Physical Chemistry

Lecture 24

Diatomic Molecules of the First Row

Molecular aufbau principle

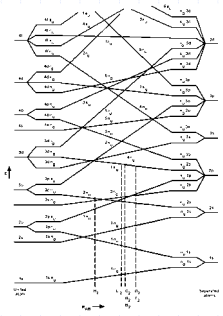
- Like atomic aufbau
- Generalized filling order (energy order) for homonuclear diatomics of the first rows

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

- Pauli's principle may be applicable
- Degeneracy of π, δ, ϕ, etc levels is 2

Multielectron configurations

- Electronic wave functions for multi-electron molecule
- Relative energy order of MOs changes from molecule to molecule
  - Changes the filling order
  - Depends on parameters like the bond length
- Pictured qualitatively in a Walsh diagram



Walsh diagram (after Noggle)

Determining terms from molecular configurations

- Determine eigenvalues of operators that commute with H
  - Angular momentum about the z axis, $L_z = \Sigma L_{zk}$
  - Inversion through the center
  - Reflection through a vertical plane
  - Total spin
- Use Greek letters, subscripts and superscripts to identify terms

Λ	Symbol
0	Σ
1	Π
2	Δ
3	Φ
4	Γ

S	Symbol
0	1
½	2
1	3
3/2	4
2	5

Inversion eigenvalue	Symbol
+1	g
-1	u

Example: ground state of H_2

- The ground state of H_2 has the configuration $(\sigma g1s)^2$
- Total angular momentum is zero
- Spins must be paired
  - Spin is zero
- Both states are even under inversion
  - Product is even under inversion

$$^1\Sigma_g^+$$

Example: excited configuration of H_2

- Excited configuration found by promotion of a single excited MO theory
  - $(\sigma_g 1s)^1 (\sigma_u 1s)^1$
- Qualities
  - $\Lambda = 0$
  - S = 0 or 1
  - Inversion ungerade
- Triplet state is of lower energy by Hund's rules

$$^1\Sigma_u$$

$$^3\Sigma_u$$

Lowest-energy configuration and term of He_2

- Lowest-energy configuration
  - $(1\sigma_g)^2(2\sigma_u)^2$
  - $\Lambda = 0$
  - Even under inversion
  - Has to be a singlet because of pairing of electrons
- Bond order of 0
  - Unstable

$$^1\Sigma_g^+$$

Ground configuration and term of Li_2

- $(1\sigma_g)^2\,(2\sigma_u)^2\,(3\sigma_g)^2$
  - $\Lambda = 0$
  - Even under inversion
  - Has to be a singlet because of pairing of electrons
- Bond order of 1
  - A stable molecule

$$^1\Sigma_g^+$$

Ground configuration and term of C_2

- $(1\sigma_g)^2\,(2\sigma_u)^2\,(3\sigma_g)^2\,(4\sigma_u)^2\,(1\pi_u)^4$
  - Note the filling of the π orbital requires four (4) electrons
- $\Lambda = 0$
- Even under inversion
- Has to be a singlet because of pairing of electrons
- Bond order of 2

$$^1\Sigma_g^+$$

Ground configuration and terms for O_2

- $(1\sigma_g)^2(2\sigma_u)^2\,(3\sigma_g)^2\,(4\sigma_u)^2\,(1\pi_u)^4(5\sigma_g)^2\,(2\pi_g)^2$
- Partially filled π shell
  - Have to determine terms from this partial shell
  - May lead to multiple terms
- Bond order of 2

Terms from the π^2 configuration

- Create all possible product functions
- Create symmetric and antisymmetric combinations
- Determine angular momentum, Λ, about axis
- Determine inversion symmetry
- Determine allowed spin
  - Must know interchange symmetry to determine this

$$\begin{aligned}
\Psi_a &= C_a(\pi_{+1}(1)\pi_{+1}(2)) \\
\Psi_b &= C_b(\pi_{+1}(1)\pi_{-1}(2) + \pi_{-1}(1)\pi_{+1}(2)) \\
\Psi_c &= C_c(\pi_{+1}(1)\pi_{-1}(2) - \pi_{-1}(1)\pi_{+1}(2)) \\
\Psi_d &= C_d(\pi_{-1}(1)\pi_{-1}(2))
\end{aligned}$$

	AM		$inversion$	$interchange$
Λ_a	=	2	*gerade*	*even*
Λ_b	=	0	*gerade*	*even*
Λ_c	=	0	*gerade*	*odd*
Λ_d	=	2	*gerade*	*even*

Terms from the π^2 configuration

- Ψ_a and Ψ_d associated
  - Two states of a Δ term
  - Must be paired with antisymmetric spin function
- Ψ_b and Ψ_c are Σ terms
  - Ψ_b associated with antisymmetric spin function
  - Ψ_c paired with symmetric spin function
- All states are gerade

$$\begin{aligned}
\Psi_a &= C_a(\pi_{+1}(1)\pi_{+1}(2)) \\
\Psi_b &= C_b(\pi_{+1}(1)\pi_{-1}(2) + \pi_{-1}(1)\pi_{+1}(2)) \\
\Psi_c &= C_c(\pi_{+1}(1)\pi_{-1}(2) - \pi_{-1}(1)\pi_{+1}(2)) \\
\Psi_d &= C_d(\pi_{-1}(1)\pi_{-1}(2))
\end{aligned}$$

$$^1\Delta_g: \quad \{\Psi_a, \Psi_d\}$$

$$^1\Sigma_g: \quad \Psi_b$$

$$^3\Sigma_g: \quad \Psi_c$$

Hund's rules applied to O_2

- Choose among the terms that arise from the ground configuration
- Hund's first rule: state of highest spin is ground term

$$^3\Sigma_g$$

Summary

- Aufbau principle permits determination of configurations of diatomic molecules
  - Must know filling order of MOs
  - Correlation (Walsh) diagrams help to know of inversion of energies of MOs
- Terms determined by
  - Angular momentum about the axis
  - Inversion symmetry
  - Spin
- Unsöld's rule applies to molecules
- Partially filled orbitals must be considered carefully
  - Follow Pauli's principle
  - Remember spatial degeneracies