

Physical Chemistry

Lecture 23

Diatomic Molecular Orbitals of H_2^+

Molecular orbitals

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

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

H_2^+ molecular orbitals

- ◆ LCAO-MO approach
 - Linear combinations of orbitals centered on each atom
 - Uses a small set of orbitals
- ◆ Normalization constant expressed in terms of an overlap integral, S_{AB}
- ◆ One-electron energy given as integrals over the one-electron orbitals
 - Can be evaluated for hydrogen-like 1s orbitals
 - No electron interaction

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

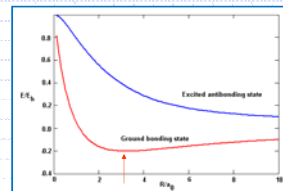
$$E_{MO,\pm} = \frac{1}{1 \pm S_{AB}} \{ H_{AA} \pm H_{AB} \}$$

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

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

Energetics of H_2^+ orbitals

- ◆ Calculation for 1s orbitals
- ◆ The bonding orbital (sum) has a stable state at a finite nuclear distance
- ◆ The antibonding orbital (difference) shows no stability, with minimum energy 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 Schroedinger's equation ■ Modern theory uses numerical solutions <ul style="list-style-type: none"> • Hartree-Fock solutions | <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 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

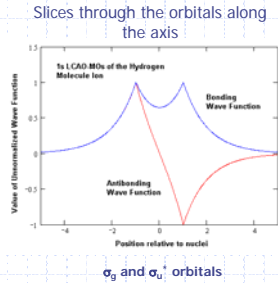
$$\sigma \Psi(x, y, z) = \Psi(x, y, -z) = \pm \Psi(x, y, z)$$
- ◆ Symmetry under rotation by θ

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

H₂⁺ 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 of H₂⁺

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

$$\Psi_{\sigma_{2s}} = N\{\Psi_{2sA} + \Psi_{2sB}\}$$

$$\Psi_{\sigma_{2s}^*} = N\{\Psi_{2sA} - \Psi_{2sB}\}$$

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

$$\Psi_{\sigma_{2p}} = N\{\Psi_{2pA} + \Psi_{2pB}\}$$

$$\Psi_{\sigma_{2p}^*} = N\{\Psi_{2pA} - \Psi_{2pB}\}$$

◆ One-electron MOs used for creating configurations

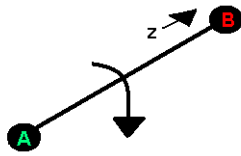
$$\Psi_{\sigma_{2p}} = N\{\Psi_{2pA} - \Psi_{2pB}\} \text{ and } N\{\Psi_{2p,A} - \Psi_{2p,B}\}$$

$$\Psi_{\sigma_{2p}^*} = N\{\Psi_{2pA} + \Psi_{2pB}\} \text{ and } N\{\Psi_{2p,A} + \Psi_{2p,B}\}$$

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
 - Take Pauli's principle into account
 - Be aware of degeneracy of π, δ, φ, etc
- ◆ Filling order (energy order) for homonuclear diatomic molecules of the first rows

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

Dihydrogen configurations

◆ Ground configuration

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

◆ First excited configuration, probably unstable

- $(1\sigma_g)^1(1\sigma_u^*)^1$
- $L_z(\sigma_g)^1(\sigma_u^*)^1 = 0(\sigma_g)^1(\sigma_u^*)^1$
- $i(\sigma_g)^1(\sigma_u^*)^1 = (i\sigma_g)(i\sigma_u^*) = (+1\sigma_g)(-1\sigma_u^*) = (-1)(\sigma_g)^1(\sigma_u^*)^1$
- Can be either a "singlet" or a "triplet" without violating Pauli's principle
- Leads to two terms

Further excited configurations of dihydrogen

◆ $(1\sigma_g)^1(2\sigma_g)^1$ or $(1\sigma_g)^1(3\sigma_g)^1$

- $L_z(\sigma_g)(\sigma_g) = L_{z1}\sigma_g + L_{z2}\sigma_g = 0(\sigma_g)(\sigma_g)$
- $(i\sigma_g)(i\sigma_g) = (+1\sigma_g)(+1\sigma_g) = (+1)^2(\sigma_g)^2$
- Can be a singlet or a triplet

◆ $(1\sigma_g)^1(1\pi_u)^1$

- $L_z(\sigma_g)^1(\pi_u)^1 = L_{z1}(\sigma_g)(\pi_u) + (\sigma_g)L_{z2}(\pi_u) = 1(\sigma_g)^1(\pi_u)^1$
- $i(\sigma_g)^1(\pi_u)^1 = (i\sigma_g)(i\pi_u) = (+1\sigma_g)(-1\pi_u) = (-1)(\sigma_g)^1(\pi_u)^1$
- 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 H_2

- ◆ 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 $(1\sigma_g)^1(2\sigma_g)^1$

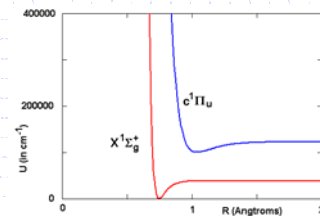
- $E^1\Sigma_g^+$

- $a^3\Sigma_g^+$

- ◆ $(1\sigma_g)^1(1\pi_u)^1$

- $C^1\Pi_u$

- $c^3\Pi_u$



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