量子力学
Quantum mechanics

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CHAPTER 7

The variational principle

Suppose you want to calculate the ground-state energy E_g for a system described by the Hamiltonian H, but you are unable to solve the (time-independent) $schr\ddot{o}dinger$ equation

What should you do ?

7.1 Theory

Theorem:

is any normalized function

$$E_g \leq \left\langle \Psi \middle| H \middle| \Psi \right\rangle \equiv \left\langle H \right\rangle$$

That is, the expectation value of H in the (presumably in correct) state Ψ is certain to overestimate the ground-state energy. Of course, if ψ just happens to be one of the excited states, then obviously $\left\langle H \right\rangle$ exceeds E_g.

Proof

Since the (unknown) eigenfunctions of H form a complete set ,we can express Ψ as a linear combination of them:

$$\Psi = \sum_n c_n \Psi_n \quad , \text{ with } \quad H\Psi_n = E_n\Psi_n$$

And Ψ is normalized,

$$1 = \langle \Psi | \Psi \rangle = \left\langle \sum_m c_m \Psi_m \middle| \sum_n c_n \Psi_n \right\rangle$$

$$= \sum_m \sum_n c^*_m c_n \langle \Psi_m | \Psi_n \rangle = \sum_n |c_n|^2$$

Meanwhile,

$$\langle H \rangle = \left\langle \sum_m c_m \Psi_m \middle| H \sum_n c_n \Psi_n \right\rangle$$

$$= \sum_m \sum_n c^*_m E_n c_n \langle \Psi_m | \Psi_n \rangle = \sum_n E_n |c_n|^2$$

Since $E_g \leq E_n$,we get

$$\langle H \rangle \geq E_g \sum_n |c_n|^2 = E_g$$

Which is what we were trying to prove.

Examples

Aim   To find the ground-state energy

Processes

Step 1.   Select a trial wave function Ψ

Step 2.   Calculate $\langle H \rangle$ in this state

Step 3.   Minimize the $\langle H \rangle$

Step 4.   Take H_{min} as the appropriate ground-state energy

Example 1.

Of course, we already know the exact answer (see chapter 2): $E_g = \dfrac{1}{2}\hbar\omega$

To find the ground-state energy for the one-dimensional harmonic oscillator:

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

Pick a Gaussian function as our trial state

$$\Psi(x) = Ae^{-bx^2}$$

where b is a constant and A is determined by normalization:

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}\,dx = |A|^2 \sqrt{\frac{\pi}{2b}} \quad \Longrightarrow \quad A = \left(\frac{2b}{\pi}\right)^{1/4}$$

The mean value of H is

$$\langle H \rangle = -\frac{\hbar^2}{2m}|A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2}\left(e^{-bx^2}\right)dx + \frac{1}{2}m\omega^2 |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} x^2 dx$$

$$= \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$$

We can get the tightest bound through minimizing $\langle H \rangle$ with

respect to b :

$$\frac{d}{db}\langle H \rangle = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \quad \Longrightarrow \quad b = \frac{m\omega}{2\hbar}$$

Putting this back into $\langle H \rangle$, we find

$$\langle H \rangle_{\min} = \frac{1}{2}\hbar\omega$$

Example 2.

Again ,we already know the exact answer (see chapter 2):

$$E_g = -\alpha \sqrt{\frac{2b}{\pi}}$$

To look for the ground state energy of the delta-function potential:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\delta(x)$$

We also Pick a Gaussian function as our trial state:

$$\Psi(x) = Ae^{-bx^2}$$

The mean value of H is

$$\langle H \rangle = -\frac{\hbar^2}{2m}|A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2}\left(e^{-bx^2}\right)dx - \alpha|A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}\delta(x)dx$$

$$= \frac{\hbar^2 b}{2m} - \alpha\sqrt{\frac{2b}{\pi}}$$

Minimizing it,

$$\frac{d}{db}\langle H \rangle = \frac{\hbar^2}{2m} - \frac{a}{\sqrt{2\pi b}} = 0 \qquad \Longrightarrow \qquad b = \frac{2m^2\alpha^2}{\pi\hbar^4}$$

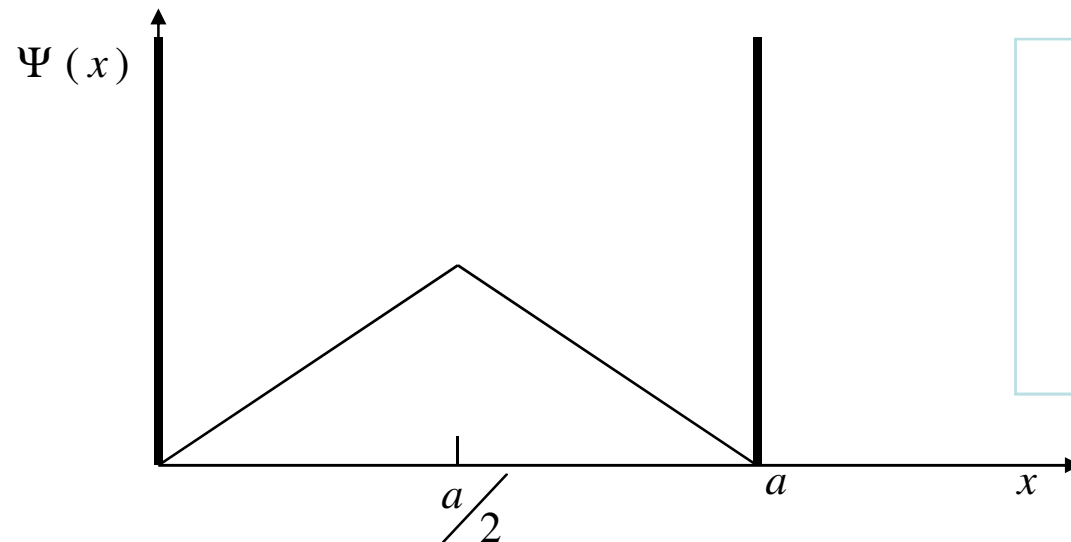So

$$\langle H \rangle_{min} = -\frac{m\alpha^2}{\pi\hbar^2}$$

which is indeed somewhat higher than E_g ,since $\pi > 2$

Example 3.

To find an upper bound on the ground-state energy of the one-dimension infinite square well, using the "triangular" trial wave function (figure 7.1):

$$\psi(x) = \begin{cases} Ax, & \text{if } 0 \leq x \leq a/2, \\ A(a-x), & \text{if } a/2 \leq x \leq a, \\ 0, & \text{otherwise,} \end{cases}$$

Figure 7.1: "triangular" trial wave function for the infinite square well

Where A is determined by normalization:

$$1 = |A|^2 \left[\int_0^{a/2} x^2 dx + \int_{a/2}^a (a-x)^2 dx \right] = |A|^2 \frac{a^3}{12} \implies A = \frac{2}{a}\sqrt{\frac{3}{a}}$$

In this case

$$\frac{d\psi}{dx} = \begin{cases} A, & \text{if } 0 \le x \le a/2, \\ -A, & \text{if } a/2 \le x \le a, \\ 0, & \text{otherwise,} \end{cases}$$

The derivative of this step function is a delta function (see problem 2.24b)

$$\frac{d\Psi}{dx^2} = A\delta(x) - 2A\delta(x - a/2) + A\delta(x-a)$$

and hence

$$\langle H \rangle = -\frac{\hbar^2 A}{2m} \int \left[\delta(x) - 2\delta(x - a/2) + \delta(x-a) \right] \Psi(x)dx$$

$$= -\frac{\hbar^2 A}{2m} \left[\Psi(0) - 2\Psi(a/2) + \Psi(a) \right] = \frac{\hbar^2 A^2}{2m} = \frac{12\hbar^2}{2ma^2}$$

The exact ground state is $E_g = \dfrac{\hbar^2 \pi^2}{2ma^2}$ (see chapter 2), so

the theorem works ($12 > \pi^2$)

Conclusions

Advantages

■ The **variational principle** is very powerful and easy to use

◆ write down a trial wave function

◆ Calculate $\langle H \rangle$

◆ tweak the parameters to get the lowest possible value

■ Even if Ψ has no relation to the true wave function, one often gets miraculously accurate values for E_g

Limitations

- It applies only to the ground state

- You never know for sure how close you are to the target and all you can certain of is that you have got an upper bound.

7.2　The ground state of helium

Our task:

> To calculate the ground–state energy by using the Variational Principle

> Theoretically reproduce the value :

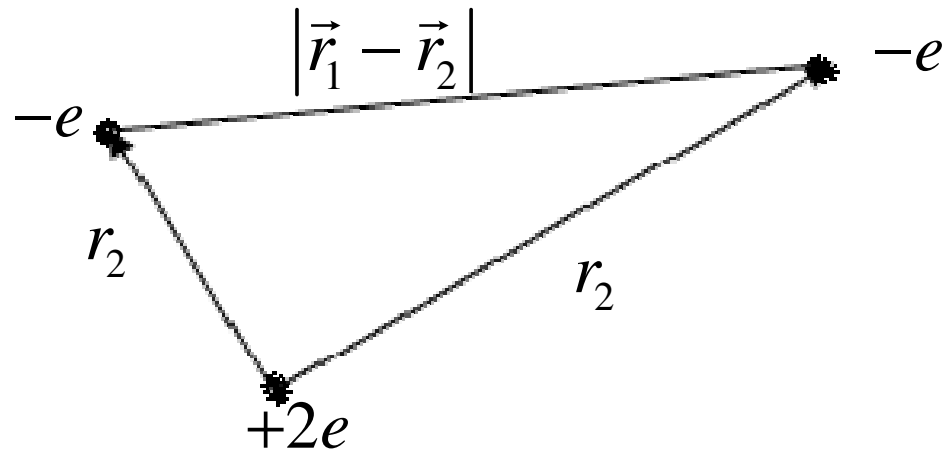$$E_g = -78.975 \text{ ev} \quad (\text{experimental})$$

Figure 7.2:the helium atom

The Hamiltonian for the helium atom system (ignoring fine structure and small correction) is

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{\left|\vec{r_1} - \vec{r_2}\right|}\right)$$

Let

$$V_{ee} = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{\left|\vec{r_1} - \vec{r_2}\right|}$$

If we ignore the electron-electron repulsion V_{ee} is, the ground-state wave function is just

$$\Psi_0\left(\vec{r_1}, \vec{r_2}\right) \equiv \Psi_{100}\left(\vec{r_1}\right) \Psi_{100}\left(\vec{r_2}\right) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$$

where Ψ_{100} is hydrogen-like wave function with $Z = 2$.

Consequently ,the energy that goes with this simplified picture is $8E_1 = -109$ ev (see Chapter 5).

In the following we will apply the variational principle , using the Ψ_0 as the trial wave function. The eigenfunction of Hamiltonian is:

$$H\Psi_0 = \left(8E_1 + V_{ee}\right)\Psi_0$$

Thus

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle$$

where

$$\langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\varepsilon_0} \right) \left(\frac{8}{\pi a^3} \right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{\left| \vec{r_1} - \vec{r_2} \right|} d^3\vec{r_1} d^3\vec{r_2}$$

To get the above integral value conveniently, we do the $\vec{r_2}$ integral first and orient the $\vec{r_2}$ coordinate system so that the $\vec{r_1}$ polar axis lies along (see Figure 7.3).

By the law of cosines,

$$\left| \vec{r_1} - \vec{r_2} \right| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}$$

and hence

$$I_2 \equiv \int \frac{e^{-4r_2/a}}{\left|\vec{r_1}-\vec{r_2}\right|}d^3\vec{r_2} = \int \frac{e^{-4r_2/a}}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}r_2^2\sin\theta_2 dr_2 d\theta_2 d\phi_2$$

The ϕ_2 integral is trivial
(2π);the ϕ_1 integral is:

$$\int_0^\pi \frac{\sin\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}d\theta_2$$

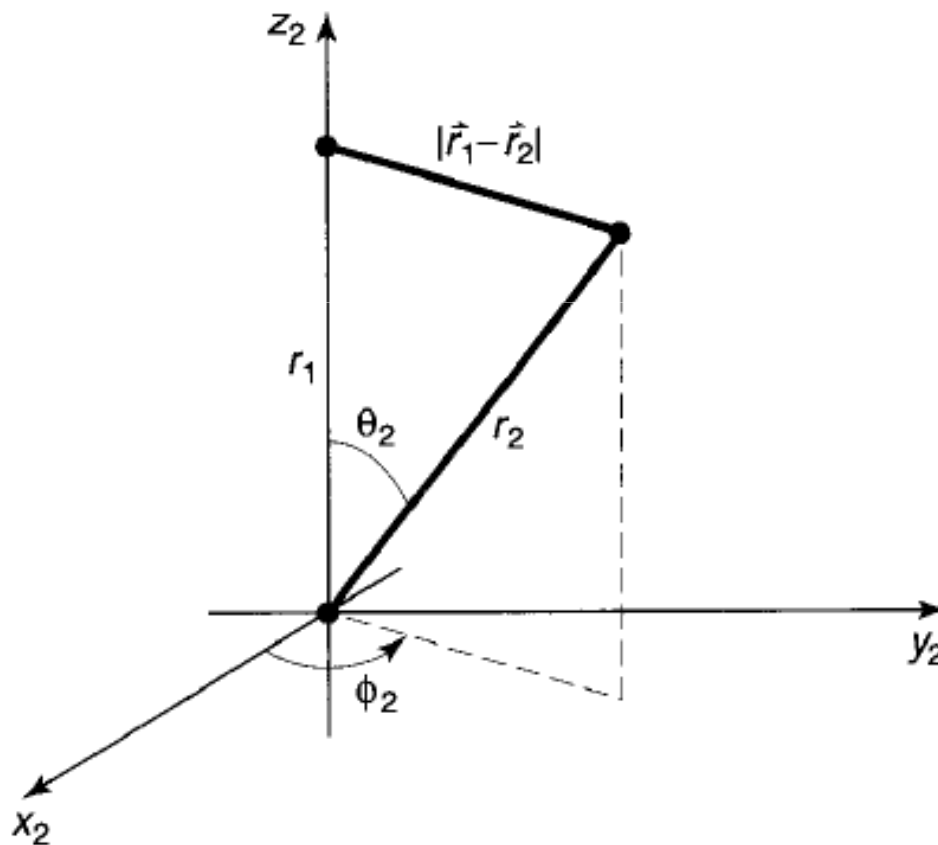$$= \frac{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}{r_1r_2}\Bigg|_0^\pi$$

Figure 7.3: choice of coordinate for the $\vec{r_2}$ integral

$$= \frac{1}{r_1 r_2} \left(\sqrt{r_1^2 + r_2^2 + 2r_1 r_2} - \sqrt{r_1^2 + r_2^2 - 2r_1 r_2} \right)$$

$$= \frac{1}{r_1 r_2} \left[(r_1 + r_2) - |r_1 - r_2| \right] = \begin{cases} 2/r_1, & \text{if } r_2 < r_1 \\ 2/r_2, & \text{if } r_2 > r_1 \end{cases}$$

Thus

$$I_2 = 4\pi \left(\frac{1}{r_1} \int_0^{r_1} e^{-4r_2/a} r_2^2 \, dr_2 + \int_{r_1}^{\infty} e^{-4r_2/a} r_2 \, dr_2 \right)$$

$$= \frac{\pi a^3}{8 r_1} \left[1 - \left(1 + \frac{2r_1}{a} \right) e^{-4r_1/a} \right]$$

It follows that $\langle V_{ee} \rangle$ is equal to

$$\left(\frac{e^2}{4\pi\varepsilon_0} \right) \left(\frac{8}{\pi a^3} \right) \int \left[1 - \left(1 + \frac{2r_1}{a} \right) e^{-4r_1/a} \right] e^{-4r_1/a} r_1 \sin\theta_1 \, dr_1 \, d\theta_1 \, d\phi_1$$

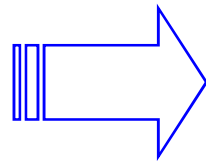The angular integals are easy(4π),and the $\vec{r_1}$ integal becomes

$$\int_0^\infty \left[re^{-4r/a} - \left(r + \frac{2r^2}{a} \right) e^{-8r/a} \right] dr = \frac{5a^2}{128}$$

Finally , then,

$$\langle V_{ee} \rangle = \frac{5}{4a} \left(\frac{e^2}{4\pi\varepsilon_0} \right) = -\frac{5}{2} E_1 = 34ev$$

And therefore

$$\langle H \rangle = -109ev + 34ev = -75ev$$

Not bad , but we can do better!

Can we think of a more realistic trial function

than Ψ_0 ?

We try the product function

$$\Psi_1(\vec{r}_1, \vec{r}_2) \equiv \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$$

and treat Z as a variable rather than setting it equal to 2.

The idea is that as each electron shields the nuclear charge seen by the other ,the effective Z is less than 2.

In the following, we will treat Z as a variational parameter, picking the value that minimizes $\langle H \rangle$.

Rewrite H in the following form:

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1{}^2 + \nabla_2{}^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{\left|\vec{r_1} - \vec{r_2}\right|}\right)$$

The expectation value of H is evidently

$$\left\langle H \right\rangle = 2Z^2 E_1 + 2(Z-2)\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left\langle \frac{1}{r}\right\rangle + \left\langle V_{ee}\right\rangle$$

Here $\left\langle \frac{1}{r}\right\rangle$ is the expectation value of $\frac{1}{r}$ in the (one-particle) hydrogenic ground state Ψ_{100} (but with nuclear charge Z).

And according to Chapter 6, we know

$$\left\langle \frac{1}{r} \right\rangle = \frac{a}{Z}$$

The expection value of V_{ee} is the same as before ,except that instead of $Z = 2$,we now want arbitrary Z—so we multiply a by $Z/2$:

$$\left\langle V_{ee} \right\rangle = \frac{5Z}{8a} \left(\frac{e^2}{4\pi\varepsilon_0} \right) = -\frac{5Z}{4} E_1$$

Putting all this together, we find

$$\left\langle H \right\rangle = \left[2Z^2 - 4Z(Z-2)(5/4)Z \right] E_1 = \left[-2Z^2 + (27/4)Z \right] E_1$$

The lowest upper bound occurs when $\langle H \rangle$ is minimized:

$$\frac{d}{dZ}\langle H \rangle = \left[-4Z + (27/4) \right] E_1 = 0$$

from which it follows that

$$Z = \frac{27}{16} = 1.69$$

Putting in this value for Z, we find

$$\langle H \rangle = \frac{1}{2}\left(\frac{3}{2}\right)^6 E_1 = -77.5 ev$$

Much nearer to experimental value !
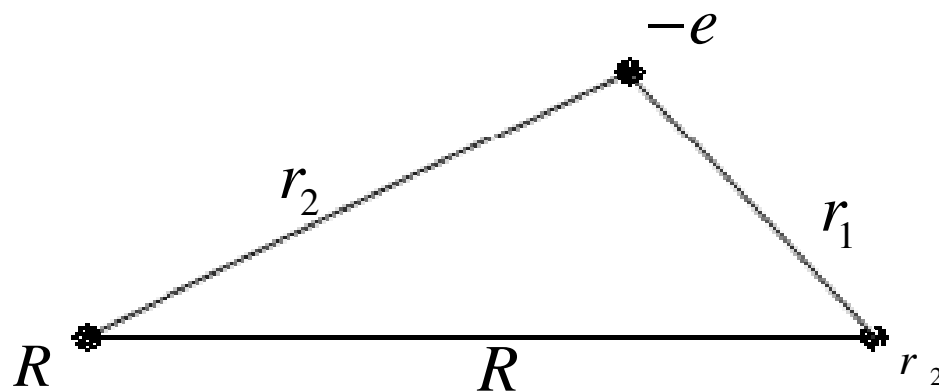
7.3 The hydrogen molecule ion

Figure 7.4 :the hydrogen molecule ion, H_2^+.

The Hamiltonian for this system is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

To construct the trial wave function , imagine that the ion is formed by taking a hydrogen atom in its ground state

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

and then bringing in proton from far away and nailing it down a distance R away. If R is substantially greatly than the Bohr radius a, the electron's wave function probably isn't changed very much. But we would like to treat the two protons equally ,so that the electron has the same probability of being associated with either one. So we consider a trial function of the form

$$\Psi = A\left[\Psi_g(r_1) + \Psi_g(r_2)\right]$$

Normalize this trial function:

$$1 = \int \left| \Psi \right|^2 d^3\vec{r} = \left| A \right|^2 \left[\int \left| \Psi_g(r_1) \right|^2 d^3\vec{r} + \int \left| \Psi_g(r_2) \right|^2 d^3\vec{r} + 2\int \Psi_g(r_1)\Psi_g(r_2) d^3\vec{r} \right]$$

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

Let

$$I \equiv \left\langle \Psi_g(r_1) \middle| \Psi_g(r_2) \right\rangle = \frac{1}{\pi a^3} \int e^{-(r_1 + r_2)/a} d^3\vec{r}$$

Picking coordinates so that the pronton 1 is at the origin and proton 2 is on the z-axis at the point R (Figure 7.5), we have

$$r_1 = r \qquad\qquad r_2 = \sqrt{r^2 + R^2 - 2rR\cos\theta}$$

and therefore

$$I = \frac{1}{\pi a^3} \int e^{-r/a} e^{-\sqrt{r^2+R^2-2rR\cos\theta}/a} \, r^2 \sin\theta \, dr \, d\theta \, d\phi$$

The ϕ integral is trivial (2π).

To do the θ integral, let

$$y \equiv \sqrt{r^2 + R^2 - 2rR\cos\theta}$$

so that

$$d(y^2) = 2y\,dy = 2rR\sin\theta\,d\theta$$
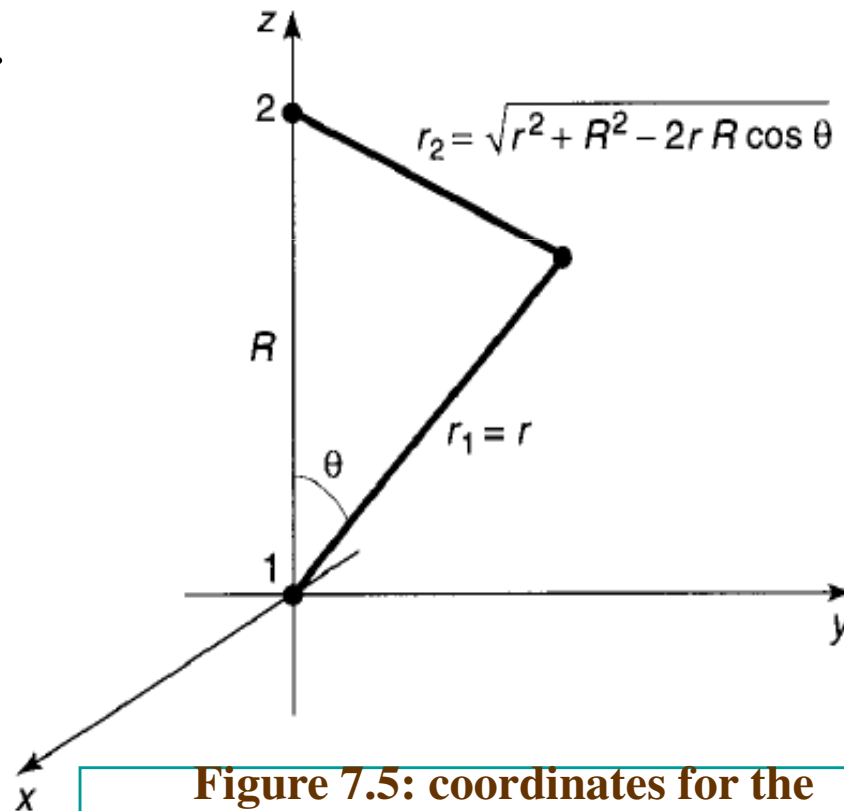

Figure 7.5: coordinates for the calculation of *I*

Then

$$\int_0^\pi e^{-\sqrt{r^2+R^2-2rR\cos\theta}/a} \sin\theta d\theta = \frac{1}{rR}\int_{|r-R|}^{r+R} e^{-y/a} y dy$$

$$= -\frac{a}{rR}\left[e^{-(r+R)/a}\left(r+R+a\right) - e^{-|r-R|/a}\left(|r-R|+a\right)\right]$$

The r integral is now straightforward:

$$I = \frac{2}{a^2R}\left[-e^{-R/a}\int_0^\infty (r+R+a)e^{-2r/a}rdr + e^{-R/a}\int_0^R (R-r+a)rdr\right.$$

$$\left. +e^{R/a}\int_R^\infty (r-R+a)e^{-2r/a}rdr\right]$$

Evaluating the integrals, we find

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

In the terms of I , the normalization factor is

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

Next we must calculate the expectation value of H in the trial state ψ. Noting that

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_1} \right)\Psi_g(r_1) = E_1\Psi_g(r_1)$$

Where $E_1 = -13.6$ ev is the ground-state energy of atomic hydrogen and the same with r_2 in place of r_1 ,we have

$$H\Psi = A\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right]\left[\Psi_g(r_1) + \Psi_g(r_2) \right]$$

$$= E_1\Psi - A\left(\frac{e^2}{4\pi\varepsilon_0} \right)\left[\frac{1}{r_2}\Psi_g(r_1) + \frac{1}{r_1}\Psi_g(r_2) \right]$$

It follows that

$$\langle H \rangle = E_1 - 2|A|^2 \left(\frac{e^2}{4\pi\varepsilon_0} \right) \left[\left\langle \Psi_g(r_1) \left| \frac{1}{r_2} \right| \Psi_g(r_1) \right\rangle + \left\langle \Psi_g(r_1) \left| \frac{1}{r_1} \right| \Psi_g(r_2) \right\rangle \right]$$

Calculate the two remaining quantities ,the so-called **direct integral,**

$$D \equiv a \left\langle \Psi_g(r_1) \left| \frac{1}{r_2} \right| \Psi_g(r_1) \right\rangle$$

and the **exchange integral,**

$$X \equiv a \left\langle \Psi_g(r_1) \left| \frac{1}{r_1} \right| \Psi_g(r_2) \right\rangle$$

The results are

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

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

Putting all this together, and recalling that $E_1 = -\left(e^0/4\pi\varepsilon_0\right)\left(1/2a\right)$ we conclude that

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

This is only the electron's energy----there is also potential energy associated with the proton-proton repulsion:

$$V_{pp} = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{R} = -\frac{2a}{R}E_1$$

Thus the *total* energy of the system, in units of $-E_1$ and expressed as a function of $x \equiv R/a$,is less than

$$F(x) = -1 + \frac{2}{x}\left\{\frac{(1-(2/3)x^2)e^{-x} + (1+x)e^{-2x}}{1+(1+x+(1/3)x^2)e^{-x}}\right\}$$
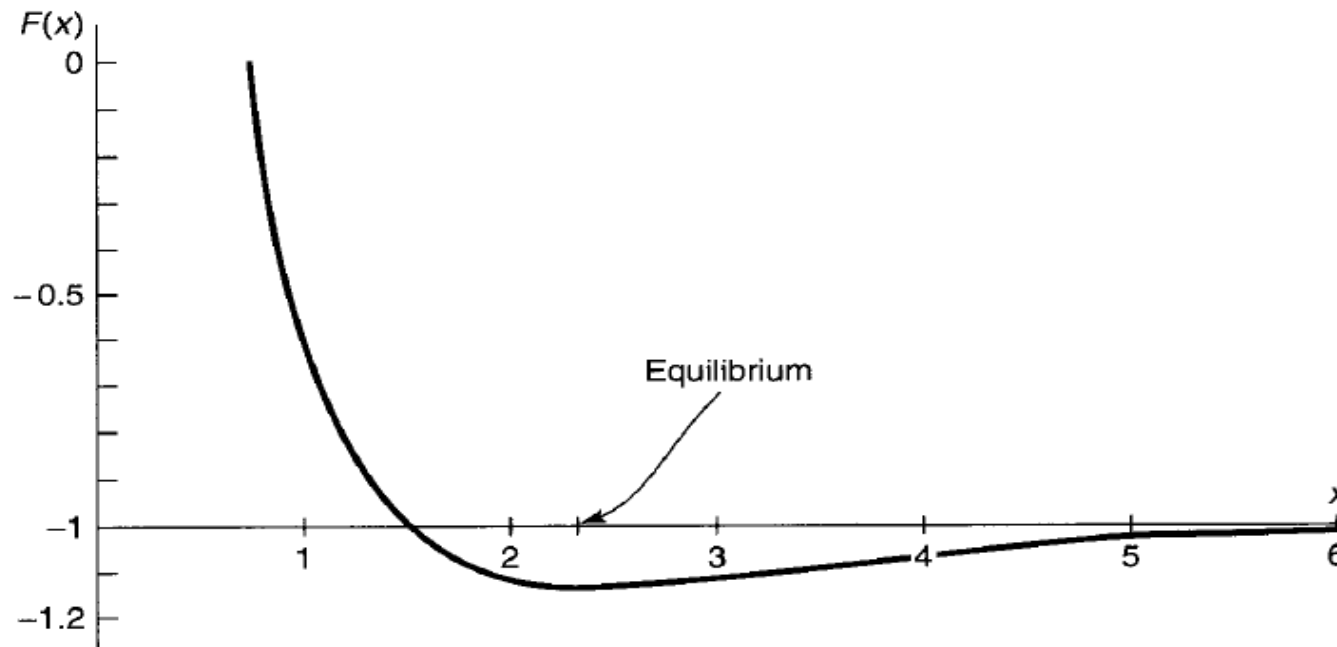
Figure 7.6: plot of the function $F(x)$, showing existence of a bound state.

Evidently bonding does occur, for there exists a region in which the graph goes below -1, indicating that the energy is less than that of a neutral atom plus a free proton (to wit, $-13.6 ev$). The Equilibrium separation of the protons is about 2.4 Bohr radii, or $1.27 \overset{\circ}{A}$.