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)
    - Hückel orbitals
    - SCF Hartree-Fock orbitals
  - Valence-bond orbitals
- Determine approximate energy as an integral of the Hamiltonian operator over the function
  \[ E = \int \Psi_{\text{MO}}^* H \Psi_{\text{MO}} d^3r \]

$H_2^+$ 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
  \[ \Psi_{\text{MO}} = \frac{1}{\sqrt{2}} (\Psi_1 \pm \Psi_2) \]
  \[ E_{\text{MO}} = \frac{1}{1 \pm S_{ab}} \left[ H_{12} \pm H_{ab} \right] \]
  \[ H_{12} = \frac{1}{4\pi} \int \mathbf{r}_1 \cdot \mathbf{r}_2 \left( \frac{1}{\mathbf{r}_1^2} \right) e^{-r_1} \left( 1 + \frac{1}{\mathbf{r}_2^2} \right) \]

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
- MO theory
  - 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
- Lewis theory
  - 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
  \[ \varphi(x,y,z) = \varphi(-x,-y,-z) = - \varphi(x,y,z) \]
- Symmetry under reflection through $x$-$y$ plane
  \[ \sigma \varphi(x,y,z) = \varphi(x,-y,z) = - \varphi(x,y,z) \]
- Symmetry under rotation by $\theta$
  \[ R_{\theta} \varphi(x,y,z) = \varphi(x \cos \theta + y \sin \theta, y \cos \theta - x \sin \theta, z) \]
**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
  - Must be symmetry-connected
  - Estimate energy by integral of Hamiltonian

**Molecular orbital nomenclature**

- Angular momentum about z (internuclear) axis
  - 0, σ state
  - ±1, π state
  - ±2, δ state
  - ±3, ψ 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, ψ, etc.
- Filling order (energy order) for homonuclear diatomic molecules of the first rows

\[ \sigma_z (1s), \sigma'_z (1s), \sigma_z (2s), \sigma'_z (2s), \pi_z (2p), \sigma_z (2p), \pi'_z (2p), \sigma'_z (2p) \]

**Dihydrogen configurations**

- **Ground configuration**
  - \((1\sigma_g)^2\)
  - \(L_z (\sigma_g) = L_{z1} \sigma_g + L_{z2} \sigma_g = 0 (\sigma_g)^2\)
  - \(i (\sigma_g)^2 = (\sigma_g) (\sigma_g) = (+1) (\sigma_g) = (+1)^2 (\sigma_g)^2\)
  - Has to be a singlet because of pairing of electrons
  - First excited configuration, probably unstable
    - \((1\sigma_g)^1 (1\sigma_u)^1\)
    - \(L_z (\sigma_g) (\sigma_u) = L_{z1} \sigma_g + L_{z2} \sigma_u = 0 (\sigma_u) (\sigma_u)\)
    - \(i (\sigma_u)^2 (\sigma_u) = (\sigma_u) (\sigma_u) = (+1) (\sigma_u) = (+1)^2 (\sigma_u)^2\)
- 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 \((1\sigma_g)^1 (3\sigma_g)^1\)
  - \(L_z (\sigma_g) (\sigma_g) = L_{z1} \sigma_g + L_{z2} \sigma_g = 0 (\sigma_g) (\sigma_g)\)
  - \(i (\sigma_g)^2 (\sigma_g) = (\sigma_g) (\sigma_g) = (+1) (\sigma_g) = (+1)^2 (\sigma_g)^2\)
  - Can be a singlet or a triplet
- \((1\sigma_g)^1 (1\pi_u)^1\)
  - \(L_z (\sigma_g) (\pi_u) = L_{z1} (\sigma_g) (\pi_u) + (\sigma_g) L_{z2} (\pi_u) = 1 (\sigma_g) (\pi_u)\)
  - \(i (\sigma_g)^2 (\pi_u) = (\sigma_g) (\pi_u) = (+1) (\sigma_g) = (+1)^2 (\sigma_g)^2\)
  - Can be either a singlet or a triplet
Labeling homonuclear diatomic terms

- Use total angular momentum about the z axis as a primary label
  \[ \Lambda = 0, 1, 2, 3, 4, \ldots \]
- Use symmetry under inversion as a further label
  \[ \text{Symbol: } \Sigma, \Pi, \Delta, \Phi, \Gamma, \ldots \]
- Use the total spin, as one does with atoms
  \[ S = 0, 1/2, 1, 3/2, 2, 5/2, \ldots \]

Terms for H\textsubscript{2}

- Ground state \((1\sigma_g)^2\)
  - \(\pi_{u}^{\perp}\)
- First excited configuration \((1\sigma_g)^1(1\pi_u)^1\)
  - \(\Delta\)
  - \(\Gamma\)
- Next configuration \((1\pi_u)^2\)
  - \(\Sigma\)
  - \(\Delta\)
- Next configuration \((1\sigma_g)^1(1\pi_u)^1\)
  - \(\Sigma\)
  - \(\Pi, \Delta\)

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