

CHEM 361B - Lecture 15 Activity

Forming Bonds and Molecular Orbitals

1. Arrange the following species in order of decreasing bond energy and bond length: O_2^+ , O_2 , O_2^- , and O_2^{2-} .
2. CO and NO are two diatomic molecules
 - (a) The ionization energy of CO is greater than that of NO. Explain this difference using molecular orbital diagrams for the two molecules.
 - (b) Using their molecular orbital diagrams, predict that CO will have a stronger bond.
3. We saw in the lecture that H_2^+ has two molecular orbitals, a bonding orbital, and an anti-bonding orbital if we only consider mixing 1s atomic orbitals. We found that the energy of the two molecular orbitals are

$$E_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S}$$

where the unit of energy used is the Hartree ($1 \text{ Hartree} = 4.3597482 \times 10^{-18} \text{ J}$) and

$$S = e^{-R} \left(1 + R + \frac{R^2}{3} \right)$$
$$H_{AA} = -\frac{1}{2} + e^{-2R} \left(1 + \frac{1}{R} \right)$$
$$H_{AB} = -\frac{S}{2} - e^{-R} (1 + R) + \frac{S}{R}$$

and $R = r/a_0$, meaning that R quantifies the internuclear distance between the two protons in units of the Bohr radius (a_0).

- (a) Show that the value of the overlap integral, S , for when $R = 1$ is 0.858, for $R = 2.493$ is 0.46, and for $R = 10$ is 2.01×10^{-3} . Do these values make sense according to what the overlap integral represents?
- (b) Show that $E_+ = -0.288 \text{ Hartree}$ and $E_- = 0.5454 \text{ Hartree}$ when $R = 1$ (meaning the protons are separated by 1 Bohr radius).
- (c) $E_+ = -0.565 \text{ Hartree}$ and $E_- = -0.289 \text{ Hartree}$ when $R = 2.493$ (meaning the protons are separated by 2.493 Bohr radii) and $E_+ = -0.5003 \text{ Hartree}$ and $E_- = -0.4997 \text{ Hartree}$ when $R = 10$ (meaning the protons are separated by 10 Bohr radii). Based on the known energy values at $R = 1, 2.493$, and 10, determine what is the equilibrium bond distance? Explain why you chose this value.
- (d) Draw a before and after molecular orbital diagram of H_2^+ in the ground state, and the first excited state. Show that the frequency of the photon required excite H_2^+ from the ground state to the first excited state at the equilibrium bond distance is $1.81 \times 10^{15} \text{ Hz}$.

- (e) Why are the energies for E_+ and E_- so close together when $R = 10$?
4. In this problem, we are going to solve for the c_A and c_B for ψ_- .
- (a) Start with E_- and plug that into the equation that results from taking the derivative of the energy of the wavefunction with respect to c_A

$$0 = c_A(H_{AA} - E) + c_B(H_{AB} - ES)$$

or c_B

$$0 = c_A(H_{AB} - ES) + c_B(H_{AA} - E)$$

and show that

$$c_B = -c_A$$

- (b) Since $c_B = -c_A$, plug this into the trial wavefunction to get

$$\psi_{el} = c_A(\psi_{1sA} - \psi_{1sB})$$

Normalize this expression and show that

$$c_A = \frac{1}{\sqrt{2(1-S)}}$$

5. Show that the operator $\hat{O} = \frac{d}{dx}$ is not Hermetian.