

7 Molecular Orbital Theory

- 11/17: 1. The bonding and antibonding potential energy surfaces of H_2^+ were derived in class by applying the linear variational principle to the trial wave function

$$\psi_{\text{trial}} = c_1 1s_A + c_2 1s_B$$

- (a) Estimate the ground-state potential energy surface by computing the first-order *perturbative* change in the energy where the reference Hamiltonian

$$\hat{H}_0 = -\frac{1}{2}\nabla^2 - \frac{1}{r_A}$$

is the Hamiltonian of the hydrogen atom at position A and the perturbation

$$\hat{V} = -\frac{1}{r_B} + \frac{1}{R}$$

is the interaction of a second proton at position B with the proton at position A where R is the internuclear distance. The reference wave function

$$\psi_0 = 1s_A$$

is the $1s$ orbital of hydrogen centered at position A .

- (b) Make a sketch of the potential energy surface from part (a) as a function of R .
- (c) Does the approximation in part (a) produce a stable, bound ground state for H_2^+ ?
- (d) In a second sketch, compare the potential energy surface in part (a) with the bonding and antibonding potential energy surfaces of H_2^+ that were derived in class from the trial wave function above.
- (e) Using the trial wave function for comparison, explain briefly in terms of bonding — the sharing of electrons — the limitation of the wave function in part (a).
- (f) Furnish the trial wave function that within the variational approximation would give the same potential energy surface as the application of first-order perturbation theory in (a).
2. The Coulomb integral for H_2^+ is given by

$$J(R) = e^{-2R} \left(1 + \frac{1}{R} \right)$$

- (a) By making a sketch of $J(R)$ as a function of the internuclear distance R , show that $J(R)$ is nonnegative for all R .
- (b) The $J(R)$ results from two competing forces: (i) the attraction of an electron on A to the proton at B and (ii) the repulsion of the proton at A from the proton at B . What does the nonnegativity of $J(R)$ in part (a) say about the relative strengths of these competing forces?
3. (a) Give the molecular orbital diagrams for the molecules N_2 , N_2^+ , O_2 , and O_2^+ .
- (b) What is the bond order for each molecule?
- (c) Explain why N_2 has a larger dissociation energy than N_2^+ , but O_2^+ has a larger dissociation energy than O_2 .
- (d) Using Grassmann notation, give the ground-state wave function for N_2 in molecular orbital theory.
4. Using the worksheet “Huckel Theory” with the Quantum Chemistry Toolbox for Maple, answer the lettered questions.
5. In photoelectron spectroscopy, radiation interacts with gaseous molecules to eject electrons whose kinetic energies are measured (recall the photoelectric effect).

- (a) Explain why measuring the kinetic energy of the ejected electrons tells us something about the molecular orbital energies.
 - (b) If the incident radiation has a frequency of 57.8 nm, what is the largest electron binding energy that can be measured?
6. (a) Sketch the hybrid orbitals of Be in the molecule BeH_2 and illustrate their role in bonding.
- (b) Using the hybrid orbitals, assemble a molecular orbital diagram for BeH_2 .
- (c) With Grassmann notation, express the MO ground-state wave function for BeH_2 .
7. Using the *hybridized* sp^3 wave functions of CH_4 on McQuarrie and Simon (1997, p. 376), give the probability that an electron in one of the sp^3 wave functions is...
- (a) In carbon's $2p_x$ orbital;
 - (b) In carbon's $2p_z$ orbital.
 - (c) By symmetry, should the results in parts (a) and (b) be the same or different?
8. The π -electrons may be approximated in conjugated and aromatic hydrocarbons through Huckel theory. Use Huckel theory to approximate the energies and the wave functions for...
- (a) The allyl radical;
 - (b) Cyclobutadiene;
 - (c) The cyclopentadienyl radical.
 - (d) For each wave function computed in parts (a), (b), and (c), give a schematic sketch of the molecular orbital contributions. Refer to Figure 10.23 on McQuarrie and Simon (1997, p. 396) for an example of such a sketch.