

Problem Set 8

Due beginning of class on Wednesday, March 21

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

1. *Atkins Exercise 10.10b.* Assume ψ_A and ψ_B are individually normalized and real.
2. *Atkins Exercise 10.11b.* You may assume that the overlap integral $S = 0$ and that A and B are individually normalized and real.
3. *Atkins Problem 10.16.*
4. The ionization energy of H is 13.6 eV, and that of Cl is 13 eV. For, N_2 , F_2 and HCl:
 - (a.) Give the ground-state electron configuration. (As in Figure 10.32, you may exclude $n=1$, except in the case of the H in HCl. You may also exclude $n=2$ for Cl). Be sure to give each molecular orbital its correct σ and π label and fill in the electrons. Include non-bonding orbitals.
 - (b.) What is the bond order for each molecule?
 - (c.) Do you expect the molecules to be stabilized or destabilized with the addition of another electron?
 - (d.) For N_2 and HCl, sketch the molecular orbitals from your diagram in part a, even those that are not filled. (You may ignore the radial component of the atomic orbital wavefunctions and just focus on the angular component. Do not worry about the sign of the lobes but be sure you have all angular nodes in the correct places.)
 - (e.) Approximately how much $1s_H$ character and how much $3p_{z,Cl}$ character do you expect the sigma orbitals to have in the HCl molecular orbitals?
5. (a) In Eqns. 10.12 and 10.15 Atkins gives explicit expressions for $\langle E_{\pm} \rangle$ for the H_2^+ molecular ion in terms of j, k and S . Show that,

$$\alpha = E_{1s} + \frac{e^2}{4\pi\epsilon_0 R} - j \quad \text{and} \quad \beta = E_{1s}S + \frac{e^2}{4\pi\epsilon_0 R}S - k.$$

Where α and β are the coulomb and resonance integrals defined in class.

Atkins also provides these explicit expressions for j , k , and S , on page 380,

$$j = \frac{e^2}{4\pi\epsilon_0 R} \left[1 - \left(1 + \frac{R}{a_0} \right) e^{-2R/a_0} \right] \quad k = \frac{e^2}{4\pi\epsilon_0 a_0} \left(1 + \frac{R}{a_0} \right) e^{-R/a_0} \quad S = \left[1 + \frac{R}{a_0} + \frac{1}{3} \left(\frac{R}{a_0} \right)^2 \right] e^{-R/a_0}.$$

Use these definitions of α and β to plot the expectation value of the energies $\langle E_{\pm} \rangle$ as a function of R from $R=a_0$ to $R=8.5 a_0$. On a separate plot show the values of α , β , and S over the same range. Comment on the energy you obtain for large values of R . Is it consistent with the physical picture of the system? Show the work you do to obtain the expressions you plot.

Advice: A convenient dimensionless variable is $z=R/a_0$. It is also useful to recognize that the Coulomb attraction at the Bohr radius is twice the energy of the $1s$ state, $-e^2/4\pi\epsilon_0 a_0 = 2E_{1s}$. (You can obtain this result by substituting the definition of a_0 and comparing to the expression for the energy of $1s$.) The energy of the $1s$ state is $E_{1s} = -13.6$ eV. You can do this plot with Excel, Mathcad, or any other software you like.

(b.) If we excited the electron from $\langle E_{+} \rangle$ to $\langle E_{-} \rangle$, what would H_2^+ subsequently do?