

Problem Set 5
CHM102A

1. (a) Which orbital of Be^{3+} has the same energy as the 2s orbital of the hydrogen atom?

For the Be^{3+} atom, $Z = 4$, and the energy is given by

$$E_n = -13.6 \frac{Z^2}{n^2} \text{eV}$$

Energy of 2s orbital of H-atom is $-13.6/4 \text{eV}$. Thus we have $16/n^2 = 1/4$ or $n = 8$.

- (b) The values of shielding constant σ for Li atom are 0.31 and 1.72 for the 1s and 2s orbitals respectively. Calculate the difference in energies between the 1s and 2s orbitals.

Effective Atomic Number, $Z_{\text{eff}} = (\text{Atomic Number } Z - \text{shielding constant } \sigma)$

Energy of Hydrogen like Energy States follow the expression:

$$E_n = -13.6 \times \frac{Z_{\text{eff}}^2}{n^2} \text{ eV}$$

So, based on the values of Shielding constant provided, we have:

$$E_{1s} = -13.6(3 - 0.31)^2 = -98.4 \text{eV}$$

$$E_{2s} = -13.6 \frac{(3 - 1.72)^2}{2^2} = -5.6 \text{eV}$$

Difference = 92.8 eV.

2. The first two ionization energies of He-atom are 2372.3 KJ/mol and 5250.4 KJ/mol. Assuming that the electron-electron repulsion in the He-atom can be neglected, calculate the effective nuclear charge of He-atom. What is the total multi-electron wavefunction of the ground state of the He-atom in this approximation (no need to normalize the wavefunction)? Include both the spatial and spin parts.

As in question 1,

$$E_n = -13.6 \times \frac{Z_{\text{eff}}^2}{n^2} \text{ eV}$$

So, for the He-atom, we have:

$$E_1 = -13.6 Z_{\text{eff}}^2 \text{eV} = -13.6 Z_{\text{eff}}^2 1.6 \times 10^{-19} \times 6.023 \times 10^{23} \text{J/mol} = 1311 Z_{\text{eff}}^2 \text{KJ/mol}$$

The first ionization energy corresponds to removal of electron from the 1s state. However, unlike in the case of the Hydrogen atom, the ionization energy is NOT the negative of E_1 . The reason is that when the electron is removed from the 1s state, the remaining electron does not have the same energy. It is effectively a hydrogen like atom and sees the entire nuclear charge. Thus, we have:

$$-13.6 * 4eV \approx 5250.4 KJ/mol.$$

The total energy required to remove both electrons should be equal to $2E_1$. Thus, we have

$$2E_1 = 2622Z_{eff}^2 = 2372.2 + 5250.4$$

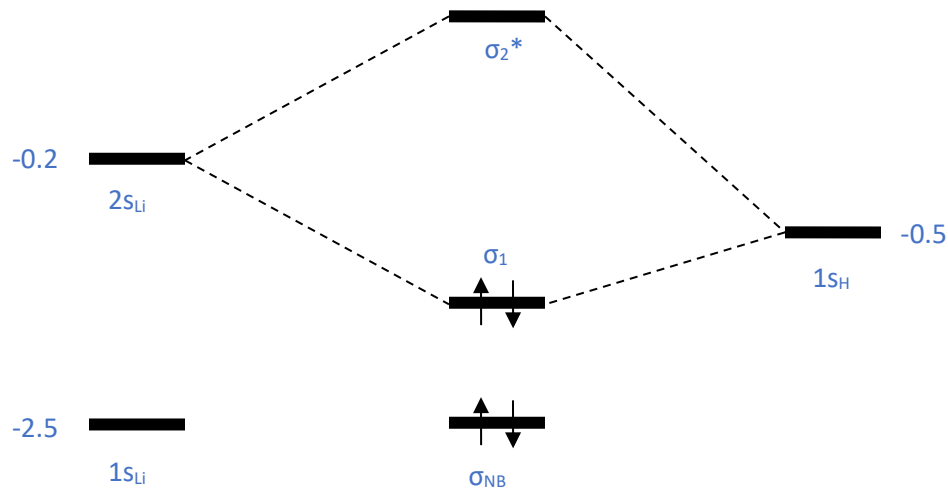
Solving we get, $Z_{eff} = 1.705$. The ground state wavefunction is:

$$\psi(\vec{r}_1, s_1; \vec{r}_2, s_2) = Ne^{-1.705r_1/a_0}e^{-1.705r_2/a_0}(\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1))$$

3. The atomic orbitals of Li have energies $E_{1s} \approx -2.5$ and $E_{2s} \approx -0.2$ Hartrees (where, 1 Hartree = 27.2 eV). Based on energetic criteria alone, qualitatively write down the occupied molecular orbitals of LiH. Given that LiH is ionic *i.e.*, Li^+H^- , what can you say about the atomic orbital coefficients of the highest occupied molecular orbital?

Given, 1 Hartree = 27.2 eV;

So, 1s level of H-atom is at -0.5 Hartree



$$\sigma_1 = c_{1s_H} |1s_H\rangle + c_{2s_{Li}} |2s_{Li}\rangle$$

From energetics as seen in the Figure, contribution of $1s_H$ is more to the bond in LiH, *i.e.*, $c_{1s_H} > c_{2s_{Li}}$ & so is the ionic nature Li^+H^- with more electron cloud of H.

4. As a part of Molecular Orbital Theory that you are studying, a useful, but qualitative concept is that of Bond Order (BO), which is given by:

$$BO = \frac{1}{2} |(\text{Number of bonding} - \text{Number of antibonding})|$$

What is the write the electronic configuration and bond order of the following species: O_2^- , N_2^{2+} , F_2 . Identify the HOMO and LUMO in the following species: O_2 , N_2^{2-} , F_2 .

According to MO theory, the electronic configurations are :

O_2^- : $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*3}$: Bond Order = $(6-3)/2 = 1.5$

N_2^{2+} : $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4$: Bond Order = $(4-0)/2 = 2$

F_2 : $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*4}$: Bond Order = $(6-4)/2 = 1$

According to MO theory, the electronic configurations are :

O_2 : $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*2}$: HOMO: $1\pi_g^*$, LUMO: $3\sigma_u^*$

N_2^{2-} : $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4 3\sigma_g^2 1\pi_g^{*2}$: HOMO: $1\pi_g^*$, LUMO: $3\sigma_u^*$

F_2 : $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*4}$: HOMO: $1\pi_g^*$, LUMO: $3\sigma_u^*$

5. The wavenumber of the $j=1 \leftarrow j=0$ rotational transitions for $^1H^{35}Cl$ and $^2H^{35}Cl$ are 20.8784 and 10.7840 cm^{-1} respectively. Accurate atomic masses are 1.007825 *amu* and 2.0140 *amu* for 1H and 2H respectively. The mass of ^{35}Cl is 34.96885 *amu*. Based on this information alone, can you conclude that the bond lengths are the same or different in the two molecules?

Ans. Given wavenumber of the $j=1 \leftarrow j=0$ transitions for $^1H^{35}Cl$ and $^2H^{35}Cl$ are 20.8784 and 10.7840 cm^{-1} respectively.

$$m(^1H) = 1.007825 \text{ amu} ; \quad m(^2H) = 2.0140 \text{ amu} ; \quad m(^{35}Cl) = 34.96885 \text{ amu}$$

$$\therefore \mu(^1H^{35}Cl) = \frac{(1.007825)(34.96885)}{(34.96885 + 1.007825)} \cong 0.97959 \text{ amu} .$$

$$\& \mu(^2H^{35}Cl) = \frac{(2.0140)(34.96885)}{(34.96885 + 2.0140)} \cong 1.90432 \text{ amu} .$$

$$\text{We know that the transition wavenumber} = 2\tilde{B} = \frac{2h}{8\pi^2 c I} = \frac{h}{4\pi^2 c \mu R_e^2}$$

$$\therefore \text{For, } {}^1H^{35}Cl : \frac{h}{4\pi^2 c \mu R_e^2} = 20.8781$$

$$\Rightarrow R_e({}^1H^{35}Cl) = \left\{ \frac{6.63 \times 10^{-34} Js}{4\pi^2 (2.998 \times 10^{10} cm s^{-1}) (20.8781 cm^{-1}) (0.97959 amu)} \right\}^{1/2}$$

$$\simeq 1.2807 \times 10^{-10} m \simeq \underline{128.07 pm}$$

$$\text{Similarly, } R_e({}^2H^{35}Cl) = 1.2780 \times 10^{-10} m \simeq 127.80 pm$$

Yes, we can distinguish (although the difference is small).