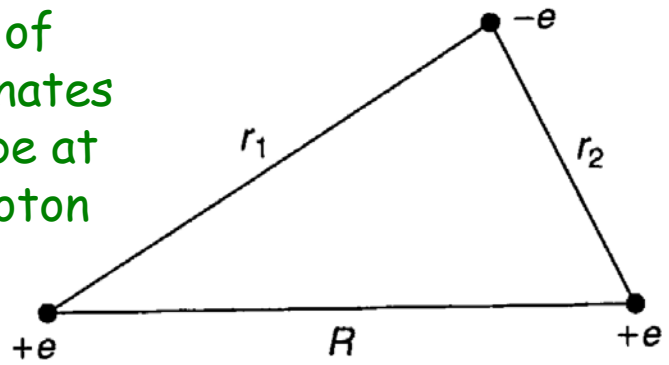
8.3: The Hydrogen Molecule Ion H_2^+

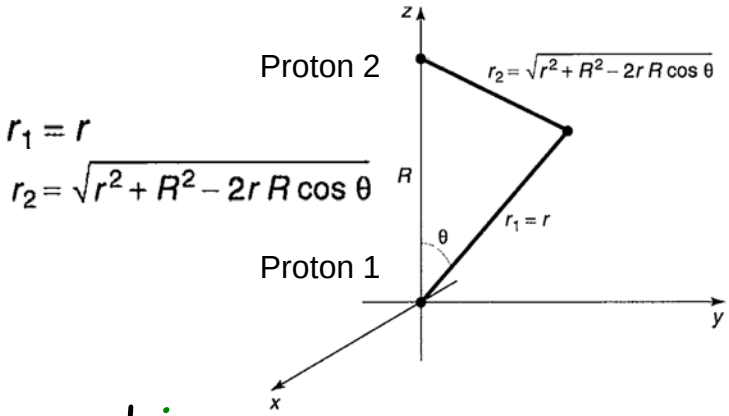
Mobile electron

Origin of coordinates could be at one proton



Fixed proton Fixed proton

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$



We wish to find the best variational energy, and *investigate if energetically the system may prefer to decompose into one neutral hydrogen and one free proton far away, or remain bounded.*

We will try:

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

where each wave function is the normalized-to-one exact ground state of hydrogen is:

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

Note it is 1e. Thus, a sum must be used, **not a product** as in He with 2e.

First normalize:

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

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Not easy, see book. It is called **overlap integral**. If R is huge, then integral is ~0.

$$I \equiv \langle \psi_0(r_1) | \psi_0(r_2) \rangle = \frac{1}{\pi a^3} \int e^{-(r_1+r_2)/a} \, d^3\mathbf{r}$$

Final result:

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

where the integral is given to you:

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

After normalization, then we need to calculate <*H*>:

$$H\psi = A\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right][\psi_0(r_1)+\psi_0(r_2)]$$
$$= E_1\psi - A\left(\frac{e^2}{4\pi\epsilon_0}\right)\left[\frac{1}{r_2}\psi_0(r_1)+\frac{1}{r_1}\psi_0(r_2)\right].$$

where we used $$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_1}\right)\psi_0(r_1) = E_1\psi_0(r_1)$$

(and same for proton 2 i.e. for r_2):

$$\langle H\rangle = E_1 - 2|A|^2\left(\frac{e^2}{4\pi\epsilon_0}\right)\left[\langle\psi_0(r_1)\left|\frac{1}{r_2}\right|\psi_0(r_1)\rangle + \langle\psi_0(r_1)\left|\frac{1}{r_1}\right|\psi_0(r_2)\rangle\right]$$

NOTE: the first sandwich arises as written, plus also with r_2 and r_1 exchanged, thus the appearance of the factor 2 in front because integrals must be the same. Same with the other integral.

Direct integral: $$D \equiv a\langle \psi_0(r_1) \left| \frac{1}{r_2} \right| \psi_0(r_1) \rangle$$

Exchange integral: $$X \equiv a\langle \psi_0(r_1) \left| \frac{1}{r_1} \right| \psi_0(r_2) \rangle$$

The results given to you are:

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

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

Final result is: $$\langle H \rangle = \left[1 + 2\frac{(D + X)}{(1 + I)}\right] E_1$$

But this is not the total energy …

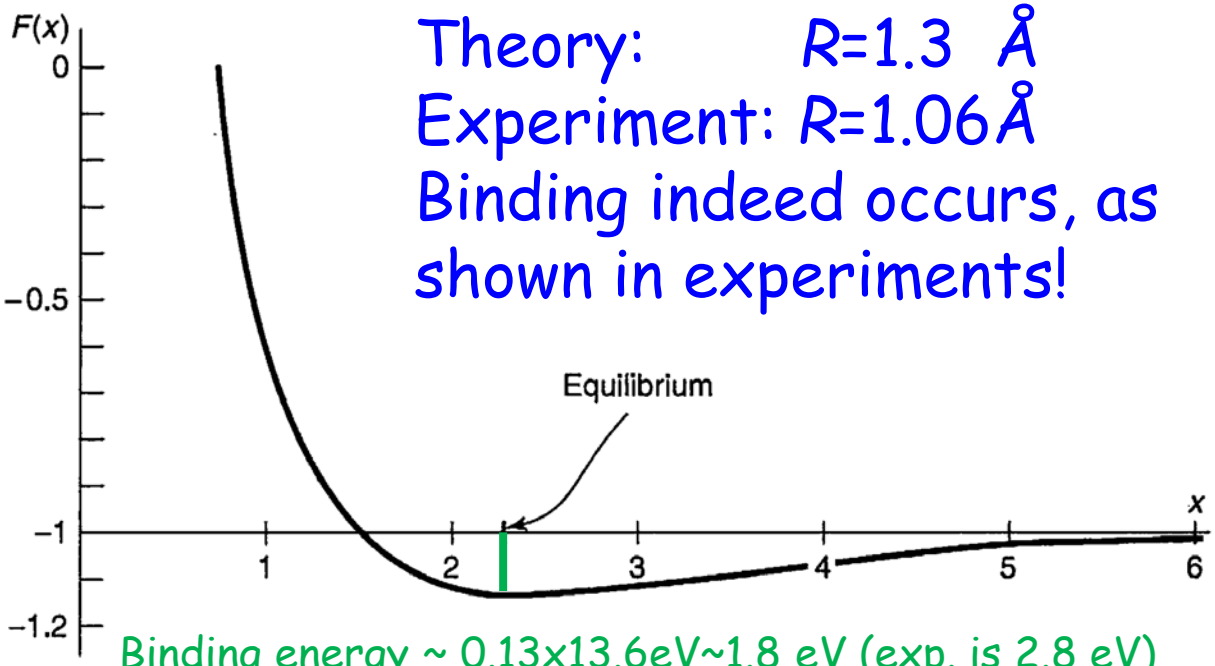
Proton-proton repulsion missing (no integrals needed):

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

$\langle H + V_{pp}\rangle/(-E_1) =$ $F(x) = -1 + \frac{2}{x}\left\{\frac{(1-(2/3)x^2)e^{-x} + (1+x)e^{-2x}}{1+(1+x+(1/3)x^2)e^{-x}}\right\}$

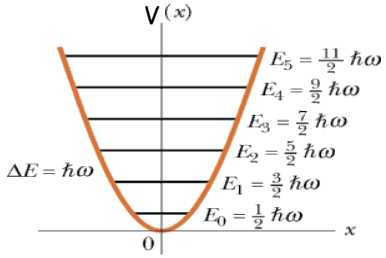
Dividing by $-E_1$ and using the dimensionless variable $x \equiv R/a$ (a is ~ 0.5Å) then the function that matters is F(x):

x=R/a→∞, i.e. F(x)=-1, is the decoupled H atom plus one free proton.



Theory: R=1.3 Å
Experiment: R=1.06Å
Binding indeed occurs, as shown in experiments!

Binding energy ~ 0.13x13.6eV~1.8 eV (exp. is 2.8 eV)



Problem 8.11: because protons are oscillating they have a zero-point energy.

Binding energy ~ 0.13x13.6eV
~1.8 eV (exp. is 2.8 eV)