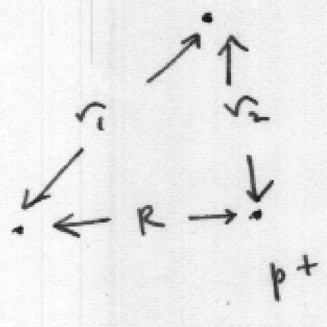
Lecture 6

We now study the H_2^+ ion using the variational method. Since this is a 3-body problem, we simplify it by making the "Born-Oppenheimer" approximation: the motion of the (heavy) protons is neglected compared to that of the (light) electron.



Here R is a fixed parameter. Specifying (r_1, r_2), along with the rotation angle φ of the $e^-p^+p^+$ plane around the p^+p^+ axis, gives the location of the electron. More convenient coordinates in place of r_1, r_2 are

$$\mu = \frac{r_1 + r_2}{R}, \quad \nu = \frac{r_1 - r_2}{R}$$

We have:

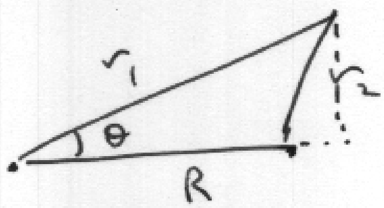
Consider the locus of fixed ν.

If we fix μ (it has to be ≥ 1!) the electron moves keeping the sum of its distances to the two protons fixed. This is an ellipse.

If we fix ν, instead the difference of the two distances is fixed. This is a hyper-bola.

Let's calculate the volume element in (μ, ν, φ) coordinates. First consider spherical polar coordinates centred at the left proton. We have:

$$d^3x = r_1^2 \, dr_1 \, \sin\theta \, d\theta \, d\varphi$$



Now $$r_2^2 = r_1^2 + R^2 - 2 r_1 R \cos\theta$$

from which $$\frac{\partial r_2}{\partial \theta} = \frac{r_1 R \sin\theta}{r_2}$$

Hence $$\sin\theta \, d\theta = \frac{r_2 \, dr_2}{r_1 R}$$

So $$d^3x = \frac{r_1 r_2}{R} \, dr_1 \, dr_2 \, d\varphi$$

Next use

$$r_1 = \tfrac{1}{2}R(\mu+\nu)$$
$$r_2 = \tfrac{1}{2}R(\mu-\nu)$$

So

$$\frac{\partial(r_1, r_2)}{\partial(\mu, \nu)} = \begin{vmatrix} \frac{1}{2}R & \frac{1}{2}R \\ \frac{1}{2}R & -\frac{1}{2}R \end{vmatrix} = \frac{1}{2}R^2$$

Thus

$$dr_1\, dr_2 = \frac{1}{2}R^2\, d\mu\, d\nu$$
$$r_1 r_2 = \frac{R^2}{4}(\mu^2-\nu^2)$$

$$\rightarrow \quad d^3x = \frac{R^3}{8}(\mu^2-\nu^2)\, d\mu\, d\nu\, d\varphi$$

The Schrödinger equation to be solved is, in (r_1, θ, φ) coordinates,

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}_1^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R}\right]\psi(r_1, \theta, \varphi)$$
$$= E\psi(r_1, \theta, \varphi)$$

where $r_2 = \sqrt{r_1^2 + r^2 - 2r_1 r\cos\theta}$

This problem is actually separable in (μ, ν, φ) coordinates. However we will use a variational method based on

$$\psi_1(r_1) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_1/a_0} \qquad a_0 = \text{Bohr radius}$$

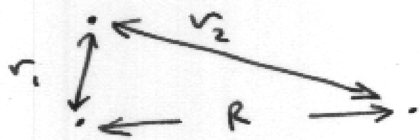
$$\psi_2(r_2) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_2/a_0}$$

the physical picture that allows us to use the variational principle in this problem (and suggests the choice of variational wave fn) is the following.

With
$$H = -\frac{\hbar^2 \vec{\nabla}^2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R}$$

we can consider the following situations:

i) $R \gg a_0$, $r_1 \sim a_0$. Then we see from the figure: $\left(a_0 = \frac{\hbar^2}{me^2}\right)$



that $r_2 \simeq R$ so $H \sim -\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{e^2}{r_1}$

which is the Hydrogen atom Hamiltonian.

Likewise when

ii) $R \gg a_0$, $r_2 \sim a_0$, we have

$r_1 \simeq R$ and $H \simeq -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_2}$

which is again the Hydrogen atom Hamiltonian but centred around the second proton.

This suggests to take the variational wave function

$$|\Psi\rangle = |\Psi_1\rangle + \alpha |\Psi_2\rangle$$

where $\Psi_1(\vec{r}) = \langle \vec{r} | \Psi_1 \rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_1/a_0}$

$$\Psi_2(\vec{r}) = \langle \vec{r} | \Psi_2 \rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_2/a_0}$$

are the ground state wave fns of the two separate Hydrogen atoms.

To apply the variational principle we write:

$$\langle H \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{H_{11} + \alpha^2 H_{22} + 2\alpha H_{12}}{1 + \alpha^2 + 2\alpha S_{12}}$$

where $H_{ij} = \langle \Psi_i | H | \Psi_j \rangle$ and

$S_{ij} = \langle \Psi_i | \Psi_j \rangle$, $S_{11} = S_{22} = 1$ (normalisation)

Note that for the present problem one is quite sure that ~~S_{ij}~~ $S_{12} \neq 0$ since the orbitals around ~~the~~ each proton certainly overlap when R is not so large.

From symmetry we have $H_{11} = H_{22}$. Using this it is a straightforward computation to find that

$$\frac{\partial \langle H \rangle}{\partial \alpha} = 0 \Rightarrow$$

$$(1 + \alpha^2 + 2\alpha S_{12})(2\alpha H_{11} + 2 H_{12}) - ((1+\alpha^2) H_{11} + 2\alpha H_{12})(2\alpha + 2 S_{12}) = 0$$

Cancelling common factors and simplifying, we get

$$(1-\alpha^2)(H_{12} - S_{12} H_{11}) = 0$$

from which $\alpha = \pm 1$. The values of $\langle H \rangle$ at $\alpha = \pm 1$ are:

$$E_{\pm} = \langle H \rangle(\alpha = \pm 1) = \frac{H_{11} \pm H_{12}}{1 \pm S_{12}}$$

We see a two-fold splitting in the formerly degenerate energy levels (they were degenerate as $R \to \infty$).

We now need to calculate H_{11}, H_{12} and S_{12}.

For S_{12}, we use the elliptic coordinates (μ, ν, φ) ~~tangent~~ where

$$\mu = \frac{r_1 + r_2}{R}, \quad \nu = \frac{r_1 - r_2}{R}$$

Thus $$\psi_1(\mu, \nu, \varphi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-R(\mu+\nu)/2a_0}$$

$$\psi_2(\mu, \nu, \varphi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-R(\mu-\nu)/2a_0}$$

So $\int d^3x \, \psi_1^* \psi_2 =$

$$\frac{R^3}{8} \iint (\mu^2 - \nu^2) \, d\mu \, d\nu \int_0^{2\pi} d\varphi \cdot \frac{1}{\pi a_0^3} e^{-\mu R/a_0}$$

Note that
$$\underbrace{\begin{aligned} r_1 + r_2 &\geq R \Rightarrow 1 \leq \mu \leq \infty \\ |r_1 - r_2| &\leq R \Rightarrow -1 \leq \nu \leq 1 \end{aligned}}_{}$$

These constraints can be inferred from the geometry

$$\therefore S_{12} = \frac{1}{8\pi}\left(\frac{R}{a_0}\right)^3 \int_0^{2\pi} d\varphi \int_1^{\infty} d\mu \left[\int_{-1}^{1} d\nu \, (\mu^2 - \nu^2) \right] e^{-\mu \frac{R}{a_0}}$$

$$= \frac{1}{4}\left(\frac{R}{a_0}\right)^3 \int_1^{\infty} d\mu \, e^{-\mu \frac{R}{a_0}} \left(2\mu^2 - \frac{2}{3}\right)$$

$$= \frac{1}{2}\left(\frac{R}{a_0}\right)^3 \int_1^{\infty} d\mu \, e^{-\mu \frac{R}{a_0}} \left(\mu^2 - \frac{1}{3}\right)$$

Now $\displaystyle\int_1^\infty d\mu \, e^{-\mu R/a_0} \left(\mu^2 - \frac{1}{3}\right) =$

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

So $S_{12} = \frac{1}{2}\left(\frac{R}{a_0}\right)^3 \int - - -$

$$\boxed{S_{12} = e^{-R/a_0}\left(1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right)}$$

Next let us calculate

$$H_{11} = H_{22} = \langle \Psi_1 | H | \Psi_1 \rangle$$

($|\Psi\rangle$ is normalized).

we have: $H_{11} = \langle \Psi_1 | \left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{e^2}{r_1} \right) | \Psi_1 \rangle$

$$- \langle \Psi_1 | \frac{e^2}{r_2} | \Psi_1 \rangle + \frac{e^2}{R}$$

The first term is minus the well-known ground-state energy of the Hydrogen atom, namely $E_I = \frac{e^2}{2a_0} = 13.6 \text{ eV}$

The second term is: $- \langle \Psi_1 | \frac{e^2}{r_2} | \Psi_1 \rangle$

$$= -e^2 \int d^3r \, \frac{|\Psi_1|^2}{r_2} \quad \text{where } \Psi_1 = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_1/a_0}$$

$$= \frac{-e^2}{\pi a_0^3} \int d^3r \, \frac{e^{-2r_1/a_0}}{r_2}.$$

Again we evaluate this using elliptic coordinates:

$$-\frac{e^2}{\pi a_0^3} \cdot \frac{R^3}{8}\int d\mu\, d\nu\, d\varphi\ (\mu^2-\nu^2)\ e^{-(\mu+\nu)R/a_0} \cdot \frac{2}{R(\mu-\nu)}$$

$$= -\frac{e^2R^2}{2a_0^3}\int_1^\infty d\mu \int_{-1}^{+1} d\nu\ (\mu+\nu)\ e^{-(\mu+\nu)R/a_0}$$

where we used $\int_0^{2\pi} d\varphi = 2\pi$

For notational simplicity we use $E_I = \frac{e^2}{2a_0}$

and also define $\rho = \frac{R}{a_0}$.

Then

$$-\langle \psi_1 | \frac{e^2}{r_2} | \psi_1 \rangle =$$

$$-E_I\,\rho^2 \int_1^\infty d\mu \int_{-1}^{+1} d\nu\ (\mu+\nu)\ e^{-(\mu+\nu)\rho}$$

The integral is tedious but elementary:

$$\int_{-1}^{+1} d\nu\ (\mu+\nu)\, e^{-(\mu+\nu)\rho} = e^{-\mu\rho}\left[\mu\int_{-1}^{+1} d\nu\, e^{-\nu\rho} + \int_{-1}^{+1} d\nu\, \nu e^{-\nu\rho}\right]$$

$$= e^{-\mu\rho}\left[\frac{\mu}{\rho}(e^{\rho}-e^{-\rho}) + \frac{1}{\rho^2}\left((1-\rho)e^{\rho} - (1+\rho)e^{-\rho}\right)\right]$$

Integrating this over $\int_1^\infty d\mu$ gives:

$$\frac{(e^{\rho}-e^{-\rho})}{\rho}\int_1^\infty d\mu\, \mu e^{-\mu\rho} + \frac{1}{\rho^2}\left((1-\rho)e^{\rho} - (1+\rho)e^{-\rho}\right)\int_1^\infty d\mu\, e^{-\mu\rho}$$

$$= \frac{e^{\rho}-e^{-\rho}}{\rho}\ \frac{1}{\rho^2}(1+\rho)e^{-\rho} + \frac{1}{\rho^2}\left((1-\rho)e^{\rho} - (1+\rho)e^{-\rho}\right)\left(\frac{e^{-\rho}}{\rho}\right)$$

$$= \frac{1}{\rho^3}\left\{ (1+\rho)(1-e^{-2\rho}) + (1-\rho) - (1+\rho)e^{-2\rho} \right\}$$

$$= \frac{1}{\rho^3}\left\{ 2 - 2(1+\rho)e^{-2\rho} \right\}$$

$$= \frac{2}{\rho^3}\left[1 - (1+\rho)e^{-2\rho} \right]$$

Hence $\quad - \langle \psi_1 | \frac{e^2}{r_2} | \psi_1 \rangle = -\frac{2E_I}{\rho}\left[1-(1+\rho)e^{-2\rho} \right]$

with $\rho = \frac{R}{a_0}$.

Therefore

$$H_{11} = -E_I - \frac{2E_I}{\rho}\left[1-(1+\rho)e^{-2\rho} \right] + \frac{e^2}{R}$$

Notice that $\frac{2E_I}{\rho} = \frac{2e^2}{2a_0}\cdot\frac{a_0}{R} = \frac{e^2}{R}$.

Thus finally,

$$\boxed{H_{11} = -\frac{e^2}{2a_0} + \frac{e^2}{R}\left(1+\frac{R}{a_0}\right)e^{-2R/a_0}}$$

Notice that the leading term from $-\langle \psi_1 | \frac{e^2}{r_2} | \psi_1 \rangle$ cancelled the contribution $\frac{e^2}{R}$.

This is because when R is large, the second proton sees no net charge: the charges of the electron & first proton effectively cancel.

Finally we need to calculate H_{12}:

$$H_{12} = \langle \Psi_1 | -\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{e^2}{r_2} | \Psi_2 \rangle$$

$$- \langle \Psi_1 | \frac{e^2}{r_1} | \Psi_2 \rangle + \frac{e^2}{R} \langle \Psi_1 | \Psi_2 \rangle$$

$$= -E_I S_{12} + \frac{e^2}{R} S_{12} - \langle \Psi_1 | \frac{e^2}{r_1} | \Psi_2 \rangle$$

Again we need to evaluate an integral:

$$- \langle \Psi_1 | \frac{e^2}{r_1} | \Psi_2 \rangle = \frac{e^2}{\pi a_0^3} \int d^3r \, \frac{e^{-r_1/a_0} \, e^{-r_2/a_0}}{r_1}$$

~~[illegible] the integrations:~~

$$= -\frac{e^2}{\pi a_0^3} \cdot \frac{R^3}{8} \cdot 2\pi \cdot \int_1^\infty d\mu \int_{-1}^{+1} d\nu \; \frac{2 e^{-\mu R/a_0}}{R(\mu+\nu)} \cdot (\mu^2 - \nu^2)$$

$$= \frac{-e^2 R^2}{2 a_0^3} \cdot \int_1^\infty d\mu \int_{-1}^{+1} d\nu \; (\mu - \nu) \, e^{-\mu R/a_0}$$

$$= -E_I \rho^2 \int_1^\infty d\mu \left[e^{-\mu\rho} \int_{-1}^{+1} d\nu \, (\mu - \nu) \right]$$

$$= -E_I \rho^2 \int_1^\infty d\mu \, e^{-\mu\rho} (2\mu - 0)$$

$$= -2E_I \, e^{-\rho} (1+\rho)$$

This integral physically corresponds to a "jumping" amplitude for the electron to go from the orbit of one proton to the other.

So we have:

$$H_{12} = S_{12}\left(-E_I + \frac{e^2}{R}\right) - 2E_I e^{-\rho}(1+\rho)$$

In the same units E_I and ρ, we found that

$$H_{11} = -E_I + \frac{e^2}{R} - \frac{2E_I}{\rho}\left[1-(1+\rho)e^{-2\rho}\right]$$

We have shown that the expectation value for the variational wave fn is:

$$E_{\mp} = \frac{H_{11} \pm H_{12}}{1 \pm S_{12}}$$

(we choose the signs so that $E_- < E_+$ as we will see)

$$\cancel{-E_I + \frac{e^2}{R}}$$

In units of E_I we have:

$$H_{11} = E_I\left[-1 + \frac{2}{\rho} - \frac{2}{\rho}\left[1-(1+\rho)e^{-2\rho}\right]\right]$$

$$H_{12} = E_I\left[\left(-1+\frac{2}{\rho}\right)S_{12} - 2e^{-\rho}(1+\rho)\right]$$

Thus finally,

$$\frac{E_{\mp}}{E_I} = -1 + \frac{2}{\rho} + \frac{2}{1 \pm S_{12}} \left\{ -\frac{1}{\rho}\left[1-(1+\rho)e^{-2\rho}\right] \mp e^{-\rho}(1+\rho) \right\}$$

Now ρ is the separation of the protons R in units of a_0. So as $\rho \to \infty$ we expect $\frac{E_{\mp}}{-E_I} \to 1$ and this is correct.

So we write $\frac{E_{\mp}}{E_I} = -1 + \frac{\Delta E_{\mp}}{E_I}$

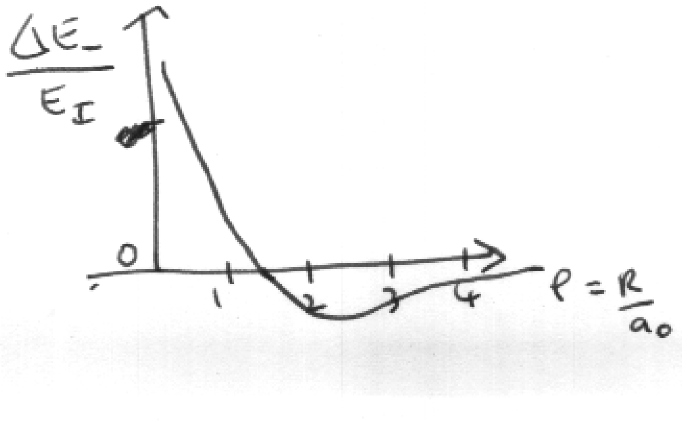
where

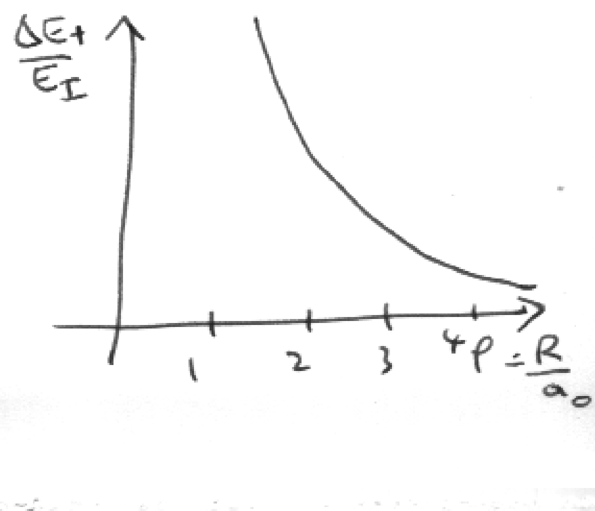
$$\frac{\Delta E_{\mp}}{E_I} = \frac{2}{\rho} + \frac{2}{1 \pm S_{12}} \left\{ -\frac{1}{\rho}\left[1-(1+\rho)e^{-2\rho}\right] \mp e^{-\rho}(1+\rho) \right\}$$

with $S_{12} = e^{-\rho}(1+\rho+\frac{1}{3}\rho^2)$

Plotting $\frac{\Delta E_-}{E_I}$, $\frac{\Delta E_+}{E_I}$ ~~we f~~ against ρ

we find:





Though we have treated ρ as a parameter, which is an approximation, we see that the energy is <u>minimized</u> as a function of ρ for $\rho \simeq 2.5$

This predicts the existence of a chemical bond. Also we see that this is due to H_{12}, S_{12} (since H_{11} as a function of ρ has no minimum). This means the <u>overlap</u> of electronic orbitals of the two atoms was crucial for the bond to form.

The normalized wave function of the bonding state Ψ_- (of energy E_-) is:

$$\Psi_- = \frac{1}{\sqrt{2(1+S_{12})}} \left[|\varphi_1\rangle + |\varphi_2\rangle \right]$$

→ sy<u>mmetrica</u>l.

while

$$\Psi_+ = \frac{1}{\sqrt{2(1-S_{12})}} \left[|\varphi_1\rangle - |\varphi_2\rangle \right]$$

which is antisymmetric, is called the anti-bonding state.