83

QM 115B Lec. 19

Variational Method

any normalized wavefunction $\langle \psi | \psi \rangle = 1$

$$E_{gs} \leq \langle \psi | H | \psi \rangle$$

$$\psi = \sum_n c_n \psi_n \qquad H \psi_n = E_n \psi_n$$

$$1 = \langle \psi | \psi \rangle = \left\langle \sum_m c_m \psi_m \middle| \sum_n c_n \psi_n \right\rangle$$

$$= \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2$$

$$\langle \psi | H | \psi \rangle = \left\langle \sum_m c_m \psi_m \middle| H \middle| \sum_n c_n \psi_n \right\rangle$$

$$= \sum_m \sum_n c_m^* c_n E_n \langle \psi_m | \psi_n \rangle$$

$$= \sum_n |c_n|^2 E_n$$

$$\geq E_{gs} \sum_n |c_n|^2 = E_{gs}$$

eg $H = \frac{-\hbar^2}{2mr^2}\frac{d}{dr}r^2\frac{d}{dr} + \hbar^2\frac{l(l+1)}{2mr^2} - \frac{\hbar\alpha c}{r}$

$l=0 \quad \psi = R(r)\, Y_0^0 \qquad R(r) = A e^{-br}$

$\int_0^\infty r^2 R^2 dr = A^2 \int_0^\infty e^{-2br} r^2 dr = A^2 \frac{2!}{(2b)^3} = 1$

$A^2 = \frac{8b^3}{2} = 4b^3$

$\frac{d}{dr}R = -bAe^{-br} \qquad \frac{d}{dr}r^2\frac{d}{dr}R = -bAe^{-br}(2r - br^2)$

$\langle\psi|H|\psi\rangle = A^2\int_0^\infty dr\, r^2 \left(\left(\frac{-\hbar^2}{2mr^2}\right)(-b(2r-br^2)) - \frac{\hbar\alpha c}{r}\right)e^{-2br}$

$= 4b^3 \int_0^\infty dr\, e^{-2br}\left(\frac{\hbar^2}{2m}(2rb - b^2r^2) - \hbar\alpha c r\right)$

$= 4b^3 \left[\frac{\hbar^2}{2m}\left(\frac{2b\,1!}{(2b)^2} - \frac{b^2\,2!}{(2b)^3} - \frac{\hbar\alpha c\, 1!}{(2b)^2}\right)\right]$

$= 4b^3\left(\frac{\hbar^2}{2m}\left(\frac{1}{2b} - \frac{1}{4b}\right) - \frac{\hbar\alpha c}{4b^2}\right)$

$= \frac{\hbar^2}{2m}b^2 - \hbar\alpha c b$

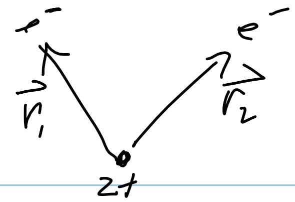
$\frac{d}{db}\langle\psi|H|\psi\rangle = \frac{\hbar^2}{m}b - \hbar\alpha c = 0$

$b = \frac{\alpha m c}{\hbar}$

$\langle\psi|H|\psi\rangle = \frac{\hbar^2}{2m}\left(\frac{\alpha m c}{\hbar}\right)^2 - \hbar\alpha c\left(\frac{\alpha m c}{\hbar}\right) = -\frac{\alpha^2 mc^2}{2}$

$= -13.6\,eV \qquad$ gaussian $\to -11\,eV$

85



Helium Ground State

$$H = -\frac{\hbar}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \hbar\alpha c\left(\frac{2}{r_1} + \frac{2}{r_2} - \underbrace{\frac{1}{|\vec{r}_1 - \vec{r}_2|}}_{= V_{ee}}\right)$$

$$E_{gs,\,exp} = -78.975\,eV$$

1st order pert
$E_{gs} = -75\,eV$

hydrogen $\quad \psi_{100} = \frac{Z^{3/2}}{\sqrt{\pi a^3}} e^{-2r/a}$

trial: $\quad \psi_0 = \psi_{100}(r_1)\,\psi_{100}(r_2) = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \hbar\alpha c\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)$$

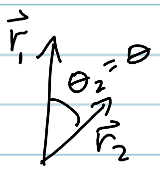
$$+\,\hbar\alpha c\left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right)$$

$$\langle\psi_0|H|\psi_0\rangle = 2Z^2E_1 + 2(Z-2)\hbar\alpha c\langle\psi_0|\tfrac{1}{r}|\psi_0\rangle$$
$$+ \langle\psi_0|V_{ee}|\psi_0\rangle$$

$$\langle\psi_0|\tfrac{1}{r}|\psi_0\rangle = \frac{Z}{a}$$

$$2(Z-2)\hbar\alpha c\langle\psi_0|\tfrac{1}{r}|\psi_0\rangle = 2(Z-2)\hbar\alpha c\frac{Z}{a}$$
$$= 2Z(Z-2)(-2E_1)$$
$$= -4Z(Z-2)E_1$$

$$\langle \psi_0 | V_{ee} | \psi_0 \rangle = \frac{\hbar \alpha c Z^6}{\pi^2 a^6} \int \frac{e^{-2Z(r_1+r_2)/a}}{|\vec{r}_1 - \vec{r}_2|} \, d^3 r_1 \, d^3 r_2$$



$$|\vec{r}_1 - \vec{r}_2| = \sqrt{(r_1 - r_2\cos\theta_2) + r_2^2 \sin^2\theta_2}$$
$$= \sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2}$$

$$I_2 = \int \frac{e^{-2Z r_2/a}}{|\vec{r}_1 - \vec{r}_2|} d^3 r_2 = \int \frac{e^{-2Z r_2/a} \, r_2^2 \sin\theta_2 \, d\theta_2 \, d\phi_2 \, dr_2}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2}}$$

$$= \int_0^\infty dr_2 \, 2\pi \int_0^\pi \frac{\sin\theta \, d\theta}{\sqrt{\underbrace{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta}_{x}}} \, r_2^2 \, e^{-2Z r_2/a} \qquad dx = 2 r_1 r_2 \sin\theta \, d\theta$$

$$= 2\pi \int_0^\infty dr_2 \, r_2^2 \, e^{-2Z r_2/a} \int_{(r_1 - r_2)^2}^{(r_1 + r_2)^2} \frac{1}{\sqrt{x}} \frac{dx}{2 r_1 r_2}$$

$$= 2\pi \int_0^\infty dr_2 \, r_2^2 \, e^{-2Z r_2/a} \left[\frac{\sqrt{x}}{r_1 r_2} \right]_{(r_1 - r_2)^2}^{(r_1 + r_2)^2}$$

$$= 2\pi \int_0^\infty dr_2 \, r_2^2 \, e^{-2Z r_2/a} \underbrace{\left(\frac{r_1 + r_2 - |r_1 - r_2|}{r_1 r_2} \right)}_{\begin{array}{ll} \frac{2}{r_1} & r_2 < r_1 \\ \frac{2}{r_2} & r_2 > r_1 \end{array}}$$

$$= 4\pi \left(\int_0^{r_1} dr_2 \, \frac{r_2^2}{r_1} \, e^{-2Z r_2/a} + \int_{r_1}^\infty dr_2 \, r_2 \, e^{-2Z r_2/a} \right)$$

$$= \frac{\pi a^3}{r_1 Z^3} \left(1 - \left(1 + \frac{r_1 Z}{a} \right) e^{-2Z r_1/a} \right)$$

8)

$$\langle V_{ee} \rangle = \hbar \alpha c \frac{Z^6}{\pi^2 a^6} \int I_2 \, e^{-2Zr_1/a} \, d^3 r_1$$

$$= \frac{\hbar \alpha c}{\pi} \frac{Z^6}{a^3} \int \left(1 - \left(1 + \frac{r_1 Z}{a}\right) e^{-2Zr_1/a}\right) \frac{r_1^2}{r_1} dr_1 \sin\theta d\theta$$

$$= \frac{5}{8} \hbar \alpha c \frac{Z}{a} = -\frac{5Z}{4} E_1$$

$$\langle \psi_0 | H | \psi_0 \rangle = 2Z^2 E_1 - 4Z(Z-2)E_1 - \frac{5}{4} Z E_1$$

$$= \left(-2Z^2 + \frac{27}{4} Z\right) E_1$$

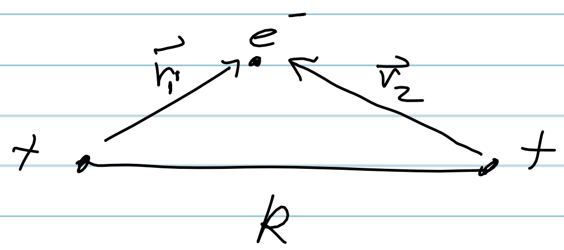
$$\frac{d}{dZ} \langle \psi_0 | H | \psi_0 \rangle = \left(-4Z + \frac{27}{4}\right) E_1 = 0$$

$$Z = \frac{27}{16} = 1.69$$

$$\langle \psi_0 | H | \psi_0 \rangle = \frac{1}{2} \left(\frac{3}{2}\right)^6 E_1 = -77.5 \text{eV}$$

within 2%

Hydrogen Molecule Ion

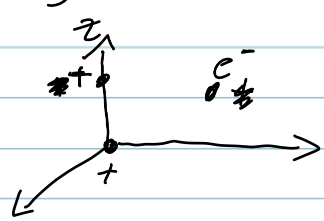


$$H = -\frac{\hbar^2\nabla^2}{2m} - \hbar\alpha c\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad H_{pp} = \frac{\hbar\alpha c}{R}$$

LCAO $\quad \psi = A\left(\psi_0(r_1) + \psi_0(r_2)\right)$

$$\psi_0(r) = \frac{1}{\sqrt{\pi a^3}}\, e^{-r/a}$$

$$1 = \int |\psi|^2 d^3r = |A|^2 \int d^3r \Big(\underbrace{|\psi_0(r_1)|^2}_{=1} + \underbrace{2\psi_0(r_1)\psi_0(r_2)}_{=2I} + \underbrace{|\psi_0(r_2)|^2}_{=1} \Big)$$



$$r_1 = r \qquad r_2 = \sqrt{r^2 + R^2 - 2rR\cos\theta}$$

$$I = \frac{1}{\pi a^3}\int e^{-r/a}\, e^{-\sqrt{r^2+R^2-2rR\cos\theta}}\, r^2 \sin\theta \, d\theta \, d\phi \, dr$$

$$y = \sqrt{r^2+R^2-2rR\cos\theta} \qquad d(y^2) = 2y\,dy = 2rR\sin\theta\, d\theta$$

$$\int_0^\pi e^{-y/a}\sin\theta\, d\theta = \frac{1}{Rr}\int_{|r-R|}^{r+R} e^{-y/a}\, y\, dy$$

$$= -\frac{a}{rR}\left(e^{-(r+R)/a}(r+R+a) - e^{-|r-R|/a}(|r-R|+a) \right)$$

(84)

$$I = \frac{2\pi}{\pi a^3}\frac{a}{R}\left(e^{-R/a}\left(\int_0^\infty (r+R+a)e^{-2r/a} r\,dr + \int_0^R (R-r+a)\, r\,d \right) + e^{R/a}\int_R^\infty (r-R+a)\,e^{-2r/a} r\,dr \right)$$

$$= e^{-R/a}\left(1+\frac{R}{a}+\frac{1}{3}\left(\frac{R}{a}\right)^2\right) \leftarrow \begin{matrix} R\to\infty\ I\to 0 \\ R\to 0\ I\to 1\end{matrix}$$

$$1 = |A|^2(1+2I+1)$$

$$|A|^2 = \frac{1}{2(1+I)}$$

$$\left(-\frac{\hbar^2\nabla^2}{2m} - \frac{\hbar\alpha c}{r}\right)\psi_0(r_1) = \underset{-13.6\,eV}{\overset{}{E_1}}\ \psi_0(r_1)$$

$$H\psi = A\left(-\frac{\hbar^2}{2m}\nabla^2 - \hbar\alpha c\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right)\left(\psi_0(r_1)+\psi_0(r_2)\right)$$

$$= E\psi - A\hbar\alpha c\left(\frac{1}{r_2}\psi_0(r_1) + \frac{1}{r_1}\psi_0(r_2)\right)$$

$$\langle\psi|H|\psi\rangle = E_1 - |A|^2\hbar\alpha c\left(\langle\psi_0(r_1)|\frac{1}{r_2}|\psi_0(r_1)\rangle + \langle\psi_0(r_1)|\frac{1}{r_1}|\psi_0(r_2)\rangle + \langle\psi_0(r_2)|\frac{1}{r_2}|\psi_0(r_1)\rangle + \langle\psi_0(r_2)|\frac{1}{r_1}|\psi_0(r_2)\rangle\right)$$

$$= E_1 - 2|A|^2\hbar\alpha c\left(\langle\psi_0(r_1)|\frac{1}{r_2}|\psi_0(r_1)\rangle + \langle\psi_0(r_1)|\frac{1}{r_1}|\psi_0(r_2)\rangle\right)$$

$D = a \langle \psi_0(r_1) | \frac{1}{r_2} | \psi_0(r_1) \rangle$ direct

$X = a \langle \psi_0(r_1) | \frac{1}{r_1} | \psi_0(r_2) \rangle$ exchange

$$D = \frac{a}{R} - \left(1 + \frac{a}{R}\right) e^{-2R/a}$$

$$X = \left(1 + \frac{R}{a}\right) e^{-R/a}$$

$$E_1 = \frac{-\alpha^2 mc^2}{2} = -\frac{\hbar \alpha c}{2a}$$

$$\langle \psi | H | \psi \rangle = E_1 - 2|A|^2 (-2aE_1)\left(\frac{D}{a} + \frac{X}{a}\right)$$

$$H_{pp} = \frac{\hbar \alpha c}{R} = -\frac{2a}{R} E_1$$

equilibrium $R = 2.4a = 1.3\,\text{Å}$

exp $1.06\,\text{Å}$