

Diatomic Molecules Part II

Chem 2430

\pm Symmetry: Behavior under $\hat{\sigma}_v$

σ_g, σ_u are + since they have no ϕ dependence

π_+ and π_- are not eigenfunctions of $\hat{\sigma}_v$

but $\pi_+ + \pi_-$ and $\pi_+ - \pi_-$ which give π_x, π_y are

$$\left. \begin{array}{l} \hat{\sigma}_v \quad \pi_x = +\pi_x \\ \hat{\sigma}_v \quad \pi_y = -\pi_y \end{array} \right\} \text{reflection in xz plane}$$

$$\left. \begin{array}{l} \sigma_v \quad \pi_x = -\pi_x \\ \sigma_v \quad \pi_y = \pi_y \end{array} \right\} \text{reflection in yz plane}$$

$$\pi_+^2 \rightarrow {}^1\Delta$$

$$(\pi_+\pi_- + \pi_-\pi_+)(\alpha\beta - \beta\alpha) \quad {}^1\Sigma_g^+$$

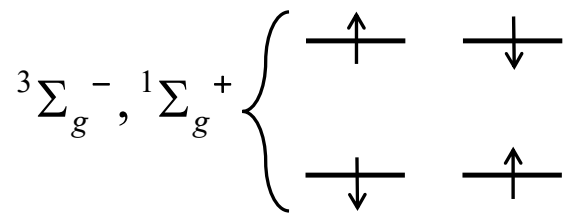
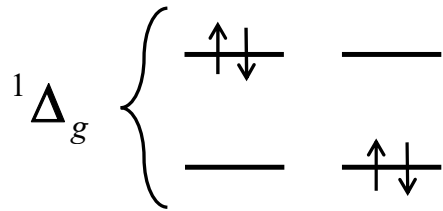
$$(\pi_+\pi_- - \pi_-\pi_+)\alpha\alpha \quad {}^3\Sigma_g^-$$

$$\begin{aligned}(\pi_+\pi_- + \pi_-\pi_+) &= (\pi_x + i\pi_y)(\pi_x - i\pi_y) + (\pi_x - i\pi_y)(\pi_x + i\pi_y) \\ &= \pi_x^2 + \pi_y^2 + i(\pi_y\pi_x - \pi_x\pi_y) + \pi_x^2 + \pi_y^2 - i(\pi_y\pi_x - \pi_x\pi_y) \\ &= \pi_x^2 + \pi_y^2\end{aligned}$$

$$\text{Hence } \sigma_v(\pi_+\pi_- + \pi_-\pi_+) = +(\pi_+\pi_- + \pi_-\pi_+)$$

$$(\pi_+\pi_- - \pi_-\pi_+) = \pi_x\pi_y - \pi_y\pi_x$$

$$\text{So } \sigma_v(\pi_+\pi_- - \pi_-\pi_+) = -(\pi_+\pi_- - \pi_-\pi_+)$$



$L_z \rightarrow \lambda$ for one el. diatomic

$L_z \rightarrow \Lambda$ for a diatomic with ≥ 2 electrons

$$\Lambda \neq 0, \quad m_i = \pm\Lambda$$

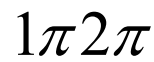


each electron has $m = \pm 1$ so $M = 2, -2, 0$



π electron $m = \pm 1$ $M = \pm 3, \pm 1$ ${}^3\Pi, {}^1\Pi, {}^3\Phi, {}^1\Phi$

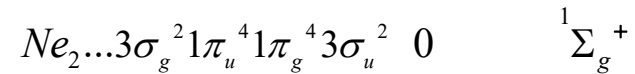
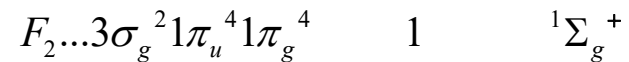
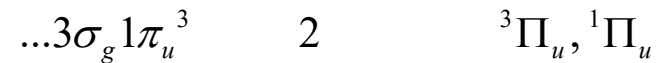
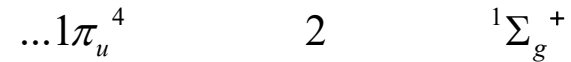
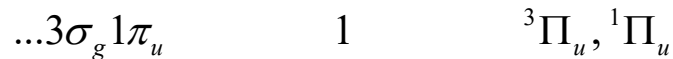
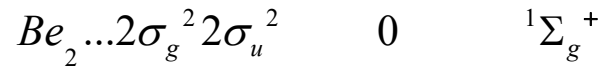
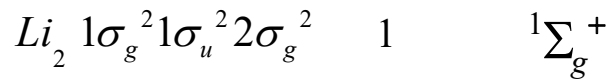
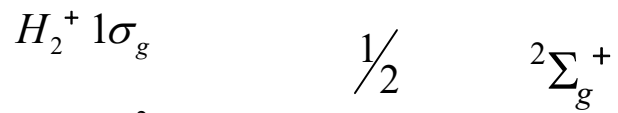
δ electron $m = \pm 2$



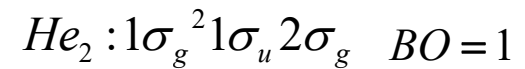
${}^1\Sigma, {}^3\Sigma, {}^1\Sigma, {}^3\Sigma, {}^1\Delta, {}^3\Delta$

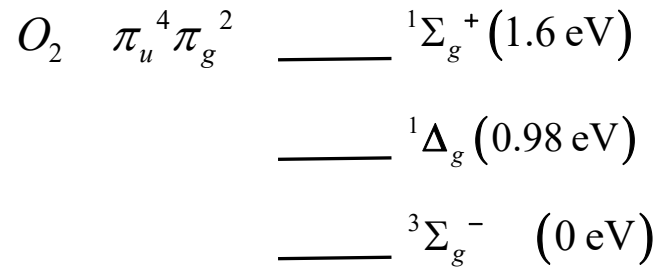
16 arrangements (4 x 4 = 16)

Species/Config Bond Order Term Symbol



Excited states





In spectroscopy the ground state is often labeled as X, and successive excited states (of a given multiplicity) by A, B, C,...

Total angular momentum: combine spin and Λ

$$\Lambda + S, \Lambda + S - 1, \dots, \Lambda - S$$

Analog to the J quantum number for atoms

H_2 molecule

$$\sigma_g = \frac{1}{\sqrt{2(1+S_{AB})}}(1s_A + 1s_B)$$

$$\psi = |\sigma_g \bar{\sigma}_g|$$

With this treatment $D_e = 3.5$ eV vs. 4.75 (exact)

Larger basis set: $D_e = 3.64$ eV

So correlation energy ~ -1.11 eV.

Correlation energy of He atom = -1.14 eV

Roughly speaking correlation energy ≈ -0.9 eV per pair of electrons

$$CI \quad \Psi = c_1 |\sigma_g \bar{\sigma}_g| + c_2 |\sigma_u^* \bar{\sigma}_u^*|$$

$$D_e = 4.03 \text{ eV.}$$

33 configuration wave function $D_e = 4.71$ eV

For the Be atom, the correlation energy is 2.5 eV

Note if one were analyzing this in terms of pair correlation energies, there are 1s-1s, 2s-2s, and 1s-2s pairs

The HF wave function of H_2 has both ionic and covalent components

$$\sigma_g^2 = (1s_a + 1s_b)(1s_a + 1s_b) = (1s_a^2 + 1s_b^2) + (1s_a 1s_b + 1s_b 1s_a)$$

This 50/50 mixture persists at all distances. So the dissociation limit corresponds to $\frac{1}{2} (H+H) + \frac{1}{2} (H^++H^-)$

$$\text{IP } H = 13.6 \text{ eV}$$

$$\text{EA } H \approx 0.7 \text{ eV}$$

So the ionic limit is $\sim 14.2 \text{ eV}$ above the covalent limit

and the $R \rightarrow \infty$ asymptote is $\sim 7.1 \text{ eV}$ too high in energy

Note
$$\sigma_u^2 = (1s_a - 1s_b)(1s_a - 1s_b) = (1s_a^2 + 1s_b^2) - (1s_a 1s_b + 1s_b 1s_a)$$

So by taking $\psi = c_1 \sigma_g^2 + c_2 \sigma_u^2$, we can vary the % of ionic character

At $R = \infty$, $c_2 = -c_1$, and the dissociation is to the purely covalent limit

Valence Bond treatment of H₂

$$\psi = (1s_a 1s_b + 1s_b 1s_a)(\alpha\beta - \beta\alpha)$$

For the simple VB wavefunction

$D_e = 3.15$ eV, which is in poorer agreement with the exact value than is the HF result

Optimize the orbital exponents: $D_e = 3.78$ eV

Expand the basis set : $D_e = 4.04$ eV

Can mix in the ionic configuration

$$\psi = c_1(1s_a 1s_b + 1s_b 1s_a) + c_2(1s_a^2 + 1s_b^2)$$

Equivalent to the two-configuration wave function
based on MOs that we considered earlier

$H_2 : 1\sigma_g \rightarrow 1\sigma_u^*$ excited states

$$\psi_S = (1\sigma_g 1\sigma_u^* + 1\sigma_u^* 1\sigma_g) (\alpha\beta - \beta\alpha) \text{ Singlet}$$

$$\psi_T = (1\sigma_g 1\sigma_u^* - 1\sigma_u^* 1\sigma_g) \begin{cases} \alpha\alpha \\ (\alpha\beta + \beta\alpha) \\ \beta\beta \end{cases}$$

Consider the triplet state

$$\begin{aligned} \psi_T &= (1s_A + 1s_B)(1s_A - 1s_B) - (1s_A - 1s_B)(1s_A + 1s_B) \\ &= (1s_A^2 - 1s_B^2) + (1s_B 1s_A - 1s_A 1s_B) \\ &\quad - (1s_A^2 - 1s_B^2) + (1s_B 1s_A - 1s_A 1s_B) \\ &= 1s_B 1s_A - 1s_A 1s_B \end{aligned}$$

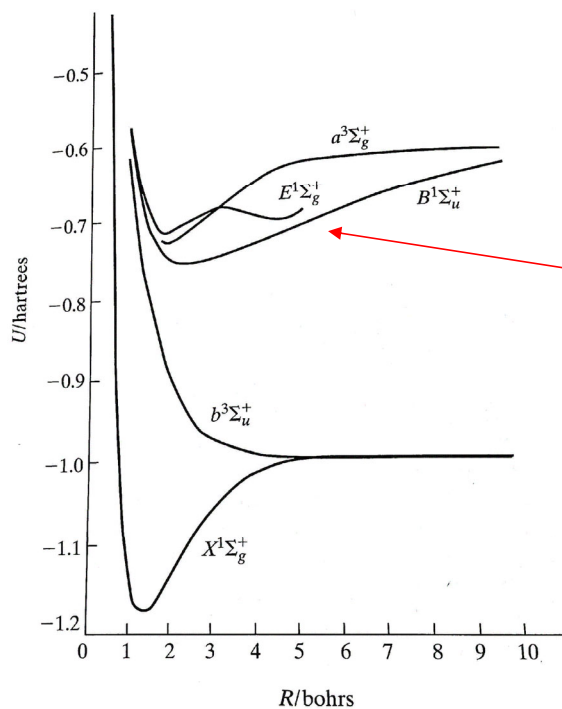
This goes to the same limit as the ground state (with ionic terms removed) as $R = \infty$ i.e., to H atoms with the electrons in their 1s orbitals.

This makes sense at $R = \infty$ we have two $2S$ H atoms, that can couple to a singlet or triplet.

Now let's consider the excited $\sigma_g \sigma_u$ singlet state

$$\psi_s = 1s_A^2 - 1s_B^2$$

This is 100% ionic (H^-H^+ and H^+H^-)



Notice the unusual shape of its potential energy curve which at long should go as R^{-1} due to the ionic nature of the wave function.

Potential energy curves of H₂
From Levine