L4

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 attemted to guess the wave function we can construct the ground state energy.

Lets assume we know Φ_n:

$$H \Phi_n = E_n \Phi_n \qquad n = 0, 1, \dots$$

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

Now lets calulate the average of H

$$\int \psi^* H \psi \, d\tau = \int \sum_m a_m^* \phi_m^* \, H \sum_n a_n \Phi_n \, dv$$

δ_{mn}!

$$= \sum_n |a_n|^2 E_n \geqslant \sum_n |a_n|^2 E_0$$

b/c if we are not in the ground state $\sum_n |a_n|^2 E_n$ is larger. For normalized Φ_n: $\sum_n \Phi_n^2 = 1 \implies$

$$\boxed{E_0 \leq \int_{\infty}^{\infty} \psi^* H \psi \, d\tau}$$ ← the variational theorem

So whatever is the form of the w.f. Ψ it is alway can be minimized if we express ψ as a function of some parameters, e.g. c_i

$$E(c_i) = \int_{\pm\infty} \phi^*(c_i)\, H\, \phi(c_i)\, d\tau$$

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

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:

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

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

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

Next we know that

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

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

$$+\, m\omega^2 A^2 \int_0^\infty x^2 e^{-2\alpha x^2} dx$$

Recall in the lecture 2 we learn that

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

!! 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

typo on page 402 eqn. 16.13

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

~~[illegible]~~

~~[illegible]~~

~~[illegible]~~

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

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

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

$$= \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = \frac{\hbar\omega}{2}\ !$$ 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.

$$\Psi_t = \Psi - \phi_0 \int \phi^* \Psi \, d\tau \Rightarrow$$

$$\langle \phi_0 | \Psi_t \rangle = \langle \phi_0 | \Psi \rangle - \overset{1}{\langle \phi_0 | \phi_0 \rangle} \langle \phi_0 | \Psi \rangle = 0$$

Hence the expression

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

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 Ψ_t gives the upper limit for the 1st excited state.

By virtue of the same argument we get that Ψ_t is orthogonal to ϕ_i $i = 0, 1 \ldots n$ and thus Ψ_t gives the upper limit for $(n+1)$th energy eigenvalue

Finite Basis expansion

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

the Ψ_t is then can be constructed as:

$$\Psi = \sum_{i=1}^{r} a_i \phi_i$$

a_i are the variational parameters.

Note: ϕ_i may not be orthogonal.

$$E = \int_{\pm\infty} \psi^* H \psi \, d\tau \Big/ \int_{+\infty} \psi^* \psi \, d\tau$$

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

or

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

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

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

If we differenteate w.r.t $\frac{\partial}{\partial a_i}(\dots) = 0$ we get a complex conjugate of

Thus we ended up with the folowing set of eqn's:

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

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

$$\sum_{i=1}^r \left(H_{ij} - ES_{ij}\right) a_j = 0 \qquad i = 1, 2, \dots$$

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:

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

The accuracy can be verified by including one more Φ_{p+1} and watching for:

$$| E_n(r) - E_n(r+1) | \cancel{=} \sim 0$$

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.

~~Example: A hydrogen Molecule~~

This will best illustrated by H_2^+ molecule.

SOME GENERAL COMMENTS AND INTERESTING EXAMPLES.

L 4

VARIATIONAL METHODS

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.

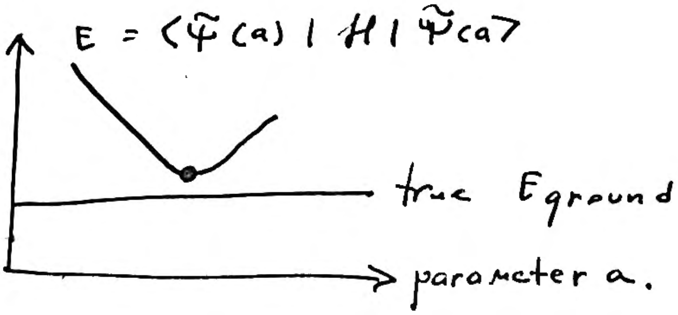
The procedure involves minimization of E w.r.t the free parameters i.e.

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

trial wave function.

Q: Why this approach works?

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



Perturbation V.S. VARIATION.

Recall for the 1st order perturbation ΔV

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

$|n\rangle$ 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:

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

$E_n = \langle \tilde{\Psi} | H | \tilde{\Psi} \rangle = \langle n | H | n \rangle = E_n^{(0} + \langle n | \lambda V | n \rangle$

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

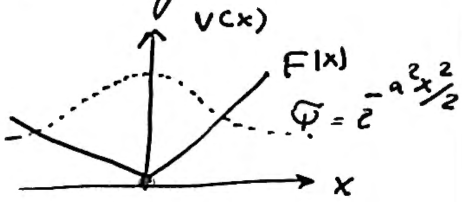
→ The 1st order perturbation theory =

NB!
= variational estimate where the trial w.f. Ψ
= the eigenstate of the unperturbed hamiltonian

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

L 4

Lets solve the symmetric ramp problem $V = F|x|$ 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

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

Math.

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

$$J_n = \int_0^\infty dy\, y^n e^{-ay^2}$$

, recall the trick is to start with $J_1 = \frac{1}{2a}$ and then use the recursion $J_{n+2} = -\frac{\partial J_n}{\partial a}$

For example:

$$\langle V \rangle = \langle \tilde{\varphi}_0 | V | \tilde{\varphi}_0 \rangle = \langle \tilde{\varphi}_0 | F|x| \, | \tilde{\varphi}_0 \rangle =$$

$$= \underline{\underline{2}} \times \sqrt{\frac{a}{\pi}} \int_0^\infty dx\, F \cancel{|}x\cancel{|}\, e^{-ax^2} = 2 \times \sqrt{\frac{a}{\pi}}\, F \underbrace{\int_0^\infty x e^{-ax^2}}_{J_1} =$$

$$= \frac{F}{\sqrt{\pi}} \frac{1}{\sqrt{a}}$$

Next lets compute $\langle T \rangle =$

$$= \frac{\hbar^2}{2m} \langle \tilde{\varphi}_0 | \frac{\partial}{\partial x^2} | \tilde{\varphi}_0 \rangle$$

as clearly seen $\langle T \rangle$ depends only on a and m and has no connection to the well.

Since the $\tilde{\varphi}_0$ is the <u>exact</u> ground state of. an oscillator in the ground state $\langle T \rangle = \langle V \rangle = \frac{E}{2} = \hbar\omega/4$

Q! But for what ω???

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

we can write down:

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

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 ↑ $\tilde{\psi}_0$ gets more narrow and more peaked, then $\underbrace{\frac{\partial^2 \tilde{\psi}_0}{\partial x^2}}_{\text{kinetic term}}$ gets very very large

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

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

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

~~We can repeat the WKB here again with a slight twist~~

A QUICK REVIEV 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 viral theorem which allows us to write the kinetic part $\langle T \rangle = \frac{E_0}{2}$ and avoid all other calculations

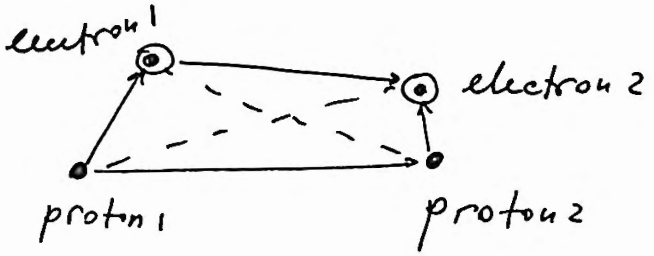
3. Do a single integration over the new potential to set up $\widetilde{E}$ and minimize it.

4. Allow more adjustable parameters if possible.

L 4

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 if 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 $M_p \sim 1000\, m_{e^-}$.

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

$E_1 = -13.6$ eV for H atom.

And the complete hamiltonian is given by:

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

$r_1 = |r - R_1|$ and $r_2 = |r - R_2|$

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

Lets apply our variational method:

$E = \langle \tilde{\Psi} | H | \tilde{\Psi} \rangle + V_{pp}$ and vary R to minimize E.

linear ↓ of atomic

As a trial function we will use the LCAO orbitals atomic orbitals:

↑ combination

$$\tilde{\Psi}(\bar{r}) = N\left(\psi_{100}(|\bar{r} - \bar{R}_1|) + \psi_{100}(|\bar{r} - R_2|)\right)$$
$$= N\left(\psi(r_1) + \psi(r_2)\right)$$

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

However we need to remember that

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

Since H_a $(r_1 \leftrightarrow r_2)$ is symmetric $\Rightarrow$

$\Rightarrow e^{i\delta} = \pm$. In terms of the symmetry operator $\hat{X}$: $\hat{X}\psi(r_1, r_2) = \psi(r_2, r_1) \Rightarrow$

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

or $\hat{X}(\psi(r_1) + e^{i\delta}\psi(r_2)) = (\underline{\psi(r_2)} + e^{i\delta}\psi(r_1) =$

$= \underline{\underline{\pm}}(\psi(r_1) + \underline{\underline{e^{i\delta}}}\psi(r_2)) \Rightarrow e^{i\delta}$ can be only ±1

L5

We select $\delta = 0$.

Next normalization:

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

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

$\equiv I$ = the overlap integral

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

$$I = \frac{1}{\pi a_B^3} \int d^3r \, \underset{z=0}{e^{-r/a_B}} \cdot \underset{\text{at } z=R}{e^{\left(-\frac{|r - R\hat{z}|}{a_B}\right)}}$$

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

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

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

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

Consider this:

$$H\psi(r_1) = \overbrace{\left\{ -\frac{\hbar^2}{2m} \nabla^2 \psi(r_1) - \frac{e^2}{r_1}\psi(r_1) \right\}}^{\text{hydrogen atom displaced by } R_1} - \underbrace{\frac{e^2}{r_2}\psi(r_1)}_{\text{acting out the atom displaced by } (r - R_1)}.$$

~~notion on~~

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

So we can write down:

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

$E_1 = E_2$ since the same H atom

LS

For total hamiltonian:

$$H\tilde{\Psi} = NH(\psi(r_1) + \psi(r_2)) =$$

$$= \underbrace{E_1\psi(r_1) + E_2\psi(r_2)}_{E_1 = E_2 \Rightarrow} - N\frac{e^2}{4\pi\epsilon_0}\left(\frac{\psi(r_1)}{r_2} + \frac{\psi(r_2)}{r_1}\right)$$

$$\Rightarrow E_1(\psi(r_1) + \psi(r_2))$$

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

$$= E_1\Psi - \frac{Ne^2}{4\pi\epsilon_0}\left(\frac{\psi(r_1)}{r_2} + \frac{\psi(r_2)}{r_1}\right)$$

$$\bar{E} = \langle\Psi|H|\Psi\rangle = E_1\langle\Psi|\Psi\rangle -$$

$$- N^2\frac{e^2}{4\pi\epsilon_0}\Big(\langle\psi(r_1) + \psi(r_2)|\frac{1}{r_2}|\psi(r_1)\rangle +$$

$$+ \langle\psi(r_1) + \psi(r_2)|\frac{1}{r_1}|\psi(r_2)\rangle\Big)$$

b/c of $r_1 \leftrightarrow r_2$ symmetry

$$E = E_1 - 2\times N^2\frac{e^2}{4\pi\epsilon_0}\Big(\langle\psi(r_1)|\frac{1}{r_2}|\psi(r_1)\rangle +$$

$$+ \langle\psi(r_1)|\frac{1}{r_1}|\psi(r_2)\rangle\Big) =$$

$$= E_1 - 4N^2\overbrace{\frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{2a_B}}^{E_1}\Big(\overset{\equiv D}{\langle\psi(r_1)|\frac{a_0}{r_2}|\psi(r_1)\rangle} +$$

$$+ \underset{\equiv X}{\langle\psi(r_1)|\frac{a_0}{r_1}|\psi(r_2)\rangle}\Big) \quad \text{or}$$

$$E = E_1 + 4E_1N^2(D + X)$$

The analytical solution of integrals D and X:

$$D = \frac{1}{\xi} - \left(1 + \frac{1}{\xi}\right)e^{-2\xi} \qquad \text{where } \xi = \frac{R}{a_B}$$

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

LS

Notice that two integrals X, I that are based on $\langle \psi(r_1) | \ldots | \psi(r_2) \rangle$ fall off as $\sim e^{-R/a_B}$ $\Rightarrow D(R \to \infty) = \frac{1}{\xi} = \frac{R}{a_B}$

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

$r_2 \to r_1$

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

$D(\xi) \to \underset{=1}{I(\xi)} \to \langle \psi(r) | \frac{a_B}{r} | \psi(r) \rangle = a_B \underset{= a_B}{\langle \frac{1}{r} \rangle}$

Now we include the V_{pp} term and $N^2 = \frac{1}{2(I+1)}$

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

Now we need to prove that the "molecular" total energy is lower than E_1, i.e.

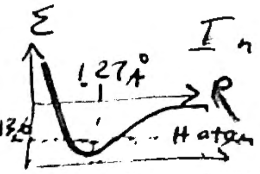
$$\frac{\mathcal{E}}{-E_1} \equiv f(\xi) = -1 + \frac{2}{\xi} \left(\frac{\left(1-(2/3)\xi^2\right)e^{-\xi} + (1+\xi)\,e^{-2\xi}}{1+\left(1+\xi+\frac{1}{3}\cdot\xi^2\right)e^{-\xi}} \right)$$

$f(\xi \to \infty)$ $D, X, I \to 0$ and $\mathcal{E}(\infty) \to E_1$

$V_{pp} \to 0$

just a superposition of hydrogen atoms and a free proton.

For $R \to 0$ $V_{pp} \uparrow \infty$ and $\mathcal{E} \uparrow +\infty$ in between



In between $\frac{\partial f}{\partial \xi} = 0 \Rightarrow \xi^*$ or R^* $\cancel{\xi} = 1.27 A°$

and $\mathcal{E} = -13.6\,eV - 1.76\,eV$! MOLECULE EXISTS !