

CHAPTER 7

THE VARIATIONAL PRINCIPLE

7.1 THEORY

Suppose you want to calculate the ground state energy, E_{gs} , for a system described by the Hamiltonian H , but you are unable to solve the (time-independent) Schrödinger equation. The **variational principle** will get you an *upper bound* for E_{gs} , which is sometimes all you need, and often, if you're clever about it, very close to the exact value. Here's how it works: Pick *any normalized function* ψ *whatsoever*; I claim that

$$E_{\text{gs}} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle. \quad [7.1]$$

That is, the expectation value of H , in the (presumably incorrect) 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* $\langle H \rangle$ exceeds E_{gs} ; the point is that the same holds for any ψ whatsoever.

Proof: Since the (unknown) eigenfunctions of H form a complete set, we can express ψ as a linear combination of them:¹

$$\psi = \sum_n c_n \psi_n, \quad \text{with } H\psi_n = E_n \psi_n.$$

¹ If the Hamiltonian admits scattering states, as well as bound states, then we'll need an integral as well as a sum, but the argument is unchanged.

Since ψ is normalized,

$$1 = \langle \psi | \psi \rangle = \left\langle \sum_m c_m \psi_m \left| \sum_n c_n \psi_n \right. \right\rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2,$$

(assuming the eigenfunctions themselves have been orthonormalized: $\langle \psi_m | \psi_n \rangle = \delta_{mn}$). Meanwhile,

$$\langle H \rangle = \left\langle \sum_m c_m \psi_m \left| H \sum_n c_n \psi_n \right. \right\rangle = \sum_m \sum_n c_m^* E_n c_n \langle \psi_m | \psi_n \rangle = \sum_n E_n |c_n|^2.$$

But the ground state energy is, by definition, the *smallest* eigenvalue, so $E_{\text{gs}} \leq E_n$, and hence

$$\langle H \rangle \geq E_{\text{gs}} \sum_n |c_n|^2 = E_{\text{gs}},$$

which is what we were trying to prove.

Example 7.1 Suppose we want to find the ground state energy for the one-dimensional harmonic oscillator:

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

Of course, we already know the *exact* answer, in this case (Equation 2.61): $E_{\text{gs}} = (1/2)\hbar\omega$; but this makes it a good test of the method. We might pick as our “trial” wave function the Gaussian,

$$\psi(x) = A e^{-bx^2}, \quad [7.2]$$

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

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} dx = |A|^2 \sqrt{\frac{\pi}{2b}} \Rightarrow A = \left(\frac{2b}{\pi}\right)^{1/4}. \quad [7.3]$$

Now

$$\langle H \rangle = \langle T \rangle + \langle V \rangle, \quad [7.4]$$

where, in this case,

$$\langle T \rangle = -\frac{\hbar^2}{2m} |A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2} (e^{-bx^2}) dx = \frac{\hbar^2 b}{2m}. \quad [7.5]$$

and

$$\langle V \rangle = \frac{1}{2} m \omega^2 |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} x^2 dx = \frac{m \omega^2}{8b},$$

so

$$\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m \omega^2}{8b}. \quad [7.6]$$

According to Equation 7.1, this exceeds E_{gs} for any b ; to get the *tightest* bound, let's *minimize* $\langle H \rangle$:

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

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

$$\langle H \rangle_{\min} = \frac{1}{2} \hbar \omega. \quad [7.7]$$

In this case we hit the ground state energy right on the nose—because (obviously) I “just happened” to pick a trial function with precisely the form of the *actual* ground state (Equation 2.59). But the gaussian is very easy to work with, so it's a popular trial function, even when it bears little resemblance to the true ground state.

Example 7.2 Suppose we're looking for the ground state energy of the delta-function potential:

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

Again, we already know the exact answer (Equation 2.129): $E_{\text{gs}} = -m\alpha^2/2\hbar^2$. As before, we'll use a gaussian trial function (Equation 7.2). We've already determined the normalization, and calculated $\langle T \rangle$; all we need is

$$\langle V \rangle = -\alpha |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} \delta(x) dx = -\alpha \sqrt{\frac{2b}{\pi}}.$$

Evidently

$$\langle H \rangle = \frac{\hbar^2 b}{2m} - \alpha \sqrt{\frac{2b}{\pi}}, \quad [7.8]$$

and we know that this exceeds E_{gs} for all b . Minimizing it,

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

So

$$\langle H \rangle_{\min} = -\frac{m\alpha^2}{\pi\hbar^2}, \quad [7]$$

which is indeed somewhat higher than E_{gs} , since $\pi > 2$.

I said you can use *any* (normalized) trial function ψ whatsoever, and this is true in a sense. However, for *discontinuous* functions it takes some fancy footwork to assign a sensible meaning to the second derivative (which you need, in order to calculate $\langle T \rangle$). Continuous functions with kinks in them are fair game, however, as long as you are careful; the next example shows how to handle them.²

Example 7.3 Find an upper bound on the ground state energy of the one-dimensional infinite square well (Equation 2.19), using the “triangular” trial wave function (Figure 7.1):³

$$\psi(x) = \begin{cases} Ax, & \text{if } 0 \leq x \leq a/2, \\ A(a-x), & \text{if } a/2 \leq x \leq a, \\ 0, & \text{otherwise,} \end{cases} \quad [7.10]$$

where A is determined by normalization:

$$1 = |A|^2 \left[\int_0^{a/2} x^2 dx + \int_{a/2}^a (a-x)^2 dx \right] = |A|^2 \frac{a^3}{12} \Rightarrow A = \frac{2}{a} \sqrt{\frac{3}{a}}. \quad [7.11]$$

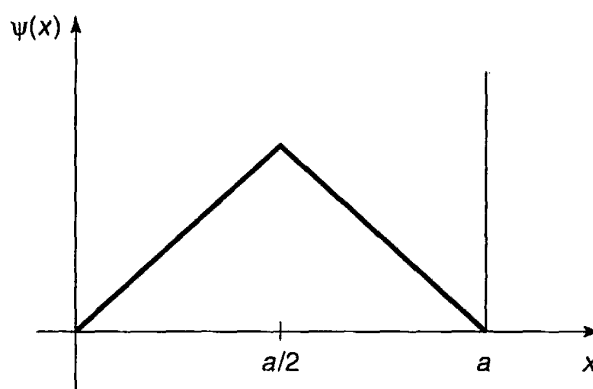


FIGURE 7.1: Triangular trial wave function for the infinite square well (Equation 7.10).

²For a collection of interesting examples see W. N. Mei, *Int. J. Educ. Sci. Tech.* **30**, 513 (1999).

³There is no point in trying a function (such as the gaussian) that “leaks” outside the well because you’ll get $\langle V \rangle = \infty$, and Equation 7.1 tells you nothing.

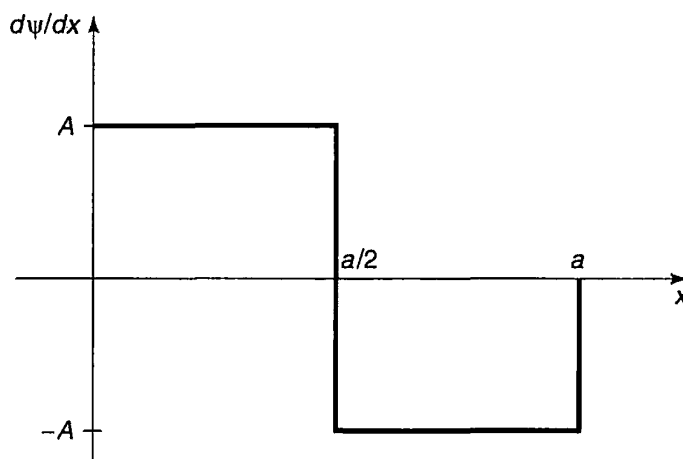


FIGURE 7.2: Derivative of the wave function in Figure 7.1.

In this case

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

as indicated in Figure 7.2. Now, the derivative of a step function is a delta function (see Problem 2.24(b)):

$$\frac{d^2\psi}{dx^2} = A\delta(x) - 2A\delta(x - a/2) + A\delta(x - a), \quad [7.12]$$

and hence

$$\begin{aligned} \langle H \rangle &= -\frac{\hbar^2 A}{2m} \int [\delta(x) - 2\delta(x - a/2) + \delta(x - a)] \psi(x) dx \\ &= -\frac{\hbar^2 A}{2m} [\psi(0) - 2\psi(a/2) + \psi(a)] = \frac{\hbar^2 A^2 a}{2m} = \frac{12\hbar^2}{2ma^2}. \end{aligned} \quad [7.13]$$

The exact ground state energy is $E_{\text{gs}} = \pi^2 \hbar^2 / 2ma^2$ (Equation 2.27), so the theorem works ($12 > \pi^2$).

The variational principle is extraordinarily powerful, and embarrassingly easy to use. What a physical chemist does to find the ground state energy of some complicated molecule is write down a trial wave function with a large number of adjustable parameters, calculate $\langle H \rangle$, and tweak the parameters to get the lowest possible value. Even if ψ has little resemblance to the true wave function, you often get miraculously accurate values for E_{gs} . Naturally, if you have some way of guessing a *realistic* ψ , so much the better. The only *trouble* with the method

is that you never know for sure how close you are to the target—all you can be *certain* of is that you've got an *upper bound*.⁴ Moreover, as it stands, the technique applies only to the ground state (see, however, Problem 7.4).⁵

***Problem 7.1** Use a gaussian trial function (Equation 7.2) to obtain the lowest upper bound you can on the ground state energy of (a) the linear potential: $V(x) = \alpha|x|$; (b) the quartic potential: $V(x) = \alpha x^4$.

****Problem 7.2** Find the best bound on E_{gs} for the one-dimensional harmonic oscillator using a trial wave function of the form

$$\psi(x) = \frac{A}{x^2 + b^2},$$

where A is determined by normalization and b is an adjustable parameter.

Problem 7.3 Find the best bound on E_{gs} for the delta-function potential $V(x) = -\alpha\delta(x)$, using a triangular trial function (Equation 7.10, only centered at the origin). This time a is an adjustable parameter.

Problem 7.4

- (a) Prove the following corollary to the variational principle: If $\langle \psi | \psi_{\text{gs}} \rangle = 0$, then $\langle H \rangle \geq E_{\text{fc}}$, where E_{fc} is the energy of the first excited state.

Thus, if we can find a trial function that is orthogonal to the exact ground state, we can get an upper bound on the *first excited state*. In general, it's difficult to be sure that ψ is orthogonal to ψ_{gs} , since (presumably) we don't *know* the latter. However, if the potential $V(x)$ is an *even* function of x , then the ground state is likewise even, and hence any *odd* trial function will automatically meet the condition for the corollary.

- (b) Find the best bound on the first excited state of the one-dimensional harmonic oscillator using the trial function

$$\psi(x) = Ax e^{-bx^2}.$$

⁴In practice this isn't much of a limitation, and there are sometimes ways of estimating the accuracy. The ground state helium has been calculated to many significant digits in this way—see for example G. W. Drake *et al.*, *Phys. Rev. A* **65**, 054501 (2002) or Vladimir I. Korobov, *Phys. Rev. A* **66**, 024501 (2002).

⁵For a systematic extension of the variational principle to the calculation of excited state energies see, for example, Linus Pauling and E. Bright Wilson, *Introduction to Quantum Mechanics, With Applications to Chemistry*, McGraw-Hill, New York (1935, paperback edition 1985), Section 26.

Problem 7.5

- (a) Use the variational principle to prove that first-order non-degenerate perturbation theory always *overestimates* (or at any rate never *underestimates*) the ground state energy.
- (b) In view of (a), you would expect that the *second*-order correction to the ground state is always negative. Confirm that this is indeed the case, by examining Equation 6.15.

7.2 THE GROUND STATE OF HELIUM

The helium atom (Figure 7.3) consists of two electrons in orbit around a nucleus containing two protons (also some neutrons, which are irrelevant to our purpose). The Hamiltonian for this system (ignoring fine structure and smaller corrections) is:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right). \quad [7.14]$$

Our problem is to calculate the ground state energy, E_{gs} . Physically, this represents the amount of energy it would take to strip off both electrons. (Given E_{gs} it is easy to figure out the “ionization energy” required to remove a *single* electron—see Problem 7.6.) The ground state energy of helium has been measured to great precision in the laboratory:

$$E_{\text{gs}} = -78.975 \text{ eV} \quad (\text{experimental}). \quad [7.15]$$

This is the number we would like to reproduce theoretically.

It is curious that such a simple and important problem has no known exact solution.⁶ The trouble comes from the electron-electron repulsion,

$$V_{ee} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad [7.16]$$

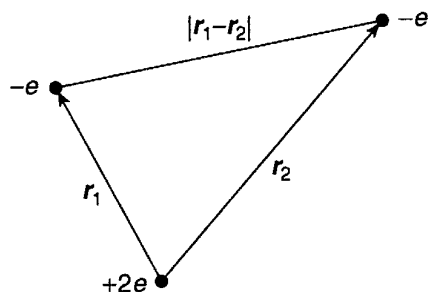


FIGURE 7.3: The helium atom.

⁶There do exist exactly soluble three-body problems with many of the qualitative features of helium, but using non-coulombic potentials (see Problem 7.17).

If we ignore this term altogether, H splits into two independent hydrogen Hamiltonians (only with a nuclear charge of $2e$, instead of e); the exact solution is just the product of hydrogenic wave functions:

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) \equiv \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}, \quad [7.17]$$

and the energy is $8E_1 = -109$ eV (Equation 5.31).⁷ This is a long way from -79 eV, but it's a start.

To get a better approximation for E_{gs} we'll apply the variational principle, using ψ_0 as the trial wave function. This is a particularly convenient choice because it's an eigenfunction of *most* of the Hamiltonian:

$$H\psi_0 = (8E_1 + V_{ee})\psi_0. \quad [7.18]$$

Thus

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle, \quad [7.19]$$

where⁸

$$\langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{8}{\pi a^3} \right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2. \quad [7.20]$$

I'll do the \mathbf{r}_2 integral first; for this purpose \mathbf{r}_1 is fixed, and we may as well orient the \mathbf{r}_2 coordinate system so that the polar axis lies along \mathbf{r}_1 (see Figure 7.4). By the law of cosines,

$$|\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}. \quad [7.21]$$

and hence

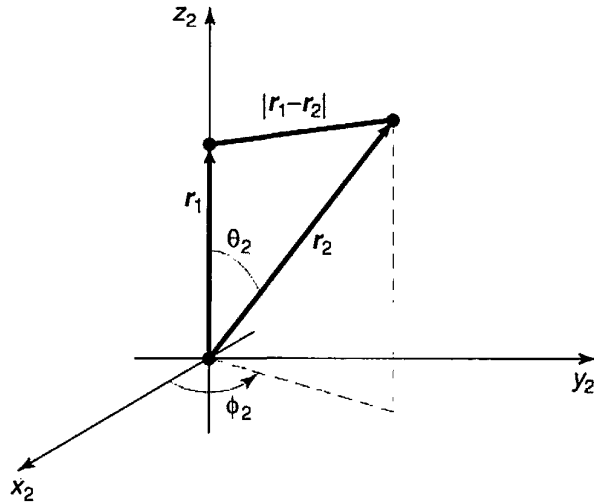
$$I_2 \equiv \int \frac{e^{-4r_2/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3r_2 = \int \frac{e^{-4r_2/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}} r_2^2 \sin \theta_2 dr_2 d\theta_2 d\phi_2. \quad [7.22]$$

The ϕ_2 integral is trivial (2π); the θ_2 integral is

$$\int_0^\pi \frac{\sin \theta_2}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}} d\theta_2 = \frac{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}}{r_1r_2} \Big|_0^\pi$$

⁷Here a is the ordinary Bohr radius and $E_n = -13.6/n^2$ eV is the n th Bohr energy: recall that for a nucleus with atomic number Z , $E_n \rightarrow Z^2 E_n$ and $a \rightarrow a/Z$ (Problem 4.16). The spin configuration associated with Equation 7.17 will be antisymmetric (the singlet).

⁸You can, if you like, interpret Equation 7.20 as first-order perturbation theory, with $H' = V_{ee}$. However, I regard this as a misuse of the method, since the perturbation is comparable in size to the unperturbed potential. I prefer, therefore, to think of it as a variational calculation, in which we are looking for an upper bound on E_{gs} .

FIGURE 7.4: Choice of coordinates for the r_2 -integral (Equation 7.20).

$$\begin{aligned}
 &= \frac{1}{r_1 r_2} \left(\sqrt{r_1^2 + r_2^2 + 2r_1 r_2} - \sqrt{r_1^2 + r_2^2 - 2r_1 r_2} \right) \\
 &= \frac{1}{r_1 r_2} [(r_1 + r_2) - |r_1 - r_2|] = \begin{cases} 2/r_1, & \text{if } r_2 < r_1, \\ 2/r_2, & \text{if } r_2 > r_1. \end{cases} \quad [7.23]
 \end{aligned}$$

Thus

$$\begin{aligned}
 I_2 &= 4\pi \left(\frac{1}{r_1} \int_0^{r_1} e^{-4r_2/a} r_2^2 dr_2 + \int_{r_1}^{\infty} e^{-4r_2/a} r_2 dr_2 \right) \\
 &= \frac{\pi a^3}{8r_1} \left[1 - \left(1 + \frac{2r_1}{a} \right) e^{-4r_1/a} \right]. \quad [7.24]
 \end{aligned}$$

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

$$\left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{8}{\pi a^3} \right) \int \left[1 - \left(1 + \frac{2r_1}{a} \right) e^{-4r_1/a} \right] e^{-4r_1/a} r_1 \sin\theta_1 dr_1 d\theta_1 d\phi_1.$$

The angular integrals are easy (4π), and the r_1 integral becomes

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

Finally, then,

$$\langle V_{ee} \rangle = \frac{5}{4a} \left(\frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5}{2} E_1 = 34 \text{ eV}, \quad [7.25]$$

and therefore

$$\langle H \rangle = -109 \text{ eV} + 34 \text{ eV} = -75 \text{ eV}. \quad [7.26]$$

Not bad (remember, the experimental value is -79 eV). But we can do better.

We need to think up a more realistic trial function than ψ_0 (which treats the two electrons as though they did not interact at all). Rather than completely *ignoring* the influence of the other electron, let us say that, on the average, each electron represents a cloud of negative charge which partially *shields* the nucleus, so that the other electron actually sees an *effective* nuclear charge (Z) that is somewhat *less* than 2. This suggests that we use a trial function of the form

$$\psi_1(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}. \quad [7.27]$$

We'll treat Z as a variational parameter, picking the value that minimizes H . (Please note that in the variational method we *never touch the Hamiltonian itself*—the Hamiltonian for helium is, and remains, Equation 7.14. But it's fine to *think* about approximating the Hamiltonian *as a way of motivating the choice of the trial wave function*.)

This wave function is an eigenstate of the “unperturbed” Hamiltonian (neglecting electron repulsion), only with Z , instead of 2, in the Coulomb terms. With this in mind, we rewrite H (Equation 7.14) as follows:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right). \quad [7.28]$$

The expectation value of H is evidently

$$\langle H \rangle = 2Z^2 E_1 + 2(Z-2) \left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle. \quad [7.29]$$

Here $\langle 1/r \rangle$ is the expectation value of $1/r$ in the (one-particle) hydrogenic ground state ψ_{100} (but with nuclear charge Z); according to Equation 6.55,

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a}. \quad [7.30]$$

The expectation value of V_{ee} is the same as before (Equation 7.25), except that instead of $Z = 2$ we now want *arbitrary* Z —so we multiply a by $2/Z$:

$$\langle V_{ee} \rangle = \frac{5Z}{8a} \left(\frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5Z}{4} E_1. \quad [7.31]$$

Putting all this together, we find

$$\langle H \rangle = \left[2Z^2 - 4Z(Z-2) - (5/4)Z \right] E_1 = [-2Z^2 + (27/4)Z] E_1. \quad [7.32]$$

According to the variational principle, this quantity exceeds E_{gs} for *any* value of Z . The *lowest* upper bound occurs when $\langle H \rangle$ is minimized:

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

from which it follows that

$$Z = \frac{27}{16} = 1.69. \quad [7.33]$$

This seems reasonable; it tells us that the other electron partially screens the nucleus, reducing its effective charge from 2 down to about 1.69. Putting in this value for Z , we find

$$\langle H \rangle = \frac{1}{2} \left(\frac{3}{2} \right)^6 E_1 = -77.5 \text{ eV}. \quad [7.34]$$

The ground state of helium has been calculated with great precision in this way, using increasingly complicated trial wave functions, with more and more adjustable parameters.⁹ But we're within 2% of the correct answer, and, frankly, at this point my own interest in the problem begins to wane.¹⁰

Problem 7.6 Using $E_{\text{gs}} = -79.0 \text{ eV}$ for the ground state energy of helium, calculate the ionization energy (the energy required to remove just *one* electron). *Hint:* First calculate the ground state energy of the helium ion, He^+ , with a single electron orbiting the nucleus; then subtract the two energies.

***Problem 7.7** Apply the techniques of this Section to the H^- and Li^+ ions (each has two electrons, like helium, but nuclear charges $Z = 1$ and $Z = 3$, respectively). Find the effective (partially shielded) nuclear charge, and determine the best upper bound on E_{gs} , for each case. *Comment:* In the case of H^- you should find that $\langle H \rangle > -13.6 \text{ eV}$, which would appear to indicate that there is no bound state at all, since it would be energetically favorable for one electron to fly off, leaving behind a neutral hydrogen atom. This is not entirely surprising, since the electrons are less strongly attracted to the nucleus than they are in helium, and the electron repulsion tends to break the atom apart. However, it turns out to be incorrect. With a more sophisticated trial wave function (see Problem 7.18) it can be shown that $E_{\text{gs}} < -13.6 \text{ eV}$, and hence that a bound state *does* exist. It's only *barely* bound,

⁹The classic studies are E. A. Hylleraas, *Z. Phys.* **65**, 209 (1930); C. L. Pekeris, *Phys. Rev.* **115**, 1216 (1959). For more recent work see footnote 4.

¹⁰The first excited state of helium can be calculated in much the same way, using a trial wave function orthogonal to the ground state. See P. J. E. Peebles, *Quantum Mechanics*, Princeton U.P., Princeton, NJ (1992), Section 40.

however, and there are no excited bound states,¹¹ so H^- has no discrete spectrum (all transitions are to and from the continuum). As a result, it is difficult to study in the laboratory, although it exists in great abundance on the surface of the sun.¹²

7.3 THE HYDROGEN MOLECULE ION

Another classic application of the variational principle is to the hydrogen molecule ion, H_2^+ , consisting of a single electron in the Coulomb field of two protons (Figure 7.5). I shall assume for the moment that the protons are fixed in position, a specified distance R apart, although one of the most interesting byproducts of the calculation is going to be the actual *value* of R . The Hamiltonian is

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right), \quad [7.35]$$

where r_1 and r_2 are the distances to the electron from the respective protons. As always, our strategy will be to guess a reasonable trial wave function, and invoke the variational principle to get a bound on the ground state energy. (Actually, our main interest is in finding out whether this system bonds at *all*—that is, whether its energy is less than that of a neutral hydrogen atom plus a free proton. If our trial wave function indicates that there *is* a bound state, a *better* trial function can only make the bonding even stronger.)

To construct the trial wave function, imagine that the ion is formed by taking a hydrogen atom in its ground state (Equation 4.80),

$$\psi_0(\mathbf{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}, \quad [7.36]$$

bringing the second proton in from “infinity,” and nailing it down a distance R away. If R is substantially greater than the Bohr radius, the electron’s wave function probably isn’t changed very much. But we would like to treat the two protons on

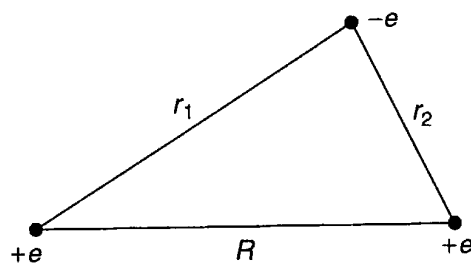


FIGURE 7.5: The hydrogen molecule ion, H_2^+ .

¹¹Robert N. Hill, *J. Math. Phys.* **18**, 2316 (1977).

¹²For further discussion see Hans A. Bethe and Edwin E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, Plenum, New York (1977), Section 34.

an equal footing, so that the electron has the same probability of being associated with either one. This suggests that we consider a trial function of the form

$$\psi = A [\psi_0(r_1) + \psi_0(r_2)]. \quad [7.37]$$

(Quantum chemists call this the **LCAO** technique, because we are expressing the molecular wave function as a linear combination of atomic orbitals.)

Our first task is to *normalize* the trial function:

$$1 = \int |\psi|^2 d^3\mathbf{r} = |A|^2 \left[\int |\psi_0(r_1)|^2 d^3\mathbf{r} + \int |\psi_0(r_2)|^2 d^3\mathbf{r} + 2 \int \psi_0(r_1)\psi_0(r_2) d^3\mathbf{r} \right]. \quad [7.38]$$

The first two integrals are 1 (since ψ_0 itself is normalized); the third is more **tricky**. Let

$$I \equiv \langle \psi_0(r_1) | \psi_0(r_2) \rangle = \frac{1}{\pi a^3} \int e^{-(r_1+r_2)/a} d^3\mathbf{r}. \quad [7.39]$$

Picking coordinates so that proton 1 is at the origin and proton 2 is on the z axis at the point R (Figure 7.6), we have

$$r_1 = r \quad \text{and} \quad r_2 = \sqrt{r^2 + R^2 - 2rR \cos \theta}. \quad [7.40]$$

and therefore

$$I = \frac{1}{\pi a^3} \int e^{-r/a} e^{-\sqrt{r^2 + R^2 - 2rR \cos \theta}/a} r^2 \sin \theta dr d\theta d\phi. \quad [7.41]$$

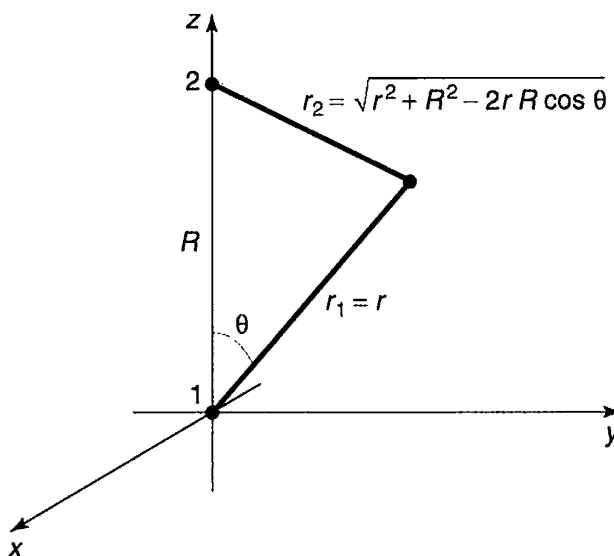


FIGURE 7.6: Coordinates for the calculation of I (Equation 7.39).

The ϕ integral is trivial (2π). To do the θ integral, let

$$y \equiv \sqrt{r^2 + R^2 - 2rR \cos \theta}, \quad \text{so that } d(y^2) = 2y dy = 2rR \sin \theta d\theta.$$

Then

$$\begin{aligned} \int_0^\pi e^{-\sqrt{r^2 + R^2 - 2rR \cos \theta}/a} \sin \theta d\theta &= \frac{1}{rR} \int_{|r-R|}^{r+R} e^{-y/a} y dy \\ &= -\frac{a}{rR} \left[e^{-(r+R)/a} (r+R+a) - e^{-|r-R|/a} (|r-R|+a) \right]. \end{aligned}$$

The r integral is now straightforward:

$$\begin{aligned} I &= \frac{2}{a^2 R} \left[-e^{-R/a} \int_0^\infty (r+R+a) e^{-2r/a} r dr + e^{-R/a} \int_0^R (R-r+a) r dr \right. \\ &\quad \left. + e^{R/a} \int_R^\infty (r-R+a) e^{-2r/a} r dr \right]. \end{aligned}$$

Evaluating the integrals, we find (after some algebraic simplification),

$$I = e^{-R/a} \left[1 + \left(\frac{R}{a} \right) + \frac{1}{3} \left(\frac{R}{a} \right)^2 \right]. \quad [7.42]$$

I is called an **overlap** integral; it measures the amount by which $\psi_0(r_1)$ overlaps $\psi_0(r_2)$ (notice that it goes to 1 as $R \rightarrow 0$, and to 0 as $R \rightarrow \infty$). In terms of I , the normalization factor (Equation 7.38) is

$$|A|^2 = \frac{1}{2(1+I)}. \quad [7.43]$$

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

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_1} \right) \psi_0(r_1) = E_1 \psi_0(r_1)$$

(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

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

It follows that

$$\langle H \rangle = E_1 - 2|A|^2 \left(\frac{e^2}{4\pi\epsilon_0} \right) \left[\langle \psi_0(r_1) \left| \frac{1}{r_2} \right| \psi_0(r_1) \rangle + \langle \psi_0(r_1) \left| \frac{1}{r_1} \right| \psi_0(r_2) \rangle \right]. \quad [7.44]$$

I'll let you calculate the two remaining quantities, the so-called **direct integral**,

$$D \equiv a \langle \psi_0(r_1) \left| \frac{1}{r_2} \right| \psi_0(r_1) \rangle, \quad [7.45]$$

and the **exchange integral**,

$$X \equiv a \langle \psi_0(r_1) \left| \frac{1}{r_1} \right| \psi_0(r_2) \rangle. \quad [7.46]$$

The results (see Problem 7.8) are

$$D = \frac{a}{R} - \left(1 + \frac{a}{R} \right) e^{-2R/a}, \quad [7.47]$$

and

$$X = \left(1 + \frac{R}{a} \right) e^{-R/a}. \quad [7.48]$$

Putting all this together, and recalling (Equations 4.70 and 4.72) that $E_1 = -(e^2/4\pi\epsilon_0)(1/2a)$, we conclude:

$$\langle H \rangle = \left[1 + 2 \frac{(D + X)}{(1 + I)} \right] E_1. \quad [7.49]$$

According to the variational principle, the ground state energy is *less* than $\langle H \rangle$. Of course, this is only the *electron's* energy—there is also potential energy associated with the proton-proton repulsion:

$$V_{pp} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} = -\frac{2a}{R} E_1. \quad [7.50]$$

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

$$F(x) = -1 + \frac{2}{x} \left\{ \frac{(1 - (2/3)x^2)e^{-x} + (1 + x)e^{-2x}}{1 + (1 + x + (1/3)x^2)e^{-x}} \right\}. \quad [7.51]$$

This function is plotted in Figure 7.7. 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 (-13.6 eV). It's a covalent bond, with the electron shared equally by the two protons. The equilibrium separation of the protons is about 2.4 Bohr radii, or 1.3 Å (the experimental value is 1.06 Å). The

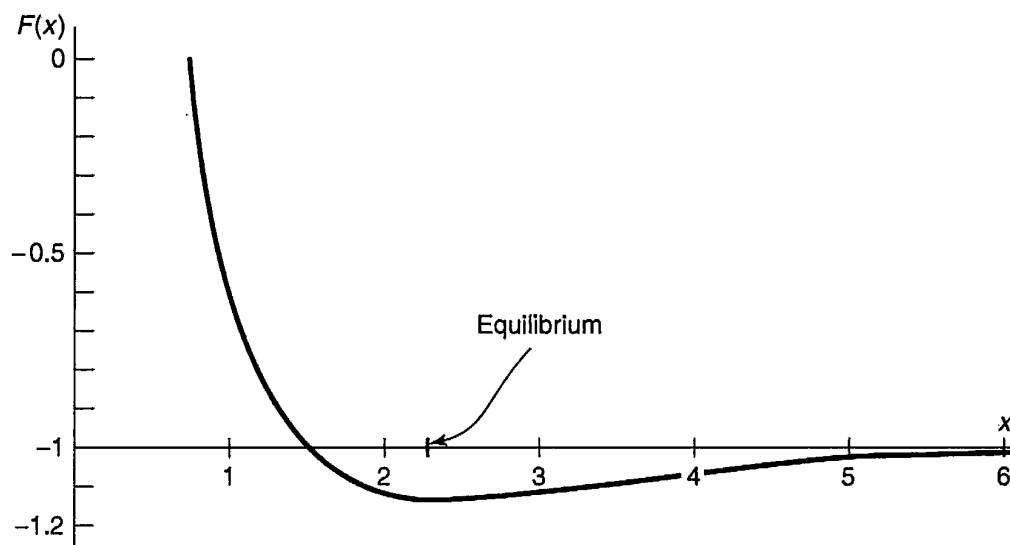


FIGURE 7.7: Plot of the function $F(x)$, Equation 7.51, showing existence of a bound state (x is the distance between the protons, in units of the Bohr radius).

calculated binding energy is 1.8 eV, whereas the experimental value is 2.8 eV (the variational principle, as always, *overestimates* the ground state energy—and hence *underestimates* the strength of the bond—but never mind: The essential point was to see whether binding occurs at all; a better variational function can only make the potential well even deeper.

***Problem 7.8** Evaluate D and X (Equations 7.45 and 7.46). Check your answers against Equations 7.47 and 7.48.

****Problem 7.9** Suppose we used a *minus* sign in our trial wave function (Equation 7.37):

$$\psi = A[\psi_0(r_1) - \psi_0(r_2)]. \quad [7.52]$$

Without doing any new integrals, find $F(x)$ (the analog to Equation 7.51) for this case, and construct the graph. Show that there is no evidence of bonding.¹³ (Since the variational principle only gives an *upper bound*, this doesn't *prove* that bonding cannot occur for such a state, but it certainly doesn't look promising). *Comment:* Actually, any function of the form

$$\psi = A[\psi_0(r_1) + e^{i\phi}\psi_0(r_2)]. \quad [7.53]$$

¹³Bonding occurs when the electron “prefers” to be between the protons, attracting them inward. But the odd linear combination (Equation 7.52) has a *node* at the center, so it's not surprising that this configuration drives the protons apart.

has the desired property that the electron is equally likely to be associated with either proton. However, since the Hamiltonian (Equation 7.35) is invariant under the interchange $P: r_1 \leftrightarrow r_2$, its eigenfunctions can be chosen to be simultaneously eigenfunctions of P . The plus sign (Equation 7.37) goes with the eigenvalue $+1$, and the minus sign (Equation 7.52) with the eigenvalue -1 ; nothing is to be gained by considering the ostensibly more general case (Equation 7.53), though you're welcome to try it, if you're interested.

- **Problem 7.10** The second derivative of $F(x)$, at the equilibrium point, can be used to estimate the natural frequency of vibration (ω) of the two protons in the hydrogen molecule ion (see Section 2.3). If the ground state energy ($\hbar\omega/2$) of this oscillator exceeds the binding energy of the system, it will fly apart. Show that in fact the oscillator energy is small enough that this will *not* happen, and estimate how many bound vibrational levels there are. *Note:* You're not going to be able to obtain the position of the minimum—still less the second derivative at that point—analytically. Do it numerically, on a computer.

FURTHER PROBLEMS FOR CHAPTER 7

Problem 7.11

- (a) Use a trial wave function of the form

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

to obtain a bound on the ground state energy of the one-dimensional harmonic oscillator. What is the “best” value of a ? Compare $\langle H \rangle_{\min}$ with the exact energy. *Note:* This trial function has a “kink” in it (a discontinuous derivative) at $\pm a/2$; do you need to take account of this, as I did in Example 7.3?

- (b) Use $\psi(x) = B \sin(\pi x/a)$ on the interval $(-a, a)$ to obtain a bound on the first excited state. Compare the exact answer.

**Problem 7.12

- (a) Generalize Problem 7.2, using the trial wave function¹⁴

$$\psi(x) = \frac{A}{(x^2 + b^2)^n},$$

¹⁴W. N. Mei, *Int. J. Educ. Sci. Tech.* **27**, 285 (1996).

for arbitrary n . *Partial answer:* The best value of b is given by

$$b^2 = \frac{\hbar}{m\omega} \left[\frac{n(4n-1)(4n-3)}{2(2n+1)} \right]^{1/2}.$$

- (b) Find the least upper bound on the first excited state of the harmonic oscillator using a trial function of the form

$$\psi(x) = \frac{Bx}{(x^2 + b^2)^n}.$$

Partial answer: The best value of b is given by

$$b^2 = \frac{\hbar}{m\omega} \left[\frac{n(4n-5)(4n-3)}{2(2n+1)} \right]^{1/2}.$$

- (c) Notice that the bounds approach the exact energies as $n \rightarrow \infty$. Why is that? *Hint:* Plot the trial wave functions for $n = 2$, $n = 3$, and $n = 4$, and compare them with the true wave functions (Equations 2.59 and 2.62). To do it analytically, start with the identity

$$e^z = \lim_{n \rightarrow \infty} \left(1 + \frac{z}{n} \right)^n.$$

Problem 7.13 Find the lowest bound on the ground state of hydrogen you can get using a gaussian trial wave function

$$\psi(\mathbf{r}) = Ae^{-br^2},$$

where A is determined by normalization and b is an adjustable parameter. *Answer:* -11.5 eV.

- **Problem 7.14** If the photon had a nonzero mass ($m_\gamma \neq 0$), the Coulomb potential would be replaced by the **Yukawa potential**,

$$V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0} \frac{e^{-\mu r}}{r}, \quad [7.54]$$

where $\mu = m_\gamma c/\hbar$. With a trial wave function of your own devising, estimate the binding energy of a “hydrogen” atom with this potential. Assume $\mu a \ll 1$, and give your answer correct to order $(\mu a)^2$.

Problem 7.15 Suppose you’re given a quantum system whose Hamiltonian H_0 admits just two eigenstates, ψ_a (with energy E_a), and ψ_b (with energy E_b). They

are orthogonal, normalized, and nondegenerate (assume E_a is the smaller of the two energies). Now we turn on a perturbation H' , with the following matrix elements:

$$\langle \psi_a | H' | \psi_a \rangle = \langle \psi_b | H' | \psi_b \rangle = 0; \quad \langle \psi_a | H' | \psi_b \rangle = \langle \psi_b | H' | \psi_a \rangle = h, \quad [7.55]$$

where h is some specified constant.

- (a) Find the exact eigenvalues of the perturbed Hamiltonian.
- (b) Estimate the energies of the perturbed system using second-order perturbation theory.
- (c) Estimate the ground state energy of the perturbed system using the variational principle, with a trial function of the form

$$\psi = (\cos \phi) \psi_a + (\sin \phi) \psi_b, \quad [7.56]$$

where ϕ is an adjustable parameter. *Note:* Writing the linear combination in this way is just a neat way to guarantee that ψ is normalized.

- (d) Compare your answers to (a), (b), and (c). Why is the variational principle so accurate, in this case?

Problem 7.16 As an explicit example of the method developed in Problem 7.15, consider an electron at rest in a uniform magnetic field $\mathbf{B} = B_z \hat{k}$, for which the Hamiltonian is (Equation 4.158):

$$H_0 = \frac{eB_z}{m} S_z. \quad [7.57]$$

The eigenspinors, χ_a and χ_b , and the corresponding energies, E_a and E_b , are given in Equation 4.161. Now we turn on a perturbation, in the form of a uniform field in the x direction:

$$H' = \frac{eB_x}{m} S_x. \quad [7.58]$$

- (a) Find the matrix elements of H' , and confirm that they have the structure of Equation 7.55. What is h ?
- (b) Using your result in Problem 7.15(b), find the new ground state energy, in second-order perturbation theory.
- (c) Using your result in Problem 7.15(c), find the variational principle bound on the ground state energy.

*****Problem 7.17** Although the Schrödinger equation for helium itself cannot be solved exactly, there exist “helium-like” systems that do admit exact solutions.

A simple example¹⁵ is “rubber-band helium,” in which the Coulomb forces are replaced by Hooke’s law forces:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \frac{1}{2}m\omega^2(r_1^2 + r_2^2) - \frac{\lambda}{4}m\omega^2|\mathbf{r}_1 - \mathbf{r}_2|^2. \quad [7.59]$$

(a) Show that the change of variables from $\mathbf{r}_1, \mathbf{r}_2$, to

$$\mathbf{u} \equiv \frac{1}{\sqrt{2}}(\mathbf{r}_1 + \mathbf{r}_2), \quad \mathbf{v} \equiv \frac{1}{\sqrt{2}}(\mathbf{r}_1 - \mathbf{r}_2), \quad [7.60]$$

turns the Hamiltonian into two independent three-dimensional harmonic oscillators:

$$H = \left[-\frac{\hbar^2}{2m}\nabla_u^2 + \frac{1}{2}m\omega^2 u^2 \right] + \left[-\frac{\hbar^2}{2m}\nabla_v^2 + \frac{1}{2}(1-\lambda)m\omega^2 v^2 \right]. \quad [7.61]$$

(b) What is the *exact* ground state energy for this system?

(c) If we didn’t know the exact solution, we might be inclined to apply the method of Section 7.2 to the Hamiltonian in its original form (Equation 7.59). Do so (but don’t bother with shielding). How does your result compare with the exact answer? *Answer:* $\langle H \rangle = 3\hbar\omega(1 - \lambda/4)$.

*****Problem 7.18** In Problem 7.7 we found that the trial wave function with shielding (Equation 7.27), which worked well for helium, is inadequate to confirm the existence of a bound state for the negative hydrogen ion. Chandrasekhar¹⁶ used a trial wave function of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) \equiv A[\psi_1(r_1)\psi_2(r_2) + \psi_2(r_1)\psi_1(r_2)], \quad [7.62]$$

where

$$\psi_1(r) \equiv \sqrt{\frac{Z_1^3}{\pi a^3}} e^{-Z_1 r/a}, \quad \text{and} \quad \psi_2(r) \equiv \sqrt{\frac{Z_2^3}{\pi a^3}} e^{-Z_2 r/a}. \quad [7.63]$$

In effect, he allowed two *different* shielding factors, suggesting that one electron is relatively close to the nucleus, and the other is farther out. (Because electrons are identical particles, the spatial wave function must be symmetrized with respect to interchange. The *spin* state—which is irrelevant to the calculation—is evidently

¹⁵For a more sophisticated model, see R. Crandall, R. Whitnell, and R. Bettge, *Am. J. Phys.* **52**, 438 (1984).

¹⁶S. Chandrasekhar, *Astrophys. J.* **100**, 176 (1944).

antisymmetric.) Show that by astute choice of the adjustable parameters Z_1 and Z_2 you can get $\langle H \rangle$ less than -13.6 eV. *Answer:*

$$\langle H \rangle = \frac{E_1}{x^6 + y^6} \left(-x^8 + 2x^7 + \frac{1}{2}x^6y^2 - \frac{1}{2}x^5y^2 - \frac{1}{8}x^3y^4 + \frac{11}{8}xy^6 - \frac{1}{2}y^8 \right),$$

where $x \equiv Z_1 + Z_2$ and $y \equiv 2\sqrt{Z_1 Z_2}$. Chandrasekhar used $Z_1 = 1.039$ (since this is larger than 1, the motivating interpretation as an effective nuclear charge cannot be sustained, but never mind—it's still an acceptable trial wave function) and $Z_2 = 0.283$.

Problem 7.19 The fundamental problem in harnessing nuclear fusion is getting the two particles (say, two deuterons) close enough together for the attractive (but short-range) nuclear force to overcome the Coulomb repulsion. The “bulldozer” method is to heat the particles up to fantastic temperatures, and allow the random collisions to bring them together. A more exotic proposal is **muon catalysis**, in which we construct a “hydrogen molecule ion,” only with deuterons in place of protons, and a *muon* in place of the electron. Predict the equilibrium separation distance between the deuterons in such a structure, and explain why muons are superior to electrons for this purpose.¹⁷

*****Problem 7.20 Quantum dots.** Consider a particle constrained to move in two dimensions in the cross-shaped region shown in Figure 7.8. The “arms” of the cross continue out to infinity. The potential is zero within the cross, and infinite in the shaded areas outside. Surprisingly, this configuration admits a positive-energy bound state.¹⁸

(a) Show that the lowest energy that can propagate off to infinity is

$$E_{\text{threshold}} = \frac{\pi^2 \hbar^2}{8ma^2};$$

any solution with energy *less* than that has to be a bound state. *Hint:* Go way out one arm (say, $x \gg a$), and solve the Schrödinger equation by separation of variables; if the wave function propagates out to infinity, the dependence on x must take the form $\exp(ik_x x)$ with $k_x > 0$.

¹⁷The classic paper on muon-catalyzed fusion is J. D. Jackson, *Phys. Rev.* **106**, 330 (1957); for a more recent popular review, see J. Rafelski and S. Jones, *Scientific American*, November 1987, page 84.

¹⁸This model is taken from R. L. Schult *et al.*, *Phys. Rev. B* **39**, 5476 (1989). In the presence of quantum tunneling a classically bound state becomes unbound; this is the reverse: A classically unbound state is quantum mechanically *bound*.

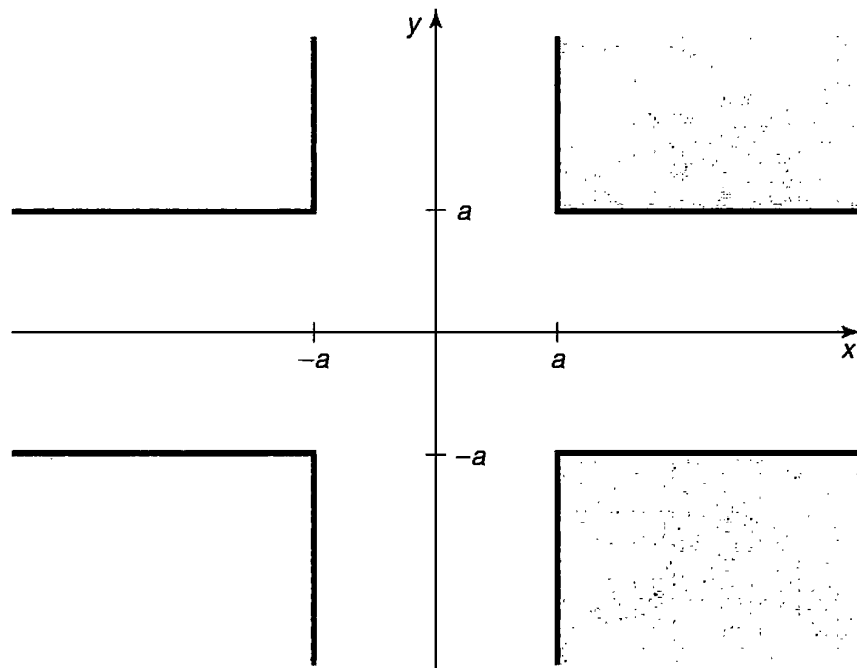


FIGURE 7.8: The cross-shaped region for Problem 7.20.

- (b) Now use the variational principle to show that the ground state has energy less than $E_{\text{threshold}}$. Use the following trial wave function (suggested by Krishna Rajagopal):

$$\psi(x, y) = A \begin{cases} (1 - |xy|/a^2)e^{-\alpha}, & |x| \leq a \text{ and } |y| \leq a \\ (1 - |x|/a)e^{-\alpha|y|/a}, & |x| \leq a \text{ and } |y| > a \\ (1 - |y|/a)e^{-\alpha|x|/a}, & |x| > a \text{ and } |y| \leq a \\ 0, & \text{elsewhere.} \end{cases}$$

Normalize it to determine A , and calculate the expectation value of H .
Answer:

$$\langle H \rangle = \frac{3\hbar^2}{ma^2} \left(\frac{\alpha^2 + 2\alpha + 3}{6 + 11\alpha} \right).$$

Now minimize with respect to α , and show that the result is less than $E_{\text{threshold}}$. *Hint:* Take full advantage of the symmetry of the problem—you only need to integrate over 1/8 of the open region, since the other 7 integrals will be the same. Note however that whereas the trial wave function is continuous, its *derivatives* are *not*—there are “roof-lines” at $x = 0$, $y = 0$, $x = \pm a$, and $y = \pm a$, where you will need to exploit the technique of Example 7.3.