ATOMS, MOLECULES & REACTIONS

QUANTUM MECHANICS - SPRING 2006 - WEEK 5

Homework sheet

① $$V_{NN} = \frac{(Ze)(Ze)}{(4\pi\varepsilon_0) R_e} = \frac{Z^2 e^2}{(4\pi\varepsilon_0) R_e}$$

For H_2^+ $\quad Z = 1 \quad R_e = 106 \text{ pm} = 106 \times 10^{-12}\text{ m}$

$$V_{NN} = \frac{(1.602 \times 10^{-19}\text{ C})^2}{(4\pi \times 8.854 \times 10^{-12}\text{ C}^2\text{N}^{-1}\text{m}^{-2})(106 \times 10^{-12}\text{ m})}$$

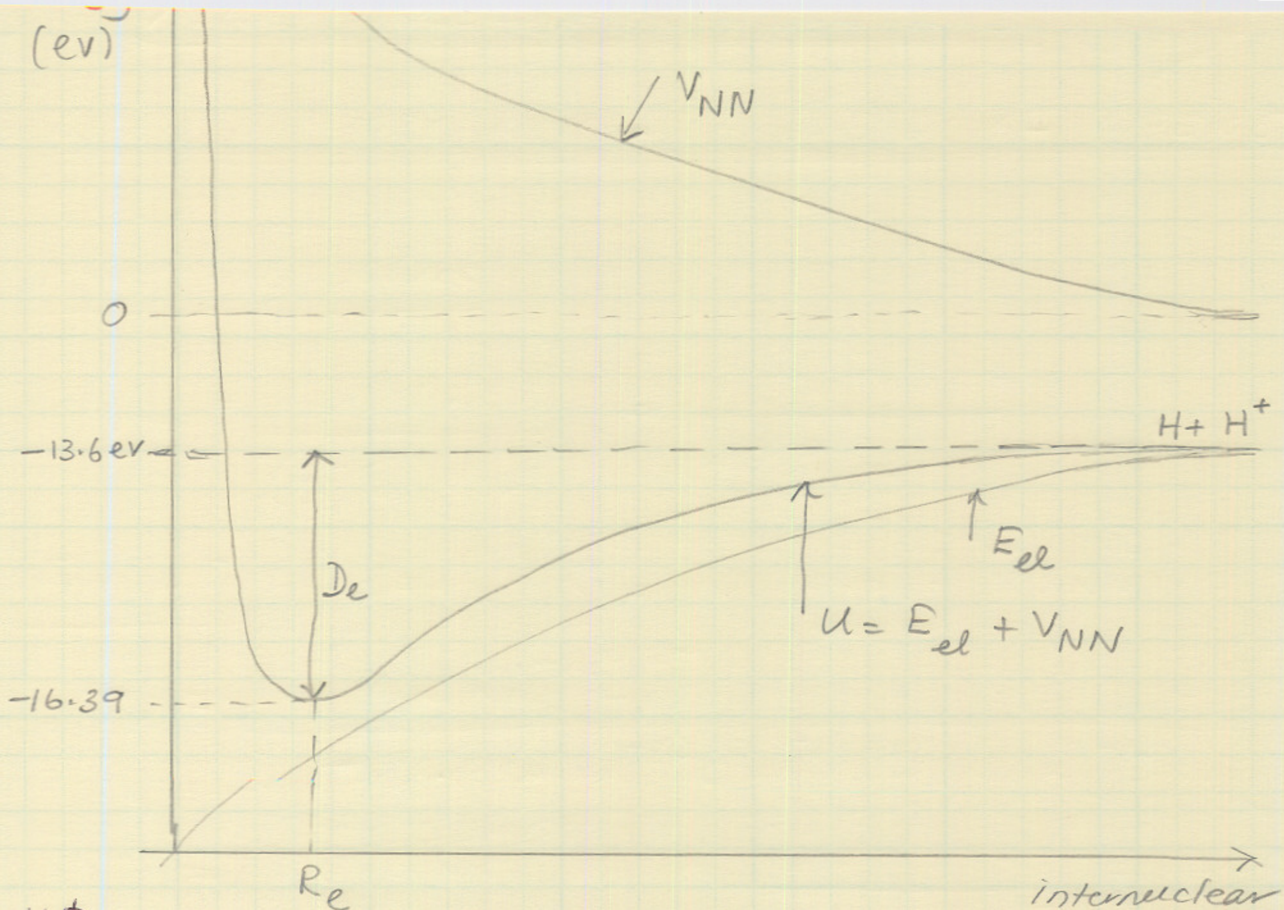
$$= 2.176 \times 10^{-18}\text{ N m} \times \frac{\text{eV}}{1.602 \times 10^{-19}\text{ J}} = \underline{\underline{13.58\text{ eV}}}$$

For H_2 $\quad Z = 1 \quad R_e = 74.1\text{ pm} = 74.1 \times 10^{-12}\text{ m}$

$$V_{NN} = \frac{(1.602 \times 10^{-19}\text{ C})^2}{(4\pi \times 8.854 \times 10^{-12}\text{ C}^2\text{N}^{-1}\text{m}^{-2})(74.1 \times 10^{-12}\text{ m})}$$

$$= 3.113 \times 10^{-18}\text{ N m} \times \frac{\text{eV}}{1.602 \times 10^{-19}\text{ J}} = \underline{\underline{19.43\text{ eV}}}$$

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



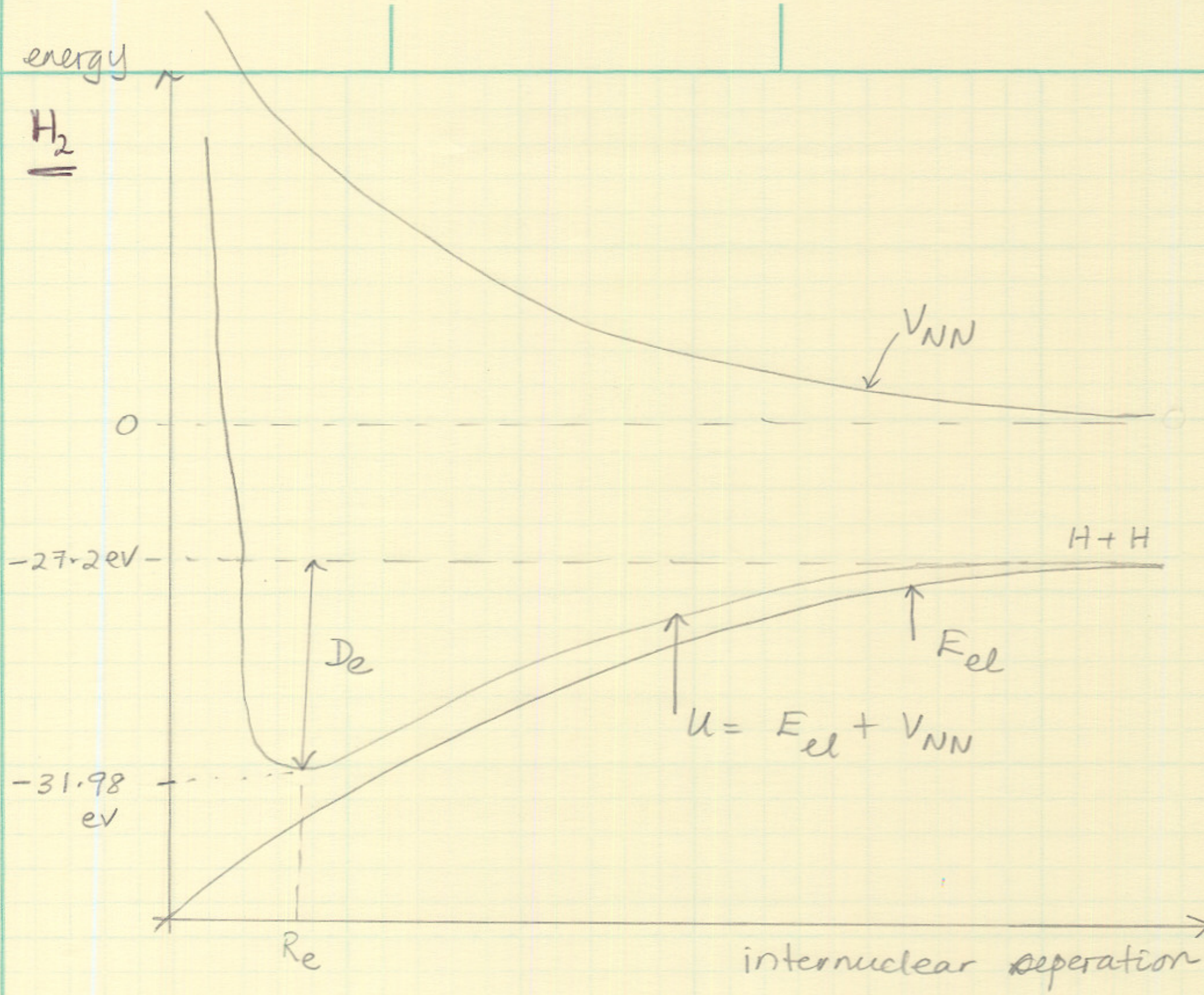
$\underline{H_2^+}$

At R_e $\quad U = E_{el} + V_{NN}$

$$= -(D_e + 13.6\, ev) = -(2.79 + 13.6)\, ev$$

$$U = -16.39\, ev$$

$$E_{el} = U - V_{NN} = -16.39\, eV - 13.583\, ev = \underline{\underline{-29.97\, eV}}$$



at R_e $\quad U = -(27.2 + 4.78)\text{ eV} = -31.98\text{ eV}$

$$E_{el} = U - V_{NN} = -31.98\text{ eV} - 19.431\text{ eV}$$

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

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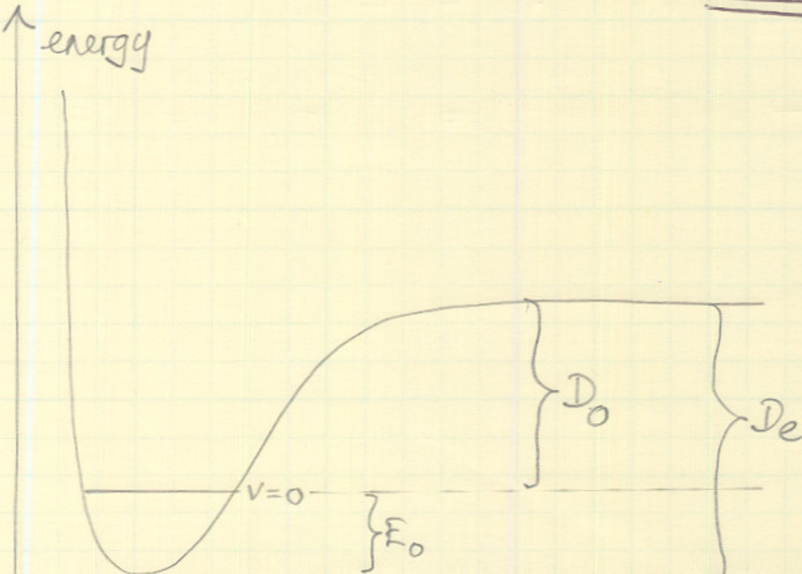

$$D_e = D_0 + E_0$$

$$= \frac{1}{2}h\nu = \frac{1}{2}\frac{hc}{\lambda} = \frac{hc}{2}\left(\frac{1}{\lambda}\right)$$

$$E_0 = \frac{(6.626\times10^{-34}\,\mathrm{J\,s})(2.99\times10^{10}\,\mathrm{cm\,s^{-1}})}{2}(2331\,\mathrm{cm^{-1}})$$

$$= 2.309\times10^{-20}\,\mathrm{J}\left(\frac{1\,\mathrm{eV}}{1.602\times10^{-19}\,\mathrm{J}}\right) = 0.144\,\mathrm{eV}$$

$$D_0 = D_e - E_0 = 9.902\,\mathrm{eV} - 0.144\,\mathrm{eV} = 9.758\,\mathrm{eV}$$

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

$$D_0 = \underline{\underline{941.07\,\mathrm{kJ\,mol^{-1}}}}$$

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① $$E = \frac{C_1^2 H_{AA} + 2C_1C_2 H_{AB} + C_2^2 H_{BB}}{C_1^2 + 2C_1C_2 S + C_2^2}$$

$$E\left[C_1^2 + 2C_1C_2 S + C_2^2\right] = C_1^2 H_{AA} + 2C_1C_2 H_{AB} + C_2^2 H_{BB} \quad \text{— (A)}$$

differentiate w.r.t. C_1

$$\frac{\partial E}{\partial C_1}\left[C_1^2 + 2C_1C_2S + C_2^2\right] + E\left[2C_1 + 2C_2S\right] = 2C_1H_{AA} + 2C_2H_{AB}$$

$$\frac{\partial E}{\partial C_1} = \frac{2C_1H_{AA} + 2C_2H_{AB} - E(2C_1 + 2C_2S)}{C_1^2 + 2C_1C_2S + C_2^2} = 0$$

$$\rightarrow \quad 2C_1H_{AA} + 2C_2H_{AB} - E(2C_1 + 2C_2S) = 0$$

$$C_1(H_{AA} - E) + C_2(H_{AB} - ES) = 0 \quad \text{— (1)}$$

differentiate equation (A) w.r.t. C_2

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

$$\frac{\partial E}{\partial C_2} = \frac{2C_1H_{AB} + 2C_2H_{BB} - 2E(C_1S + C_2)}{C_1^2 + 2C_1C_2S + C_2^2} = 0$$

$$C_1H_{AB} + C_2H_{BB} - E(C_1S + C_2) = 0$$

$$C_1(H_{AB} - ES) + C_2(H_{BB} - E) = 0 \quad \text{— (2)}$$

Secular determinant

$$\begin{vmatrix} H_{AA} - E & H_{AB} - SE \\ H_{BA} - SE & H_{BB} - E \end{vmatrix} = 0$$

$$(H_{AA} - E)(H_{BB} - E) - (H_{BA} - SE)(H_{AB} - SE) = 0$$

since $H_{AA} = H_{BB}$ and $H_{BA} = H_{AB}$

$$(H_{AA} - E)^2 - (H_{AB} - SE)^2 = 0$$

$$(H_{AA} - E + H_{AB} - SE)(H_{AA} - E - H_{AB} + SE) = 0$$

$$\Rightarrow H_{AA} - E + H_{AB} - SE = 0 \quad \text{OR} \quad H_{AA} - E - H_{AB} + SE = 0$$

$$\Rightarrow E_1 = \frac{H_{AA} + H_{AB}}{1+S} \quad \text{OR} \quad E_2 = \frac{H_{AA} - H_{AB}}{1-S}$$

Substitute E_1 in the equation

$$c_1(H_{AA} - E) + c_2(H_{AB} - SE) = 0$$

$$c_1\left[H_{AA} - \frac{H_{AA} + H_{AB}}{1+S}\right] + c_2\left[H_{AB} - \left(\frac{SH_{AA} + SH_{AB}}{1+S}\right)\right] = 0$$

$$c_1\left[\frac{\cancel{H_{AA}} + H_{AA}S - \cancel{H_{AA}} - H_{AB}}{1+S}\right] + c_2\left[\frac{H_{AB} + S\cancel{H_{AB}} - SH_{AA} - S\cancel{H_{AB}}}{1+S}\right] = 0$$

$$c_1\frac{(SH_{AA} - H_{AB})}{(1+S)} + c_2\frac{(H_{AB} - SH_{AA})}{(1+S)} = 0$$

$$c_1(SH_{AA} - H_{AB}) - c_2(SH_{AA} - H_{AB}) = 0$$

$$\Rightarrow \quad \underline{\underline{c_1 = c_2}}$$

use E_2 in the equation

$$c_1(H_{AA} - E) + c_2(H_{AB} - SE) = 0$$

$$c_1\left[H_{AA} - \frac{H_{AA} - H_{AB}}{1-S}\right] + c_2\left[H_{AB} - \left(\frac{SH_{AA} - SH_{AB}}{1-S}\right)\right] = 0$$

$$c_1\left[\frac{\cancel{H_{AA}} - SH_{AA} - \cancel{H_{AA}} + H_{AB}}{1-S}\right] + c_2\left[\frac{H_{AB} - S\cancel{H_{AB}} - SH_{AA} + S\cancel{H_{AB}}}{1-S}\right] = 0$$

$$c_1[H_{AB} - SH_{AA}] + c_2[H_{AB} - SH_{AA}] = 0$$

$$\Rightarrow \quad c_1 = -c_2 \qquad \therefore \quad \underline{\underline{c_1 = \pm c_2}}$$

$$\psi_{H_2^+} = c_1\, 1s_A + c_2\, 1s_B = (c_1\, 1s_A \pm c_1\, 1s_B)$$

$$= c_1 (1s_A \pm 1s_B)$$

$$\int \psi_{H_2^+}^* \psi_{H_2^+}\, d\tau = 1$$

$$\Rightarrow \int c_1^* (1s_A^* \pm 1s_B^*)\, c_1 (1s_A \pm 1s_B)\, d\tau = 1$$

$$c_1^2 \int (1s_A^*\, 1s_A \pm 1s_A^*\, 1s_B \pm 1s_B^*\, 1s_A + 1s_B^*\, 1s_B)\, d\tau = 1$$

$$c_1^2 \left[\int 1s_A^*\, 1s_A\, d\tau \pm \int 1s_A^*\, 1s_B\, d\tau \pm \int 1s_B^*\, 1s_A\, d\tau + \int 1s_B^*\, 1s_B\, d\tau \right] = 1$$

$$c_1^2 [1 \pm s \pm s + 1] = 1$$

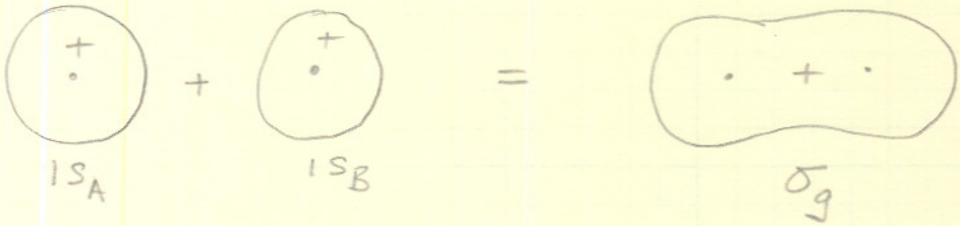
$$2 c_1^2 (1 \pm s) = 1$$

$$c_1^2 = \frac{1}{2(1+s)}$$

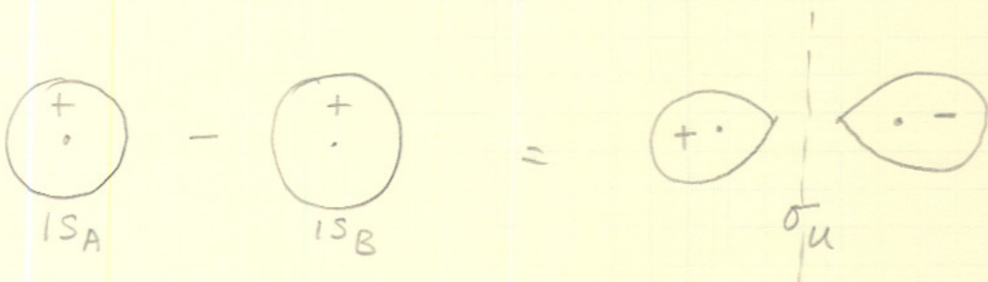
$$\therefore\ c_1 = \frac{1}{\sqrt{2(1+s)}} \quad \text{OR} \quad \frac{1}{\sqrt{2(1-s)}}$$

$$\psi_{H_2^+} = \frac{1}{\sqrt{2(1+S)}}\left(1s_A + 1s_B\right) = \sigma_g$$

$$\psi_{H_2^+} = \frac{1}{\sqrt{2(1-S)}}\left(1s_A - 1s_B\right) = \sigma_u$$



no nodes.



one node ∴ Higher in energy than σ_u