

## CHAPTER 7

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# THE VARIATIONAL PRINCIPLE

### 7.1 THEORY

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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) Schrödinger equation. Pick *any normalized function  $\psi$  whatsoever*.

**Theorem:**

$$E_g \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle. \quad [7.1]$$

That is, the expectation value of  $H$  in the (presumably incorrect) state  $\psi$  is certain to *overestimate* the ground-state energy. Of course, if  $\psi$  just happens to be one of the *excited* states, then *obviously*  $\langle H \rangle$  exceeds  $E_g$ ; but the theorem says that the same holds for any  $\psi$  whatsoever.

**Proof:** Since the (unknown) eigenfunctions of  $H$  form a complete set, we can express  $\psi$  as a linear combination of them<sup>1</sup>:

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

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<sup>1</sup>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  $\psi$  is normalized,

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

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

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

But the ground-state energy is, by definition, the *smallest* eigenvalue, so  $E_g \leq E_n$ , and hence

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

QED

**Example 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 2.49):  $E_g = (1/2)\hbar\omega$ ; 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,

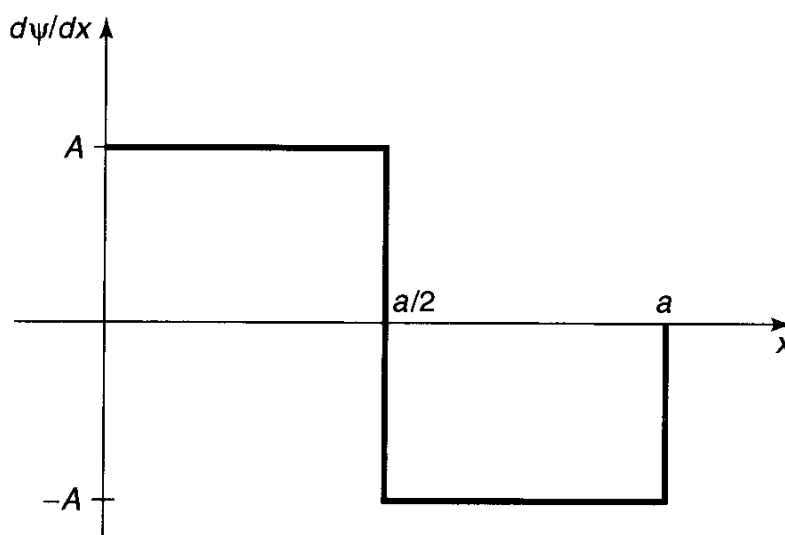
$$\langle T \rangle = -\frac{\hbar^2}{2m} |A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2} (e^{-bx^2}) dx = \frac{\hbar^2 b}{2m}, \quad [7.5]$$

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

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



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

The exact ground state is  $E_g = \pi^2 \hbar^2 / 2ma^2$  (Equation 2.23), so the theorem works ( $12 > \pi^2$ ).

The **variational principle** (as Equation 7.1 is called) is extremely powerful, and embarrassingly easy to use. What a 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  $\psi$  has no relation to the true wave function, one often gets miraculously accurate values for  $E_g$ . Naturally, if you have some way of guessing a *realistic*  $\psi$ , 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*. Moreover, the technique applies only to the ground state (see, however, Problem 7.4).

**\*Problem 7.1** Use the 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  $E_g$  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  $E_g$  for the delta-function potential  $-\alpha\delta(x - a/2)$ , using the triangle trial function (Equation 7.10). (This time  $a$  is an adjustable parameter.)

function (see Problem 7.16) it can be shown that  $E_g < -13.6$  eV, and hence that a bound state does exist. It's only *barely* bound, however, and there are no excited bound states,<sup>7</sup> so  $\text{H}^-$  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.<sup>8</sup>

### 7.3 THE HYDROGEN MOLECULE ION

Another classic application of the variational principle is to the hydrogen molecule ion,  $\text{H}_2^+$ , consisting of a single electron in the Coulomb field of two protons (Figure 7.5). We 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

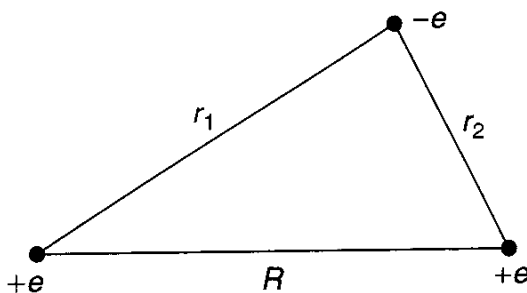
$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} \right), \quad [7.35]$$

where  $r_1$  and  $r_2$  are the distances to the electron from the respective protons. As always, the 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),

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

and then bringing in a proton from far away and nailing it down a distance  $R$  away. If  $R$  is substantially greater than the Bohr radius,  $a$ , the electron's wave function



**Figure 7.5:** The hydrogen molecule ion,  $\text{H}_2^+$ .

<sup>7</sup>Robert N. Hill, *J. Math. Phys.* **18**, 2316 (1977).

<sup>8</sup>For further discussion, see Hans A. Bethe and Edwin E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (New York: Plenum 1977), Section 34.

probably isn't changed very much. But we would like to treat the two protons on 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

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

(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:

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

The first two integrals are 1 (since  $\psi_g$  itself is normalized); the third is more tricky. Let

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

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

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

and therefore

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

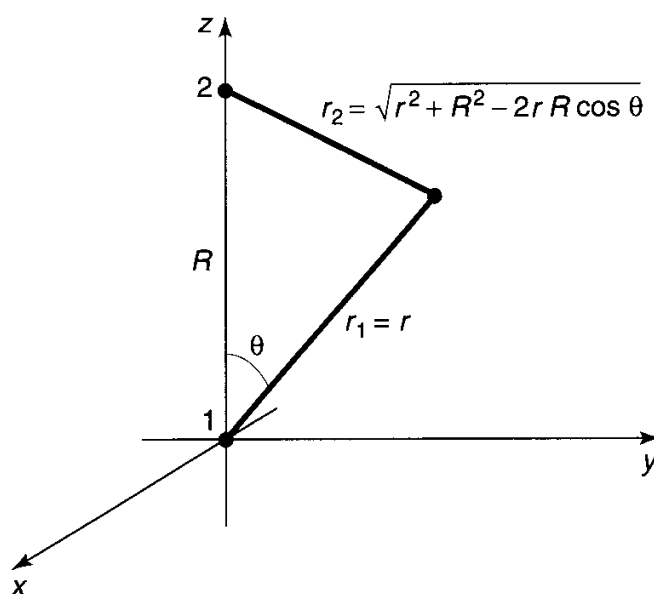


Figure 7.6: Coordinates for the calculation of  $I$  (Equation 7.39).

The  $\phi$  integral is trivial ( $2\pi$ ). To do the  $\theta$  integral, let

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

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  $\psi_g(r_1)$  overlaps  $\psi_g(r_2)$  (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  $\psi$ . Noting that

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

(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

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

It follows that

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

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

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

and the **exchange integral**,

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

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 that

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

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 (to wit,  $-13.6$  eV). The equilibrium separation of the protons is about 2.4 Bohr radii, or 1.27 Å.

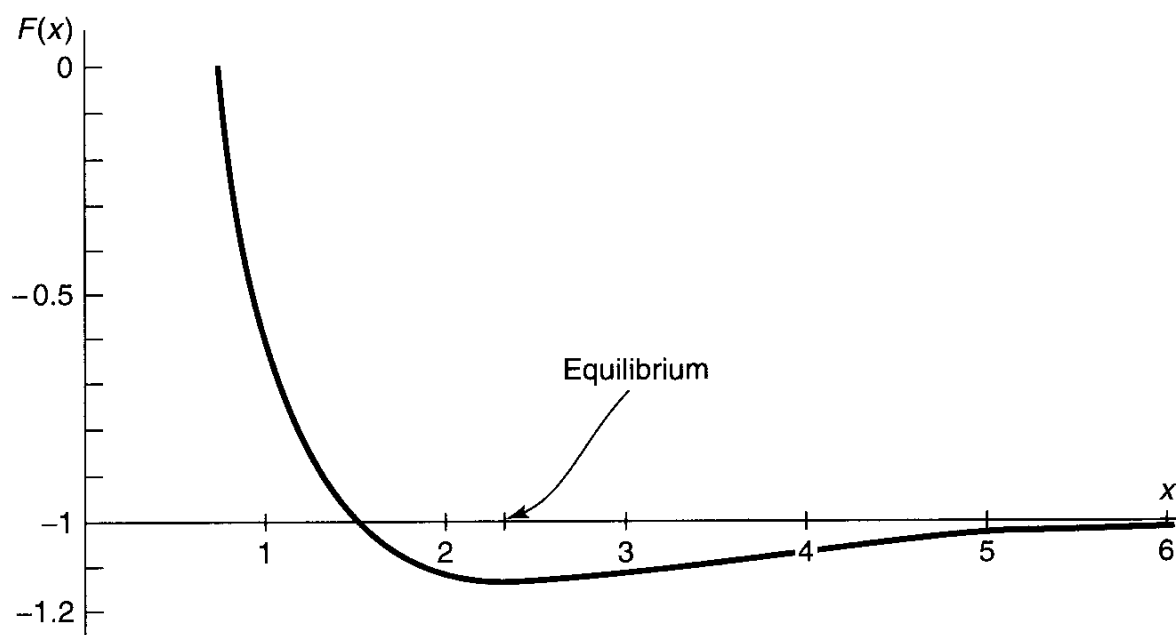
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**\*Problem 7.8** Evaluate  $D$  and  $X$  (Equations 7.45 and 7.46). Check your answers against Equations 7.47 and 7.48.

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

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



**Figure 7.7:** Plot of the function  $F(x)$ , Equation 7.51, showing existence of a bound state.

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. (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). *Note:* Actually, any function of the form

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

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.

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**\*\*\*Problem 7.10** The second derivative of  $F(x)$ , at the equilibrium point, can be used to estimate the natural frequency of vibration ( $\omega$ ) 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.

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