ADVANCED CHEMISTRY – 2008

QUANTUM MECHANICS - SPRING - WEEK 2

Chapter 11

(1) $$V_{NN} = \frac{Z_A Z_B e^2}{(4\pi\varepsilon_0) R_{AB}}$$

H_2 (at $R_e = 74.1\,pm$)

$$V_{NN} = \frac{(1)(1)\,e^2}{(4\pi\varepsilon_0)\,74.1\times10^{-12}\,m} = \cancel{\frac{(1.602\times10^{-19}C)}{4\pi(8.854\times10^{-12}C^2N^{-1}m^{-2})}}$$

$$= \frac{(1.602\times10^{-19}C)^2}{4\pi(8.854\times10^{-12}C^2N^{-1}m^{-2})(74.1\times10^{-12}m)}$$

$$= 3.112845\times10^{-18}\,NM$$

$$= \underline{\underline{3.112845\times10^{-18}\,J}}$$

H_2^+ ($R_e = 106\,pm$)

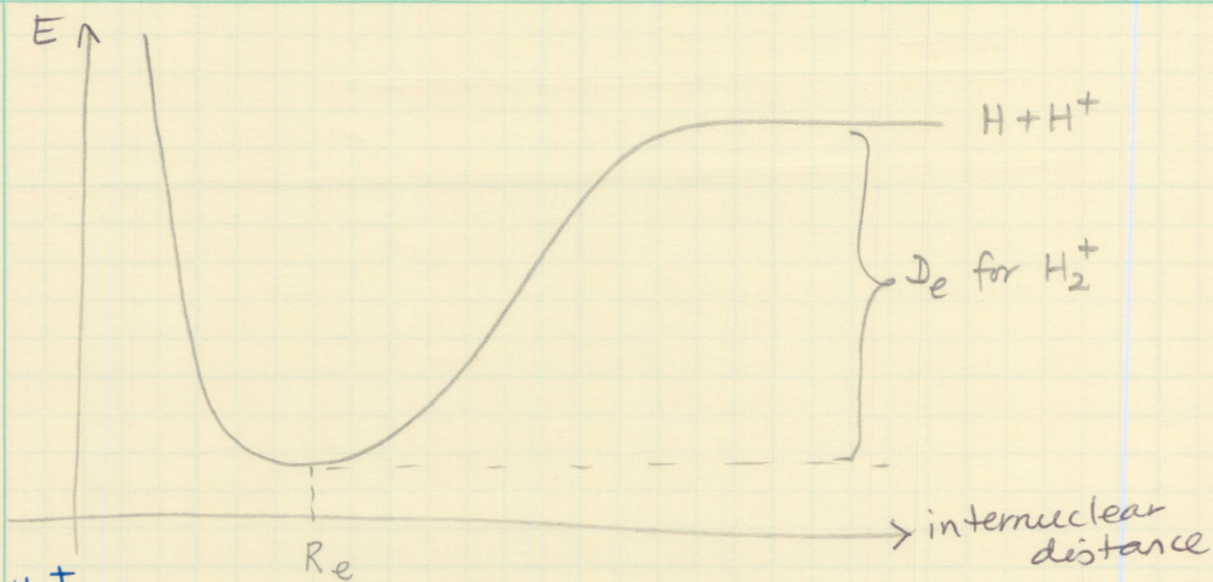
$$V_{NN} = \frac{(1.602\times10^{-19}C)^2}{4\pi(8.854\times10^{-12}C^2N^{-1}m^{-2})(106\times10^{-12}m)}$$

$$= \underline{2.17605\times10^{-18}\,J}$$

$$V_{NN} \text{ for } H_2 = 3.112845\times10^{-18}\,J\left(\frac{eV}{1.602\times10^{-19}\,J}\right)$$

$$= \cancel{19} \;\underline{19.43099\,eV}$$

$$\text{for } H_2^+ \quad V_{NN} = 2.17605\times10^{-18}\,J\times\left(\frac{eV}{1.602\times10^{-19}\,J}\right) = \underline{13.58336\,eV}$$



For H_2^+

D_e ~~for~~ = (energy of H_2^+ at $R = \infty$) − (energy of H_2^+ at Re)

energy of H_2^+ at $(R = \infty)$ = energy of $H + H^+$

$= (-13.6\,eV + 0\,eV)$

$= -13.6\,eV$

$\therefore\ D_e = -13.6\,eV - $ energy of H_2^+ at R_e

$\underbrace{\text{energy of } H_2^+ \text{ at } R_e}_{= U \text{ of } H_2^+ \text{ at } R_e} = -13.6\,eV - De$

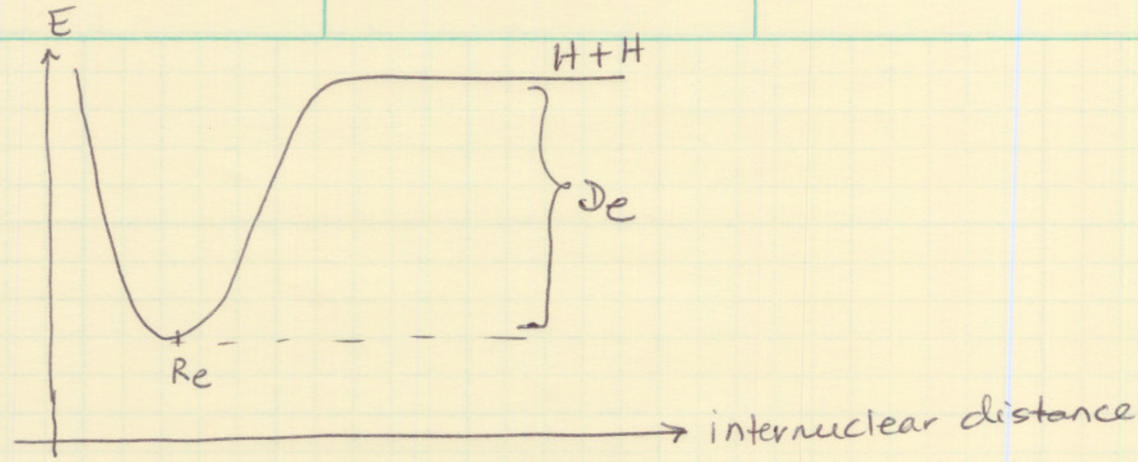
$= -13.6\,eV - 2.79\,eV = -16.39\,eV$

$U = E_{el} + V_{NN}$

$\therefore\ E_{el}$ of H_2^+ at R_e = U of H_2^+ at $R_e - V_{NN}$

$= -16.39\,eV - 13.58336\,eV$

$= \underline{\underline{-29.97\,eV}}$



For H_2

energy of H_2 at $(R = \infty)$ = energy of H + H

$= -2(13.6)\text{ eV} = -27.2\text{ eV}$

$\therefore D_e$ = energy of H_2 at $(R = \infty)$ − energy of H_2 at R_e

$\underbrace{\text{energy of } H_2 \text{ at } R_e}_{= U \text{ of } H_2 \text{ at } R_e} = -D_e +$ energy of H_2 at $R = \infty$

$= -4.78\text{ eV} - 27.2\text{ eV}$

$= -31.98\text{ eV}$

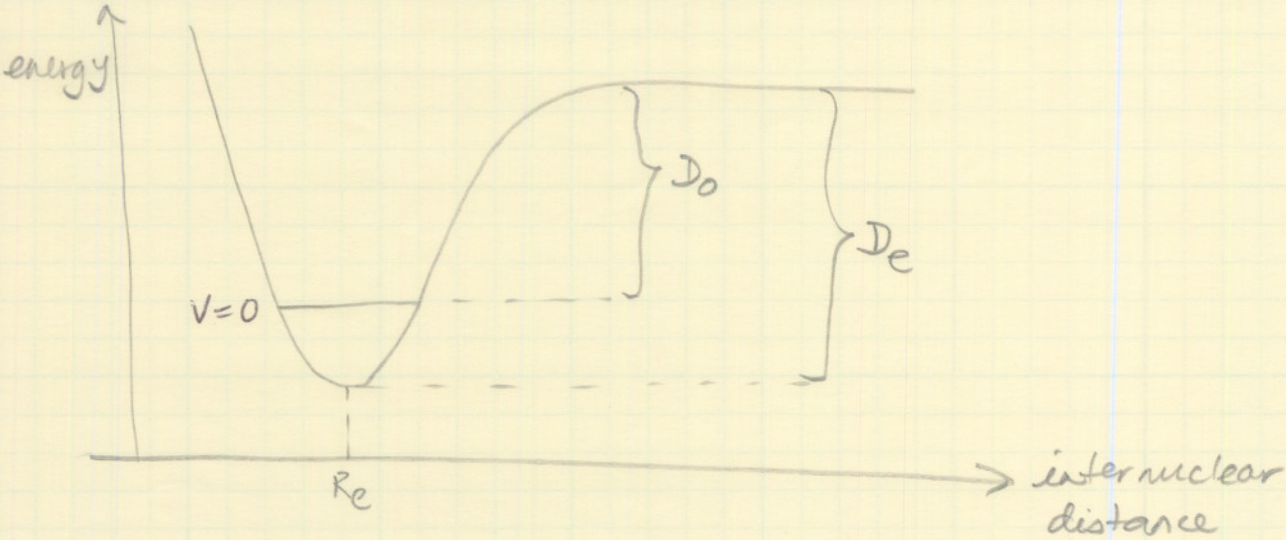
$$U = E_{el} + V_{NN}$$

E_{el} of H_2 at R_e = U of H_2 at $R_e - V_{NN}$

$= -31.98\text{ eV} - 19.43099\text{ eV}$

$= \underline{\underline{-51.41\text{ eV}}}$

(2)



$$D_0 = D_e - (\text{energy of } v=0 \text{ level})$$

$$E_v = \left(v+\tfrac{1}{2}\right)h\nu \Rightarrow E_0 = \tfrac{1}{2}h\nu$$

$$\Rightarrow D_0 = D_e - \tfrac{1}{2}h\nu = 9.902\,\text{eV} - \tfrac{1}{2}\frac{hc}{\lambda}$$

$$= 9.902\,\text{eV} - \tfrac{1}{2}(6.626\times10^{-34}\,\text{Js})(2.99\times10^{8}\,\text{ms}^{-1})(2331\,\text{cm}^{-1})$$

$$= 9.902\,\text{eV} - 9.9059\times10^{-26}\,\text{Jm}\,(2331\,\text{cm}^{-1})\left(\frac{100\,\text{cm}}{\text{m}}\right)$$

$$= 9.902\,\text{eV} - 2.3091\times10^{-20}\,\text{J}\times\left(\frac{\text{eV}}{1.602\times10^{-19}\,\text{J}}\right)$$

$$= 9.758\,\text{eV}\times\left(\frac{1.602\times10^{-19}\,\text{J}}{1\,\text{eV}}\right)\left(\frac{\text{KJ}}{10^{3}\,\text{J}}\right)(6.02\times10^{23}\,\text{mol}^{-1})$$

$$= \underline{\underline{941.05\,\text{KJ}\,\text{mol}^{-1}}}$$

From the worksheet

$$\langle E \rangle = \frac{C_1^2 H_{AA} + 2C_1C_2 H_{AB} + C_2^2 H_{BB}}{C_1^2 + 2C_1C_2 S + C_2^2}$$

$$\langle E \rangle \left[C_1^2 + 2C_1C_2 S + C_2^2\right] = C_1^2 H_{AA} + 2C_1C_2 H_{AB} + C_2^2 H_{BB} \qquad \text{A}$$

$$\frac{\partial}{\partial C_1}\left[\langle E \rangle \left[C_1^2 + 2C_1C_2 S + C_2^2\right]\right] = \frac{\partial}{\partial C_1}\left(C_1^2 H_{AA} + 2C_1C_2 H_{AB} + C_2^2 H_{BB}\right)$$

$$\langle E \rangle \left[2C_1 + 2C_2 S\right] + \frac{\partial \langle E \rangle}{\partial C_1}\left[C_1^2 + 2C_1C_2 S + C_2^2\right] =$$

$$2C_1 H_{AA} + 2C_2 H_{AB}$$

$$\frac{\partial \langle E \rangle}{\partial C_1}\left[C_1^2 + 2C_1C_2 S + C_2^2\right] = 2C_1 H_{AA} + 2C_2 H_{AB} - \langle E \rangle \left[2C_1 + 2C_2 S\right]$$

$$= 2\left(C_1 H_{AA} + C_2 H_{AB}\right) - 2\langle E \rangle \left(C_1 + C_2 S\right)$$

$$\frac{\partial \langle E \rangle}{\partial C_1} = \frac{2\left(C_1 H_{AA} + C_2 H_{AB}\right) - 2\langle E \rangle \left(C_1 + C_2 S\right)}{C_1^2 + 2C_1C_2 S + C_2^2}$$

Similarly using equation (A) and taking the derivative w.r.t. C_2 we get

$$\frac{\partial}{\partial C_2}\left[\langle E\rangle\left[C_1^2 + 2C_1C_2S + C_2^2\right]\right] = \frac{\partial}{\partial C_2}\left[C_1^2H_{AA} + 2C_1C_2H_{AB} + C_2^2H_{BB}\right]$$

$$\langle E\rangle\left[2C_1S + 2C_2\right] + \left[C_1^2 + 2C_1C_2S + C_2^2\right]\left[\frac{\partial\langle E\rangle}{\partial C_2}\right] =$$

$$2C_1H_{AB} + 2C_2H_{BB}$$

$$\left[C_1^2 + 2C_1C_2S + C_2^2\right]\frac{\partial\langle E\rangle}{\partial C_2} = 2C_1H_{AB} + 2C_2H_{BB} - \langle E\rangle\left[2C_1S + 2C_2\right]$$

$$= 2\left(C_1H_{AB} + C_2H_{BB}\right) - 2\langle E\rangle\left(C_1S + C_2\right)$$

$$\frac{\partial\langle E\rangle}{\partial C_2} = \frac{2\left(C_1H_{AB} + C_2H_{BB}\right) - 2\langle E\rangle\left(C_1S + C_2\right)}{C_1^2 + 2C_1C_2S + C_2^2}$$