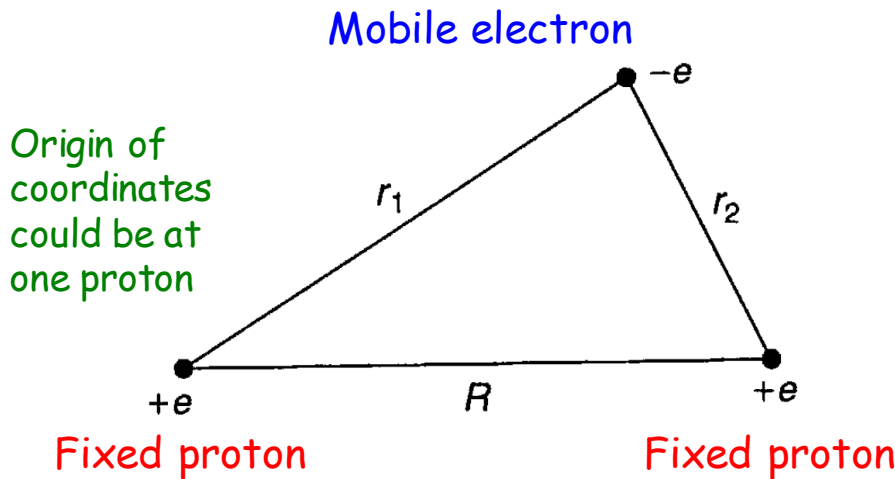
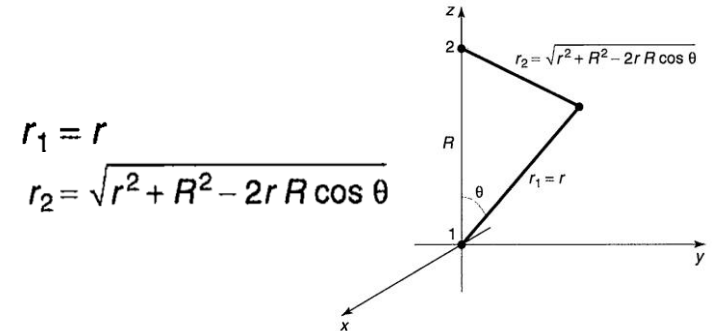


7.3: The Hydrogen Molecule Ion H_2^+



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



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

We will try:

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

where each wave function is the normalized to 1 exact ground state of H:

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

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

First normalize:

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

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

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

Final result:

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

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

After normalization, then we need to calculate $\langle H \rangle$:

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

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

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

NOTE: the first sandwich arises as written, plus also with r_2 and r_1 exchanged, thus the factor 2 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: $X \equiv a \langle \psi_0(r_1) \left| \frac{1}{r_1} \right| \psi_0(r_2) \rangle$

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

The results are:

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

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

But this is not the total energy ...

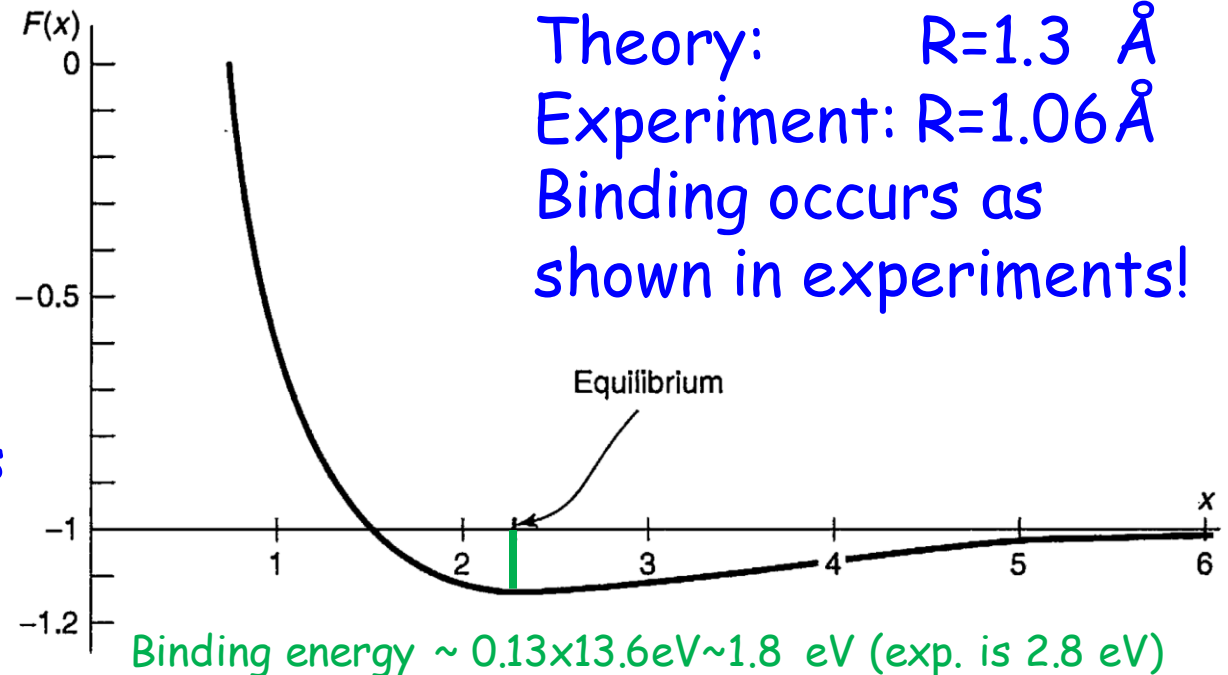
Proton-proton repulsion missing (no integrals needed):

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

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

Dividing by $-E_1$ and using the dimensionless variable $x \equiv R/a$ (a is $\sim 0.5\text{\AA}$) then the function that matters is:

$x=R/a \rightarrow \infty$, i.e. $F(x)=-1$, is the decoupled H atom plus one free proton.



Chapter 9: Time Dependent Perturbation Theory

Thus far, our potentials $V(\mathbf{r})$ have been time independent. Now we will use $V(\mathbf{r},t)$.

These type of problems are very difficult so we will work in the context of **perturbation theory**. The most dominant portion of H will be time independent, while only the perturbation will be time dependent.

By this procedure we will study the emission and absorption of radiation by an atom.

To study emission and absorption we need at least two states. Consider two eigenstates of H^0 :

$$H^0 \psi_a = E_a \psi_a \quad H^0 \psi_b = E_b \psi_b \quad \langle \psi_a | \psi_b \rangle = \delta_{ab}$$

We will assume these two states are the only ones that really matter. Thus, any arbitrary state can be a linear combination of "a" and "b" at time $t=0$:

$$\Psi(0) = c_a \psi_a + c_b \psi_b \quad |c_a|^2 + |c_b|^2 = 1$$

You can imagine these two states as for example the 1s and 2s states of the hydrogen atom. Or they can be spinors, describing a static spin in a magnetic field. Etc.

If there is NO perturbation, you learned in class 411 (Test 1, 2018 for instance) that the time dependence is easy:

$$\Psi(t) = c_a \psi_a e^{-iE_a t/\hbar} + c_b \psi_b e^{-iE_b t/\hbar}$$

So far nothing new ...

Now we will introduce a **perturbation $H'(t)$** that depends on time, such as an **small external field**.

The two original states are still a complete basis. But the time dependence is not so easy. **We will consider the new time dependence by making the coefficients, that before were fixed numbers, time dependent...**

$$\Psi(t) = c_a(t)\psi_a e^{-iE_a t/\hbar} + c_b(t)\psi_b e^{-iE_b t/\hbar}$$

We know ψ_a , ψ_b , E_a , and E_b . Thus, the challenge is to find the coefficients as a function of time.

For example if at time $t=0$, $c_a(0)=1$ and $c_b(0)=0$, then the electron is at "a" initially. If at a later time T the coefficients are $c_a(T)=0$ and $c_b(T)=1$ a transition occurred from ψ_a to ψ_b .