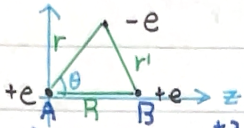
The Hydrogen Molecule Ion



$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_A^2+\nabla_B^2) - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}+\frac{1}{r'}\right) + \frac{e^2}{4\pi\epsilon_0 R}$$

$$\approx -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}+\frac{1}{r'}\right)$$

assume trial wave function $\psi_0(\vec{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{r}{a}}$

$\psi = A[\psi_0(r)+\psi_0(r')]$ ⇐ LCAO technique : molecular wave function as a linear combination of atomic orbitals

$$1 = \int|\psi|^2 d^3\vec{r} = |A|^2\Big[\cancel{\int\psi_0(r)^2 d^3\vec{r}}^{\,1} + \cancel{\int\psi_0(r')^2 d^3\vec{r}}^{\,1} + 2\underbrace{\int\psi_0(r)\psi_0(r')d^3\vec{r}}_{I}\Big]$$

$$I = \frac{1}{\pi a^3}\int e^{-\frac{r+r'}{a}} d^3\vec{r}, \quad r' = \sqrt{r^2+R^2-2rR\cos\theta} \equiv y, \quad d(y^2) = 2y\,dy = 2rR\sin\theta\, d\theta$$

$$= \frac{1}{\pi a^3}\int_0^{\pi} \underbrace{e^{-\frac{r}{a}} e^{-\frac{\sqrt{r^2+R^2-2rR\cos\theta}}{a}}}_{\frac{1}{rR}\int_{|r-R|}^{r+R} e^{-\frac{y}{a}} y\,dy = -\frac{a}{rR}\left[e^{-\frac{r+R}{a}}(r+R+a) - e^{-\frac{|r-R|}{a}}(|r-R|+a)\right]} r^2\sin\theta\, dr\, d\theta\, \underbrace{d\phi}_{2\pi}$$

$$= \frac{2}{a^2R} - e^{-\frac{R}{a}}\int_0^\infty (r+R+a)e^{-\frac{2r}{a}} r\,dr + e^{-\frac{R}{a}}\int_0^R (R-r+a) r\,dr + e^{\frac{R}{a}}\int_R^\infty (r-R+a)e^{-\frac{2r}{a}} r\,dr$$

$$\approx e^{-\frac{R}{a}}\left[1+\frac{R}{a}+\frac{1}{3}\left(\frac{R}{a}\right)^2\right]$$ overlap integral, $R\to 0,\ I=1$; $R\to\infty,\ I=0$

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

$$H\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}+\frac{1}{r'}\right)\right]A[\psi_0(r)+\psi_0(r')] = E_1\psi - A\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r'}\psi_0(r)+\frac{1}{r}\psi_0(r')\right]$$

$$\langle H\rangle = E_1 - 2|A|^2\frac{e^2}{4\pi\epsilon_0}\left[\langle\psi_0(r)|\frac{1}{r'}|\psi_0(r)\rangle + \langle\psi_0(r)|\frac{1}{r}|\psi_0(r')\rangle\right]$$

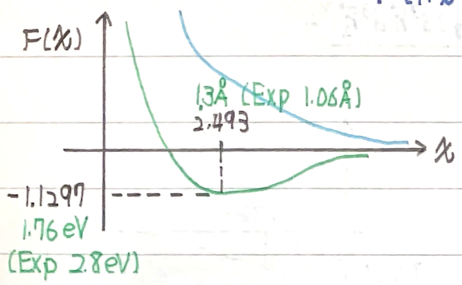
define direct integral, $D \equiv a\langle\psi_0(r)|\frac{1}{r'}|\psi_0(r)\rangle$ exchange integral $X \equiv a\langle\psi_0(r)|\frac{1}{r}|\psi_0(r')\rangle$

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

$$\Rightarrow \langle H\rangle = \left(1+\frac{D+X}{1+I}2\right)E_1$$

$$V_{pp} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{R} = -\frac{2a}{R}E_1$$

total energy $F(x) = \left(-1+\frac{2}{x}\,\frac{(1-\frac{2}{3}x^2)e^{-x}+(1+\underset{\frac{R}{a}}{x})e^{-2x}}{1+(1+x+\frac{1}{3}x^2)e^{-x}}\right)E_1$



if $\psi = A[\psi_0(r)-\psi_0(r')]$

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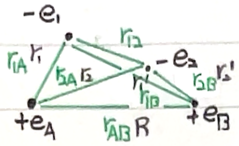
The Hydrogen Molecule



$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) + \frac{e^2}{4\pi\epsilon_0}\left(-\frac{1}{r_{1A}}-\frac{1}{r_{1B}}-\frac{1}{r_{2A}}-\frac{1}{r_{2B}}+\frac{1}{r_{12}}\right) - \frac{e^2}{4\pi\epsilon_0 r_{AB}}$$

$$\left.\begin{aligned} \psi_+(\vec{r}_1,\vec{r}_2) &= A_+\left[\psi_0(r_{1A})\psi_0(r_{2B}) + \psi_0(r_{1B})\psi_0(r_{2A})\right] \\ \psi_-(\vec{r}_1,\vec{r}_2) &= A_-\left[\psi_0(r_{1A})\psi_0(r_{2B}) - \psi_0(r_{1B})\psi_0(r_{2A})\right]\end{aligned}\right\}\ \text{Heitler-London approximation}$$

$$|\psi_\pm(\vec{r}_1,\vec{r}_2)|^2 = A_\pm^2\left[\psi_0(r_{1A})^2\psi_0(r_{2B})^2 + \psi_0(r_{1B})^2\psi_0(r_{2A})^2 \pm 2\psi_0(r_{1A})\psi_0(r_{2B})\psi_0(r_{1B})\psi_0(r_{2A})\right]$$

$$1 = \iint |\psi_\pm(\vec{r}_1,\vec{r}_2)|^2 d^3\vec{r}_1 d^3\vec{r}_2 = \underbrace{A_\pm^2}_{\frac{1}{\sqrt{2(1\pm I^2)}}}\Big[\int\psi_0(r_{1A})^2 d^3\vec{r}_1\int\psi_0(r_{2B})^2 d^3\vec{r}_2 + \int\psi_0(r_{1B})^2 d^3\vec{r}_1\int\psi_0(r_{2A})^2 d^3\vec{r}_2 \pm 2\int\psi_0(r_{1A})\psi_0(r_{2B})d^3\vec{r}_1\int\psi_0(r_{1B})\psi_0(r_{2A})d^3\vec{r}_2\Big]$$

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi_\pm = A_\pm\left\{\left[-\frac{\hbar^2}{2m}\nabla_1^2\psi_0(r_{1A})\right]\psi_0(r_{2B}) \pm \left[-\frac{\hbar^2}{2m}\nabla_1^2\psi_0(r_{1B})\right]\psi_0(r_{2A})\right\} =$$

$$A_\pm\left[\left(E_1+\frac{e^2}{4\pi\epsilon_0 r_{1A}}\right)\psi_0(r_{1A})\psi_0(r_{2B}) \pm \left(E_1+\frac{e^2}{4\pi\epsilon_0 r_{1B}}\right)\psi_0(r_{1B})\psi_0(r_{2A})\right]$$

$$= E_1\psi_\pm + \frac{e^2}{4\pi\epsilon_0 a}A_\pm\left[\frac{a}{r_{1A}}\psi_0(r_{1A})\psi_0(r_{2B}) \pm \frac{a}{r_{1B}}\psi_0(r_{1A})\psi_0(r_{2B})\right] = E_1 + \frac{e^2}{4\pi\epsilon_0 a}\,\frac{1\pm IX}{1\pm I^2}$$

$$\Rightarrow \left\langle -\frac{\hbar^2}{2m}\nabla_1^2\right\rangle = E_1 + \frac{e^2}{4\pi\epsilon_0 a}A_\pm^2\Big[\langle\psi_0(r_{1A})|\frac{a}{r_{1A}}|\psi_0(r_{1A})\rangle\langle\psi_0(r_{2B})|\psi_0(r_{2B})\rangle \pm \langle\psi_0(r_{1B})|\frac{a}{r_{1A}}|\psi_0(r_{1A})\rangle\langle\psi_0(r_{2A})|\psi_0(r_{2B})\rangle$$
$$\pm \langle\psi_0(r_{1A})|\frac{a}{r_{1B}}|\psi_0(r_{1B})\rangle\langle\psi_0(r_{2B})|\psi_0(r_{2A})\rangle \pm \langle\psi_0(r_{1B})|\frac{a}{r_{1B}}|\psi_0(r_{1B})\rangle\langle\psi_0(r_{2A})|\psi_0(r_{2A})\rangle\Big]$$

$$\left\langle -\frac{e^2}{4\pi\epsilon_0 r_{1A}}\right\rangle_\pm = -\frac{e^2}{4\pi\epsilon_0 a}A_\pm^2\Big[\langle\psi_0(r_{1A})|\frac{a}{r_{1A}}|\psi_0(r_{1A})\rangle\langle\psi_0(r_{2B})|\psi_0(r_{2B})\rangle + \langle\psi_0(r_{1B})|\frac{a}{r_{1A}}|\psi_0(r_{1B})\rangle\langle\psi_0(r_{2A})|\psi_0(r_{2A})\rangle$$
$$\pm 2\langle\psi_0(r_{1A})|\frac{a}{r_{1A}}|\psi_0(r_{1B})\rangle\langle\psi_0(r_{2B})|\psi_0(r_{2A})\rangle\langle\psi_0(r_{2B})|\psi_0(r_{2A})\rangle\Big]$$

$$= -\frac{e^2}{4\pi\epsilon_0 a}\,\frac{1}{2(1\pm I^2)}(1\times 1 + D\times 1 \pm 2XI) = -\frac{1}{2}\,\frac{e^2}{4\pi\epsilon_0 a}\,\frac{1+D\pm 2IX}{1\pm I^2}$$

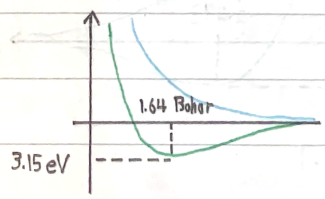
$$\langle V_{ee}\rangle = \frac{e^2}{4\pi\epsilon_0 a}\iint|\psi_\pm(\vec{r}_1,\vec{r}_2)|^2\frac{a}{r_{12}}d^3\vec{r}_1 d^3\vec{r}_2$$

$$= \frac{e^2}{4\pi\epsilon_0 a}A_\pm^2\Big[\overbrace{\iint\psi_0(r_{1A})^2\frac{a}{r_{12}}\psi_0(r_{2B})^2 d^3\vec{r}_1 d^3\vec{r}_2}^{D_2} + \iint\psi_0(r_{1B})^2\frac{a}{r_{12}}\psi_0(r_{2A})d^3\vec{r}_1 d^3\vec{r}_2 \pm 2\underbrace{\iint\psi_0(r_{1A})\psi_0(r_{1B})\frac{a}{r_{12}}\psi_0(r_{2A})\psi_0(r_{2B})d^3\vec{r}_1 d^3\vec{r}_2}_{X_2}\Big]$$

$$= \frac{e^2}{4\pi\epsilon_0 a}\,\frac{D_2\pm X_2}{1\pm I^2}$$

+ singlet − triplet

$$\Rightarrow \langle H\rangle_\pm = 2E_1\left[1-\frac{a}{r_{AB}}+\frac{2D-D_2\pm(2IX-X_2)}{1\pm I^2}\right]$$



exchange splitting $J = \langle H\rangle_+ - \langle H\rangle_-$

$$= 4E_1\frac{(D_2-2D)I^2-(X_2-2IX)}{1-I^4} \approx -10\text{ eV}$$