Lecture 23

Last time, applied variational method to He atom

This time, look at hydrogen <u>molecule</u> ion
- on of my favorite problems

He: 2 electrons, 1 proton
H_2^+: 1 electron, 2 protons

Complete H: Protons at R_1, R_2, mass M
Electron at $\vec{r}$, mass m

$$H = -\frac{\hbar^2}{2M}\left(\nabla_{R_1}^2 + \nabla_{R_2}^2\right) - \frac{\hbar^2}{2m}\nabla_r^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{|r-R_1|} + \frac{1}{|r-R_2|} - \frac{1}{|R_1-R_2|}\right)$$

3 particles: kind of hard

However: we haven't normally worried about QM of nuclear motion
Nuclei are ~2000× heavier than e^-
So nuclei can be well localized at definite R_1, R_2

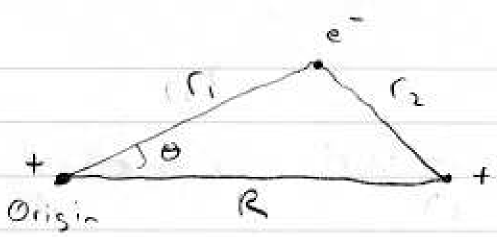
So only treat e^- using QM

Still, need to decide <u>where</u> nuclei should be
In particular, need $R = |\vec{R}_1 - \vec{R}_2|$

Solution: treat R as variational parameter

For electron, $H \to -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$

Set up:



$r = r_1$

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

Need a trial wave function

If $R \gg a$, expect $\psi \sim \psi_{100}(r) \equiv \psi_0(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$

But electron could be on either proton, so use

$$\psi = A\left[\psi_0(r_1) + \psi_0(r_2)\right]$$

(Note only one electron, no symmetrization issues)

First step: Normalization

Since $\psi_0(r_1)$ & $\psi_0(r_2)$ are not orthogonal, A is not trivial

Need $1 = \int |\psi|^2 d^3r = |A|^2 \int \left[|\psi_0(r_1)|^2 + |\psi_0(r_2)|^2 + 2\psi_0(r_1)\psi_0(r_2)\right] d^3r_1$

First two terms give 1

3rd term: $I \equiv \int \psi_0(r_1)\psi_0(r_2)\, d^3r = \frac{1}{\pi a^3}\int e^{-(r_1+r_2)/a} d^3r$

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

Do θ integral first:

Substitute $y = \sqrt{r^2+R^2-2rR\cos\theta}$

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

When $\theta = 0$, $\quad y = |r-R|$
when $\theta = \pi$, $\quad y = r+R$

Shorter if needed

So θ integral becomes

$$\int_0^{\pi} e^{-\frac{1}{a}\sqrt{r^2+R^2-2rR\cos\theta}} \sin\theta \, d\theta = \frac{1}{rR}\int_{|r-R|}^{r+R} e^{-y/a}\, y\, dy$$

$$= -\frac{a}{rR}\Big[e^{-(r+R)/a}(r+R+a) - e^{-|r-R|/a}(|r-R|+a) \Big]$$

and then

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

Use formula in back of book, get

$$\boxed{I = e^{-R/a}\left[1 + \left(\frac{R}{a}\right) + \frac{1}{3}\left(\frac{R}{a}\right)^2\right]}$$

and then $A = \dfrac{1}{\sqrt{2(1+I)}}$ Whew!

Now calculate $\langle H \rangle$:

$$H\psi = A\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right]\left[\psi_0(r_1)+\psi_0(r_2)\right]$$

$$= A\left[\left(E_1 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_2}\right)\psi_0(r_1) + \left(E_1 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_1}\right)\psi_0(r_2)\right]$$

$$= E_1\psi - A\frac{e^2}{4\pi\varepsilon_0}\left[\frac{1}{r_2}\psi_0(r_1) + \frac{1}{r_1}\psi_0(r_2)\right]$$

That gives $\langle H \rangle = \langle \psi | H | \psi \rangle$

$$= E_1 - A \frac{e^2}{4\pi\varepsilon_0} \left[\langle \psi | \frac{1}{r_2} | \psi_0(r_1) \rangle + \langle \psi | \frac{1}{r_1} | \psi_0(r_2) \rangle \right]$$

first term: $A \left[\langle \psi_0(r_1) | \frac{1}{r_2} | \psi_0(r_1) \rangle + \langle \psi_0(r_2) | \frac{1}{r_2} | \psi_0(r_1) \rangle \right]$

$\hookrightarrow = \langle \psi_0(r_1) | \frac{1}{r_1} | \psi_0(r_2) \rangle$

by symmetry $r_1 \leftrightarrow r_2$

second term: $A \left[\langle \psi_0(r_1) | \frac{1}{r_1} | \psi_0(r_2) \rangle + \langle \psi_0(r_2) | \frac{1}{r_1} | \psi_0(r_2) \rangle \right]$

$\hookrightarrow = \langle \psi_0(r_1) | \frac{1}{r_2} | \psi_0(r_1) \rangle$

Then $\langle H \rangle = E_1 - 2A^2 \overbrace{\frac{e^2}{4\pi\varepsilon_0 a}}^{-2E_1} (D + X)$

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

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

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

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

So $\langle H \rangle = \left[1 + 2 \frac{D + X}{1 + I} \right] E_1$

This is the electron's energy.

Also need to include energy of proton-proton interaction

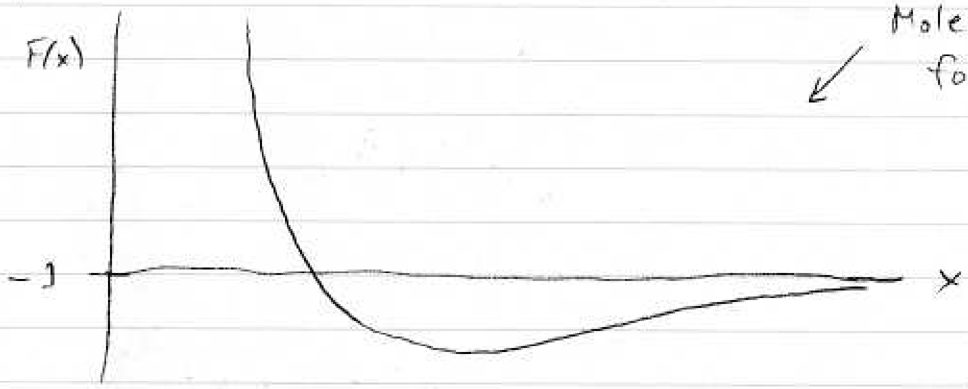
$$V_{pp} = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{R} = -\frac{2a}{R} E_1$$

Gives total energy

$$\langle H \rangle + V_{pp} = F(x)\,(-E_1) \quad , \quad x = \frac{R}{a}$$

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

Plot:



Molecular potential for H_2^-

Get minimum numerically:

$X_{min} = 2.4a$

$E_{min} = E_1 - 1.8\,eV$

binding energy of molecule

Experimentally, $X_{min} = 2.0a$

$E_{min} = E_1 - 2.8\,eV$

Not great agreement, but calculation does prove that bound state should exist.

(Since actually ground state must be more tightly bound than our calculation)