Problem 7.4

(a) Prove the following **corollary** to the variational principle: If $\langle\psi|\psi_g\rangle = 0$, then $\langle H\rangle \geq E_f$, where E_f 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_g, 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

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

Problem 7.5

(a) Use the variational principle to prove that first-order nondegenerate 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 6.14.

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

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

Our problem is to calculate the ground-state energy, E_g—the amount of energy it would take to strip off the two electrons. (Given E_g it is easy to figure out the "ionization energy" required to remove a *single* electron—see Problem 7.6.) E_g has been measured very accurately in the laboratory:

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

This is the number we would like to reproduce theoretically.

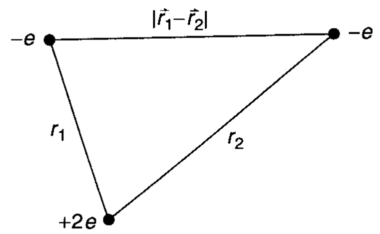

Figure 7.3: The helium atom.

It is curious that such a simple and important problem has no known exact solution.[3] The trouble comes from the electron-electron repulsion,

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

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:

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

and the energy is $8E_1 = -109$ eV (Eq. [5.31]).[4] This is a long way from -79 eV, but it's a start.

To get a better approximation for E_g, 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:

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

Thus

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

where[5]

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

---

[3]There do exist exactly soluble three-body problems with many of the qualitative features of helium, but using non-Coulombic potentials (see Problem 7.15).

[4]Here a is the ordinary Bohr radius and $E_n = -13.6/n^2$ eV is the nth Bohr energy; recall that for a nucleus with atomic number Z, $E_n \rightarrow Z^2 E_n$ and $a \rightarrow a/Z$ (Problem 4.17). The spin configuration associated with Equation 7.17 will be antisymmetric (the singlet).

[5]You can, if you like, interpret Equation 7.19 as first-order perturbation theory, with V_{ee} as H'. However, I regard this as a misuse of the method, since the perturbation is roughly equal 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_g.

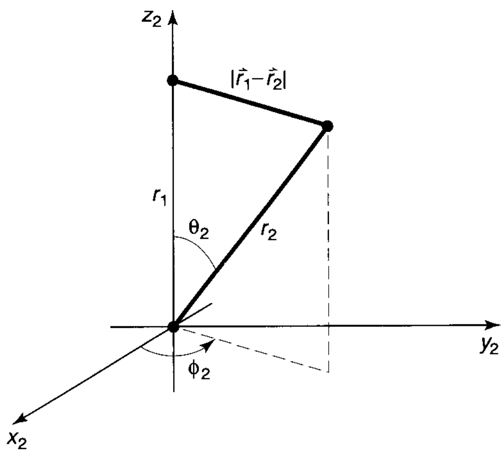

Figure 7.4: Choice of coordinates for the $\mathbf{r}_2$ integral (Equation 7.20).

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,

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

and hence

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

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

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

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

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

Thus

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

$$= \frac{\pi a^3}{8r_1} \left[1 - \left(1 + \frac{2r_1}{a} \right) e^{-4r_1/a} \right]. \qquad [7.24]$$

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

$$\left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{8}{\pi a^3}\right)\int\left[1-\left(1+\frac{2r_1}{a}\right)e^{-4r_1/a}\right]e^{-4r_1/a}r_1\sin\theta_1\,dr_1d\theta_1d\phi_1.$$

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

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

and therefore

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

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

Can we think of 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

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

We'll treat Z as a variational parameter, picking the value that minimizes $\langle H\rangle$.

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

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

The expectation value of H is evidently

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

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 6.54,

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

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 $2/Z$:

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

Putting all this together, we find

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

According to the variational principle, this quantity exceeds E_g 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

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

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

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

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.[6] But we're within 2% of the correct answer, and, frankly, at this point my own interest in the problem begins to fade.

Problem 7.6 Using $E_g = -79.0$ 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 orbitting 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_g, for each case. *Note*: In the case of H^- you should find that $\langle H\rangle > -13.6$ eV, which would appear to indicate that there is no bound state at all, since it is 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

[6] E. A. Hylleraas, *Z. Phys.* **65**, 209 (1930); C. L. Pekeris, *Phys. Rev.* **115**, 1216 (1959).