

CHEMISTRY 373 –TUTORIAL 10  
PRACTICE FOR MANY-ELECTRON ATOMS AND THE H<sub>2</sub><sup>+</sup> MOLECULE  
March 22

1.

A. The H<sub>2</sub><sup>+</sup> molecule.

2. Given the equilibrium distance in H<sub>2</sub><sup>+</sup> 106 pm and that of H<sub>2</sub> is 74.1 pm, calculate the internuclear repulsion in both cases at  $R_e$ . Using  $D_e(\text{H}_2^+) = 2.79$  eV and  $D_e(\text{H}_2) = 4.78$  eV, calculate  $E_{el}$  in both cases. (Question 12.1 in Alberty and Silbey.)

(Answer: For H<sub>2</sub><sup>+</sup>, we have for internuclear repulsion:

$$\frac{e^2}{(4\pi\epsilon_0)R_e} = \frac{(1.602 \times 10^{-19})^2}{1.06 \times 10^{-10}} (0.8988 \times 10^{10}) = 2.1761 \times 10^{-18} \text{ J or}$$

$$((2.1761 \times 10^{-18}) \div (1.602177 \times 10^{-19})) = 13.582 \text{ eV. Therefore } E_{el} = E(R) - \frac{e^2}{(4\pi\epsilon_0)R}. \text{ At}$$

$$R_e = 106 \text{ pm, } E_{el} = D_e - \frac{e^2}{(4\pi\epsilon_0)R_e} = 2.79 - 13.582 = -10.792 \text{ eV. For H}_2,$$

$$E_{el} = 4.78 - \frac{(1.602 \times 10^{-19})^2}{(7.41 \times 10^{-11})} (0.8988 \times 10^{10}) \div (1.602177 \times 10^{-19}) = -14.649 \text{ eV}$$

3. Derive the values of the normalization constants for both  $\psi_g$  and  $\psi_u$ . (Question 12.3 in Alberty and Silbey.)

(ANS. The normalization constant for  $\psi_g = N_g(1s_A + 1s_B)$  is calculated as follows:

$$\int d\tau \psi_g^* \psi_g = 1,$$

$$N_g^2 \int d\tau (1s_A + 1s_B)^* (1s_A + 1s_B) = 1,$$

$$N_g^2 \left[ \int d\tau 1s_A^* 1s_A + \int d\tau 1s_A^* 1s_B + \int d\tau 1s_B^* 1s_A + \int d\tau 1s_B^* 1s_B \right] = 1.$$

Now, we have

$$\int d\tau 1s_A^* 1s_A = \int d\tau 1s_B^* 1s_B = 1,$$

since the 1s orbitals are normalized. Also, we have

$$\int d\tau 1s_A^* 1s_B = \int d\tau 1s_B^* 1s_A = S,$$

where  $S$  is called the overlap integral. It is a measure of the amount of interpenetration of the 1s orbitals. Therefore, the normalization integral is

$$N_g^2 [2 + 2S] = 1.$$

Therefore, we obtain

$$N_g = \sqrt{\frac{1}{2(1+S)}}.$$

The calculation is the same for  $\psi_u = N_u(1s_A - 1s_B)$ , and we find that

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

and that completes the calculation.)

4. The overlap integral,  $S$ , for the H<sub>2</sub><sup>+</sup> molecule can be evaluated as

$$S = \left( 1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2} \right) e^{-R/a_0}.$$

(a) For what value of  $R$  is  $S$  a maximum?

(b) For what value of  $R$  is  $S$  a minimum?

(c) What is the value of  $S$  at the equilibrium nuclear separation,  $R_e = 106$  pm?

(Answers: Set  $x = R/a_0$ . Then  $0 \leq x < \infty$ , and

$$\frac{d}{dx} \left(1 + x + \frac{1}{3}x^2\right) \exp(-x) = \left(1 + \frac{2}{3}x\right)e^{-x} - \left(1 + x + \frac{1}{3}x^2\right)e^{-x} = -\frac{1}{3}e^{-x}x - \frac{1}{3}e^{-x}x^2$$

$\left(1 + x + \frac{1}{3}x^2\right) \exp(-x)$  Extrema:  $\left\{1, \frac{1}{3}e\right\}$ , at  $\{x = 0\}, \{x = -1\}$ . The extremum at  $x = -1$  has no meaning since  $x \geq 0$ . Furthermore, as  $x \rightarrow \infty$ ,  $S \rightarrow 0$ , which is its minimum value in the range of  $x$ .

$$S = \left(1 + x + \frac{1}{3}x^2\right) \exp(-x)$$

5. Using diagrams, describe why the  $\psi_u$  molecular orbital describes an antibonding situation for  $\text{H}_2^+$ .

(ANS. See Atkins, pages 476 & 478, Figure 14.16 & 14.17)

6. For  $\text{H}_2^+$ , describe how  $E(R)$  varies with the internuclear separation  $R$ . What is the difference between  $D_0$  and  $D_e$ ? What is  $R_e$ ?

(ANS. See Atkins, page 462, Figure 14.1, applied to  $\text{H}_2^+$ . Note that  $D_0$  is not given and is the spectroscopic dissociation constant and is measured from the ground vibrational and rotational level (zero-point energy) to the energy of the dissociated atoms.)