Chemistry 562 **Spring 2012**

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,

$$\alpha = E_{1s} + \frac{e^2}{4\pi\varepsilon_0 R} - j \qquad \text{and} \qquad \beta = E_{1s}S + \frac{e^2}{4\pi\varepsilon_0 R}S - k.$$

   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,

$$j = \frac{e^2}{4\pi\varepsilon_0 R}\left[1 - \left(1 + \frac{R}{a_0}\right)e^{-2R/a_0}\right] \qquad k = \frac{e^2}{4\pi\varepsilon_0 a_0}\left(1 + \frac{R}{a_0}\right)e^{-R/a_0} \qquad S = \left[1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right]e^{-R/a_0}.$$

1) $\int \Psi \Psi = \int (\psi_a + \lambda \psi_b)(\psi_a + \lambda \psi_b) = \overbrace{\int \psi_a \psi_a}^{1} + \int \psi_a \lambda \psi_b$

$\textcircled{+} \int \lambda \psi_b \psi_a + \int \lambda \psi_b \lambda \psi_b$

$$= 1 + \lambda \underbrace{\int \psi_a \psi_b}_{\equiv S} + \lambda \underbrace{\int \psi_a \psi_b}_{\equiv S} + \lambda^2 \underbrace{\int \psi_b \psi_b}_{1}$$

$$= 1 + 2\lambda S + \lambda^2$$

Set equal to $1/N2$ for normalization

$1 + 2\lambda S + \lambda^2 = 1/N^2 \qquad N = \frac{1}{\sqrt{1 + 2\lambda S + \lambda^2}}$

$$\Psi = \frac{1}{(1 + 2\lambda S + \lambda^2)^{1/2}} (\psi_a + \lambda \psi_b)$$

2) if orthogonal, then $\int \psi_a \psi_b = 0$

let $\psi_a = N(\overset{c_1}{0.145}A + \overset{c_2}{0.844}B)$

$\psi_b = M(c_3 A + c_4 B)$

$$N \cdot M \int (c_1 A + c_2 B)(c_3 A + c_4 B) = 0$$

$$c_1 c_3 \int AA + c_1 c_4 \int AB + c_2 c_3 \int BA + c_2 c_4 \int B^2 = 0$$

$$\int AA = 1 \quad , \int BB = 1, \quad \int AB = \int BA = S = 0$$

$$0.145\, c_3 + 0.844\, c_4 = 0 \qquad c_3 = \frac{-0.844\, c_4}{0.145}$$

$$c_3^2 + c_4^2 = 1$$

$$\left(\frac{-.844\, c_4}{0.145}\right)^2 + c_4^2 = 1 \qquad 34.88\, c_4^2 = 1 \qquad c_4 = \pm 0.169$$

$$c_3 = \mp 0.983$$

3) $h_z = s + \left(\frac{3}{2}\right)^{1/2} p_x + \left(\frac{1}{2}\right)^{1/2} p_y$

$$p_x = \frac{1}{\sqrt{2}}\left(p_{+1} - p_{-1}\right) = r\sin\theta\cos\phi\, f(r)$$

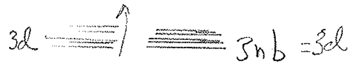
$$p_y = \frac{i}{\sqrt{2}}\left(p_{+1} + p_{-1}\right) = r\sin\theta\sin\phi\, f(r)$$

$$\frac{dh_z}{d\phi} = \cancelto{0}{\frac{ds}{d\phi}} + \sqrt{\frac{3}{2}}\, r\sin\theta\,\frac{d\cos\phi}{d\phi} + \sqrt{\frac{1}{2}}\, r\sin\theta\,\frac{d\sin\phi}{d\phi} = 0$$

(angle to x axis is ϕ)

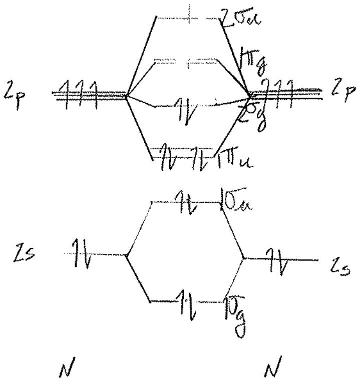
$$+\frac{\sqrt{3}}{\sqrt{2}}\sin\phi = \sqrt{\frac{1}{2}}\cos\phi \qquad \frac{\sin\phi}{\cos\phi} = \sqrt{\frac{1}{2}}\sqrt{\frac{2}{3}} = \tan\phi$$

$\phi = 210°, +30°$ from <u>x-axis</u>

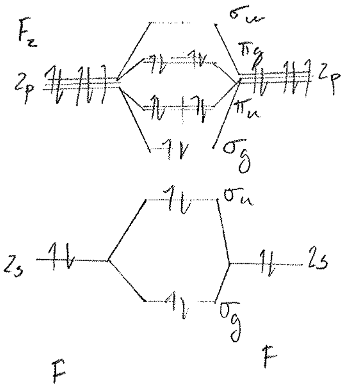


4) a)

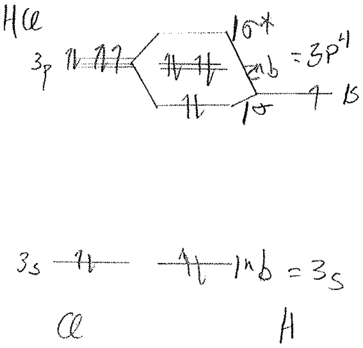
N_2



F_2



HCl



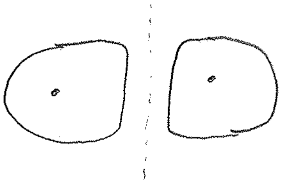
b) BO: 3 1 1

c) All will be destabilized with another e^-. In all cases the LUMO is an anti-bonding orbital

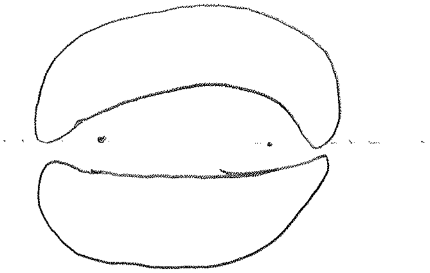
d) N_2:

$1\sigma_g$

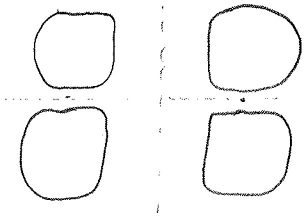
$1\sigma_u$



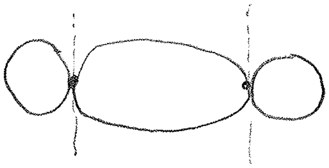
$1\pi_u$



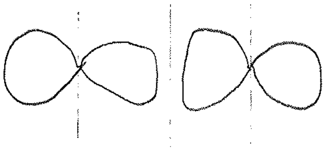
$1\pi_g$



$2\sigma_g$

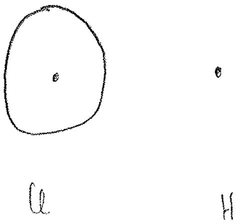


$2\sigma_u$

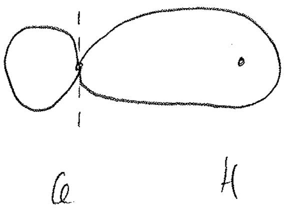


HCl:

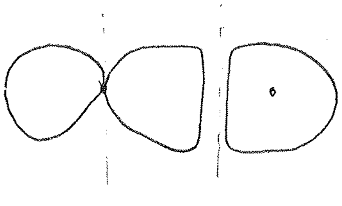
3s



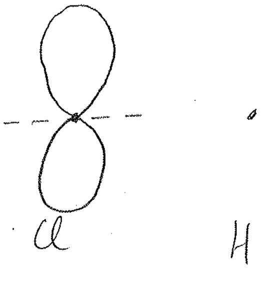
1σ



1σ*



3p



5) $\alpha = \int AHA \qquad \beta = \int AHB \qquad A = \frac{e^{-r_A/a_0}}{\sqrt{\pi a_0^3}}$

$$\alpha = \int A\left(\frac{-\hbar^2}{2m_e}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0 r_{1A}}\right)A \qquad H = \frac{-\hbar^2}{2m_e}\nabla_1^2 + V$$

$$\textcircled{+}\int A \frac{-e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1B}} - \frac{1}{R}\right)A \qquad V = \frac{-e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} - \frac{1}{R}\right)$$

$$= \int A E_{1s} A - \frac{e^2}{4\pi\varepsilon_0}\int \frac{e^{-2r_A/a_0}}{\pi a_0^3}\left(\frac{1}{r_{1B}} - \frac{1}{R}\right) dr$$

$$= E_{1s} - \frac{e^2}{4\pi\varepsilon_0}\left(\int \frac{1}{\pi a_0^3}\frac{e^{-2r_A/a_0}}{r_{1B}} - \frac{1}{R}\int A^2\right)$$

$$= E_{1s} + \frac{e^2}{4\pi\varepsilon_0 R} - \underbrace{\frac{e^2}{4\pi\varepsilon_0}\int \frac{A^2}{r_{1B}}\,d\tau}_{j} = E_{1s} + \frac{e^2}{4\pi\varepsilon_0 R} - j$$

$$\beta = \int A\left(\hat{H}_e - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A} + \frac{-1}{R}\right)\right)B\,d\tau = E_{1s}\int AB + \frac{e^2}{4\pi\varepsilon_0 R}\int AB\,d\tau - \overbrace{\frac{e^2}{4\pi\varepsilon_0}\int \frac{AB}{r_{1A}}\,d\tau}^{k}$$

$$= E_{1s} S + \frac{e^2}{4\pi\varepsilon_0 R}\cdot S - k$$

Problem Set 8

#2 As always, let's define some constants and conversion factors.

$eV := 1.609 \cdot 10^{-19} J$ $\quad e_c := 1.609 \cdot 10^{-19} C$

I need to differentiate between *e* (the charge of an electron) and e (the base of ln)

$A := 10^{-10} m$ $\quad a_0 := 0.53A$

$\varepsilon_0 := 8.854 \cdot 10^{-12} \frac{F}{m}$ $\quad E_{1s} := -13.6eV$

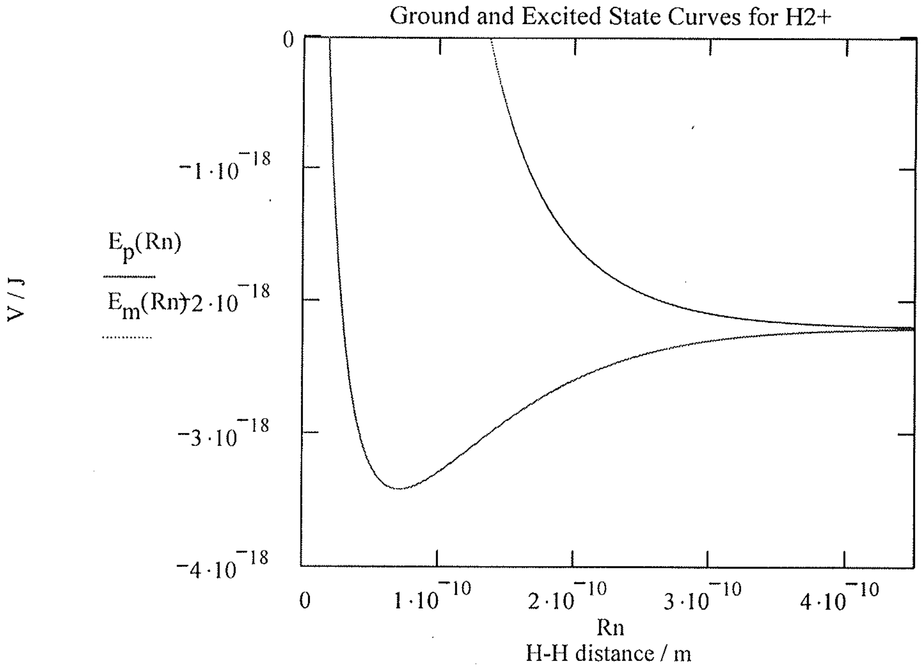
$$j(Rn) := \frac{e_c^{\,2}}{4 \cdot \pi \cdot \varepsilon_0 \cdot Rn} \cdot \left[1 - \left(1 + \frac{Rn}{a_0} \right) \cdot e^{-2\frac{Rn}{a_0}} \right]$$

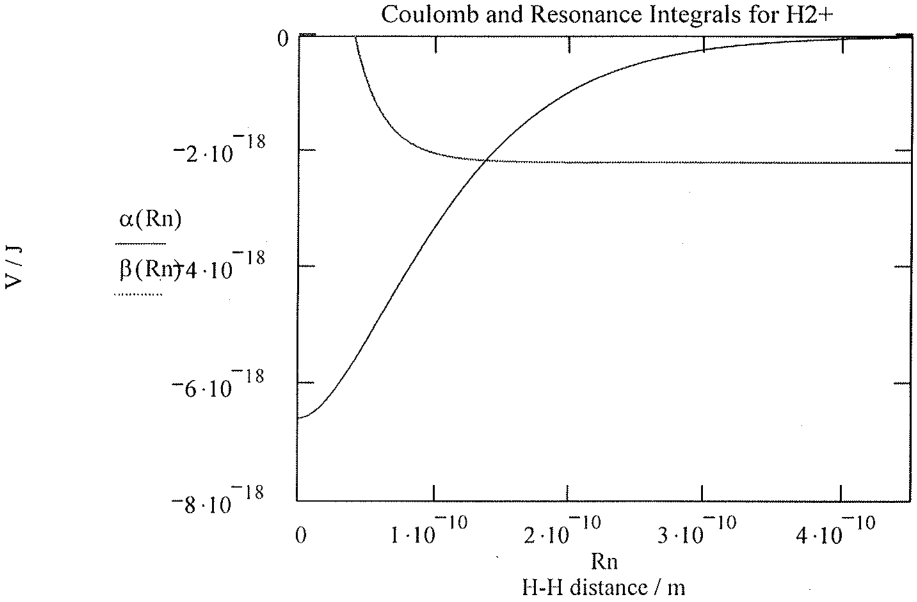
I have used 'Rn' as I found that 'R' was predefined as a conversion between Rankine and Kelvin.

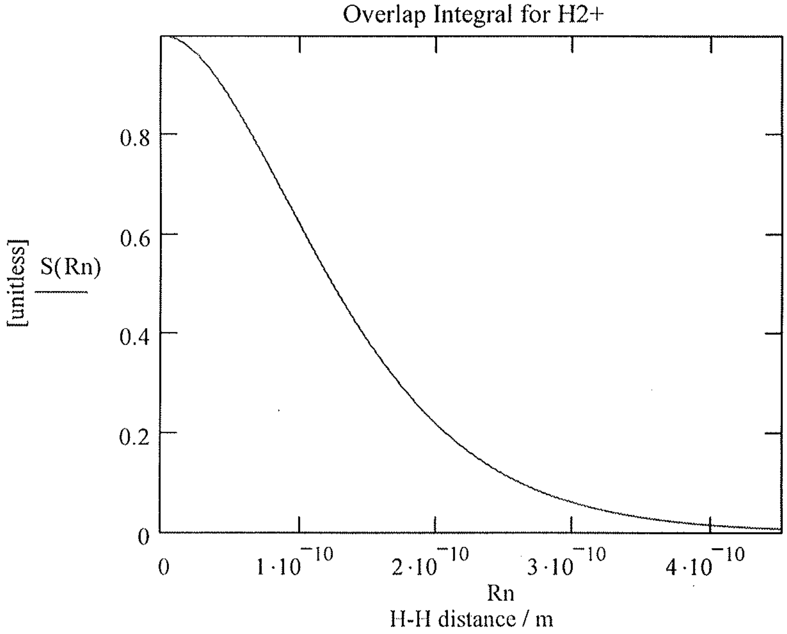
$$k(Rn) := \frac{e_c^{\,2}}{4 \cdot \pi \cdot \varepsilon_0 \cdot a_0} \cdot \left(1 + \frac{Rn}{a_0} \right) e^{\frac{-Rn}{a_0}} \qquad S(Rn) := \left[1 + \frac{Rn}{a_0} + \frac{1}{3} \left(\frac{Rn}{a_0} \right)^2 \right] e^{\frac{-Rn}{a_0}}$$

$$\alpha(Rn) := E_{1s} + \frac{e_c^{\,2}}{4 \cdot \pi \cdot \varepsilon_0 \cdot Rn} - j(Rn) \qquad \beta(Rn) := E_{1s} \cdot S(Rn) + \frac{e_c^{\,2}}{4 \cdot \pi \cdot \varepsilon_0 \cdot R} \cdot S(Rn) - k(Rn)$$

$$E_p(Rn) := \frac{\alpha(Rn) + \beta(Rn)}{1 + S(Rn)} \qquad E_m(Rn) := \frac{\alpha(Rn) - \beta(Rn)}{1 - S(Rn)}$$







At large values of R, the energy of the excited state converges to the same energy as the ground state. This is equivalent to saying that pulling the molecule apart from the ground state will lead to the same products as letting the excited state fly apart. In this case, that would be one proton and one hydrogen atom, with the hydrogen atom in its ground state. *see PS 9*

b) As stated above, we would expect the two nuclei to fly apart after being excited to the upper state. This is easily visualized by noting that these are potential energy curves and the negative of the slope at all points on Eplus points to larger distance. That is to say there is no bound minimum; H2+* is not stable.