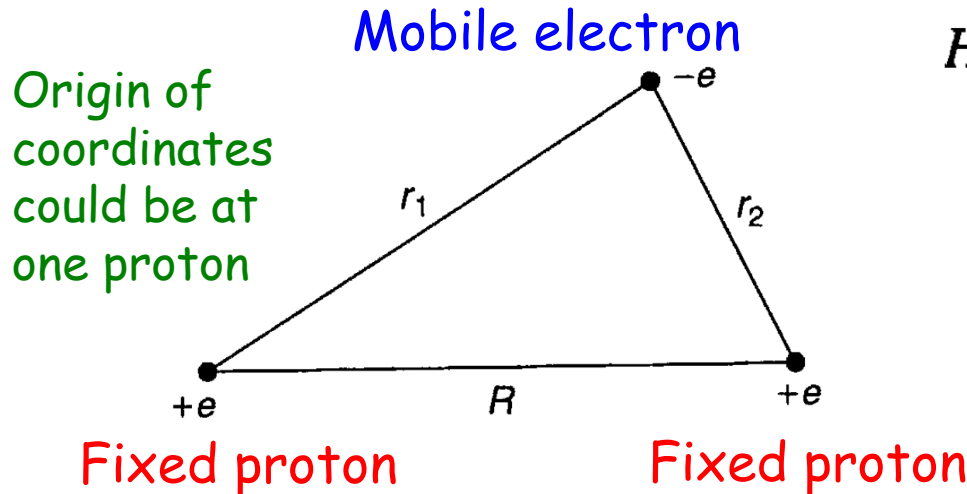
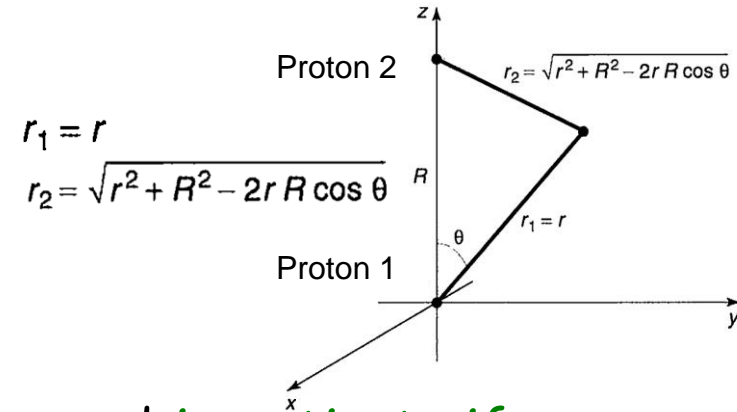


8.3: The Hydrogen Molecule Ion H_2^+



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



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

We will try:

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

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

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

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

but centered at different places.

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 . Overlap integrals are crucial in molecular physics and condensed matter physics.

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 $\langle H \rangle$:

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

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 by symmetry. 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 given
to you 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 yet ...

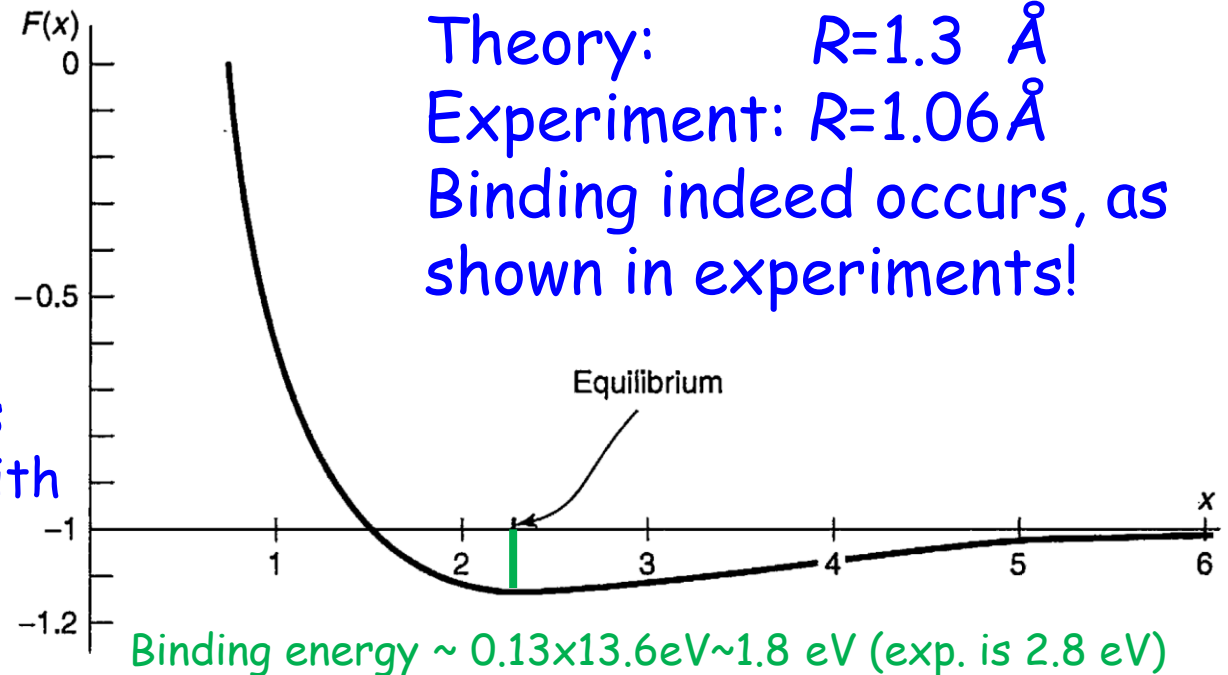
Proton-proton repulsion missing (no integrals needed):

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

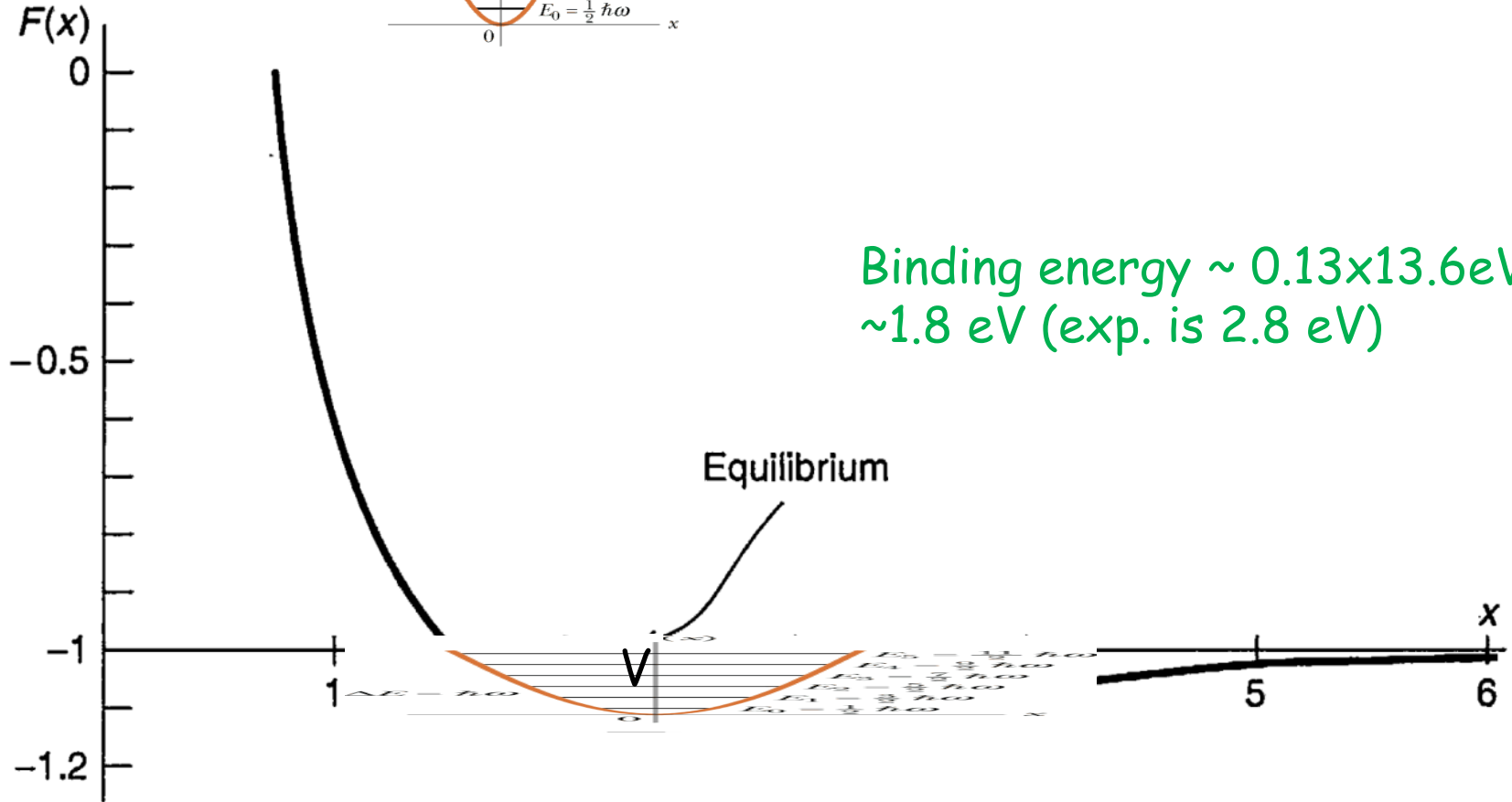
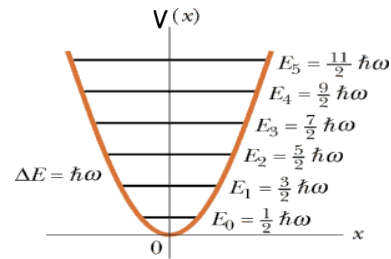
$$\langle H + V_{pp} \rangle / (-E_1) = F(x) = -1 + \frac{2}{x} \left\{ \frac{(1 - (2/3)x^2)e^{-x} + (1+x)e^{-2x}}{1 + (1+x + (1/3)x^2)e^{-x}} \right\}$$

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 $F(x)$:

$x=R/a \rightarrow \infty$, i.e. $F(x)=-1$, is the decoupled H atom with energy -13.6 eV plus one free static proton at ∞ .



Protons are always vibrating because they have a zero-point energy.



Binding energy $\sim 0.13 \times 13.6 \text{ eV}$
 $\sim 1.8 \text{ eV}$ (exp. is 2.8 eV)

Chapter 11: Quantum Dynamics

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

These type of problems are often 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 (photons) by an atom.

Often we have casually spoken about transitions from high energy states to low. And you have learned about this since probably High School. But mathematically, if we are in an excited state, THUS FAR we stay there forever.

Then, how do we describe the transitions between levels, such as when an electron decays from a state, say, $n=3$ $l=1$ to the ground state $n=1$ $l=0$, by emitting a photon?

At the minimum, we have to “shake” a little bit the electron at $n=3$ $l=1$ to allow for the transition to occur. How do we shake the electron? By placing the electron in an external electromagnetic field, which often is time dependent. Then, “quantum jumps” - that are almost instantaneous - can occur.

11.1: Two-level systems

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 $t=0$:

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

Again, you can imagine these two states as for example the *1s* and *2p* states of the hydrogen atom. Or they can be spinors up and down, describing a spin in a magnetic field.

If there is NO perturbation, you learned in the fall P411 class 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 obvious. **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 t .

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 become $c_a(T)=0$ and $c_b(T)=1$, then a full transition occurred from ψ_a to ψ_b .