g)¹(3σ_g)¹

- L_z(σ_g)(σ_g) = L_{z1}σ_g + L_{z2}σ_g = 0 (σ_g)(σ_g)
- (iσ_g)(iσ_g) = (+1σ_g)(+1σ_g) = (+1)²(σ_g)²
- Can be a singlet or a triplet

◆ (1σ_g)¹(1π_u)¹

- L_z(σ_g)¹(π_u)¹ = L_{z1}(σ_g)(π_u) + (σ_g)L_{z2}(π_u) = 1 (σ_g)¹(π_u)¹
- i(σ_g)¹(π_u)¹ = (iσ_g)(iπ_u) = (+1σ_g)(-1π_u) = (-1)(σ_g)¹(π_u)¹
- Can be either a singlet or a triplet

Labeling homonuclear diatomic terms

- ◆ Use total angular momentum about the z axis as a primary label

Λ	0	1	2	3	4	...
Symbol	Σ	Π	Δ	Φ	Γ	...

- ◆ Use symmetry under inversion as a further label

Eigenvalue +1 -1

Symbol g u

- ◆ Use the total spin, as one does with atoms

S	0	1/2	1	3/2	2	5/2	...
Symbol	1	2	3	4	5	6	...

Terms for H₂

- ◆ Ground state $(1\sigma_g)^2$

- $X^1\Sigma_g^+$

- ◆ First excited configuration $(1\sigma_g)^1(1\sigma_u)^1$

- $B^1\Sigma_u^+$

- $b^3\Sigma_u^+$

- ◆ Next configuration $(1\sigma_g)^1(2\sigma_g)^1$

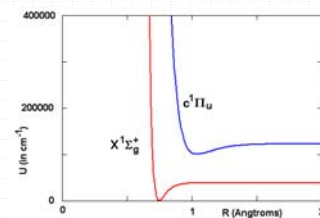
- $E^1\Sigma_g^+$

- $a^3\Sigma_g^+$

- ◆ $(1\sigma_g)^1(1\pi_u)^1$

- $C^1\Pi_u$

- $c^3\Pi_u$



Example potential-energy diagrams for two hydrogen-molecule states

Summary

- ◆ Molecular orbitals describe one-electron states of a molecule
 - LCAO-MO provides a convenient "picture"
 - Hydrogen-molecule-ion states are a simple basis
- ◆ Estimate energies for the approximate states by integration
- ◆ Can use more sophisticated functions with variation principle to get better representations of the states
- ◆ Create configurations by filling via the aufbau principle
 - Must know filling order (i.e. relative energies of states)
 - Remember spatial degeneracies
 - Ensure Pauli's principle is not violated
- ◆ Multi-electron state labeled by
 - Angular momentum about the z axis
 - Inversion symmetry
 - Total spin