

# Approximation methods IV.

## VARIATIONAL APPROACH (VMA)

VMA is used to construct the ground state eigenfunction and approximate energy of the ground state.

Unlike the previous methods we will GUESS the ground state and more of an art than a mathematically rigid construction.

As the result will study it mostly by considering various examples.

Once you have attempted to guess the wave function we can construct the ground state energy.

Lets assume we know  $\phi_n$ :

$$1) \quad H \phi_n = E_n \phi_n \quad n=0,1,\dots$$

and we can write down for any  $\psi = \sum_n a_n \phi_n$

Now lets calculate the average of  $H$

$$2) \quad \int \psi^* H \psi d\tau = \int \sum_m a_m^* \phi_m^* H \sum_n a_n \phi_n d\tau$$

$$\stackrel{\delta_{mn}}{=} \sum_n |a_n|^2 E_n \geq \sum_n |a_n|^2 E_0$$

b/c if we are not in the ground state

$\sum_n |a_n|^2 E_n$  is larger. For normalized

$$\phi_n : \sum_n \phi_n^2 = 1 \Rightarrow$$

$$E_0 \leq \int_{-\infty}^{\infty} \psi^* H \psi d\tau \quad \leftarrow \text{the variational theorem}$$

So whatever is the form of the w.f.  $\psi$ , it is always can be minimized if we express  $\psi$  as a function of some parameters, e.g.  $c_i$

$$E(c_i) = \int_{-\infty}^{\infty} \psi^*(c_i) H \psi(c_i) dx$$

to be a minimum  $\frac{\partial E}{\partial c_i} = 0$  and  $\frac{\partial^2 E}{\partial c_i^2} > 0$

the math idea of the method

to determine the minimum value of  $E$ .

Consider some important examples

①

### Harmonic oscillator

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m \omega^2 x^2$$

by some reason we decided to try:

$$\psi = A e^{-\alpha x^2} \Rightarrow A?$$

$\alpha$  is real to be varied.

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 2A^2 \int_0^{\infty} e^{-2\alpha x^2} dx =$$

$$\int_0^{\infty} e^{-\beta x^2} dx = \sqrt{\pi/(4\beta)} \Rightarrow A = \left(\frac{2\alpha}{\pi}\right)^{1/4}$$

Next we know that

$$E = \int \psi^* H \psi dx = A^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right)$$

$$e^{-\alpha x^2} = \frac{2\hbar^2 A^2 \alpha}{m} \int_0^{\infty} (1 - 2x^2) e^{-2\alpha x^2} dx + m\omega^2 A^2 \int_0^{\infty} x^2 e^{-2\alpha x^2} dx$$

Recall in the lecture 2 we learn that

$$\int_0^{\infty} x^{2n} e^{-\beta x^2} dx = \frac{(2n-1)!! \sqrt{\pi/\beta}}{2^{n+1} \beta^n}$$

$$n!! = \begin{cases} n(n-2) \dots 5 \cdot 3 \cdot 1 & n = \text{odd} \\ n(n-2) \dots 6 \cdot 4 \cdot 2 & n = \text{even} \\ 1 & n = -1, 0 \end{cases}$$

!! means  $n!! = 1$  if  $n=0$ , or 1

and  $(n-2) \cdot n!!$  if  $n \geq 2$

from  $(2n-1)!! = (2n)! / (2^n n!)$  we get

$$E = \frac{\hbar^2 \alpha^2}{2m} + \frac{m\omega^2}{8\alpha^2} \quad \text{and from}$$

! typo!  
on page  
402  
eqn. 16.13

$$\frac{\partial E}{\partial \alpha} = \left[ \frac{\hbar^2 \alpha}{2m} + \frac{m\omega^2}{8\alpha^2} \right]'_{\alpha} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0 \Rightarrow$$

$$\alpha^2 = \frac{m\omega^2}{4\hbar^2} \Rightarrow \alpha = \frac{m\omega}{2\hbar}$$

$$E \left( \alpha = \frac{m\omega}{2\hbar} \right) = \frac{\hbar^2 \frac{m\omega}{2\hbar}}{2m} + \frac{m\omega^2}{8 \left( \frac{m\omega}{2\hbar} \right)^2} =$$

$$= \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = \frac{\hbar\omega}{2} \quad \text{! zero-energy ground state.}$$

The answer is exact b/c we selected

$\phi = A e^{-x^2 \alpha}$  is exact too!

★ go in details over 16.2.4. and 16.2.5

### TRIAL FUNCTIONS FOR THE EXCITING STATES.

When the same method is applied to the exciting states, we assume that the exciting state trial w.f. is orthogonal to the ground state w.f.

$$\psi_t = \psi - \phi_0 \int \phi_0^* \psi d\tau \Rightarrow$$

$$\langle \phi_0 | \psi_t \rangle = \langle \phi_0 | \psi \rangle - \langle \phi_0 | \phi_0 \rangle \langle \phi_0 | \psi \rangle = 0$$

Hence the expression

$$\Psi_t = \sum_{n=1}^{\infty} a_n \phi_n \quad \text{will not contain } \phi_0$$

therefore we get:

$$\langle E_t \rangle = \langle \Psi_t | H | \Psi_t \rangle = \sum_{n=1}^{\infty} |a_n|^2 E_n \Rightarrow$$

$$\boxed{\langle E_t \rangle \geq E_1}$$

So the trial  $\Psi_t$  gives the upper limit for the 1<sup>st</sup> excited state.

By virtue of the same argument we get that  $\Psi_t$  is orthogonal to  $\phi_i$   $i=0, 1, \dots, n$  and thus  $\Psi_t$  gives the upper limit for  $(n+1)^{\text{th}}$  energy eigenvalue

### Finite Basis expansion

Following this idea we assume that we have a known complete set  $\{\phi_n\}$  ← any!

The  $\Psi_t$  is then can be constructed as

$$\Psi = \sum_{i=1}^r a_i \phi_i \quad a_i \text{ are the variational parameters.}$$

Note:  $\phi_i$  may not be orthogonal.

$$E = \frac{\int_{-\infty}^{\infty} \Psi^* H \Psi d\tau}{\int_{-\infty}^{\infty} \Psi^* \Psi d\tau}$$

$$E = \frac{\sum_{i=1}^r \sum_{j=1}^r a_i^* a_j H_{ij}}{\sum_{i=1}^r \sum_{j=1}^r a_i^* a_j S_{ij}} \rightarrow \begin{matrix} \langle \phi_i | H | \phi_j \rangle \\ \langle \phi_i | \phi_j \rangle \end{matrix}$$



or

$$\frac{\partial}{\partial a_i^*} \left| \sum_i^r \sum_j^r E a_i^* a_j S_{ij} - \sum_i^r \sum_j^r a_i^* a_j H_{ij} \right| = 0$$

$$\sum_{j=1}^r E a_j S_{ij} - \sum_{j=1}^r a_j H_{ij} = 0,$$

$$\sum_{j=1}^r (E S_{ij} - H_{ij}) a_j = 0 \quad i = 1, 2, \dots, r$$

If we differentiate w.r.t  $\frac{\partial}{\partial a_i^*} (\dots) = 0$

we get a complex conjugate of

Thus we ended up with the following

set of eqns:

$$\begin{vmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} & \dots & H_{1r} - E S_{1r} \\ \vdots & \vdots & \ddots & \vdots \\ H_{r1} - E S_{r1} & \dots & \dots & H_{rr} - E S_{rr} \end{vmatrix} = 0$$

After we solve this set for  $E$  we

get  $E_0, E_1, \dots, E_{r-1}$

where  $E_0$  is the ground state,  $E_1$  - excited etc.

Next we can insert  $E_0, \dots$  into

$$\sum_{j=1}^r (H_{ij} - E S_{ij}) a_j = 0 \quad i = 1, 2, \dots$$

and solve for  $a_j$  for each  $E$

Note: if we select the orthogonal basis

then  $S_{ij} = \delta_{ij}$

And the matrix is simplified as:

$$\begin{vmatrix} H_{11} - E & H_{12} & \dots & H_{1r} \\ \vdots & \vdots & \ddots & \vdots \\ H_{r1} & H_{r2} & \dots & H_{rr} - E \end{vmatrix} = 0$$

The accuracy can be verified by including one more  $\phi_{r+1}$  and watching for:

$$|E_n(r) - E_n(r+1)| \sim 0$$

The basis set should be expanded more and more till the convergence is realized

Any basis can be used but

if  $H^{(0)} + H_1$  then eigenstates of  $H^{(0)}$  can be used if they are exactly known.

This will best illustrated by  $H_2$  molecule.

SOME GENERAL COMMENTS AND INTERESTING EXAMPLES.

## Intro:

- Some interesting observations:

The method involves - guessing - the ground state in a parametric form.

For example  $\tilde{\psi}(x, a) = \sqrt{\frac{a}{\pi}} e^{-ax^2/2}$

$a$  is the inverse width of the wave packet.

So the idea is to use a trial wave function which is an exact solution for some other potential is often a good choice.

e.g. - a harmonic oscillator g.s. is good for 1D square wells

-  $\psi_{100}(\vec{r})$  of H atom is a good choice for radially symmetric 3D problems.

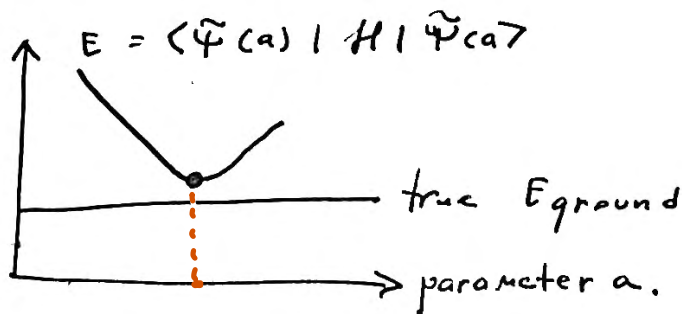
The procedure involves minimization of  $E$  w.r.t the free parameters i.e.

$$\tilde{E} = \langle \tilde{\psi} | H | \tilde{\psi} \rangle$$

↑ trial wave function.

Q: Why this approach works?

> Follow the lecture L4 p.1 .....



## Perturbation U.S. VARIATION.

Recall for the 1<sup>st</sup> order perturbation  $\Delta V$

$$H^0 + \Delta V \quad E_n^{(1)} = E_n^{(0)} + \langle n | V | n \rangle$$

- $|n\rangle$  is the unperturbed state of  $H^{(0)}$
- $H^{(0)} |n\rangle = E_n^{(0)} |n\rangle$

Lets cast this solution in a form that looks like the variational method:

$$E_n = \langle n | H | n \rangle = \langle n | H_0 + \Delta V | n \rangle \Rightarrow$$

$$E_n = \langle \tilde{\psi} | H | \tilde{\psi} \rangle = \langle n | H | n \rangle = E_n^{(0)} + \langle n | \Delta V | n \rangle$$

where  $\tilde{\psi} \equiv |n\rangle$

→ The 1<sup>st</sup> order perturbation theory =  
 = variational estimate where the trial w.  $\psi$ .  
 = the eigenstate of the unperturbed hamiltonian

But unlike perturbation we can alter  
the shape of  $\tilde{\psi}(x)$  to get as close as  
 possible to the ground state.

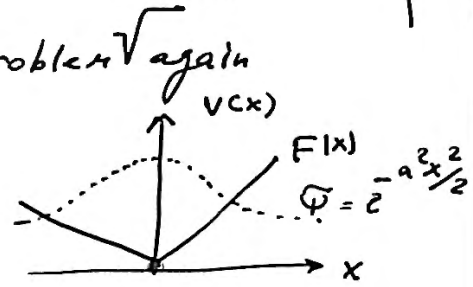


L 4

$V = F|x|$

9

Lets solve the symmetric ramp problem  $\sqrt{\text{again}}$  but via the variational way.



As a trial wave function we will use:

$$\tilde{\Psi}_0 = \left[ \sqrt{\frac{a}{\pi}} \right]^{1/2} e^{-ax^2/2}$$

So our main job is to evaluate

$$\langle \tilde{\Psi}_0 | H | \tilde{\Psi}_0 \rangle = \langle T \rangle + \langle V \rangle$$

Some math detour: To evaluate  $\langle V \rangle$  we need to calculate integrals like:

Math.

$$I_n = \int_0^{\infty} dy y^n e^{-ay^2} \quad \leftarrow \text{the trick}$$

is to start with  $I_1 = \frac{1}{2a}$  and then

$$\text{use the recursion } I_{n+2} = -\frac{\partial I_n}{\partial a}$$

For example:

$$\begin{aligned} \langle V \rangle &= \langle \tilde{\Psi}_0 | V | \tilde{\Psi}_0 \rangle = \langle \tilde{\Psi}_0 | F|x| | \tilde{\Psi}_0 \rangle = \\ &= \frac{2}{\sqrt{\pi}} \sqrt{\frac{a}{\pi}} \int_0^{\infty} dx F x e^{-ax^2} = 2 \times \sqrt{\frac{a}{\pi}} F \underbrace{\int_0^{\infty} x e^{-ax^2}}_{I_1} = \\ &= \frac{F}{\sqrt{\pi}} \frac{1}{\sqrt{a}} \end{aligned}$$

Next lets compute  $\langle T \rangle =$

$$= \frac{\hbar^2}{2m} \langle \tilde{\Psi}_0 | \frac{\partial^2}{\partial x^2} | \tilde{\Psi}_0 \rangle, \text{ as clearly seen}$$

$\langle T \rangle$  depends only on  $a$  and  $m$  and

has no connection to the well.

Since the  $\tilde{\Psi}_0$  is the exact ground state of an oscillator in the ground

$$\text{state } \langle T \rangle = \langle V \rangle = \frac{E}{2} = \hbar \omega / 4$$

Q! But for what  $\omega$ ???

about

Virial theorem:  
if  $V(x) = cx^n$   
 $2 \langle T \rangle = n \langle V \rangle$

For harmonic oscillator since  $a = \hbar\omega/\hbar$

we can write down

$$\langle T \rangle = \frac{\hbar\omega}{4} = \frac{\hbar}{4} \left( \frac{\hbar\omega}{m} \right) = \frac{\hbar^2 a}{4m}$$

So the final form of  $\langle H \rangle = \frac{\hbar^2 a}{4m} + \frac{F}{\sqrt{\pi}} a^{-1/2}$

The minimum  $\tilde{E}$  is clearly depends on  $a$   
 as  $a \uparrow$   $\tilde{\psi}_0$  gets more narrow and more peaked then  $\frac{\partial^2 \tilde{\psi}_0}{\partial x^2}$  gets very very large  
 kinetic term

But also narrow  $\tilde{\psi}_0$  means we probe states closer to the bottom of the well and thus the potential energy goes down.

Now we can minimise it w.r.t  $a$ :

$$\frac{\partial \langle H \rangle}{\partial a} = \frac{\partial}{\partial a} \left\{ \frac{\hbar^2 a}{4m} + \frac{F}{\sqrt{\pi}} a^{-1/2} \right\} = 0 \rightarrow$$

$$\frac{\hbar^2}{4m} = \frac{F}{2\sqrt{\pi}} a^{*-3/2} \rightarrow a^* = \left( \frac{2mF}{\hbar^2 \sqrt{\pi}} \right)^{2/3}$$

and finally  $E = \langle H \rangle_{\text{for } a^*} =$

$$E = \left( \frac{27}{16\pi} \right)^{1/3} \left( \frac{\hbar^2 F}{\sqrt{\pi}} \right)^{2/3}$$

Compare this answer to the solution we obtained for the Ai special function and WKB.

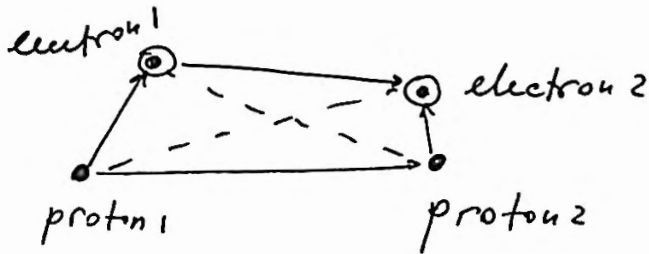
A QUICK REVIEW OF VARIATIONAL STRATEGY

1. Pick a trial wave function which is normalized ground state of a system that solves a potential close to the unknown one
2. Use a virial theorem, which allows us to write the kinetic part  $\langle T \rangle = \frac{E_0}{2}$  and avoid all other calculations
3. Do a single integration over the new potential to set up  $\tilde{E}$  and minimize it.
4. Allow more adjustable parameters if possible

*[Faint handwritten notes and equations, including  $\frac{E_0}{2}$  and other mathematical expressions, are visible but mostly illegible.]*

The  $H_2^+$  molecule

We want to solve this very realistic and rather non-trivial problem of 2 electrons localized around 2-nuclei centers.



This problem also appears in terms of a COVALENT BOND in chemistry.

So the question we are concerned with is such a "hybrid" object would even exist?

Q: We can restate the problem in  $H_2$  molecule is it possible that 2 electrons will be able to overcome a mutual Coulomb repulsion and repulsion between two protons & make a bound object we call a molecule?

↑  
or the state with negative energy.

The problem we about to solve is even more interesting can a single electron stabilize  $H_2^+$ .

To start lets place two protons at  $R$  and assume they are "pinned" since  $M_p \sim 1000 m_e$ .

$$V_{pp} = \frac{e^2}{4\pi\epsilon_0 R} = -\frac{2a_0}{R} \frac{-e^2}{4\pi\epsilon_0 2a_0} = -\frac{2a_0}{R} E_1$$

$$E_1 = -13.6 \text{ eV for H atom.}$$



And the complete hamiltonian is given by:

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

$$r_1 = |r - R_1| \quad \text{and} \quad r_2 = |r - R_2|$$

$r$  is the coordinate of  $e^-$  and  $\bar{R}_1, \bar{R}_2$  for protons and the distance between pp =  $R = |\bar{R}_2 - \bar{R}_1|$

Let's apply our variational method:

$$E = \langle \bar{\Psi} | H | \bar{\Psi} \rangle + V_{pp} \quad \text{and vary } R$$

to minimize  $E$ .

As a trial function we will use the  $\downarrow$  linear combination of atomic orbitals  $\uparrow$  atomic orbitals:

$$\bar{\Psi}(r) = N (\psi_{100}(|r - \bar{R}_1|) + \psi_{100}(|r - \bar{R}_2|)) \\ = N (\psi(r_1) + \psi(r_2))$$

here I assume that electrons have equal probability to be around either ~~proton~~ proton:

However we need to remember that

$\bar{\Psi} = N (\psi(r_1) + e^{i\delta} \psi(r_2))$  is the most general form of the wave function.

since  $H_0(r_1 \leftrightarrow r_2)$  is symmetric  $\Rightarrow$

$\Rightarrow e^{i\delta} = \pm 1$ . In terms of the symmetry

operator  $\hat{X}$ :  $\hat{X} \psi(r_1, r_2) = \psi(r_2, r_1) \Rightarrow$

$$\hat{X} [\hat{X} \psi(r_1, r_2)] = \psi(r_1, r_2) = \lambda^2 \psi(r_1, r_2) \Rightarrow \lambda^2 = 1 \Rightarrow \lambda = \pm 1$$

$$\text{or } \hat{X} (\psi(r_1) + e^{i\delta} \psi(r_2)) = (\psi(r_2) + e^{i\delta} \psi(r_1)) = \\ = \pm (\psi(r_1) + e^{i\delta} \psi(r_2)) \Rightarrow e^{i\delta} \text{ can be only } \pm 1$$

LS

We select  $\delta = 0$ .

Next normalization:

$$N^2 \langle \psi(r_1) + \psi(r_2) | \psi(r_1) + \psi(r_2) \rangle = 1 \Rightarrow$$

$$\Rightarrow N^2 (2 + 2 \langle \psi(r_1) | \psi(r_2) \rangle) = 1 \Rightarrow$$

$\equiv I = \text{the overlap integral}$

One popular way to express this overlap is to place 1 proton at  $z=0$  and other one at  $z$

$$I = \frac{1}{\pi a_0^3} \int d^3r e^{-r/a_0} \cdot e^{-\frac{|r-R\hat{z}|}{a_0}}$$

at  $z=R$

By introducing  $\xi = R/a_0$  we can show that

Show this!

$$\Rightarrow I = e^{-\xi} \left( 1 + \xi + \frac{\xi^3}{3} \right) \text{ and}$$

$$\text{thus } N = \frac{1}{\sqrt{2(I+1)}}$$

How to deal with the Schr. equation when our  $\psi$  is constructed from two hydrogen atom like w.f.?

Consider this: hydrogen atom ~~action on~~ displaced by  $R_1$

$$H \psi(r_1) = \left\{ -\frac{\hbar^2}{2m} \nabla^2 \psi(r_1) - \frac{e^2}{r_1} \psi(r_1) \right\} - \frac{e^2}{r_2} \psi(r_1)$$

Comment: our w.f. is constructed of  $\psi(r_1)$  and  $\psi(r_2)$  which are eigenfunctions of pieces of  $\hat{H}$ .

acting out the atom displaced by  $(r-R_1)$

So we can write down:

$$H \psi(r_1) = E_1 \psi(r_1) - \frac{e^2}{r_2} \psi(r_1) \text{ and } H \psi(r_2) = E_2 \psi(r_2) - \frac{e^2}{r_1} \psi(r_2)$$

$E_1 = E_2$  since the same H atom

For total hamiltonian:

$$\begin{aligned}
 H\bar{\Psi} &= NH(\Psi(r_1) + \Psi(r_2)) = \\
 &= \underbrace{E_1\Psi(r_1) + E_2\Psi(r_2)}_{E_1=E_2 \Rightarrow} - N \frac{e^2}{4\pi\epsilon_0} \left( \frac{\Psi(r_1)}{r_2} + \frac{\Psi(r_2)}{r_1} \right) \\
 &\Rightarrow E_1(\Psi(r_1) + \Psi(r_2)) \\
 &= E_1\Psi - \frac{Ne^2}{4\pi\epsilon_0} \left( \frac{\Psi(r_1)}{r_2} + \frac{\Psi(r_2)}{r_1} \right)
 \end{aligned}$$

where  $E_1 = \frac{-e^2}{4\pi\epsilon_0 2a_B}$   
 $= -13.6 \text{ eV}$

$$\begin{aligned}
 \bar{E} &= \langle \Psi | H | \Psi \rangle = E_1 \langle \Psi | \Psi \rangle - \\
 &- N^2 \frac{e^2}{4\pi\epsilon_0} \left( \langle \Psi(r_1) + \Psi(r_2) | \frac{1}{r_2} | \Psi(r_1) \rangle + \right. \\
 &\left. + \langle \Psi(r_1) + \Psi(r_2) | \frac{1}{r_1} | \Psi(r_2) \rangle \right)
 \end{aligned}$$

b/c of  $r_1 \leftrightarrow r_2$  symmetry

$$\begin{aligned}
 \bar{E} &= E_1 - 2 \times N^2 \frac{e^2}{4\pi\epsilon_0} \left( \langle \Psi(r_1) | \frac{1}{r_2} | \Psi(r_1) \rangle + \right. \\
 &\left. + \langle \Psi(r_1) | \frac{1}{r_1} | \Psi(r_2) \rangle \right) = E_1 - \underbrace{2}_{\equiv D} N^2 \frac{e^2}{4\pi\epsilon_0} \cdot \underbrace{\frac{1}{2a_B}}_{\equiv X} \left( \langle \Psi(r_1) | \frac{a_0}{r_2} | \Psi(r_1) \rangle + \right. \\
 &\left. + \langle \Psi(r_1) | \frac{a_0}{r_1} | \Psi(r_2) \rangle \right) \text{ or}
 \end{aligned}$$

$$\bar{E} = E_1 + 4E_1 N^2 (D + X)$$

The analytical solution of integrals D and X:

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

$$X = \left(1 + \xi\right) e^{-\xi}$$

where  $\xi = \frac{R}{a_B}$

Notice that two integrals  $X, I$

that are based on  $\langle \psi(r_1) | \dots | \psi(r_2) \rangle$

fall off as  $\sim e^{-R/a_B} \Rightarrow D(R \rightarrow \infty) = \frac{1}{\xi} = \frac{R}{a_B}$

in the opposite limit:  $\xi \rightarrow 0$  or  $R \rightarrow 0$

$r_2 \rightarrow r_1$

$I(\xi) \rightarrow \langle \psi(r) | \psi(r) \rangle = 1$

$D(\xi) \rightarrow I(\xi) \rightarrow \langle \psi(r) | \frac{a_B}{r} | \psi(r) \rangle = a_B \left( \frac{1}{r} \right) = 1 = a_B$

Now we include the  $V_{pp}$  term

and  $N^2 = \frac{1}{2(I+1)}$

$\epsilon = E + V_{pp} = -\frac{2}{3} E_1 + E_1 + 2E_1 \frac{D+X}{I+1}$

Now we need to prove that the "molecular" total energy is lower

than  $E_1$ , i.e.

$$-\frac{\epsilon}{E_1} \equiv f(\xi) = -1 + \frac{2}{\xi} \left( \frac{(1 - (2/3)\xi^2)\xi^2 e^{-\xi} + (1 + \xi) e^{-2\xi}}{1 + (1 + \xi + \frac{1}{3}\xi^2) e^{-\xi}} \right)$$

$f(\xi \rightarrow \infty) \quad D, X, I \rightarrow 0 \quad \text{and} \quad \epsilon(\infty) \rightarrow E_1$   
 $V_{pp} \rightarrow 0$

just a superposition of hydrogen atoms and a free proton.

For  $R \rightarrow 0 \quad V_{pp} \uparrow \infty$  and  $\epsilon \uparrow +\infty$  in between

In between  $\frac{\partial f}{\partial \xi} = 0 \Rightarrow \xi^* \quad \text{or} \quad R^*$

and  $\epsilon = -13.6 \text{ eV} - 1.76 \text{ eV}!$

$R^* = 1.27 \text{ \AA}$   
**MOLECULE EXISTS!**

