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**Problem 5.7** Suppose you could find a solution $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)$ to the Schrödinger (Equation 5.25) for the Hamiltonian in Equation 5.24. Describe how you could construct from it a completely symmetric function and a completely antisymmetric function, which also satisfy the Schrödinger equation, with the same energy.

---

### 5.2.1 Helium

After hydrogen, the simplest atom is helium ($Z = 2$). The Hamiltonian,

$$H = \left\{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1}\right\} + \left\{-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2}\right\} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad [5.27]$$

consists of two *hydrogenic* Hamiltonians (with nuclear charge $2e$), one for electron 1 and one for electron 2, together with a final term describing the repulsion of the two electrons. It is this last term that causes all the problems. If we simply *ignore* it, the Schrödinger equation separates, and the solutions can be written as products of *hydrogen* wave functions:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2), \quad [5.28]$$

only with half the Bohr radius (Equation 4.72), and four times the Bohr energies (Equation 4.70). The total energy would be

$$E = 4(E_n + E_{n'}), \quad [5.29]$$

where $E_n = -13.6/n^2$ eV. In particular, the ground state would be

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3}e^{-2(r_1+r_2)/a} \quad [5.30]$$

(see Equation 4.80), and its energy would be

$$E_0 = 8(-13.6\,\text{eV}) = -109\,\text{eV}. \quad [5.31]$$

Because $\psi_0$ is a symmetric function, the spin state has to be *antisymmetric*, so the ground state of helium is a *singlet* configuration, with the spins "oppositely aligned". The *actual* ground state of helium is indeed a singlet, but the experimentally determined energy is $-78.975$ eV, so the agreement is not very good. But this is hardly surprising: We ignored electron repulsion, which is certainly *not* a small contribution. It is clearly *positive* (see Equation 5.27), which is comforting—evidently it brings the total energy up from $-109$ to $-79$ eV (see Problem 5.10).

The excited states of helium consist of one electron in the hydrogenic ground state and the other in an excited state:

$$\psi_{nlm}\psi_{100}. \quad [5.32]$$

[If you try to put *both* electrons in excited states, one immediately drops to the ground state, releasing enough energy to knock the other one into the continuum ($E > 0$), leaving you with a helium *ion* ($He^+$) and a free electron. This is an interesting system in its own right—see Problem 5.8—but it is not our present concern.] We can construct from this both symmetric and antisymmetric combinations, in the usual way (Equation 5.10); the former go with the *antisymmetric* spin configuration (the singlet), and they are called **parahelium**, while the latter require a *symmetric* spin configuration (the triplet), and they are known as **orthohelium**. The ground state is necessarily parahelium; the excited states come in both forms. Because the symmetric spatial state brings the electrons closer together (as we discovered in Section 5.1.2), we expect a higher interaction energy in parahelium, and indeed it is experimentally confirmed that the parahelium states have somewhat higher energy than their orthohelium counterparts (see Figure 5.2).

---

**Problem 5.8**

**(a)** Suppose you put both electrons in a helium atom into the $n = 2$ state; what would the energy of the emitted electron be?

**(b)** Describe (quantitatively) the spectrum of the helium ion, $He^+$.

---

**Problem 5.9** Discuss (qualitatively) the energy level scheme for helium (a) if electrons were identical bosons, and (b) if electrons were distinguishable particles (but still with the same mass and charge). Pretend the electrons still have spin 1/2.

---

****Problem 5.10**

**(a)** Calculate $\langle (1/|\mathbf{r}_1 - \mathbf{r}_2|) \rangle$ for the state $\psi_0$ (Equation 5.30). *Hint*: Do the $d^3\mathbf{r}_2$ integral first, using spherical coordinates and setting the polar axis along $\mathbf{r}_1$, so that

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

The $\theta_2$ integral is easy, but be careful to take the *positive root*. You'll have to break the $r_2$ integral into two pieces, one ranging from 0 to $r_1$, the other from $r_1$ to $\infty$. *Answer*: $5/4a$.

**(b)** Use your result in (a) to estimate the electron interaction energy in the ground state of helium. Express your answer in electron volts, and add it to $E_0$ (Equation 5.31) to get a corrected estimate of the ground-state energy. Compare the experimental value. *Note*: Of course, we're still working with an approximate wave function, so don't expect *perfect* agreement.

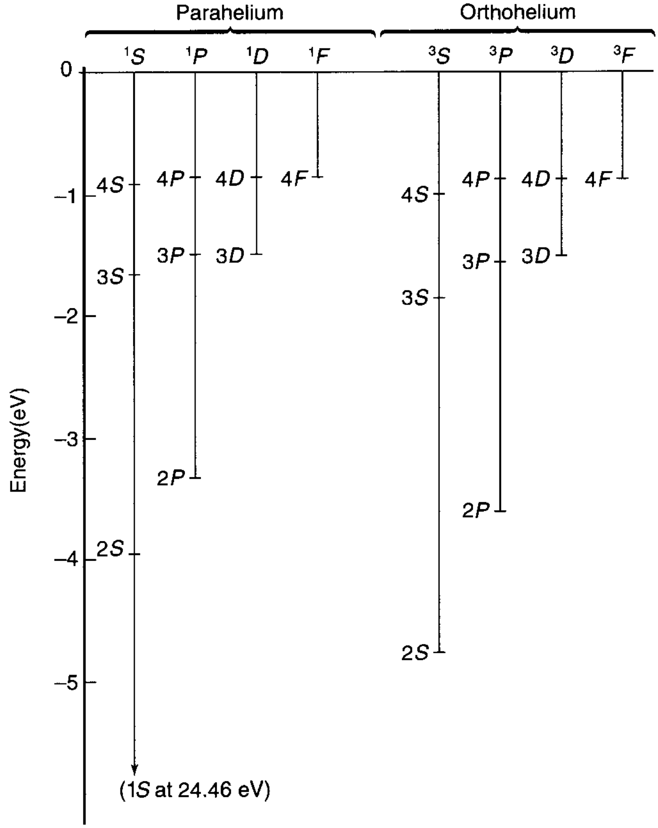

**Figure 5.2:** Energy level diagram for helium (the notation is explained in Section 5.2.2). Note that parahelium energies are uniformly higher than their orthohelium counterparts. The numerical values on the vertical scale are *relative* to the ground state of ionized helium ($He^+$): $4 \times (-13.6 \text{ eV}) = -54.4$ eV; to get the *total* energy of the state, subtract 54.4 eV.

### 5.2.2 The Periodic Table

The ground-state electron configurations for heavier atoms can be pieced together in much the same way. To first approximation (ignoring their mutual repulsion altogether), the individual electrons occupy one-particle hydrogenic states $(n, l, m)$, called **orbitals**, in the Coulomb potential of a nucleus with charge $Ze$. If electrons were bosons (or distinguishable particles), they would all shake down to the ground state (1,0,0), and chemistry would be very dull indeed. But electrons are in fact identical fermions, subject to the Pauli exclusion principle, so only *two* can occupy any given orbital (one with spin up, and one with spin down—or, more precisely, in the singlet configuration). There are $n^2$ hydrogenic wave functions (all with the same energy $E_n$) for a given value of $n$, so the $n = 1$ **shell** has room for two electrons, the $n = 2$ shell holds eight, $n = 3$ takes 18, and in general the $n$th shell can accomodate $2n^2$ electrons. Qualitatively, the horizontal rows on the **Periodic Table** correspond to filling out each shell (if this were the whole story, they would have lengths 2, 8, 18, 32, 50, etc., instead of 2, 8, 8, 18, 18, etc.; we'll see in a moment how the electron-electron repulsion throws the counting off).

With helium, the $n = 1$ shell is filled, so the next atom, lithium ($Z = 3$), has to put one electron into the $n = 2$ shell. Now, for $n = 2$ we can have $l = 0$ or $l = 1$; which of these will the third electron choose? In the absence of electron-electron interactions, they both have the same energy (the Bohr energies depend on $n$, remember, but not on $l$). But the effect of electron repulsion is to favor the lowest value of $l$, for the following reason: Angular momentum tends to throw the electron outward (more formally, the expectation value of $r$ increases with increasing $l$, for a given $n$), and the farther out an electron gets, the more effectively the inner electrons **screen** the nucleus (roughly speaking, the innermost electron "sees" the full nuclear charge $Ze$, but the outermost electron sees an effective charge hardly greater than $e$). Within a given shell, therefore, the state with lowest energy (which is to say, the most tightly bound electron) is $l = 0$, and the energy increases with increasing $l$. Thus the third electron in lithium occupies the orbital (2,0,0). The next atom (beryllium, with $Z = 4$) also fits into this state (only with "opposite spin"), but boron ($Z = 5$) has to make use of $l = 1$.

Continuing in this way, we reach neon ($Z = 10$), at which point the $n = 2$ shell is filled, and we advance to the next row of the periodic table and begin to populate the $n = 3$ shell. First there are two atoms (sodium and magnesium) with $l = 0$, and then there are six with $l = 1$ (aluminum through argon). Following argon there "should" be 10 atoms with $n = 3$ and $l = 2$; however, by this time the screening effect is so strong that it overlaps the next shell, so potassium ($Z = 19$) and calcium ($Z = 20$) choose $n = 4$, $l = 0$, in preference to $n = 3$, $l = 2$. After that we drop back to pick up the $n = 3$, $l = 2$ stragglers (scandium through zinc), followed by $n = 4$, $l = 1$ (gallium through krypton), at which point we again make a premature jump to the next row ($n = 5$) and wait until later to slip in the $l = 2$ and $l = 3$ orbitals from the $n = 4$ shell. For details of this intricate counterpoint, refer to any book on atomic physics.[7]

I would be delinquent if I failed to mention the archaic nomenclature for atomic states, because all chemists and most physicists use it (and the people who make up the Graduate Record Exam *love* this kind of thing). For reasons known best to nineteenth-century spectroscopists, $l = 0$ is called $s$ (for "sharp"), $l = 1$ is $p$ (for "principal"), $l = 2$ is $d$ ("diffuse"), and $l = 3$ is $f$ ("fundamental"); after that I guess they ran out of

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[7] See, for example, U. Fano and L. Fano, *Basic Physics of Atoms and Molecules* (New York: John Wiley & Sons, 1959), Chapter 18, or the classic by G. Herzberg, *Atomic Spectra and Atomic Structure* (New York: Dover, 1944).

imagination, because the list just continues alphabetically ($g, h, i$, etc.).[8] The state of a particular electron is represented by the pair $nl$, with $n$ (the number) giving the shell and $l$ (the letter) specifying the orbital angular momentum; the magnetic quantum number $m$ is not listed, but an exponent is used to indicate the number of electrons that occupy the state in question. Thus the configuration

$$(1s)^2(2s)^2(2p)^2 \qquad [5.33]$$

tells us that there are two electrons in the orbital (1,0,0), two in the orbital (2,0,0), and two in some combination of the orbitals (2,1,1), (2,1,0), and (2,1,−1). This happens to be the ground state of carbon.

In that example there are two electrons with orbital angular momentum quantum number 1, so the total orbital angular momentum quantum number $L$ (capital $L$, instead of $l$, to indicate that this pertains to the *total*, not to any one particle) could be 2, 1, or 0. Meanwhile, the two $(1s)$ electrons are locked together in the singlet state, with total spin zero, and so are the two $(2s)$ electrons, but the two $(2p)$ electrons could be in the singlet configuration or the triplet configuration. So the total spin quantum number $S$ (capital, again, because it's the *total*) could be 1 or 0. Evidently the *grand* total (orbital plus spin) $J$ could be 3, 2, 1, or 0. There exist rituals (**Hund's rules**[9]) for figuring out what these totals will be, for a particular atom. The result is recorded as the following hieroglyphic:

$$^{2S+1}L_J \qquad [5.34]$$

(where $S$ and $J$ are the numbers, and $L$ the letter—capitalized, this time, because we're talking about the *totals*). The ground state of carbon happens to be $^3P_0$: The total spin is 1 (hence the 3), the total orbital angular momentum is 1 (hence the $P$), and the *grand* total angular momentum is zero (hence the 0). In Table 5.1 the individual configurations and the total angular momenta (in the notation of Equation 5.34) are listed, for the first four rows of the Periodic Table.

## ∗∗∗Problem 5.11

**(a)** Figure out the electron configurations (in the notation of Equation 5.33) for the first two rows of the Periodic Table (up to neon), and check your results against Table 5.1.

**(b)** Figure out the corresponding total angular momenta, in the notation of Equation [5.34], for the first four elements. List all the possibilities for boron, carbon, and nitrogen.

---

[8] The shells themselves are assigned equally arbitrary nicknames, starting (don't ask me why) with $K$: the $K$ shell is $n = 1$, the $L$ shell is $n = 2$, $M$ is $n = 3$, and so on (at least they're in alphabetical order).

[9] See, for example, Stephen Gasiorowicz, *Quantum Physics* (New York: John Wiley & Sons, 1974), Chapters 18 and 19.

**Table 5.1:** Ground-state electron configurations for the first four rows of the Periodic Table.

| Z | Element | Configuration | |
|---|---|---|---|
| 1 | H | $(1s)$ | $^2S_{1/2}$ |
| 2 | He | $(1s)^2$ | $^1S_0$ |
| 3 | Li | $(\mathrm{He})\,(2s)$ | $^2S_{1/2}$ |
| 4 | Be | $(\mathrm{He})(2s)^2$ | $^1S_0$ |
| 5 | B | $(\mathrm{He})(2s)^2(2p)$ | $^2P_{1/2}$ |
| 6 | C | $(\mathrm{He})(2s)^2(2p)^2$ | $^3P_0$ |
| 7 | N | $(\mathrm{He})(2s)^2(2p)^3$ | $^4S_{3/2}$ |
| 8 | O | $(\mathrm{He})(2s)^2(2p)^4$ | $^3P_2$ |
| 9 | F | $(\mathrm{He})(2s)^2(2p)^5$ | $^2P_{3/2}$ |
| 10 | Ne | $(\mathrm{He})(2s)^2(2p)^6$ | $^1S_0$ |
| 11 | Na | $(\mathrm{Ne})(3s)$ | $^2S_{1/2}$ |
| 12 | Mg | $(\mathrm{Ne})(3s)^2$ | $^1S_0$ |
| 13 | Al | $(\mathrm{Ne})(3s)^2(3p)$ | $^2P_{1/2}$ |
| 14 | Si | $(\mathrm{Ne})(3s)^2(3p)^2$ | $^3P_0$ |
| 15 | P | $(\mathrm{Ne})(3s)^2(3p)^3$ | $^4S_{3/2}$ |
| 16 | S | $(\mathrm{Ne})(3s)^2(3p)^4$ | $^3P_2$ |
| 17 | Cl | $(\mathrm{Ne})(3s)^2(3p)^5$ | $^2P_{3/2}$ |
| 18 | Ar | $(\mathrm{Ne})(3s)^2(3p)^6$ | $^1S_0$ |
| 19 | K | $(\mathrm{Ar})(4s)$ | $^2S_{1/2}$ |
| 20 | Ca | $(\mathrm{Ar})(4s)^2$ | $^1S_0$ |
| 21 | Sc | $(\mathrm{Ar})(4s)^2(3d)$ | $^2D_{3/2}$ |
| 22 | Ti | $(\mathrm{Ar})(4s)^2(3d)^2$ | $^3F_2$ |
| 23 | V | $(\mathrm{Ar})(4s)^2(3d)^3$ | $^4F_{3/2}$ |
| 24 | Cr | $(\mathrm{Ar})(4s)(3d)^5$ | $^7S_3$ |
| 25 | Mn | $(\mathrm{Ar})(4s)^2(3d)^5$ | $^6S_{3/2}$ |
| 26 | Fe | $(\mathrm{Ar})(4s)^2(3d)^6$ | $^5D_4$ |
| 27 | Co | $(\mathrm{Ar})(4s)^2(3d)^7$ | $^4F_{9/2}$ |
| 28 | Ni | $(\mathrm{Ar})(4s)^2(3d)^8$ | $^3F_4$ |
| 29 | Cu | $(\mathrm{Ar})(4s)(3d)^{10}$ | $^2S_{1/2}$ |
| 30 | Zn | $(\mathrm{Ar})(4s)^2(3d)^{10}$ | $^1S_0$ |
| 31 | Ga | $(\mathrm{Ar})(4s)^2(3d)^{10}(4p)$ | $^2P_{1/2}$ |
| 32 | Ge | $(\mathrm{Ar})(4s)^2(3d)^{10}(4p)^2$ | $^3P_0$ |
| 33 | As | $(\mathrm{Ar})(4s)^2(3d)^{10}(4p)^3$ | $^4S_{3/2}$ |
| 34 | Se | $(\mathrm{Ar})(4s)^2(3d)^{10}(4p)^4$ | $^3P_2$ |
| 35 | Br | $(\mathrm{Ar})(4s)^2(3d)^{10}(4p)^5$ | $^2P_{3/2}$ |
| 36 | Kr | $(\mathrm{Ar})(4s)^2(3d)^{10}(4p)^6$ | $^1S_0$ |

**(c)** **Hund's first rule** says that, all other things being equal, the state with the highest total spin will have the lowest energy. What would this predict in the case of the excited states of helium?

**(d)** **Hund's second rule** says that if a subshell $(n, l)$ is no more than half filled, then the lowest energy level has $J = |L - S|$; if it is more than half filled, then $J = L + S$ has the lowest energy. Use this to resolve the boron ambiguity in (b).

**(e)** Use Hund's rules and the fact that a symmetric spin state must go with an antisymmetric position state (and vice versa) to resolve the carbon ambiguity in (b). What can you say about nitrogen?

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**Problem 5.12** The ground state of dysprosium (element 66, in the sixth row of the Periodic Table) is listed as ${}^5I_8$. What are the total spin, total orbital, and grand total angular momentum quantum numbers? Suggest a likely electron configuration for dysprosium.

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## 5.3 SOLIDS

In the solid state, a few of the loosely bound outermost **valence** electrons in each atom become detached and roam around throughout the material, no longer subject only to the Coulomb field of a specific "parent" nucleus, but rather to the combined potential of the entire crystal lattice. In this section we will examine two extremely primitive models: first, the electron gas theory of Sommerfeld, which ignores *all* forces (except the confining boundaries), treating the wandering electrons as free particles in a box (the three-dimensional analog to an infinite square well); and second, Bloch's theory, which introduces a periodic potential representing the electrical attraction of the regularly spaced, positively charged, nuclei (but still ignores electron-electron repulsion). These models are no more than the first halting steps toward a quantum theory of solids, but already they reveal the critical role of the Pauli exclusion principle in accounting for the "solidity" of solids, and provide illuminating insight into the remarkable electrical properties of conductors, semiconductors, and insulators.

### 5.3.1 The Free Electron Gas

Suppose the object in question is a rectangular solid, with dimensions $l_x$, $l_y$, $l_z$, and imagine that an electron inside experiences no forces at all, except at the impenetrable walls:

$$V(x, y, z) = \begin{cases} 0, & \text{if } (0 < x < l_x, 0 < y < l_y, 0 < z < l_z); \\ \infty, & \text{otherwise.} \end{cases} \qquad [5.35]$$

The Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi,$$

separates in Cartesian coordinates: $\psi(x, y, z) = X(x)Y(y)Z(z)$, with

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_xX, \ -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} = E_yY, \ -\frac{\hbar^2}{2m}\frac{d^2Z}{dz^2} = E_zZ,$$

and $E = E_x + E_y + E_z$. Letting

$$k_x \equiv \frac{\sqrt{2mE_x}}{\hbar}, \ k_y \equiv \frac{\sqrt{2mE_y}}{\hbar}, \ k_z \equiv \frac{\sqrt{2mE_z}}{\hbar},$$

we obtain the general solutions

$$X(x) = A_x \sin(k_xx) + B_x \cos(k_xx), \ Y(y) = A_y \sin(k_yy) + B_y \cos(k_yy),$$

$$Z(z) = A_z \sin(k_zz) + B_z \cos(k_zz).$$

The boundary conditions require that $X(0) = Y(0) = Z(0) = 0$, so $B_x = B_y = B_z = 0$, and $X(l_x) = Y(l_y) = Z(l_z) = 0$, so

$$k_xl_x = n_x\pi, \ k_yl_y = n_y\pi, \ k_zl_z = n_z\pi, \qquad [5.36]$$

where each $n$ is a positive integer:

$$n_x = 1, 2, 3, \ldots, \ n_y = 1, 2, 3, \ldots, \ n_z = 1, 2, 3, \ldots. \qquad [5.37]$$

The (normalized) wave functions are

$$\psi_{n_xn_yn_z} = \sqrt{\frac{8}{l_xl_yl_z}} \sin\left(\frac{n_x\pi}{l_x}x\right) \sin\left(\frac{n_y\pi}{l_y}y\right) \sin\left(\frac{n_z\pi}{l_z}z\right), \qquad [5.38]$$

and the allowed energies are

$$E_{n_xn_yn_z} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right) = \frac{\hbar^2k^2}{2m}, \qquad [5.39]$$

where $k$ is the magnitude of the **wave vector** $\mathbf{k} = (k_x, k_y, k_z)$.

If you imagine a three-dimensional space, with axes $k_x, k_y, k_z$, and planes drawn in at $k_x = (\pi/l_x), (2\pi/l_x), (3\pi/l_x), \ldots$, at $k_y = (\pi/l_y), (2\pi/l_y), (3\pi/l_y), \ldots$, and at $k_z = (\pi/l_z), (2\pi/l_z), (3\pi/l_z), \ldots$, each intersection point represents a distinct (one-particle) stationary state (Figure 5.3). Each block in this grid, and hence also each state, occupies a volume

$$\frac{\pi^3}{l_xl_yl_z} = \frac{\pi^3}{V} \qquad [5.40]$$

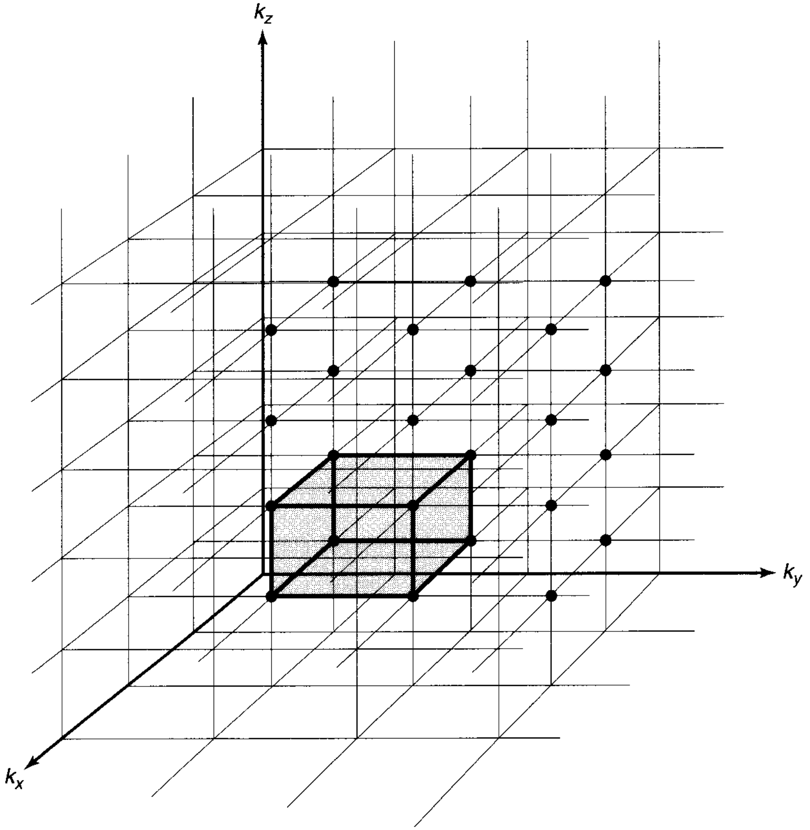

**Figure 5.3:** Free electron gas. Each intersection on the grid represents an allowed energy. Shading indicates one block; there is one state for every block.

of "$k$-space," where $V \equiv l_x l_y l_z$ is the spatial volume of the object itself. Now suppose our sample contains $N$ atoms, and each atom contributes $q$ free electrons. (In practice, $N$ will be enormous—on the order of Avogadro's number, for an object of macroscopic size.) If electrons were bosons (or distinguishable particles), they would all settle down to the ground state, $\psi_{111}$.[10] But electrons are in fact identical fermions subject to the Pauli exclusion principle, so only two of them can occupy any given state. They will fill up one octant of a *sphere* in $k$-space,[11] whose radius $k_F$ is determined by the fact that each pair of electrons requires a volume $\pi^3/V$ (Equation 5.40):

---

[10] I'm assuming there is no appreciable thermal excitation, or other disturbance, to lift the solid out of its collective ground state. If you like, I'm talking about a "cold" solid, though (as you will show in Problem 5.13c), typical solids are still "cold," in this sense, far above room temperature.

[11] Because $N$ is such a huge number, we need not worry about the distinction between the actual jagged edge of the grid and the smooth spherical surface that approximates it.

$$\frac{1}{8}\left(\frac{4}{3}\pi k_F^3\right) = \frac{Nq}{2}\left(\frac{\pi^3}{V}\right).$$

Thus

$$k_F = (3\rho\pi^2)^{1/3}, \qquad [5.41]$$

where

$$\rho \equiv \frac{Nq}{V} \qquad [5.42]$$

is the *free electron density* (the number of free electrons per unit volume).

The boundary separating occupied and unoccupied states, in $k$-space, is called the **Fermi surface** (hence the subscript $F$). The maximum occupied energy is called the **Fermi energy** $E_F$; evidently, for a free electron gas,

$$E_F = \frac{\hbar^2}{2m}(3\rho\pi^2)^{2/3}. \qquad [5.43]$$

The *total* energy of the electron gas can be calculated as follows: a shell of thickness $dk$ (Figure 5.4) contains a volume

$$\frac{1}{8}(4\pi k^2)dk,$$

so the number of electron states in the shell is

$$\frac{2[(1/2)\pi k^2\,dk]}{(\pi^3/V)} = \frac{V}{\pi^2}k^2\,dk.$$

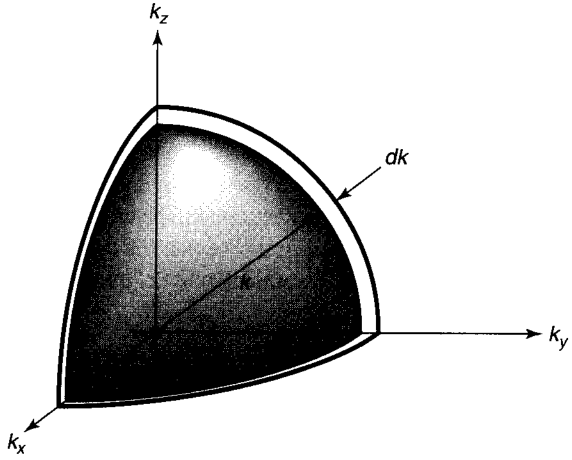

**Figure 5.4:** One octant of a spherical shell in $k$-space.

Each of these states carries an energy $\hbar^2k^2/2m$ (Equation 5.39), so the energy of the shell is

$$dE = \frac{\hbar^2k^2}{2m}\frac{V}{\pi^2}k^2\,dk, \tag{5.44}$$

and hence the total energy is

$$E_{\text{tot}} = \frac{\hbar^2 V}{2\pi^2 m}\int_0^{k_F} k^4\,dk = \frac{\hbar^2 k_F^5 V}{10\pi^2 m} = \frac{\hbar^2(3\pi^2 Nq)^{5/3}}{10\pi^2 m}V^{-2/3}. \tag{5.45}$$

This quantum mechanical energy plays a role rather analogous to the internal thermal energy ($U$) of an ordinary gas. In particular, it exerts a pressure on the walls, for if the box expands by an amount $dV$, the total energy decreases:

$$dE_{\text{tot}} = -\frac{2}{3}\frac{\hbar^2(3\pi^2 Nq)^{5/3}}{10\pi^2 m}V^{-5/3}\,dV = -\frac{2}{3}E_{\text{tot}}\frac{dV}{V},$$

and this shows up as work done on the outside ($dW = P\,dV$) by the quantum pressure $P$. Evidently

$$P = \frac{2}{3}\frac{E_{\text{tot}}}{V} = \frac{2}{3}\frac{\hbar^2 k_F^5}{10\pi^2 m} = \frac{(3\pi^2)^{2/3}\hbar^2}{5m}\rho^{5/3}. \tag{5.46}$$

Here, then, is a partial answer to the question of why a cold solid object doesn't simply *collapse*: There is a stabilizing internal pressure that has nothing to do with electron-electron repulsion (which we have ignored) or thermal motion (which we have excluded) but is strictly quantum mechanical, and derives ultimately from the antisymmetrization requirement for the wave functions of identical fermions. It is sometimes called **degeneracy pressure**, although "exclusion pressure" might be a better term.[12]

---

**Problem 5.13** The density of copper is 8.96 gm/cm$^3$, and its atomic weight is 63.5 gm/mole.

**(a)** Calculate the Fermi energy for copper (Equation 5.43). Assume $q = 1$, and give your answer in electron volts.

**(b)** What is the corresponding electron velocity [set $E_F = (1/2)mv^2$]? Is it safe to assume that the electrons in copper are nonrelativistic?

**(c)** At what temperature would the characteristic thermal energy ($k_BT$, where $k_B$ is the Boltzmann constant and $T$ is the Kelvin temperature) equal the Fermi energy, for copper? *Note*: This is called the **Fermi temperature**. As long as the *actual* temperature is substantially below the Fermi temperature, the material can be regarded as "cold", with most of the electrons in the ground-state configuration. Since the melting point of copper is 1356 K, solid copper is *always* cold.

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[12] We derived Equations 5.41, 5.43, 5.45, and 5.46 for the special case of an infinite rectangular well; but they hold for containers of any shape as long as the number of particles is extremely large.

**(d)** Calculate the degeneracy pressure (Equation 5.46) of copper, in the electron gas model.

---

**Problem 5.14** The **bulk modulus** of a substance is the ratio of a small decrease in pressure to the resulting fractional increase in volume:

$$B = -V\frac{dP}{dV}.$$

Show that $B = (5/3)P$, in the free electron gas model, and use your result in Problem 5.13(d) to estimate the bulk modulus of copper. *Note*: The observed value is $13.4 \times 10^{10}\ \mathrm{N/m^2}$, but don't expect perfect agreement—after all, we're neglecting all electron-nucleus and electron-electron forces! Actually, it is rather surprising that this calculation comes as close as it *does*.

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### 5.3.2 Band Structure

We're now going to improve on the free electron model by including the forces exerted on the electrons by the regularly spaced, positively charged, essentially stationary nuclei. The qualitative behavior of solids is dictated to a remarkable degree by the mere fact that this potential is *periodic*—its actual *shape* is relevant only to the finer details. To show you how it goes, I'm going to develop the simplest possible example: a one-dimensional **Dirac comb**, consisting of evenly spaced delta-function wells (Figure 5.5). But before I get to that, we need to know a bit about the general theory of periodic potentials.

Consider, then, a single particle subject to a periodic potential in one dimension:

$$V(x+a) = V(x). \tag{5.47}$$

**Bloch's theorem** tells us that the solutions to the Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi, \tag{5.48}$$

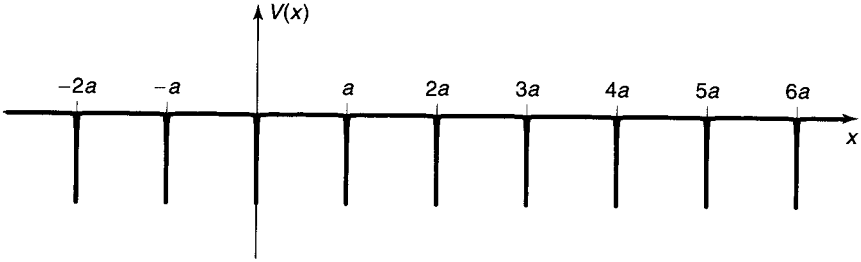

Figure 5.5: The Dirac comb, Equation 5.57.

for such a potential, can be taken to satisfy the condition

$$\psi(x+a) = e^{iKa}\psi(x) \tag{5.49}$$

for some constant $K$.

**Proof:** Let $D$ be the "displacement" operator:

$$Df(x) = f(x+a). \tag{5.50}$$

By virtue of Equation 5.47, $D$ commutes with the Hamiltonian:

$$[D, H] = 0, \tag{5.51}$$

and hence (see Section 3.4.1) we are free to choose eigenfunctions of $H$ that are simultaneously eigenfunctions of $D$: $D\psi = \lambda\psi$, or

$$\psi(x+a) = \lambda\psi(x). \tag{5.52}$$

Now $\lambda$ is certainly not *zero* [if it *were*, then—since Equation 5.52 holds for *all* $x$—we would immediately obtain $\psi(x) = 0$, which is not a permissible eigenfunction], so, like any nonzero complex number, it can be expressed as an exponential:

$$\lambda = e^{iKa} \tag{5.53}$$

for some constant $K$. QED.

At this stage Equation 5.53 is merely a strange way to write the eigenvalue $\lambda$, but in a moment we will discover that $K$ is in fact *real*, so that although $\psi(x)$ itself is not periodic, $|\psi(x)|^2$ *is*:

$$|\psi(x+a)|^2 = |\psi(x)|^2, \tag{5.54}$$

as one would certainly expect.[13]

Of course, no *real* solid goes on forever, and the edges are going to spoil the periodicity of $V(x)$ and render Bloch's theorem inapplicable. However, for any macroscopic crystal, containing something on the order of Avogadro's number of atoms, it is hardly imaginable that edge effects can significantly influence the behavior of electrons deep inside. This suggests the following device to salvage Bloch's theorem: We wrap the $x$-axis around in a circle and connect it onto its tail, after a large number $N \approx 10^{23}$ of periods; formally, we impose the boundary condition

$$\psi(x+Na) = \psi(x). \tag{5.55}$$

---

[13] Indeed, you might be tempted to reverse the argument, *starting* with Equation 5.54, as a way of proving Bloch's theorem. It doesn't work, for Equation 5.54 alone would allow the phase factor in Equation 5.49 to be a *function of* $x$.

It follows (from Equation 5.49) that

$$e^{iNKa}\psi(x) = \psi(x),$$

so $e^{iNKa} = 1$, or $NKa = 2\pi n$, or

$$K = \frac{2\pi n}{Na}, \quad (n = 0,\ \pm 1,\ \pm 2,\ \ldots). \tag{5.56}$$

In particular, for this arrangement $K$ is necessarily real. The virtue of Bloch's theorem is that we need only solve the Schrödinger equation within *a single cell* (say, on the interval $0 \le x \le a$); recursive application of Equation 5.49 generates the solution everywhere else.

Now suppose the potential consists of a long string of delta-function wells (the Dirac comb):

$$V(x) = -\alpha \sum_{j=0}^{N-1} \delta(x - ja). \tag{5.57}$$

The wells are supposed to represent, very crudely, the electrical attraction of the nuclei in the lattice. (In Figure 5.5 you must imagine that the $x$-axis has been "wrapped around," as suggested in the previous paragraph, so the $N$th well actually appears at $x = -a$.) No one would pretend that this is a *realistic* model, but remember, it is only the effect of *periodicity* that concerns us here; the classic study[14] used a repeating *rectangular* pattern, and many authors still prefer that one.[15] In the region $0 < x < a$ the potential is zero, so

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi,$$

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi,$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar}, \tag{5.58}$$

as usual. (I'll work out the positive-energy solutions; the negative-energy states can be obtained in exactly the same way, using $\kappa \equiv \sqrt{-2mE}/\hbar$, or by simply substituting $k \to i\kappa$ in the final result [5.64].)

The general solution is

$$\psi(x) = A\sin(kx) + B\cos(kx), \quad (0 < x < a). \tag{5.59}$$

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[14] R. de L. Kronig and W. G. Penney, *Proc. R. Soc. Lond.*, ser. A, **130**, 499 (1930).

[15] See, for instance, D. Park, *Introduction to the Quantum Theory*, 3rd ed., (New York: McGraw-Hill, 1992).

According to Bloch's theorem, the wave function in the cell immediately to the *left* of the origin is

$$\psi(x) = e^{-iKa}[A\sin k(x+a) + B\cos k(x+a)], \quad (-a < x < 0). \quad [5.60]$$

At $x = 0$, $\psi$ must be continuous, so

$$B = e^{-iKa}[A\sin(ka) + B\cos(ka)]; \quad [5.61]$$

its derivative suffers a discontinuity proportional to the strength of the delta function (see Equation 2.107):

$$kA - e^{-iKa}k[A\cos(ka) - B\sin(ka)] = -\frac{2m\alpha}{\hbar^2}B. \quad [5.62]$$

Solving Equation 5.61 for $A\sin(ka)$ yields

$$A\sin(ka) = [e^{iKa} - \cos(ka)]B. \quad [5.63]$$

Substituting this into Equation 5.62, and canceling $kB$, we find

$$[e^{iKa} - \cos(ka)][1 - e^{-iKa}\cos(ka)] + e^{-iKa}\sin^2(ka) = -\frac{2m\alpha}{\hbar^2 k}\sin(ka),$$

which simplifies to

$$\cos(Ka) = \cos(ka) - \frac{m\alpha}{\hbar^2 k}\sin(ka). \quad [5.64]$$

This is the fundamental result from which all else follows. For the Kronig-Penney potential (see footnote 15), the formula is more complicated, but it shares the qualitative features we are about to explore.

Equation 5.64 determines the possible values of $k$, and hence the allowed energies. To simplify the notation, let

$$z \equiv ka, \quad \text{and} \quad \beta \equiv \frac{m\alpha a}{\hbar^2}, \quad [5.65]$$

so the right side of Equation 5.64 can be written

$$f(z) = \cos(z) - \beta\frac{\sin(z)}{z}. \quad [5.66]$$

The constant $\beta$ is a dimensionless measure of the "strength" of the delta function. In Figure 5.6 I have plotted $f(z)$ for the case $\beta = 1$. The important thing to notice is that $f(z)$ strays outside the range $(-1, +1)$, and in such regions there is no hope of solving Equation 5.64, since $|\cos(Ka)| \leq 1$. These **gaps** represent forbidden energies; they are separated by **bands** of allowed energies. Within a given band, virtually any energy is allowed, for according to Equation 5.56 $Ka = 2\pi n/N$, where $N$ is a huge number,

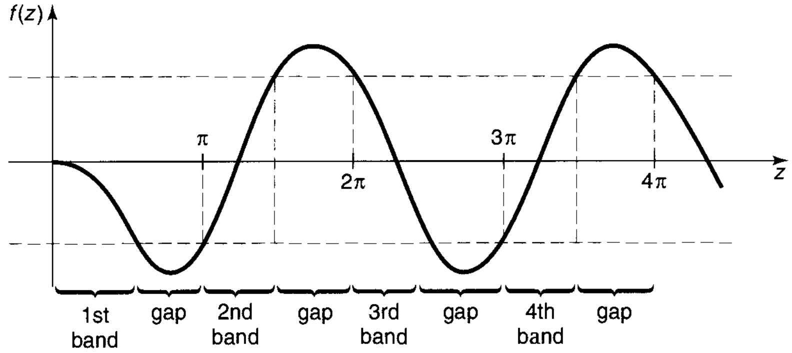

**Figure 5.6:** Graph of $f(z)$ (Equation 5.66) for $\beta = 1$, showing allowed bands separated by forbidden gaps.

and $n$ can be any integer. You might imagine drawing $N$ horizontal lines on Figure 5.6, at values of $\cos(2\pi n/N)$ ranging from $+1$ ($n = 0$) down to $-1$ ($n = N/2$), and back almost to $+1$ ($n = N-1$)—at this point the Bloch factor $e^{iKa}$ recycles, so no new solutions are generated by further increasing $n$. The intersection of each of these lines with $f(z)$ yields an allowed energy. Evidently there are $N/2$ positive-energy states in the first band (joined by $N/2$ negative-energy states) and $N$ in all the higher bands; they are so closely spaced that for most purposes we can regard them as forming a continuum (Figure 5.7).

So far, we've only put *one* electron in our potential. In practice there will be $Nq$ of them, where $q$ is again the number of "free" electrons per atom. Because of

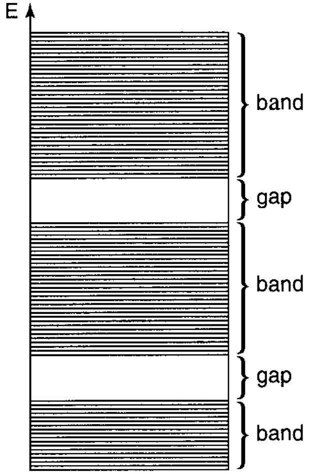

**Figure 5.7:** The allowed positive energies for a periodic potential.

the Pauli exclusion principle, only two electrons can occupy a given spatial state, so if $q = 1$, they will just fill the negative-energy half of the first band, if $q = 2$ they will completely fill the first band, if $q = 3$ they half fill the second band, and so on. (In three dimensions, and with more realistic potentials, the band structure may be more complicated, but the *existence* of bands, separated by forbidden gaps, persists—band structure is the *signature* of a periodic potential.) Now, if a band is entirely filled, it takes a relatively large energy to excite an electron, since it has to jump across the forbidden zone. Such materials will be electrical **insulators**. On the other hand, if a band is only *partly* filled, it takes very little energy to excite an electron, and such materials are typically **conductors**. If you **dope** an insulator with a few atoms of larger or smaller $q$, this puts some "extra" electrons into the next higher band, or creates some **holes** in the previously filled one, allowing in either case for weak electric currents to flow; such materials are called **semiconductors**. In the free electron model *all* solids should be excellent conductors, since there are no large gaps in the spectrum of allowed energies. It takes the band theory to account for the extraordinary range of electrical conductivities exhibited by the solids in nature.

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**Problem 5.15**

**(a)** Using Equations 5.59 and 5.63, show that the wave function for a particle in the periodic delta function potential can be written in the form

$$\psi(x) = C[\sin(kx) + e^{-iKa} \sin k(a - x)], \quad (0 \leq x \leq a).$$

(Don't bother to determine the normalization constant $C$.)

**(b)** There is an exception: At the bottom of a band, where $ka = Ka = j\pi$, (a) yields $\psi(x) = 0$. Find the correct wave function for this case. Note what happens to $\psi$ at each delta function.

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**Problem 5.16** Find the energy at the top of the first allowed band, for the case $\beta = 5$, correct to three significant digits. For the sake of argument, assume $\alpha/a = 1$ eV.

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**Problem 5.17** Suppose we used delta-function *spikes*, instead of *wells* (so that the electrons are *repelled*, instead of attracted, by the nuclei). Draw the analogs to Figures 5.6 and 5.7 (using the same values of the parameters—except for their signs). How many allowed energies are there in each band? What is the energy at the top of the $j$th band?

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**Problem 5.18** Show that *most* of the energies determined by Equation 5.64 are doubly degenerate. What are the exceptional cases? *Hint*: Try it for $N = 1, 2, 3, 4, \ldots$, to see how it goes. What are the possible values of $\cos(Ka)$ in each case?

## 5.4 QUANTUM STATISTICAL MECHANICS

At absolute zero, a physical system occupies its lowest energy configuration. As we turn up the temperature, random thermal activity will begin to populate the excited states, and this raises the following question: If we have a large number $N$ of particles in thermal equilibrium at temperature $T$, what is the probability that a given particle would be found to have a specific energy $E_j$? Note that the "probability" in question has nothing to do with quantum indeterminacy—exactly the same question arises in *classical* statistical mechanics. The reason we must be content with a *probabilistic* answer is that we are typically dealing with enormous numbers of particles, and we could not possibly expect to keep track of each one separately, whether or *not* the underlying mechanics is deterministic.

The **fundamental assumption of statistical mechanics** is that in **thermal equilibrium** every distinct state with the same *total* energy $E$ is equally probable. Random thermal motions constantly shift energy from one particle to another and from one form (rotational, kinetic, vibrational, etc.) to another, but (absent external influences) the *total* is fixed by conservation of energy. The assumption (and it's a *deep* one, worth thinking about) is that this continual redistribution of energy does not favor any particular state. The **temperature** $T$ is simply a measure of the total energy, for a system in thermal equilibrium. The only new twist introduced by quantum mechanics has to do with *how we count the distinct states*, and this depends critically on whether the particles involved are distinguishable, identical bosons, or identical fermions. The arguments are relatively straightforward, but the *arithmetic* gets pretty dense, so I'm going to begin with an absurdly simple example, so you'll have a clear sense of what is at issue when we come to the general case.

### 5.4.1 Example

Suppose we have just *three* noninteracting particles (all of mass $m$) in the one-dimensional infinite square well (Section 2.2). The total energy is

$$E = E_A + E_B + E_C = \frac{\pi^2\hbar^2}{2ma^2}(n_A^2 + n_B^2 + n_C^2) \qquad [5.67]$$

(see Equation 2.23), where $n_A$, $n_B$, and $n_C$ are positive integers. Now suppose, for the sake of argument, that $E = 243(\pi^2\hbar^2/2ma^2)$, which is to say,

$$n_A^2 + n_B^2 + n_C^2 = 243. \qquad [5.68]$$

There are, as it happens, 10 combinations of positive integers, the sum of whose squares is 243: All three could be 9, or two could be 3 and one 15 (which occurs in three permutations), or one could be 5, one 7, and one 13 (six permutations). Thus $(n_A, n_B, n_C)$ is one of the following:

$$(9, 9, 9),$$

$$(3, 3, 15),\ (3, 15, 3),\ (15, 3, 3),$$

$$(5, 7, 13),\ (5, 13, 7),\ (7, 5, 13),\ (7, 13, 5),\ (13, 5, 7),\ (13, 7, 5).$$

If the particles are *distinguishable*, each of these represents a distinct quantum state, and the fundamental assumption of statistical mechanics says that in thermal equilibrium[16] they are all equally likely. But I'm not interested in knowing *which* particle is in *which* (one-particle) state, only the total *number* of particles in each state—the **occupation number** $N_n$ for the state $\psi_n$. The collection of all occupation numbers for a given three-particle state we will call the **configuration**. If all three are in $\psi_9$, the configuration is

$$(0, 0, 0, 0, 0, 0, 0, 0, 3, 0, 0, 0, 0, 0, 0, 0, 0, 0, \ldots) \qquad [5.69]$$

(i.e., $N_9 = 3$, all others zero). If two are in $\psi_3$ and one is in $\psi_{15}$, the configuration is

$$(0, 0, 2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, 0, \ldots) \qquad [5.70]$$

(i.e., $N_3 = 2$, $N_{15} = 1$, all others zero). And if there is one particle in $\psi_5$, one in $\psi_7$, and one in $\psi_{13}$, the configuration is

$$(0, 0, 0, 0, 1, 0, 1, 0, 0, 0, 0, 0, 1, 0, 0, 0, \ldots) \qquad [5.71]$$

(i.e., $N_5 = N_7 = N_{13} = 1$, all others zero.) Of these, the third is the *most probable* configuration, because it can be achieved in six different ways, whereas the second occurs three ways, and the first only one.

Returning now to my original question, if we select one of these three particles at random, what is the probability ($P_n$) of getting a specific (allowed) energy $E_n$? Well, the chances are 1 in 10 that the system is in the first configuration (Equation 5.69), and in that event we are certain to get $E_9$, so $P_9 = 1/10$. The chances are 3 in 10 that the system is in the second configuration (Equation 5.70), and in that case there is a 2/3 probability of getting $E_3$, and 1/3 probability of getting $E_{15}$, so $P_3 = (3/10) \times (2/3) = 1/5$, and $P_{15} = (3/10) \times (1/3) = 1/10$. And the chances are 6 in 10 that the system is in the third configuration, in which case the probability is 1/3 each that we'll get $E_5$, $E_7$, and $E_{13}$, so $P_5 = P_7 = P_{13} = (6/10) \times (1/3) = 1/5$. As a check, we note that

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[16] How the particles maintain thermal equilibrium, if they really don't interact at all, is a problem I'd rather not worry about—maybe God reaches in periodically and stirs things up (being careful not to add or remove any energy). In real life, of course, the continual redistribution of energy is caused precisely by interactions between the particles, so if you don't approve of divine intervention let there be extremely weak interactions—sufficient to thermalize the system (at least, over long time periods) but too small to alter the stationary states and the allowed energies appreciably.

$$P_3 + P_5 + P_7 + P_9 + P_{13} + P_{15} = \frac{1}{5} + \frac{1}{5} + \frac{1}{5} + \frac{1}{10} + \frac{1}{5} + \frac{1}{10} = 1.$$

But that's when the particles are distinguishable. If in fact they are *identical fermions*, the antisymmetrization requirement (leaving aside spin, for simplicity) excludes the first and second configurations (which assign two—or, worse still, three—particles into the same state), and there is just *one* state with the third configuration (see Problem 5.19). For identical fermions, then, $P_5 = P_7 = P_{13} = 1/3$ (and again the sum of the probabilities is 1). On the other hand, if they are *identical bosons* the symmetrization requirement allows for one state with each configuration (see Problem 5.19), so $P_9 = 1/3$, $P_3 = (1/3) \times (2/3) = 2/9$, $P_{15} = (1/3) \times (1/3) = 1/9$, and $P_5 = P_7 = P_{13} = (1/3) \times (1/3) = 1/9$. As always, the sum is 1.

The purpose of this example was to show you how the counting of states depends on the nature of the particles. In one respect it was actually *more complicated* than the realistic situation, in which $N$ is a huge number. For as $N$ grows, the most probable configuration (in this example, $N_5 = N_7 = N_{13} = 1$, for the case of distinguishable particles) becomes *overwhelmingly* more likely than its competitors, so that, for statistical purposes, we can afford to ignore the others altogether. *The distribution of individual particle energies*, at equilibrium, *is simply their distribution in the most probable configuration.* (If this were true for $N = 3$—which, obviously, it is *not*—we would conclude that $P_5 = P_7 = P_{13} = 1/3$ for the case of distinguishable particles.) I'll return to this point in Section 5.4.3, but first we need to generalize the counting procedure itself.

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**∗Problem 5.19**

**(a)** Construct the completely antisymmetric wave function $\psi(x_A, x_B, x_C)$ for three identical fermions, one in the state $\psi_5$, one in the state $\psi_7$, and one in the state $\psi_{13}$.

**(b)** Construct the completely symmetric wave function $\psi(x_A, x_B, x_C)$ for three identical bosons, (i) if all three are in state $\psi_9$, (ii) if two are in state $\psi_3$ and one is in state $\psi_{13}$, and (iii) if one is in state $\psi_5$, one in state $\psi_7$, and one in state $\psi_{13}$.

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**∗Problem 5.20** Suppose you had three particles in a one-dimensional harmonic oscillator potential, in thermal equilibrium, with a total energy $E = (9/2)\hbar\omega$.

**(a)** If they are distinguishable particles (but all with the same mass), what are the possible occupation-number configurations, and how many distinct (three-particle) states are there for each one? What is the most probable configuration? If you picked a particle at random and measured its energy, what values might you get, and what is the probability of each one? What is the most probable energy?

**(b)** Do the same for the case of identical fermions (ignoring spin, as in the Example in Section 5.4.1).

**(c)** Do the same for the case of identical bosons (ignoring spin).

### 5.4.2 The General Case

Now consider an arbitrary potential, for which the one-particle energies are $E_1$, $E_2$, $E_3, \ldots$, with degeneracies $d_1, d_2, d_3, \ldots$ (i.e., there are $d_n$ distinct one-particle states with the same energy $E_n$). Suppose we put $N$ particles (all with the same mass) into this potential; we are interested in the configuration $(N_1, N_2, N_3, \ldots)$, for which there are $N_1$ particles with energy $E_1$, $N_2$ particles with energy $E_2$, and so on. *Question:* How many different ways can this be achieved (or, more precisely, how many distinct states correspond to this particular configuration)? The answer, $Q(N_1, N_2, N_3, \ldots)$, depends on whether the particles are distinguishable, identical fermions, or identical bosons, so we'll treat the three cases separately.[17]

First, assume the particles are *distinguishable*. How many ways are there to select (from the $N$ available candidates) the $N_1$ to be placed in the first "bin"? *Answer:* the **binomial coefficient**, "$N$ choose $N_1$":

$$\binom{N}{N_1} \equiv \frac{N!}{N_1!(N-N_1)!}. \qquad [5.72]$$

For there are $N$ ways to pick the first particle, leaving $(N-1)$ for the second, and so on:

$$N(N-1)(N-2)\cdots(N-N_1+1) = \frac{N!}{(N-N_1)!}.$$

However, this counts separately the $N_1!$ different *permutations* of the $N_1$ particles, whereas we don't care whether number 37 was picked on the first draw, or on the twenty-ninth draw; so we divide by $N_1!$, confirming Equation 5.72. Now, how many different ways can those $N_1$ particles be arranged *within* the first bin? Well, there are $d_1$ states in the bin, so each particle has $d_1$ choices; evidently there are $(d_1)^{N_1}$ possibilities in all. Thus the number of ways to put $N_1$ particles, selected from a total population of $N$, into a bin containing $d_1$ distinct options, is

$$\frac{N! d_1^{N_1}}{N_1!(N-N_1)!}.$$

The same goes for bin 2, of course, except that there are now only $(N-N_1)$ particles left to work with:

$$\frac{(N-N_1)! d_2^{N_2}}{N_2!(N-N_1-N_2)!};$$

---

[17] The presentation here follows closely that of Amnon Yariv, *An Introduction to Theory and Applications of Quantum Mechanics* (New York: John Wiley & Sons, 1982).

and so on. It follows that

$$
\begin{aligned}
&Q(N_1, N_2, N_3, \ldots)\\
&= \frac{N!d_1^{N_1}}{N_1!(N-N_1)!}\frac{(N-N_1)!d_2^{N_2}}{N_2!(N-N_1-N_2)!}\frac{(N-N_1-N_2)!d_3^{N_3}}{N_3!(N-N_1-N_2-N_3)!}\cdots\\
&= N!\frac{d_1^{N_1}d_2^{N_2}d_3^{N_3}\cdots}{N_1!N_2!N_3!\cdots} = N!\prod_{n=1}^{\infty}\frac{d_n^{N_n}}{N_n!}.
\end{aligned}
\tag{5.73}
$$

(You should pause right now and *check* this result for the Example in Section 5.4.1—see Problem 5.21.)

The problem is a lot easier for *identical fermions*. Because they are indistinguishable, it doesn't matter *which* particles are in *which* states—the antisymmetrization requirement means that there is just *one* $N$-particle state in which a specific set of one-particle states is occupied. Moreover, only one particle can occupy any given state. There are

$$\binom{d_n}{N_n}$$

ways to choose the $N_n$ occupied states in the $n$th bin,[18] so

$$Q(N_1, N_2, N_3, \ldots) = \prod_{n=1}^{\infty}\frac{d_n!}{N_n!(d_n-N_n)!}. \tag{5.74}$$

(Check it for the Example in Section 5.4.1—see Problem 5.21.)

The calculation is hardest for the case of *identical bosons*. Again, the symmetrization requirement means that there is just one $N$-particle state in which a specific set of one-particle states is occupied, but this time there is no restriction on the number of particles that can share the same one-particle state. For the $n$th bin, the question becomes: how many different ways can we assign $N_n$ identical particles to $d_n$ different slots? There are many ways to solve this combinatorial problem; an especially clever method involves the following trick: Let dots represent particles and crosses represent partitions, so that, for example, if $d_n = 5$ and $N_n = 7$,

$$\bullet\;\bullet\;\times\;\bullet\;\times\;\bullet\;\bullet\;\bullet\;\times\;\bullet\;\times$$

would indicate that there are two particles in the first state, one in the second, three in the third, one in the fourth, and none in the fifth. Note that there are $N_n$ dots and $(d_n - 1)$ crosses (partitioning the dots into $d_n$ groups). If the individual dots and crosses were *labeled*, there would be $(N_n + d_n - 1)!$ different ways to arrange them. But for our purposes the dots are all equivalent—permuting them ($N_n!$ ways) does not

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[18] This should be zero, of course, if $N_n > d_n$, and it *is*, provided that we consider the factorial of a negative integer to be infinite.

change the state. Likewise, the crosses are all equivalent—permuting them [$(d_n - 1)!$ ways] changes nothing. So there are in fact

$$\frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!} = \binom{N_n + d_n - 1}{N_n} \qquad [5.75]$$

distinct ways of assigning the $N_n$ particles to the $d_n$ one-particle states in the $n$th bin, and we conclude that

$$Q(N_1, N_2, N_3, \ldots) = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}. \qquad [5.76]$$

(Check it for the Example in Section 5.4.1—see Problem 5.21.)

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∗**Problem 5.21** Check Equations 5.73, 5.74, and 5.76 for the Example in Section 5.4.1.

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∗∗**Problem 5.22** Obtain Equation 5.75 by induction. The combinatorial question is this: How many different ways can you put $N$ identical balls into $d$ baskets (never mind the subscript $n$ for this problem). You could stick all $N$ of them into the third basket, or all but one in the second basket and one in the fifth, or two in the first and three in the third and all the rest in the seventh, etc. Work it out explicitly for the cases $N = 1$, $N = 2$, $N = 3$, and $N = 4$; by that stage you should be able to deduce the general formula.

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### 5.4.3 The Most Probable Configuration

In thermal equilibrium, every state with a given total energy $E$ and a given particle number $N$ is equally likely. So the *most probable configuration* $(N_1, N_2, N_3, \ldots)$ is the one that can be achieved in the largest number of different ways—it is that particular configuration for which $Q(N_1, N_2, N_3, \ldots)$ is a maximum, subject to the constraints

$$\sum_{n=1}^{\infty} N_n = N \qquad [5.77]$$

and

$$\sum_{n=1}^{\infty} N_n E_n = E. \qquad [5.78]$$

The problem of maximizing a function $F(x_1, x_2, x_3, \ldots)$ of several variables, subject to the constraints $f_1(x_1, x_2, x_3, \ldots) = 0$, $f_2(x_1, x_2, x_3, \ldots) = 0$, etc., is most conveniently handled by the method of **Lagrange multipliers**[19]: We introduce the new function

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[19] See, for example, Mary Boas, *Mathematical Methods in the Physical Sciences*, 2nd ed. (New York: John Wiley & Sons, 1983), Chapter 4, Section 9.

$$G(x_1, x_2, x_3, \ldots, \lambda_1, \lambda_2, \ldots) \equiv F + \lambda_1 f_1 + \lambda_2 f_2 + \cdots \qquad [5.79]$$

and set *all* its derivatives equal to zero:

$$\frac{\partial G}{\partial x_n} = 0; \quad \frac{\partial G}{\partial \lambda_n} = 0. \qquad [5.80]$$

In our case it's a little easier to work with the *logarithm* of $Q$, instead of $Q$ itself—this turns the *products* into *sums*. Since the logarithm is a monotonic function of its argument, the maxima of $Q$ and $\ln(Q)$ occur at the same point. So we let

$$G \equiv \ln(Q) + \alpha\left[N - \sum_{n=1}^{\infty} N_n\right] + \beta\left[E - \sum_{n=1}^{\infty} N_n E_n\right], \qquad [5.81]$$

where $\alpha$ and $\beta$ are the Lagrange multipliers. Setting the derivatives with respect to $\alpha$ and $\beta$ equal to zero merely reproduces the constraints (Equations 5.77 and 5.78): it remains, then, to set the derivative with respect to $N_n$ equal to zero.

If the particles are *distinguishable*, then $Q$ is given by Equation 5.73, and we have

$$G = \ln(N!) + \sum_{n=1}^{\infty}[N_n \ln(d_n) - \ln(N_n!)]$$
$$+ \alpha\left[N - \sum_{n=1}^{\infty} N_n\right] + \beta\left[E - \sum_{n=1}^{\infty} N_n E_n\right]. \qquad [5.82]$$

Assuming that the relevant occupation numbers ($N_n$) are large, we can invoke **Stirling's approximation**[20]:

$$\ln(z!) \approx z\ln(z) - z \quad \text{for } z >> 1 \qquad [5.83]$$

to write

$$G \approx \sum_{n=1}^{\infty}[N_n \ln(d_n) - N_n \ln(N_n) + N_n - \alpha N_n - \beta E_n N_n]$$
$$+ \ln(N!) + \alpha N + \beta E. \qquad [5.84]$$

It follows that

$$\frac{\partial G}{\partial N_n} = \ln(d_n) - \ln(N_n) - \alpha - \beta E_n. \qquad [5.85]$$

---

[20] See George Arfken, *Mathematical Methods for Physicists*, 3rd ed. (Orlando, FL: Academic Press, 1985), Section 10.3. If the relevant occupation numbers are *not* large—as in the Example of Section 5.4.1—then statistical mechanics simply doesn't apply. The whole point is to deal with such enormous numbers that statistical inference is a reliable predictor. Of course, there will always be one-particle states of extremely high energy that are not populated at *all*; fortunately, Stirling's approximation holds also for $z = 0$. I use the word "relevant" to exclude any stray states right at the margin, for which $N_n$ is neither huge nor zero.

Setting this equal to zero and solving for $N_n$, we conclude that the *most probable occupation numbers* for distinguishable particles are

$$N_n = d_n e^{-(\alpha+\beta E_n)}. \tag{5.86}$$

If the particles are *identical fermions*, then $Q$ is given by Equation 5.74, and we have

$$G = \sum_{n=1}^{\infty} \{\ln(d_n!) - \ln(N_n!) - \ln[(d_n - N_n)!]\} \\ + \alpha\left[N - \sum_{n=1}^{\infty} N_n\right] + \beta\left[E - \sum_{n=1}^{\infty} N_n E_n\right]. \tag{5.87}$$

This time we must assume not only that $N_n$ is large, but also that $d_n \gg N_n$,[21] so that Stirling's approximation applies to both terms. In that case

$$G \approx \sum_{n=1}^{\infty}\Big[\ln(d_n!) - N_n \ln(N_n) + N_n - (d_n - N_n)\ln(d_n - N_n) \\ + (d_n - N_n) - \alpha N_n - \beta E_n N_n\Big] + \alpha N + \beta E, \tag{5.88}$$

so

$$\frac{\partial G}{\partial N_n} = -\ln(N_n) + \ln(d_n - N_n) - \alpha - \beta E_n. \tag{5.89}$$

Setting this equal to zero and solving for $N_n$, we find the *most probable occupation numbers* for identical fermions:

$$N_n = \frac{d_n}{e^{(\alpha+\beta E_n)} + 1}. \tag{5.90}$$

Finally, if the particles are *identical bosons*, then $Q$ is given by Equation 5.76, and we have

$$G = \sum_{n=1}^{\infty} \{\ln[(N_n + d_n - 1)!] - \ln(N_n!) - \ln[(d_n - 1)!]\} \\ + \alpha\left[N - \sum_{n=1}^{\infty} N_n\right] + \beta\left[E - \sum_{n=1}^{\infty} N_n E_n\right]. \tag{5.91}$$

---

[21] In *one* dimension the energies are nondegenerate (see Problem 2.42), but in three dimensions $d_n$ typically increases rapidly with increasing $n$ (for example, in the case of hydrogen, $d_n = n^2$). So it is not unreasonable to assume that for *most* of the occupied states $d_n \gg 1$. On the other hand, $d_n$ is certainly *not* much greater than $N_n$ at absolute zero, where all states up to the Fermi level are filled, and hence $d_n = N_n$. Here again we are rescued by the fact that Stirling's formula holds also for $z = 0$.

Assuming (as always) that $N_n \gg 1$, and using Stirling's approximation:

$$G \approx \sum_{n=1}^{\infty} \{ (N_n + d_n - 1)\ln(N_n + d_n - 1) - (N_n + d_n - 1) - N_n \ln(N_n)$$

$$+ N_n - \ln[(d_n - 1)!] - \alpha N_n - \beta E_n N_n \} + \alpha N + \beta E, \qquad [5.92]$$

so

$$\frac{\partial G}{\partial N_n} = \ln(N_n + d_n - 1) - \ln(N_n) - \alpha - \beta E_n. \qquad [5.93]$$

Setting this equal to zero and solving for $N_n$, we find the *most probable occupation numbers* for identical bosons:

$$N_n = \frac{d_n - 1}{e^{(\alpha + \beta E_n)} - 1}. \qquad [5.94]$$

(For consistency with the approximations already invoked, we should really drop the 1 in the numerator, and I shall do so from now on.)

**Problem 5.23** Use the method of Lagrange multipliers to find the area of the largest rectangle, with sides parallel to the axes, that can be inscribed in the ellipse $(x/a)^2 + (y/b)^2 = 1$.

**Problem 5.24**

**(a)** Find the percent error in Stirling's approximation for $z = 10$.

**(b)** What is the smallest integer $z$ such that the error is less than 1%?

### 5.4.4 Physical Significance of $\alpha$ and $\beta$

The parameters $\alpha$ and $\beta$ came into the story as Lagrange multipliers, associated with the total number of particles and the total energy, respectively. Mathematically, they are determined by substituting the occupation numbers (Equations 5.86, 5.90, and 5.94) back into the constraint equations (Equations 5.77 and 5.78). To carry out the summation, however, we need to know the allowed energies ($E_n$) and their degeneracies ($d_n$) for the potential in question. As an example, I'll work out the case of a three-dimensional infinite square well; this will enable us to infer the physical significance of $\alpha$ and $\beta$.

In Section 5.3.1 we determined the the allowed energies (Equation 5.39):

$$E_k = \frac{\hbar^2}{2m}k^2, \qquad [5.95]$$

where

$$\mathbf{k} = \left(\frac{\pi n_x}{l_x}, \frac{\pi n_y}{l_y}, \frac{\pi n_z}{l_z}\right).$$

As before, we convert the sum into an integral, treating **k** as a continuous variable, with one state (or, for spin $s$, $2s+1$ states) per volume $\pi^3/V$ of $k$-space. Taking as our "bins" the spherical shells in the first octant (see Figure 5.4), the "degeneracy" (that is, the number of states in the bin) is

$$d_k = \frac{1}{8}\frac{4\pi k^2\,dk}{(\pi^3/V)} = \frac{V}{2\pi^2}k^2\,dk. \qquad [5.96]$$

For distinguishable particles (Equation 5.86), the first constraint (Equation 5.77) becomes

$$N = \frac{V}{2\pi^2}e^{-\alpha}\int_0^\infty e^{-\beta\hbar^2k^2/2m}k^2\,dk = Ve^{-\alpha}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2},$$

so

$$e^{-\alpha} = \frac{N}{V}\left(\frac{2\pi\beta\hbar^2}{m}\right)^{3/2}. \qquad [5.97]$$

The second constraint (Equation 5.78) says

$$E = \frac{V}{2\pi^2}e^{-\alpha}\frac{\hbar^2}{2m}\int_0^\infty e^{-\beta\hbar^2k^2/2m}k^4\,dk = \frac{3V}{2\beta}e^{-\alpha}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2},$$

or, putting in Equation 5.97 for $e^{-\alpha}$,

$$E = \frac{3N}{2\beta}. \qquad [5.98]$$

(If you include the spin factor, $2s+1$, in Equation 5.96, it cancels out at this point, so Equation 5.98 is correct regardless of spin.)

Equation 5.98 is reminiscent of the classical formula for the average kinetic energy of an atom at temperature $T$[22]:

$$\frac{E}{N} = \frac{3}{2}k_BT, \qquad [5.99]$$

where $k_B$ is the Boltzmann constant. This suggests that $\beta$ is related to the *temperature*:

$$\beta = \frac{1}{k_BT}. \qquad [5.100]$$

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[22] See, for example, David Halliday and Robert Resnick, *Fundamentals of Physics*, 3rd ed. extended (New York: John Wiley & Sons, 1988), Section 21-5.

To prove that this holds in general, and not simply for distinguishable particles in the three-dimensional infinite square well, we would have to demonstrate that different substances in thermal equilibrium with one another have the same value of $\beta$. The argument is sketched in many books,[23] but I shall not reproduce it here—I will simply adopt equation [5.100] as the *definition* of $T$.

It is customary to replace $\alpha$ (which, as is clear from the special case of Equation 5.97, is a function of $T$) by the so-called **chemical potential,**

$$\mu(T) \equiv -\alpha k_B T, \qquad [5.101]$$

and rewrite Equations 5.86, 5.90, and 5.94 as formulas for the *most probable number of particles in a particular (one-particle) state with energy* $\epsilon$ (to go from the number of particles with a given energy to the number of particles in a particular *state* with that energy, we simply divide by the degeneracy of the state):

$$\boxed{n(\epsilon) = \begin{cases} e^{-(\epsilon-\mu)/k_B T}, & \text{MAXWELL-BOLTZMANN} \\ \dfrac{1}{e^{(\epsilon-\mu)/k_B T}+1}, & \text{FERMI-DIRAC} \\ \dfrac{1}{e^{(\epsilon-\mu)/k_B T}-1}. & \text{BOSE-EINSTEIN} \end{cases}} \qquad [5.102]$$

The **Maxwell-Boltzmann distribution** is the classical result for *distinguishable* particles; the **Fermi-Dirac distribution** applies to *identical fermions*, and the **Bose-Einstein distribution** is for *identical bosons.*

The Fermi-Dirac distribution has a particularly simple behavior as $T \to 0$:

$$e^{(\epsilon-\mu)/k_B T} \to \begin{cases} 0, & \text{if } \epsilon < \mu(0), \\ \infty, & \text{if } \epsilon > \mu(0), \end{cases}$$

so

$$n(\epsilon) \to \begin{cases} 1, & \text{if } \epsilon < \mu(0), \\ 0, & \text{if } \epsilon > \mu(0). \end{cases} \qquad [5.103]$$

All states are filled, up to an energy $\mu(0)$, and none are occupied for energies above this (Figure 5.8). Evidently the chemical potential at absolute zero is precisely the Fermi energy:

$$\mu(0) = E_F. \qquad [5.104]$$

As the temperature rises, the Fermi-Dirac distribution "softens" the cutoff, as indicated by the rounded curve in Figure 5.8.

For distinguishable particles in the three-dimensional infinite square well, we found (Equation 5.98) that the total energy at temperature $T$ is

$$E = \frac{3}{2} N k_B T; \qquad [5.105]$$

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[23] See, for example, Yariv, footnote 17, Section 15.4.

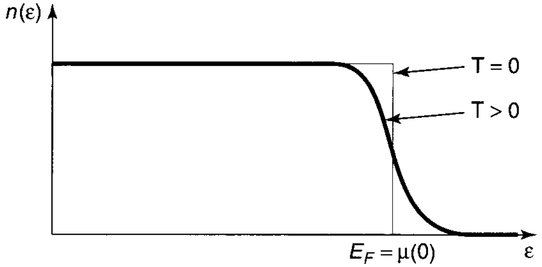

**Figure 5.8:** Fermi-Dirac distribution for $T = 0$ and for $T$ somewhat above zero.

from Equation 5.97 it follows that

$$\mu(T) = k_B T\left[\ln\left(\frac{N}{V}\right) + \frac{3}{2}\ln\left(\frac{mk_BT}{3\pi\hbar^2}\right)\right]. \qquad [5.106]$$

I would like to work out the corresponding formulas for identical fermions and bosons, using Equations 5.90 and 5.94 in place of Equation 5.86. The first constraint (Equation 5.77) becomes

$$N = \frac{V}{2\pi^2}\int_0^\infty \frac{k^2}{e^{[(\hbar^2k^2/2m)-\mu]/k_BT} \pm 1}\,dk \qquad [5.107]$$

(with the plus sign for fermions and minus for bosons), and the second constraint (Equation 5.78) reads

$$E = \frac{V}{2\pi^2}\frac{\hbar^2}{2m}\int_0^\infty \frac{k^4}{e^{[(\hbar^2k^2/2m)-\mu]/k_BT} \pm 1}\,dk. \qquad [5.108]$$

The first of these determines $\mu(T)$, and the second determines $E(T)$ (from the latter we obtain, for instance, the heat capacity $C = \partial E/\partial T$). Unfortunately, the integrals cannot be evaluated in terms of elementary functions, and I shall leave it for you to explore the matter further (see Problems 5.25 and 5.26).

---

**Problem 5.25** Evaluate the integrals (Equations 5.107 and 5.108) for the case of identical fermions at absolute zero. Compare your results with Equations 5.43 and 5.45. (Note that for electrons there is an extra factor of 2 in Equations 5.107 and 5.108, to account for the spin degeneracy.)

---

******Problem 5.26***

**(a)** Show that for bosons the chemical potential must always be less than the minimum allowed energy. *Hint*: $n(\epsilon)$ cannot be negative.

**(b)** In particular, for the ideal bose gas (identical bosons in the three-dimensional infinite square well), $\mu(T) < 0$ for all $T$. Show that in this case $\mu(T)$ monotonically increases as $T$ decreases, assuming that $N$ and $V$ are held constant. *Hint*: Study Equation 5.107, with the minus sign.

**(c)** A crisis (called **bose condensation**) occurs when (as we lower $T$) $\mu(T)$ hits zero. Evaluate the integral, for $\mu = 0$, and obtain the formula for the critical temperature $T_c$ at which this happens. *Note*: Below the critical temperature, the particles crowd into the ground state, and the calculational device of replacing the discrete sum (Equation 5.77) by a continuous integral (Equation 5.107) loses its validity. See F. Mandl, *Statistical Physics* (London: John Wiley & Sons, 1971), Section 11.5. *Hint*:

$$\int_0^\infty \frac{x^{s-1}}{e^x - 1}\, dx = \Gamma(s)\zeta(s), \qquad [5.108]$$

where $\Gamma$ is Euler's **gamma function** and $\zeta$ is the **Riemann zeta function**. Look up the appropriate numerical values.

**(d)** Find the critical temperature for $^4$He. Its density, at this temperature, is 0.15 gm/cm$^3$. *Note*: The experimental value of the critical temperature in $^4$He is 2.17 K. The remarkable properties of $^4$He in the neighborhood of $T_c$ are discussed in the reference cited in (c).

### 5.4.5 The Blackbody Spectrum

Photons (quanta of the electromagnetic field) are identical bosons with spin 1, but they are a very special case because they are *massless* particles, and hence intrinsically relativistic. We can include them here, if you are prepared to accept four assertions that do not really belong to nonrelativistic quantum mechanics:

**(1)** The energy of a photon is related to its frequency by the Planck formula $E = h\nu = \hbar\omega$.

**(2)** The wave number $k$ is related to the frequency by $k = 2\pi/\lambda = \omega/c$, where $c$ is the speed of light.

**(3)** Only two spin states occur (the quantum number $m$ can be $+1$ or $-1$, but not 0).

**(4)** The *number* of photons is not a conserved quantity; when the temperature rises the number of photons (per unit volume) increases.

In view of item 4, the first constraint equation (Equation 5.77) does not apply. We can take account of this by simply setting $\alpha \to 0$, in Equation 5.81 and everything that follows. Thus the most probable occupation number for photons is (Equation 5.94)

$$N_\omega = \frac{d_k}{e^{\hbar\omega/k_BT} - 1}. \qquad [5.110]$$

For free photons in a box of volume $V$, $d_k$ is given by Equation 5.96,[24] multiplied by 2 for spin (item 3), and expressed in terms of $\omega$ instead of $k$ (item 2):

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[24] In truth, we have no business using this formula, which came from the (nonrelativistic) Schrödinger equation; fortunately, the degeneracy is exactly the same for the relativistic case. See Problem 5.3.2.

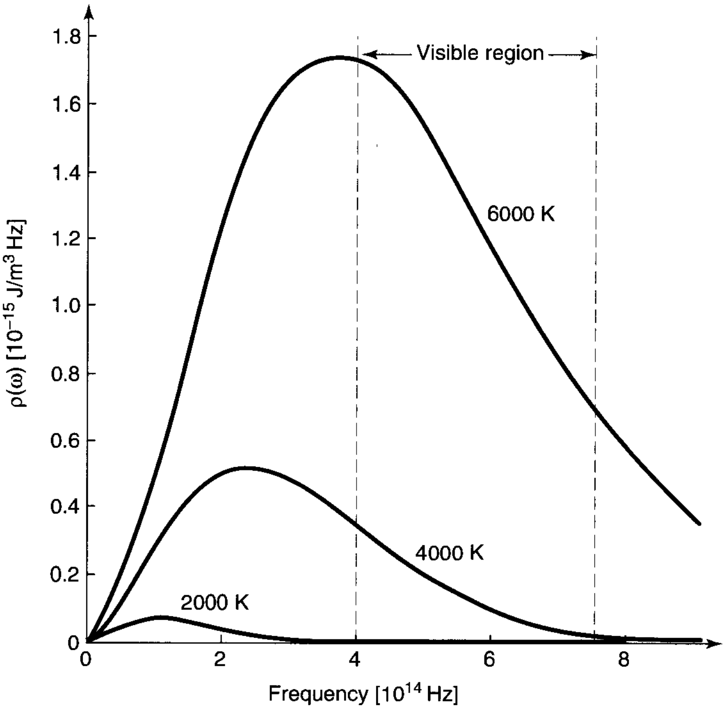

**Figure 5.9:** Planck's formula for the blackbody spectrum, Equation 5.112.

$$d_k = \frac{V}{\pi^2 c^3}\omega^2\, d\omega. \qquad [5.111]$$

So the energy density $N_\omega \hbar\omega/V$, in the frequency range $d\omega$, is $\rho(\omega)\, d\omega$, where

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3 \left(e^{\hbar\omega/k_B T} - 1\right)}. \qquad [5.112]$$

This is Planck's famous **blackbody spectrum**, giving the energy per unit volume, per unit frequency, in an electromagnetic field at equilibrium at temperature $T$. It is plotted, for three different temperatures, in Figure 5.9.

---

**Problem 5.27** Use Equation 5.112 to determine the energy density in the *wavelength* range $d\lambda$. *Hint*: set $\rho(\omega)d\omega = \overline{\rho}(\lambda)d\lambda$, and solve for $\overline{\rho}(\lambda)$. Derive the **Wien displacement law** for the wavelength at which the blackbody energy density is a maximum:

$$\lambda_{\max} = \frac{2.90 \times 10^{-3}\ \mathrm{mK}}{T}. \qquad [5.113]$$

You'll need to solve the transcendental equation $(5 - x) = 5e^{-x}$, using a calculator (or a computer); get the numerical answer accurate to three significant digits.

---

**Problem 5.28** Derive the **Stefan-Boltzmann formula** for the total energy density in blackbody radiation:

$$\frac{E}{V} = \left(\frac{\pi^2 k_B^4}{15\hbar^3 c^3}\right) T^4 = \left(7.57 \times 10^{-16}\,\mathrm{Jm^{-3}K^{-4}}\right) T^4. \qquad [5.114]$$

*Hint*: Use the hint in Problem 5.26(c) to evaluate the integral. Note that $\zeta(4) = \pi^4/90$.

## FURTHER PROBLEMS FOR CHAPTER 5

**Problem 5.29** Suppose you have three particles, and three distinct one-particle states ($\psi_a(x)$, $\psi_b(x)$, and $\psi_c(x)$) are available. How many different three-particle states can be constructed (a) if they are distinguishable particles, (b) if they are identical bosons, and (c) if they are identical fermions? [The particles need not be in *different* states—$\psi_a(x_1)\psi_a(x_2)\psi_a(x_3)$ would be one possibility if the particles are distinguishable.]

---

**Problem 5.30** Calculate the Fermi energy for electrons in a *two*-dimensional infinite square well. (Let $\sigma$ be the number of free electrons per unit area.)

---

*****Problem 5.31** Certain cold stars (called **white dwarfs**) are stabilized against gravitational collapse by the degeneracy pressure of their electrons (Equation 5.46). Assuming constant density, the radius $R$ of such an object can be calculated as follows:

**(a)** Write the total electron energy (Equation 5.45) in terms of the radius, the number of nucleons (protons and neutrons) $N$, the number of electrons per nucleon $q$, and the mass of the electron $m$.

**(b)** Look up, or calculate, the gravitational energy of a uniformly dense sphere. Express your answer in terms of $G$ (the constant of universal gravitation), $R$, $N$, and $M$ (the mass of a nucleon). Note that the gravitational energy is *negative*.

**(c)** Find the radius for which the total energy, (a) plus (b), is a minimum. *Answer:*

$$R = \left(\frac{9\pi}{4}\right)^{2/3} \frac{\hbar^2 q^{5/3}}{GmM^2N^{1/3}}.$$

(Note that the radius *decreases* as the total mass *increases*!) Put in the actual numbers, for everything except $N$, using $q = 1/2$ (actually, $q$ decreases a bit as the atomic number increases, but this is close enough for our purposes). *Answer:* $R = 7.6 \times 10^{25} N^{-1/3}$.

**(d)** Determine the radius, in kilometers, of a white dwarf with the mass of the sun.

**(e)** Determine the Fermi energy, in electron volts, for the white dwarf in (d), and compare it with the rest energy of an electron. Note that this system is getting dangerously relativistic (see Problem 5.32).

---

*****Problem 5.32** We can extend the theory of a free electron gas (Section 5.3.1) to the relativistic domain by replacing the classical kinetic energy, $E = p^2/2m$, with the relativistic formula, $E = \sqrt{p^2c^2 + m^2c^4} - mc^2$. Momentum is related to the wave vector in the usual way: $\mathbf{p} = \hbar\mathbf{k}$. In particular, in the *extreme* relativistic limit, $E \approx pc = \hbar ck$.

**(a)** Replace $\hbar^2k^2/2m$ in Equation 5.44 by the ultrarelativistic expression, $\hbar ck$, and calculate $E_{\text{tot}}$ in this regime.

**(b)** Repeat parts (a) and (b) of Problem 5.31 for the ultrarelativistic electron gas. Notice that in this case there is *no* stable minimum, regardless of $R$; if the total energy is positive, degeneracy forces exceed gravitational forces and the star will expand, whereas if the total is negative, gravitational forces win out and the star will collapse. Find the critical number of nucleons $N_c$ such that gravitational collapse occurs for $N > N_c$. This is called the **Chandrasekhar limit**. *Answer:* $2.0 \times 10^{57}$. What is the corresponding stellar mass (give your answer as a multiple of the sun's mass). Stars heavier than this will not form white dwarfs, but collapse further, becoming (if conditions are right) **neutron stars**.

**(c)** At extremely high density, **inverse beta decay**, $e^- + p^+ \rightarrow n + \nu$, converts virtually all of the protons and electrons into neutrons (liberating neutrinos, which carry off energy, in the process). Eventually *neutron* degeneracy pressure stabilizes the collapse, just as *electron* degeneracy does for the white dwarf (see Problem 5.31). Calculate the radius of a neutron star with the mass of the sun. Also calculate the (neutron) Fermi energy, and compare it to the rest energy of a neutron. Is it reasonable to treat such a star nonrelativistically?

---

## ∗∗∗Problem 5.33

**(a)** Find the chemical potential and the total energy for distinguishable particles in the three-dimensional harmonic oscillator potential (Problem 4.39). *Hint*: The sums in Equations 5.77 and 5.78 can be evaluated exactly in this case—no need to use an integral approximation, as we did for the infinite square well. Note that by differentiating the geometric series,

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n, \qquad [5.115]$$

you can get

$$\frac{d}{dx}\left(\frac{x}{1-x}\right) = \sum_{n=0}^{\infty}(n+1)x^n$$

and similar results for higher derivatives. *Answer:*

$$E = \frac{3}{2}N\hbar\omega\left(\frac{1+e^{-\hbar\omega/k_BT}}{1-e^{-\hbar\omega/k_BT}}\right). \qquad [5.116]$$

**(b)** Discuss the limiting case $k_BT \ll \hbar\omega$.

**(c)** Discuss the classical limit, $k_BT \gg \hbar\omega$, in the light of the **equipartition theorem** (see, for example, Halliday and Resnick, footnote 22, Section 21-9). How many **degrees of freedom** does a particle in the three-dimensional harmonic oscillator possess?

# PART II

# APPLICATIONS

## CHAPTER 6

# TIME-INDEPENDENT PERTURBATION THEORY

## 6.1 NONDEGENERATE PERTURBATION THEORY

### 6.1.1 General Formulation

Suppose we have solved the (time-independent) Schrödinger equation for some potential (say, the one-dimensional infinite square well):

$$H^0\psi_n^0 = E_n^0\psi_n^0, \qquad [6.1]$$

obtaining a complete set of orthonormal eigenfunctions, $\psi_n^0$,

$$\langle\psi_n^0|\psi_m^0\rangle = \delta_{nm}, \qquad [6.2]$$

and the corresponding eigenvalues $E_n^0$. Now we perturb the potential slightly (say, by putting a little bump in the bottom of the well—Figure 6.1). We'd *like* to solve for the new eigenfunctions and eigenvalues:

$$H\psi_n = E_n\psi_n, \qquad [6.3]$$

but unless we are very lucky, we're unlikely to be able to solve the Schrödinger equation exactly, for this more complicated potential. **Perturbation theory** is a systematic procedure for obtaining *approximate* solutions to the perturbed problem by building on the known exact solutions to the *unperturbed* case.

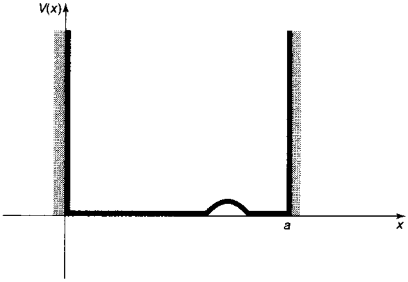

**Figure 6.1:** Infinite square well with small perturbation.

To begin with, we write the new Hamiltonian as the sum of two terms:

$$H = H^0 + \lambda H', \tag{6.4}$$

where $H'$ is the perturbation. For the moment we'll take $\lambda$ to be a small number; later we'll crank it up to 1, and $H$ will be the true, exact Hamiltonian. Writing $\psi_n$ and $E_n$ as power series in $\lambda$, we have

$$\psi_n = \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \cdots; \tag{6.5}$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots. \tag{6.6}$$

Here $E_n^1$ is the **first-order correction** to the $n^{\text{th}}$ eigenvalue, and $\psi_n^1$ is the first-order correction to the $n^{\text{th}}$ eigenfunction; $E_n^2$ and $\psi_n^2$ are the **second-order corrections**, and so on. Plugging Equations 6.4, 6.5, and 6.6 into Equation 6.3, we have

$$(H^0 + \lambda H')[\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \cdots]$$
$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots)[\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \cdots],$$

or (collecting like powers of $\lambda$):

$$H^0\psi_n^0 + \lambda(H^0\psi_n^1 + H'\psi_n^0) + \lambda^2(H^0\psi_n^2 + H'\psi_n^1) + \cdots$$
$$= E_n^0\psi_n^0 + \lambda(E_n^0\psi_n^1 + E_n^1\psi_n^0) + \lambda^2(E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0) + \cdots.$$

To lowest order ($\lambda^0$) this yields $H^0\psi_n^0 = E_n^0\psi_n^0$, which is nothing new (just Equation 6.1). To first order ($\lambda^1$),

$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0. \tag{6.7}$$

To second order ($\lambda^2$),

$$H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0, \tag{6.8}$$

and so on. (I'm done with $\lambda$, now—it was just a device to keep track of the different orders—so crank it up to 1.)

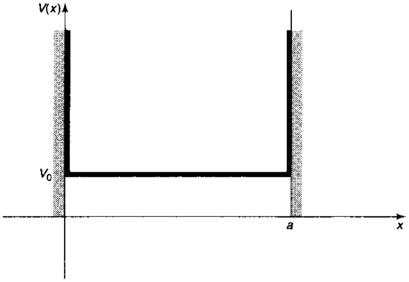

**Figure 6.2:** Constant perturbation over the whole well.

### 6.1.2 First-Order Theory

Taking the inner product of Equation 6.7 with $\psi_n^0$ [that is, multiplying by $(\psi_n^0)^*$ and integrating],

$$\langle\psi_n^0|H^0\psi_n^1\rangle + \langle\psi_n^0|H'\psi_n^0\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle + E_n^1\langle\psi_n^0|\psi_n^0\rangle.$$

But $H^0$ is Hermitian, so

$$\langle\psi_n^0|H^0\psi_n^1\rangle = \langle H^0\psi_n^0|\psi_n^1\rangle = \langle E_n^0\psi_n^0|\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle,$$

and this cancels the first term on the right. Moreover, $\langle\psi_n^0|\psi_n^0\rangle = 1$, so[1]

$$\boxed{E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle.} \qquad [6.9]$$

This is the fundamental result of first-order perturbation theory; as a *practical* matter, it may well be the most important equation in quantum mechanics. It says that the first-order correction to the energy is the *expectation value* of the perturbation in the *unperturbed* state.

---

**Example.** The unperturbed wave functions for the infinite square well are (Equation 2.24)

$$\psi_n^0(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right).$$

Suppose first that we perturb the system by simply raising the "floor" of the well by a constant amount $V_0$ (Figure 6.2). In that case $H' = V_0$, and the first-order correction to the energy of the $n^{\text{th}}$ state is

$$E_n^1 = \langle\psi_n^0|V_0|\psi_n^0\rangle = V_0\langle\psi_n^0|\psi_n^0\rangle = V_0.$$

---

[1] In this context it doesn't matter whether we write $\langle\psi_n^0|H'\psi_n^0\rangle$ or $\langle\psi_n^0|H'|\psi_n^0\rangle$ (with the extra vertical bar) because we are using the wave function itself to "label" the state. But the latter notation is preferable because it frees us from this specific convention.

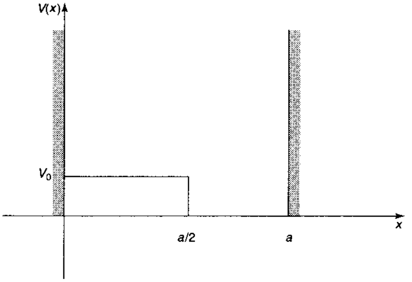

**Figure 6.3:** Constant perturbation over half the well.

The corrected energy levels, then, are $E_n \cong E_n^0 + V_0$; they are simply lifted by the amount $V_0$. Of *course*! The only surprising thing is that in this case the first-order theory yields the *exact* answer. Evidently, for a *constant* perturbation all the higher corrections vanish.[2] If, on the other hand, the perturbation extends only halfway across the well (Figure 6.3), then

$$E_n^1 = \frac{2V_0}{a}\int_0^{a/2} \sin^2\left(\frac{n\pi}{a}x\right)dx = \frac{V_0}{2}.$$

In this case every energy level is lifted by $V_0/2$. That's not the *exact* result, presumably, but it does seem reasonable as a first-order approximation.

---

Equation 6.9 is the first-order correction to the *energy*; to find the first-order correction to the *wave function* we first rewrite Equation 6.7:

$$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0. \tag{6.10}$$

The right side is a known function, so this amounts to an inhomogeneous differential equation for $\psi_n^1$. Now, the unperturbed wave functions constitute a complete set, so $\psi_n^1$ (like any other function) can be expressed as a linear combination of them:

$$\psi_n^1 = \sum_{m\neq n} c_m^{(n)}\psi_m^0. \tag{6.11}$$

[There is no need to include $m = n$ in the sum, for if $\psi_n^1$ satisfies Equation 6.10, so too does $(\psi_n^1 + \alpha\psi_n^0)$, for any constant $\alpha$, and we can use this freedom to subtract off the $\psi_n^0$ term.[3]] If we could determine the coefficients $c_m^{(n)}$, we'd be done. Well, putting Equation 6.11 into Equation 6.10, and using the fact that the $\psi_m^0$ satisfies the

---

[2] Incidentally, nothing here depends on the specific nature of the infinite square well—the same result applies for *any* potential, when the perturbation is constant.

[3] Alternatively, a glance at Equation 6.5 reveals that any $\psi_n^0$ component in $\psi_n^1$ might as well be pulled out and combined with the first term. We are *only* concerned, for the moment, with solving the Schrödinger equation (Equation 6.3), and the $\psi_n$ we get will not, in general, be normalized.

unperturbed Schrödinger equation (Equation 6.1), we have

$$\sum_{m\neq n}(E_m^0 - E_n^0)c_m^{(n)}\psi_m^0 = -(H' - E_n^1)\psi_n^0.$$

Taking the inner product with $\psi_l^0$,

$$\sum_{m\neq n}(E_m^0 - E_n^0)c_m^{(n)}\langle\psi_l^0|\psi_m^0\rangle = -\langle\psi_l^0|H'|\psi_n^0\rangle + E_n^1\langle\psi_l^0|\psi_n^0\rangle.$$

If $l = n$, the left side is zero, and we recover Equation 6.9; if $l \neq n$, we get

$$(E_l^0 - E_n^0)c_l^{(n)} = -\langle\psi_l^0|H'|\psi_n^0\rangle,$$

or

$$c_m^{(n)} = \frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{E_n^0 - E_m^0}, \qquad [6.12]$$

so

$$\boxed{\psi_n^1 = \sum_{m\neq n}\frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{(E_n^0 - E_m^0)}\psi_m^0.} \qquad [6.13]$$

Notice that the denominator is safe, since there is no coefficient with $m = n$, *as long as the unperturbed energy spectrum is nondegenerate.* But if two different unperturbed states share the same energy, we're in serious trouble (we divided by zero to get Equation 6.12); in that case we need **degenerate perturbation theory**, which I'll come to in Section 6.2.

That completes first-order perturbation theory: $E_n^1$ is given by Equation 6.9, and $\psi_n^1$ is given by Equation 6.13. I should warn you that whereas perturbation theory often yields surprisingly accurate energies (that is, $E_n^0 + E_n^1$ is quite close to the exact value $E_n$), the wave functions are notoriously poor.

---

**∗Problem 6.1** Suppose we put a delta-function bump in the center of the infinite square well:

$$H' = \alpha\delta(x - a/2),$$

where $\alpha$ is a constant. Find the first-order correction to the allowed energies. Explain why the energies are not perturbed for even $n$.

---

**∗Problem 6.2** For the harmonic oscillator $[V(x) = (1/2)kx^2]$, the allowed energies are

$$E_n = (n + 1/2)\hbar\omega, \qquad (n = 0, 1, 2, \ldots),$$

where $\omega = \sqrt{k/m}$ is the classical frequency. Now suppose the spring constant increases slightly: $k \to (1 + \epsilon)k$. (Perhaps we cool the spring, so it becomes less flexible.)

**(a)** Find the *exact* new energies (trivial, in this case). Expand your formula a power series in $\epsilon$, up to second order.

**(b)** Now calculate the first-order perturbation in the energy, using Equation 6. What is $H'$ here? Compare your result with part (a). *Hint:* It is not necessar in fact, it is not *permitted*—to calculate a single integral in doing this problem.

---

**Problem 6.3** Two identical bosons are placed in an infinite square well (Equati 2.15). They interact weakly with one another, via the potential

$$V(x_1, x_2) = -aV_0\delta(x_1 - x_2)$$

(where $V_0$ is a constant with the dimensions of energy and $a$ is the width of the well

**(a)** First, ignoring the interaction between the particles, find the ground state an first excited state—both the wave functions and the associated energies.

**(b)** Use first-order perturbation theory to calculate the effect of the particle-particl interaction on the ground and first excited state energies.

---

### 6.1.3 Second-Order Energies

Proceeding as before, we take the inner product of the *second*-order equation (Equation 6.8) with $\psi_n^0$:

$$\langle\psi_n^0|H^0\psi_n^2\rangle + \langle\psi_n^0|H'\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^2\rangle + E_n^1\langle\psi_n^0|\psi_n^1\rangle + E_n^2\langle\psi_n^0|\psi_n^0\rangle.$$

Again, we exploit the Hermiticity of $H^0$:

$$\langle\psi_n^0|H^0\psi_n^2\rangle = \langle H^0\psi_n^0|\psi_n^2\rangle = E_n^0\langle\psi_n^0|\psi_n^2\rangle,$$

so the first term on the left cancels the first term on the right. Meanwhile, $\langle\psi_n^0|\psi_n^0\rangle = 1$, and we are left with a formula for $E_n^2$:

$$E_n^2 = \langle\psi_n^0|H'|\psi_n^1\rangle - E_n^1\langle\psi_n^0|\psi_n^1\rangle.$$

But

$$\langle\psi_n^0|\psi_n^1\rangle = \sum_{m\neq n} c_m^{(n)}\langle\psi_n^0|\psi_m^0\rangle = 0,$$

so

$$E_n^2 = \langle\psi_n^0|H'|\psi_n^1\rangle = \sum_{m\neq n} c_m^{(n)}\langle\psi_n^0|H'|\psi_m^0\rangle = \sum_{m\neq n}\frac{\langle\psi_m^0|H'|\psi_n^0\rangle\langle\psi_n^0|H'|\psi_m^0\rangle}{E_n^0 - E_m^0},$$

or, finally,

$$\boxed{E_n^2 = \sum_{m\neq n}\frac{|\langle\psi_m^0|H'|\psi_n^0\rangle|^2}{E_n^0 - E_m^0}.} \qquad [6.14]$$

This is the fundamental result of second-order perturbation theory. We could proceed to calculate the second-order correction to the wave function ($\psi_n^2$), the third-order correction to the energy, and so on, but in practice Equation 6.14 is ordinarily as high as it is useful to pursue this method.

---

****Problem 6.4**

**(a)** Find the second-order correction to the energies ($E_n^2$) for the potential in Problem 6.1. *Note*: You can sum the series explicitly to obtain the result $-2m(\alpha/\pi\hbar n)^2$, for odd $n$.

**(b)** Calculate the second-order correction to the ground-state energy ($E_0^2$) for the potential in Problem 6.2. Check that your result is consistent with the exact solution.

---

****Problem 6.5** Consider a charged particle in the one-dimensional harmonic oscillator potential. Suppose we turn on a weak electric field ($E$) so that the potential energy is shifted by an amount $H' = -qEx$.

**(a)** Show that there is no first-order change in the energy levels, and calculate the second-order correction. *Hint*: See Problem 3.50.

**(b)** The Schrödinger equation can be solved exactly in this case by a change of variables: $x' \equiv x - (qE/m\omega^2)$. Find the exact energies, and show that they are consistent with the perturbation theory approximation.

---

## 6.2 DEGENERATE PERTURBATION THEORY

If the unperturbed states are degenerate—that is, if two (or more) distinct states ($\psi_a^0$ and $\psi_b^0$) share the same energy—then ordinary perturbation theory fails: $c_a^{(b)}$ (Equation 6.12) and $E_a^2$ (Equation 6.14) blow up (unless, possibly, the numerator vanishes, $\langle\psi_a^0|H'|\psi_b^0\rangle = 0$—a loophole that will be important to us later on). In the degenerate case, therefore, there is no reason to trust even the *first*-order correction to the energy (Equation 6.9), and we must look for some other way to handle the problem.

### 6.2.1 Twofold Degeneracy

Suppose that

$$H^0\psi_a^0 = E^0\psi_a^0, \quad H^0\psi_b^0 = E^0\psi_b^0, \quad \text{and } \langle\psi_a^0|\psi_b^0\rangle = 0. \qquad [6.15]$$

Note that any linear combination of these states,

$$\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0, \qquad [6.16]$$

is still an eigenstate of $H^0$, with the same eigenvalue $E^0$:

$$H^0\psi^0 = E^0\psi^0. \qquad [6.1$$

Typically, the perturbation ($H'$) will "break" the degeneracy: As we increase $\lambda$ (from 0 to 1), the common unperturbed energy $E^0$ splits into two (Figure 6.4). The essential problem is this: When we turn *off* the perturbation, the "upper" state reduces down to *one* linear combination of $\psi_a^0$ and $\psi_b^0$, and the "lower" state reduces to some *other* linear combination, but we don't know a priori *what* these **"good"** linear combinations will be. For this reason we can't even calculate the *first*-order energy (Equation 6.9) because we don't know what unperturbed states to use.

For the moment, therefore, let's just write the "good" unperturbed states in the general form (Equation 6.16), keeping $\alpha$ and $\beta$ adjustable. We want to solve the Schrödinger equation,

$$H\psi = E\psi, \qquad [6.18]$$

with $H = H^0 + \lambda H'$ and

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \cdots, \qquad \psi = \psi^0 + \lambda\psi^1 + \lambda^2\psi^2 + \cdots. \qquad [6.19]$$

Plugging these into Equation 6.18, and collecting like powers of $\lambda$, as before, we find

$$H^0\psi^0 + \lambda(H'\psi^0 + H^0\psi^1) + \cdots = E^0\psi^0 + \lambda(E^1\psi^0 + E^0\psi^1) + \cdots.$$

But $H^0\psi^0 = E^0\psi^0$ (Equation 6.17), so the first terms cancel; at order $\lambda^1$ we have

$$H^0\psi^1 + H'\psi^0 = E^0\psi^1 + E^1\psi^0. \qquad [6.20]$$

Taking the inner product with $\psi_a^0$:

$$\langle\psi_a^0|H^0\psi^1\rangle + \langle\psi_a^0|H'\psi^0\rangle = E^0\langle\psi_a^0|\psi^1\rangle + E^1\langle\psi_a^0|\psi^0\rangle.$$

Because $H^0$ is Hermitian, the first term on the left cancels the first term on the right. Putting in Equation 6.16 and exploiting the orthonormality condition Equation 6.15, we obtain

$$\alpha\langle\psi_a^0|H'|\psi_a^0\rangle + \beta\langle\psi_a^0|H'|\psi_b^0\rangle = \alpha E^1,$$

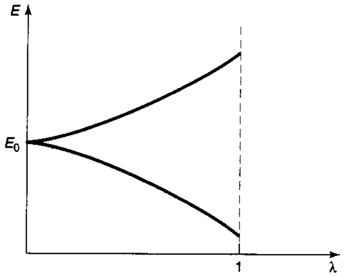

**Figure 6.4:** "Lifting" of a degeneracy by a perturbation.

or, more compactly,

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1, \tag{6.21}$$

where

$$W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle, \quad (i, j = a, b). \tag{6.22}$$

Similarly, the inner product with $\psi_b^0$ yields

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1. \tag{6.23}$$

Notice that the $W$'s are (in principle) *known*—they are just the "matrix elements" of $H'$, with respect to the unperturbed wave functions $\psi_a^0$ and $\psi_b^0$. Multiplying Equation 6.23 by $W_{ab}$, and using Equation 6.21 to eliminate $\beta W_{ab}$, we find

$$\alpha[W_{ab}W_{ba} - (E^1 - W_{aa})(E^1 - W_{bb})] = 0. \tag{6.24}$$

If $\alpha$ is *not* zero, Equation 6.24 yields an equation for $E^1$:

$$(E^1)^2 - E^1(W_{aa} + W_{bb}) + (W_{aa}W_{bb} - W_{ab}W_{ba}) = 0. \tag{6.25}$$

Invoking the quadratic formula, and noting (from Equation 6.22) that $W_{ba} = W_{ab}^*$, we conclude that

$$\boxed{E_{\pm}^1 = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2}\right].} \tag{6.26}$$

This is the fundamental result of degenerate perturbation theory; the two roots correspond to the two perturbed energies.

But what if $\alpha$ *is* zero? In that case $\beta = 1$, Equation 6.21 says $W_{ab} = 0$, and Equation 6.23 gives $E^1 = W_{bb}$. This is actually included in the general result (Equation 6.26), with the plus sign (the minus sign corresponds to $\alpha = 1$, $\beta = 0$). What's more, the *answers*,

$$E_+^1 = W_{bb} = \langle \psi_b^0 | H' | \psi_b^0 \rangle, \quad E_-^1 = W_{aa} = \langle \psi_a^0 | H' | \psi_a^0 \rangle,$$

are precisely what we would have obtained using *non*degenerate perturbation theory (Equation 6.9)—we have simply been *lucky*: The states $\psi_a^0$ and $\psi_b^0$ were *already* the "correct" linear combinations. Obviously, it would be greatly to our advantage if we could somehow *guess* the "good" states right from the start. In practice, we can often do so by exploiting the following theorem:

> **Theorem:** Let $A$ be a Hermitian operator that commutes with $H'$. If $\psi_a^0$ and $\psi_b^0$ are eigenfunctions of $A$ with distinct eigenvalues,
>
> $$A\psi_a^0 = \mu\psi_a^0, \quad A\psi_b^0 = \nu\psi_b^0, \quad \text{and } \mu \neq \nu,$$
>
> then $W_{ab} = 0$ (and hence $\psi_a^0$ and $\psi_b^0$ are the "good" states to use in perturbation theory).

**Proof:** By assumption, $[A, H'] = 0$, so

$$\begin{aligned}
\langle\psi_a^0|[A, H']\psi_b^0\rangle &= 0 \\
&= \langle\psi_a^0|AH'\psi_b^0\rangle - \langle\psi_a^0|H'A\psi_b^0\rangle \\
&= \langle A\psi_a^0|H'\psi_b^0\rangle - \langle\psi_a^0|H'\nu\psi_b^0\rangle \\
&= (\mu - \nu)\langle\psi_a^0|H'\psi_b^0\rangle = (\mu - \nu)W_{ab}.
\end{aligned}$$

But $\mu \neq \nu$, so $W_{ab} = 0$. QED

**Moral:** If you're faced with degenerate states, look around for some Hermitian operator $A$ that commutes with $H'$; pick as your unperturbed states ones that are simultaneously eigenfunctions of $H^0$ and $A$. Then use *ordinary* first-order perturbation theory. If you can't find such an operator, you'll have to resort to Equation 6.26, but in practice this is seldom necessary.

---

**Problem 6.6** Let the two "good" unperturbed states be

$$\psi_\pm^0 = \alpha_\pm\psi_a^0 + \beta_\pm\psi_b^0,$$

where $\alpha_\pm$ and $\beta_\pm$ are determined (up to normalization) by Equation 6.21 (or Equation 6.23), with Equation 6.26 for $E_\pm$. Show explicitly that

**(a)** $\psi_\pm^0$ are orthogonal ($\langle\psi_+^0|\psi_-^0\rangle = 0$);

**(b)** $\langle\psi_+^0|H'|\psi_-^0\rangle = 0$;

**(c)** $\langle\psi_\pm^0|H'|\psi_\pm^0\rangle = E_\pm^1$.

---

**Problem 6.7** Consider a particle of mass $m$ that is free to move in a one-dimensional region of length $L$ that closes on itself (for instance, a bead which slides frictionlessly on a circular wire of circumference $L$; Problem 2.43).

**(a)** Show that the stationary states can be written in the form

$$\psi_n(x) = \frac{1}{\sqrt{L}}e^{2\pi i n x/L}, \quad (-L/2 < x < L/2),$$

where $n = 0, \pm 1, \pm 2, \ldots$, and the allowed energies are

$$E_n = \frac{2}{m}\left(\frac{n\pi\hbar}{L}\right)^2.$$

Notice that—with the exception of the ground state ($n = 0$)—these are all doubly degenerate.

**(b)** Now suppose we introduce the perturbation

$$H' = -V_0 e^{-x^2/a^2},$$

where $a \ll L$. (This puts a little "dimple" in the potential at $x = 0$, as though we bent the wire slightly to make a "trap.") Find the first-order correction to $E_n$, using Equation 6.26. *Hint*: To evaluate the integrals, exploit the fact that $a \ll L$ to extend the limits from $\pm L/2$ to $\pm\infty$; after all, $H'$ is essentially zero outside $-a < x < a$.

**(c)** What are the "good" linear combinations of $\psi_n$ and $\psi_{-n}$ for this problem? Show that with these states you get the first-order correction using Equation 6.9.

**(d)** Find a Hermitian operator $A$ that fits the requirements of the theorem, and show that the simultaneous eigenstates of $H^0$ and $A$ are precisely the ones you found in (c).

---

### 6.2.2 Higher-Order Degeneracy

In the previous section I assumed the degeneracy was twofold, but it is easy to see how the method generalizes. Rewrite Equations 6.21 and 6.23 in matrix form:

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \qquad [6.27]$$

Evidently the $E^1$'s are nothing but the *eigenvalues* of the $W$-matrix; Equation 6.25 is the characteristic equation (Equation 3.70) for this matrix, and the "good" linear combinations of the unperturbed states are the eigenvectors of $W$. In the case of $n$-fold degeneracy, we look for the eigenvalues of the $n \times n$ matrix

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle. \qquad [6.28]$$

In the language of linear algebra, finding the "good" unperturbed wave functions amounts to constructing a basis in the degenerate subspace that *diagonalizes* the perturbation $H'$. Once again, if you can think of an operator $A$ that *commutes* with $H'$, and use the simultaneous eigenfunctions of $A$ and $H^0$, then the $W$ matrix will *automatically* be diagonal, and you won't have to fuss with solving the characteristic equation.

---

**Example.** Consider the three-dimensional infinite cubical well (Problem 4.2):

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < a, 0 < y < a, \text{and } 0 < z < a; \\ \infty & \text{otherwise.} \end{cases} \qquad [6.29]$$

The stationary states are

$$\psi^0_{n_x n_y n_z}(x, y, z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right), \qquad [6.30]$$

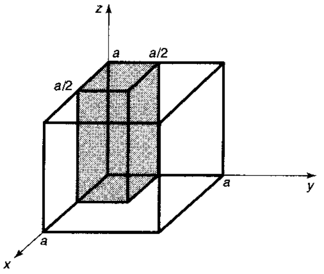

**Figure 6.5:** The perturbation increases the potential by an amount $V_0$ in the shaded sector.

where $n_x$, $n_y$, and $n_z$ are positive integers. The corresponding allowed energies are

$$E^0_{n_x n_y n_z} = \frac{\pi^2\hbar^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2). \qquad [6.31]$$

Notice that the ground state ($\psi_{111}$) is nondegenerate; its energy is

$$E^0_0 \equiv 3\frac{\pi^2\hbar^2}{2ma^2}. \qquad [6.32]$$

But the first excited state is (triply) degenerate:

$$\psi_a \equiv \psi_{112}, \quad \psi_b \equiv \psi_{121}, \text{ and } \psi_c \equiv \psi_{211}, \qquad [6.33]$$

all share the energy

$$E^0_1 \equiv 3\frac{\pi^2\hbar^2}{ma^2}. \qquad [6.34]$$

Now let's introduce the perturbation

$$H' = \begin{cases} V_0, & \text{if } 0 < x < a/2 \text{ and } 0 < y < a/2; \\ 0, & \text{otherwise.} \end{cases} \qquad [6.35]$$

This raises the potential by an amount $V_0$ in one quarter of the box (see Figure 6.5). The first-order correction to the ground state energy is given by Equation 6.9:

$$E^1_0 = \langle\psi_{111}|H'|\psi_{111}\rangle = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right)dx$$
$$\int_0^{a/2} \sin^2\left(\frac{\pi}{a}y\right)dy \int_0^{a} \sin^2\left(\frac{\pi}{a}z\right)dz = \frac{1}{4}V_0, \qquad [6.36]$$

which is just what we would expect.

For the first excited state we need the full machinery of degenerate perturbation theory. The first step is to construct the matrix $W$. The diagonal elements are the same as for the ground state (except that the argument of one of the sines is doubled); you can check for yourself that

$$W_{aa} = W_{bb} = W_{cc} = \frac{1}{4}V_0.$$

The off-diagonal elements are more interesting:

$$\begin{aligned} W_{ab} &= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right) dx \\ &\int_0^{a/2} \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{2\pi}{a}y\right) dy \int_0^{a} \sin\left(\frac{2\pi}{a}z\right) \sin\left(\frac{\pi}{a}z\right) dz. \end{aligned}$$

But the $z$ integral is zero (as it will be also for $W_{ac}$), so

$$W_{ab} = W_{ac} = 0.$$

Finally,

$$W_{bc} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) dx$$

$$\int_0^{a/2} \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{\pi}{a}y\right) dy \int_0^{a} \sin^2\left(\frac{\pi}{a}z\right) dz = \frac{16}{9\pi^2}V_0.$$

Thus

$$W = \frac{V_0}{4}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix}, \qquad [6.37]$$

where $\kappa \equiv (8/3\pi)^2 \approx 0.7205$.

The characteristic equation for $W$ (or rather, for $4W/V_0$, which is easier to work with) is

$$(1-w)^3 - \kappa^2(1-w) = 0,$$

and the eigenvalues are

$$w_1 = 1; \quad w_2 = 1 + \kappa \approx 1.7205; \quad w_3 = 1 - \kappa \approx 0.2795.$$

To first order in $\lambda$, then,

$$E_1(\lambda) = \begin{cases} E_1^0 + \lambda V_0/4, \\ E_1^0 + \lambda(1+\kappa)V_0/4, \\ E_1^0 + \lambda(1-\kappa)V_0/4, \end{cases} \qquad [6.38]$$

where $E_1^0$ is the (common) unperturbed energy (Equation 6.34). The perturbation lifts the degeneracy, splitting $E_1^0$ into three distinct energy levels (see Figure 6.6). Notice that if we had naively applied *non*degenerate perturbation theory to this problem, we would have concluded that the first-order correction (Equation 6.9) is the

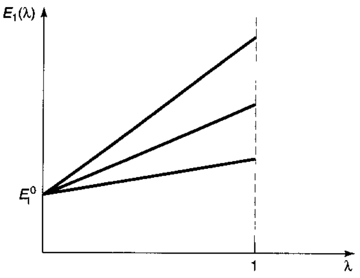

**Figure 6.6:** Lifting of the degeneracy in the example (Equation 6.38).

same for all three states, and equal to $V_0/4$—which is actually correct only for the middle state.

Meanwhile, the "good" unperturbed states are linear combinations of the form

$$\psi^0 = \alpha\psi_a + \beta\psi_b + \gamma\psi_c, \qquad [6.39]$$

where the coefficients ($\alpha$, $\beta$, and $\gamma$) form the eigenvectors of the matrix $W$:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = w \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}.$$

For $w = 1$ we get $\alpha = 1, \beta = \gamma = 0$; for $w = 1 \pm \kappa$ we get $\alpha = 0, \beta = \pm\gamma = 1/\sqrt{2}$. (I normalized them as I went along.) Thus the "good" states are[4]

$$\psi^0 = \begin{cases} \psi_a, \\ (\psi_b + \psi_c)/\sqrt{2}, \\ (\psi_b - \psi_c)/\sqrt{2}. \end{cases} \qquad [6.40]$$

---

**Problem 6.8** Suppose we perturb the infinite cubical well (Equation 6.29) by putting a delta-function "bump" at the point $(a/4, a/2, 3a/4)$:

$$H' = a^3 V_0 \delta(x - a/4)\delta(y - a/2)\delta(z - 3a/4).$$

Find the first-order corrections to the energy of the ground state and the (triply degenerate) first excited states.

---

[4] We might have guessed this result right from the start by noting that the operator $P_{xy}$, which interchanges $x$ and $y$, commutes with $H'$. Its eigenvalues are +1 (for functions that are *even* under the interchange) and −1 (for functions that are odd). In this case $\psi_a$ is *already* even, $(\psi_b + \psi_c)$ is even, and $(\psi_b - \psi_c)$ is odd. However, this is not quite conclusive, since any linear combination of the even states would still be even. What we'd *really* like is an operator with *three* distinct eigenvalues in the degenerate subspace.

---

**∗Problem 6.9** Consider a quantum system with just *three* linearly independent states. The Hamiltonian, in matrix form, is

$$H = V_0 \begin{pmatrix} (1-\epsilon) & 0 & 0 \\ 0 & 1 & \epsilon \\ 0 & \epsilon & 2 \end{pmatrix},$$

where $V_0$ is a constant and $\epsilon$ is some small number ($\epsilon \ll 1$).

**(a)** Write down the eigenvectors and eigenvalues of the *unperturbed* Hamiltonian ($\epsilon = 0$).

**(b)** Solve for the *exact* eigenvalues of $H$. Expand each of them as a power series in $\epsilon$, up to second order.

**(c)** Use first- and second-order *non*degenerate perturbation theory to find the approximate eigenvalue for the state that grows out of the nondegenerate eigenvector of $H^0$. Compare the exact result from (b).

**(d)** Use *degenerate* perturbation theory to find the first-order correction to the two initially degenerate eigenvalues. Compare the exact results.

---

## 6.3 THE FINE STRUCTURE OF HYDROGEN

In our study of the hydrogen atom (Section 4.2), we took the Hamiltonian to be

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \qquad [6.41]$$

(electron kinetic energy plus Coulombic potential energy). But this is not quite the whole story. We have already learned how to correct for the motion of the nucleus: Just replace $m$ by the reduced mass (Problem 5.1). More significant is the so-called **fine structure**, which is actually due to two distinct mechanisms: a **relativistic correction**, and **spin-orbit coupling**. Compared to the Bohr energies (Equation 4.70), fine structure is a tiny perturbation—smaller by a factor of $\alpha^2$, where

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \cong \frac{1}{137.036} \qquad [6.42]$$

is the famous **fine structure constant**. Smaller still (by another factor of $\alpha$) is the **Lamb shift**, associated with the quantization of the Coulomb field, and smaller by yet another order of magnitude is the **hyperfine structure**, which is due to the magnetic interaction between the dipole moments of the electron and the proton. This hierarchy is summarized in Table 6.1.

**Table 6.1:** Hierarchy of corrections to the Bohr energies of hydrogen.

| | | |
|---|---|---|
| Bohr energies: | of order | $\alpha^2 mc^2$ |
| Fine structure: | of order | $\alpha^4 mc^2$ |
| Lamb shift: | of order | $\alpha^5 mc^2$ |
| Hyperfine splitting: | of order | $(m/m_p)\alpha^4 mc^2$ |

In the present section we will analyze the fine structure of hydrogen, as an application of time-independent perturbation theory.

---

## Problem 6.10

**(a)** Express the Bohr energies in terms of the fine structure constant and the rest energy ($mc^2$) of the electron.

**(b)** Calculate the fine structure constant from first principles (i.e. without recourse to the empirical values of $\epsilon_0$, $e$, $\hbar$, and $c$). *Note*: The fine structure constant is undoubtedly the most fundamental pure (dimensionless) number in all of physics: It relates the basic constants of electromagnetism (the charge of the electron), relativity (the speed of light), and quantum mechanics (Planck's constant). If you can solve part (b), you have the most certain Nobel Prize in history waiting for you. But I wouldn't recommend spending a lot of time on it right now; many smart people have tried and given up.

---

### 6.3.1 The Relativistic Correction

The first term in the Hamiltonian is supposed to represent kinetic energy:

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}, \qquad [6.43]$$

and the canonical substitution $\mathbf{p} \rightarrow (\hbar/i)\nabla$ yields the operator

$$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2. \qquad [6.44]$$

But Equation 6.43 is the *classical* equation for kinetic energy; the *relativistic* formula is

$$T = \frac{mc^2}{\sqrt{1-(v/c)^2}} - mc^2. \qquad [6.45]$$

The first term is the *total* relativistic energy (not counting *potential* energy, which we aren't concerned with at the moment), and the second term is the *rest* energy—the *difference* is the energy attributable to motion. We need to express $T$ in terms of the (relativistic) momentum,

$$p = \frac{mv}{\sqrt{1-(v/c)^2}}, \qquad [6.46]$$

instead of velocity. Notice that

$$p^2c^2 + m^2c^4 = \frac{m^2v^2c^2 + m^2c^4[1-(v/c)^2]}{1-(v/c)^2} = \frac{m^2c^4}{1-(v/c)^2} = (T+mc^2)^2,$$

so

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2. \qquad [6.47]$$

This relativistic equation for kinetic energy reduces (of course) to the classical result (Equation 6.43), in the nonrelativistic limit $p \ll mc$; expanding in powers of the small number $(p/mc)$, we have

$$T = mc^2\left[\sqrt{1+\left(\frac{p}{mc}\right)^2} - 1\right] = mc^2\left[1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 \cdots - 1\right]$$

$$= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots. \qquad [6.48]$$

The lowest-order[5] relativistic contribution to the Hamiltonian is evidently

$$H_r' = -\frac{\hat{p}^4}{8m^3c^2}. \qquad [6.49]$$

In first-order perturbation theory, the correction to $E_n$ is given by the expectation value of $H'$ in the unperturbed state (Equation 6.9):

$$E_r^1 = \langle H_r' \rangle = -\frac{1}{8m^3c^2}\langle \psi | \hat{p}^4 \psi \rangle = -\frac{1}{8m^3c^2}\langle \hat{p}^2\psi | \hat{p}^2\psi \rangle. \qquad [6.50]$$

Now the Schrödinger equation (for the unperturbed states) says

$$\hat{p}^2\psi = 2m(E-V)\psi, \qquad [6.51]$$

and hence[6]

$$E_r^1 = -\frac{1}{2mc^2}\langle (E-V)^2 \rangle = -\frac{1}{2mc^2}[E^2 - 2E\langle V \rangle + \langle V^2 \rangle]. \qquad [6.52]$$

---

[5] The kinetic energy of the electron in hydrogen is on the order of 10 eV, which is miniscule compared to its rest energy (511,000 eV), so the hydrogen atom is basically nonrelativistic, and we can afford to keep only the lowest-order correction. In Equation 6.48, $p$ is the *relativistic* momentum (Equation 6.46), *not* the classical momentum $mv$. It is the former that we now associate with the quantum operator $-i\hbar\nabla$, in Equation 6.49.

[6] There is some sleight-of-hand in this maneuver, which exploits the Hermiticity of $\hat{p}^2$ and of $(E-V)$. In truth, the operator $\hat{p}^4$ is not Hermitian, for states with $l=0$, and the applicability of perturbation theory to Equation 6.49 is therefore called into question. Fortunately, the *exact* solution is available; it can be obtained by using the (relativistic) Dirac equation in place of the (nonrelativistic) Schrödinger equation, and it confirms the results we obtain here by less rigorous means. (See Problem 6.17.)

So far, this is entirely general; but we're interested in the case of hydrogen, for which $V(r) = -(1/4\pi\epsilon_0)e^2/r$:

$$E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\langle\frac{1}{r}\rangle + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\langle\frac{1}{r^2}\rangle\right], \qquad [6.53]$$

where $E_n$ is the Bohr energy of the state in question.

To complete the job, we need the expectation values of $1/r$ and $1/r^2$ in the (unperturbed) state $\psi_{nlm}$ (Equation 4.89). The first is easy (see Problem 6.11):

$$\langle\frac{1}{r}\rangle = \frac{1}{n^2 a}, \qquad [6.54]$$

where $a$ is the Bohr radius (Equation 4.72). The second is not so simple to derive (see Problem 6.28), but the answer is[7]

$$\langle\frac{1}{r^2}\rangle = \frac{1}{(l+1/2)n^3a^2}. \qquad [6.55]$$

It follows that

$$E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{n^2a} + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{(l+1/2)n^3a^2}\right],$$

or, eliminating $a$ (using Equation 4.72) and expressing everything in terms of $E_n$ (using Equation 4.70),

$$E_r^1 = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l+1/2} - 3\right]. \qquad [6.56]$$

Notice that the relativistic correction is smaller than $E_n$ by a factor of $E_n/mc^2 \approx 2\times10^{-5}$.

You might have noticed that I used *non*degenerate perturbation theory in this calculation even though the hydrogen atom is highly degenerate. But the perturbation is spherically symmetrical, so it commutes with $L^2$ and $L_z$. Moreover, the eigenfunctions of these operators (taken together) have distinct eigenvalues for the $n^2$ states with a given $E_n$. Luckily, then, the wave functions $\psi_{nlm}$ *are* "good" states for this problem, so as it happens the use of nondegenerate perturbation theory was legitimate.

---

***Problem 6.11** Use the virial theorem (Problem 4.41) to prove Equation 6.54.

---

[7] The general formula for the expectation value of *any* power of $r$ is given in Hans A. Bethe and Edwin E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, (New York: Plenum, 1977), p. 17.

---

**Problem 6.12** In Problem 4.43, you calculated the expectation value of $r^s$ in the state $\psi_{321}$. Check your answer for the special cases $s = 0$ (trivial), $s = -1$ (Equation 6.54), $s = -2$ (Equation 6.55), and $s = -3$ (Equation 6.63). Comment on the case $s = -7$.

---

****Problem 6.13** Find the (lowest-order) relativistic correction to the energy levels of the one-dimensional harmonic oscillator. *Hint:* Use the technique of Problem 2.37.

---

### 6.3.2 Spin-Orbit Coupling

Imagine the electron in orbit around the nucleus; from the *electron's* point of view, the proton is circling around *it* (Figure 6.7). This orbiting positive charge sets up a magnetic field **B** in the electron frame, which exerts a torque on the spinning electron, tending to align its magnetic moment ($\boldsymbol{\mu}$) along the direction of the field. The Hamiltonian (Equation 4.157) is

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}. \qquad [6.57]$$

**The Magnetic Field of the Proton.** If we picture the proton (from the electron's perspective) as a continuous current loop (Figure 6.7), its magnetic field can be calculated from the Biot-Savart law:

$$B = \frac{\mu_0 I}{2r},$$

with an effective current $I = e/T$, where $e$ is the charge of the proton and $T$ is the period of the orbit. On the other hand, the orbital angular momentum of the *electron* (in the rest frame of the *nucleus*) is $L = rmv = 2\pi m r^2/T$. Moreover, **B** and **L** point in the same direction (up, in Figure 6.7), so

$$\mathbf{B} = \frac{1}{4\pi\epsilon_0}\frac{e}{mc^2r^3}\mathbf{L}. \qquad [6.58]$$

(I used $c = 1/\sqrt{\epsilon_0\mu_0}$ to eliminate $\mu_0$ in favor of $\epsilon_0$.)

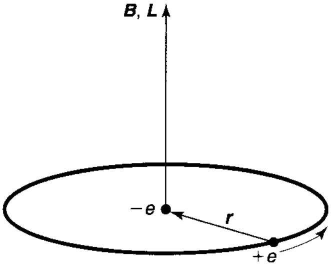

**Figure 6.7:** Hydrogen atom, from the electron's perspective.

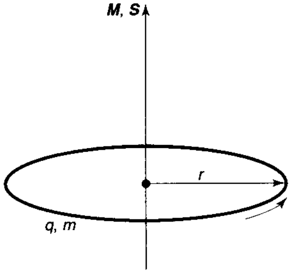

**Figure 6.8:** A ring of charge, rotating about its axis.

**The Magnetic Dipole Moment of the Electron.** The magnetic dipole moment of a spinning charge is related to its (spin) angular momentum; the proportionality factor is the gyromagnetic ratio (which we already encountered in Section 4.4.2 Let's derive it, using classical electrodynamics. Consider first a charge $q$ smeared out around a ring of radius $r$, which rotates about the axis with period $T$ (Figure 6.8 The magnetic dipole moment of the ring is defined as the current $(q/T)$ times the area $(\pi r^2)$:

$$\mu = \frac{q\pi r^2}{T}.$$

If the mass of the ring is $m$, its angular momentum is the moment of inertia $(mr^2$ times the angular velocity $(2\pi/T)$:

$$S = \frac{2\pi m r^2}{T}.$$

The gyromagnetic ratio for this configuration is evidently $\mu/S = q/2m$. Notice that it is independent of $r$ (and $T$). If I had some more complicated object, such as a sphere (all I require is that it be a figure of revolution, rotating about its axis), I could calculate $\boldsymbol{\mu}$ and $\mathbf{S}$ by chopping it into little rings and adding their contributions. As long as the mass and the charge are distributed in the same manner (so that the charge-to-mass ratio is uniform), the gyromagnetic ratio will be the same for each ring, and hence also for the object as a whole. Moreover, the directions of $\boldsymbol{\mu}$ and $\mathbf{S}$ are the same (or opposite, if the charge is negative), so

$$\boldsymbol{\mu} = \left(\frac{q}{2m}\right)\mathbf{S}.$$

That was a purely *classical* calculation, however; as it turns out, the electron's magnetic moment is *twice* the classical answer:

$$\boldsymbol{\mu}_e = -\frac{e}{m}\mathbf{S}. \qquad [6.59]$$

The "extra" factor of 2 was explained by Dirac in his relativistic theory of the electron.[8]

**The Spin-Orbit Interaction.** Putting all this together, we have

$$H = \left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\mathbf{S}\cdot\mathbf{L}.$$

But there is a serious fraud in this calculation: I did the analysis in the rest frame of the electron, but that's *not an inertial system*—it *accelerates* as the electron orbits around the nucleus. You can get away with this if you make an appropriate kinematic correction, known as the **Thomas precession.**[9] In this context it throws in a factor of 1/2:

$$H'_{\mathrm{so}} = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\mathbf{S}\cdot\mathbf{L}. \qquad [6.60]$$

This is the spin-orbit interaction; apart from two corrections (the modified gyromagnetic ratio for the electron and the Thomas precession factor—which, coincidentally, exactly cancel one another), it is just what you would expect on the basis of a naive classical model. Physically, it is attributable to the torque exerted on the magnetic dipole moment of the spinning electron, by the magnetic field of the proton, in the electron's instantaneous rest frame.

Now the quantum mechanics. In the presence of spin-orbit coupling, the Hamiltonian no longer commutes with **L** and **S**, so the spin and orbital angular momenta are not separately conserved (see Problem 6.14). However, $H'_{\mathrm{so}}$ *does* commute with $L^2$, $S^2$, and the *total* angular momentum

$$\mathbf{J} \equiv \mathbf{L} + \mathbf{S}, \qquad [6.61]$$

and hence these quantities *are* conserved (Equation 3.148). To put it another way, the eigenstates of $L_z$ and $S_z$ are not "good" states to use in perturbation theory, but the eigenstates of $L^2$, $S^2$, $J^2$, and $J_z$ are. Now

$$J^2 = (\mathbf{L}+\mathbf{S})\cdot(\mathbf{L}+\mathbf{S}) = L^2 + S^2 + 2\mathbf{L}\cdot\mathbf{S},$$

---

[8] We have already noticed that it can be dangerous to picture the electron as a spinning sphere (see Problem 4.26), and it is not too surprising that this naive classical model gets the gyromagnetic ratio wrong. Incidentally, quantum electrodynamics reveals tiny corrections to Equation 6.59; the calculation of the so-called **anomalous magnetic moment** of the electron stands as one of the greatest achievements of theoretical physics.

[9] One way of thinking of it is that we are continually stepping from one inertial system to another; Thomas precession amounts to the cumulative effect of all these Lorentz transformations. We could avoid this problem, of course, by staying in the *lab* frame, in which the nucleus is at rest. In that case the field of the proton is purely *electric*, and you may well wonder why it exerts any torque on the electron. Well, the fact is that a moving *magnetic* dipole acquires an *electric* dipole moment, and in the lab frame the spin-orbit coupling is due to the interaction of the *electric* field of the nucleus with the *electric* dipole moment of the electron. Because this analysis requires more sophisticated electrodynamics, it seems best to adopt the electron's perspective, where the physical mechanism is more transparent. For a related discussion, see V. Namias, *Am. J. Phys.*, **57**, 171 (1989).

so

$$\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2), \tag{6.62}$$

and therefore the eigenvalues of $\mathbf{L}\cdot\mathbf{S}$ are

$$\frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)].$$

In this case, of course, $s = 1/2$. Meanwhile, the expectation value of $1/r^3$ (see Problem 6.30) is

$$\left\langle\frac{1}{r^3}\right\rangle = \frac{1}{l(l+1/2)(l+1)n^3a^3}, \tag{6.63}$$

and we conclude that

$$E^1_{\text{so}} = \langle H'_{\text{so}}\rangle = \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2}\frac{(\hbar^2/2)[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)n^3a^3},$$

or, expressing it all in terms of $E_n$:

$$E^1_{\text{so}} = \frac{E_n^2}{mc^2}\left\{\frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)}\right\}. \tag{6.64}$$

It is remarkable, considering the totally different physical mechanisms involved, that the relativistic correction and the spin-orbit coupling are of the same order ($E_n^2/mc^2$). Adding them together, we get the complete fine-structure formula (see Problem 6.15):

$$E^1_{\text{fs}} = \frac{E_n^2}{2mc^2}\left(3 - \frac{4n}{j+1/2}\right). \tag{6.65}$$

Combining this with the Bohr formula, we obtain the grand result for the energy levels of hydrogen, including fine structure:

$$\boxed{E_{nj} = -\frac{13.6\,\text{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right].} \tag{6.66}$$

Fine structure breaks the degeneracy in $l$ (that is, for a given $n$, the different allowed values of $l$ do not all carry the same energy); the energies are determined by $n$ and $j$ (see Figure 6.9). The azimuthal eigenvalues for orbital and spin angular momentum ($m_l$ and $m_s$) are no longer "good" quantum numbers—the stationary states are linear combinations of states with different values of these quantities; the "good" quantum numbers are $n$, $l$, $s$, $j$, and $m_j$.[10]

---

[10] To write $|j\,m_j\rangle$ (for given $l$ and $s$) as a linear combination of $|l\,m_l\rangle|s\,m_s\rangle$ we would use the appropriate Clebsch-Gordan coefficients (Equation 4.185).

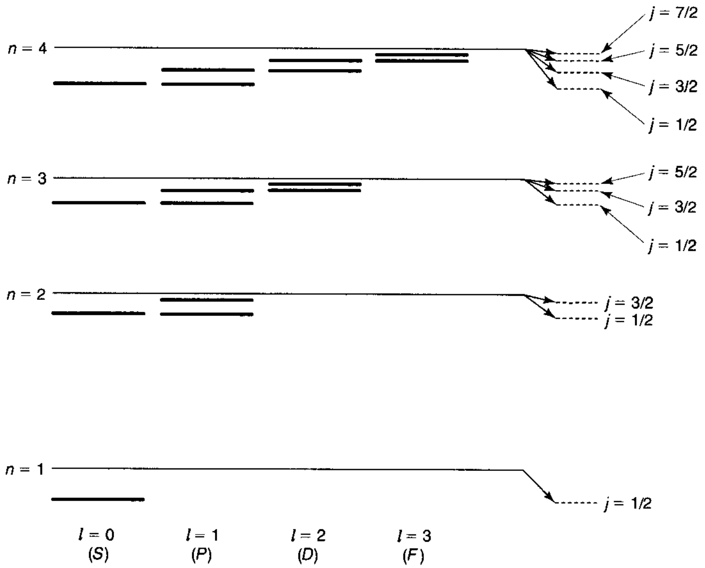

**Figure 6.9:** Energy levels of hydrogen, including fine structure (not to scale).

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**Problem 6.14** Evaluate the following commutators: (a) $[\mathbf{L}\cdot\mathbf{S}, \mathbf{L}]$, (b) $[\mathbf{L}\cdot\mathbf{S}, \mathbf{S}]$, (c) $[\mathbf{L}\cdot\mathbf{S}, \mathbf{J}]$, (d) $[\mathbf{L}\cdot\mathbf{S}, L^2]$, (e) $[\mathbf{L}\cdot\mathbf{S}, S^2]$, (f) $[\mathbf{L}\cdot\mathbf{S}, J^2]$. *Hint*: **L** and **S** satisfy the fundamental commutation relations for angular momentum (Equations 4.98, 4.99, and 4.134), but they commute with each other.

---

***Problem 6.15** Derive the fine structure formula (Equation 6.65) from the relativistic correction (Equation 6.56) and the spin-orbit coupling (Equation 6.64). *Hint*: Note that $j = l \pm 1/2$; treat the plus sign and the minus sign separately, and you'll find that you get the same final answer either way.

---

****Problem 6.16** The most prominent feature of the hydrogen spectrum in the visible region is the red Balmer line, coming from the transition $n = 3$ to $n = 2$. First of all, determine the wavelength and frequency of this line, according to the Bohr theory. Fine structure splits this line into several closely spaced lines; the question is: *How many*, and *what is their spacing*? *Hint*: First determine how many sublevels the $n = 2$ level splits into, and find $E^1_{fs}$ for each of these, in eV. Then do the same for $n = 3$. Draw an energy level diagram showing all possible transitions from $n = 3$ to $n = 2$. The energy released (in the form of a photon) is $(E_3 - E_2) + \Delta E$, the first part being common to all of them, and the $\Delta E$ (due to fine structure) varying from one transition to the next. Find $\Delta E$ (in eV) for each transition. Finally, convert to photon frequency, and determine the spacing between adjacent spectral lines (in Hz)—*not* the frequency interval between each line and the *unperturbed* line (which is, of course, unobservable), but the frequency interval between each line and the next one. Your final answer should take the form, "The red Balmer line splits into (??? lines. In order of increasing frequency, they come from the transitions (1) $j =$ (??? to $j =$ (???), (2) $j =$ (???) to $j =$ (???), and so on. The frequency spacing between line (1) and line (2) is (???) Hz, the spacing between line (2) and line (3) is (???) Hz, and so on."

---

**Problem 6.17** The *exact* fine-structure formula for hydrogen (obtained from the Dirac equation without recourse to perturbation theory) is[11]

$$E_{nj} = mc^2\left\{\left[1+\left(\frac{\alpha}{n-(j+1/2)+\sqrt{(j+1/2)^2-\alpha^2}}\right)^2\right]^{-1/2}-1\right\}.$$

Expand to order $\alpha^4$ (noting that $\alpha \ll 1$), and show that you recover Equation 6.66.

---

## 6.4 THE ZEEMAN EFFECT

When an atom is placed in a uniform external magnetic field $\mathbf{B}_{\text{ext}}$, the energy levels are shifted. This phenomenon is known as the **Zeeman effect**. For a single electron, the perturbation is

$$H_Z' = -(\boldsymbol{\mu}_l + \boldsymbol{\mu}_s)\cdot\mathbf{B}_{\text{ext}}, \tag{6.67}$$

where

$$\boldsymbol{\mu}_s = -\frac{e}{m}\mathbf{S} \tag{6.68}$$

is the magnetic dipole moment associated with electron spin, and

$$\boldsymbol{\mu}_l = -\frac{e}{2m}\mathbf{L} \tag{6.69}$$

is the dipole moment associated with orbital motion.[12] Thus

$$H_Z' = \frac{e}{2m}(\mathbf{L}+2\mathbf{S})\cdot\mathbf{B}_{\text{ext}}. \tag{6.70}$$

The nature of the Zeeman splitting depends critically on the strength of the external field in comparison with the *internal* field (Equation 6.58) that gives rise to spin-orbit coupling. For if $B_{\text{ext}} \ll B_{\text{int}}$, then fine structure dominates, and $H_Z'$ can be treated as a small perturbation, whereas if $B_{\text{ext}} \gg B_{\text{int}}$, then the Zeeman

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[11] Bethe and Salpeter (footnote 7) page 83.

[12] The gyromagnetic ratio for *orbital* motion is just the classical value $(q/2m)$—it is only for *spin* that there is an "extra" factor of 2.

effect dominates, and fine structure becomes the perturbation. In the intermediate zone, where the two fields are comparable, we need the full machinery of degenerate perturbation theory, and it is necessary to diagonalize the relevant portion of the Hamiltonian "by hand". In the following sections we shall explore each of these regimes briefly, for the case of hydrogen.

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**Problem 6.18** Use Equation 6.58 to estimate the internal field in hydrogen, and characterize quantitatively a "strong" and "weak" Zeeman field.

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### 6.4.1 Weak-Field Zeeman Effect

If $B_{\text{ext}} \ll B_{\text{int}}$, fine structure dominates (Equation 6.66); the "good" quantum numbers are $n$, $l$, $j$, and $m_j$ (but not $m_l$ and $m_s$, because—in the presence of spin-orbit coupling—**L** and **S** are not separately conserved). In first-order perturbation theory, the Zeeman correction to the energy is

$$E_Z^1 = \langle n\, l\, j\, m_j | H_Z' | n\, l\, j\, m_j \rangle = \frac{e}{2m}\mathbf{B}_{\text{ext}} \cdot \langle \mathbf{L} + 2\mathbf{S} \rangle. \qquad [6.71]$$

Now $\mathbf{L} + 2\mathbf{S} = \mathbf{J} + \mathbf{S}$; unfortunately, we do not immediately know the expectation value of **S**. But we can figure it out as follows: The total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is constant (Figure 6.10); **L** and **S** precess rapidly about this fixed vector. In particular, the (time) *average* value of **S** is just its projection along **J**:

$$\mathbf{S}_{\text{ave}} = \frac{(\mathbf{S} \cdot \mathbf{J})}{J^2}\mathbf{J}. \qquad [6.72]$$

But $\mathbf{L} = \mathbf{J} - \mathbf{S}$, so $L^2 = J^2 + S^2 - 2\mathbf{J} \cdot \mathbf{S}$, and hence

$$\mathbf{S} \cdot \mathbf{J} = \frac{1}{2}(J^2 + S^2 - L^2) = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - l(l+1)], \qquad [6.73]$$

from which it follows that

$$\langle \mathbf{L} + 2\mathbf{S} \rangle = \left\langle \left(1 + \frac{\mathbf{S} \cdot \mathbf{J}}{J^2}\right)\mathbf{J} \right\rangle = \left[1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)}\right] \langle \mathbf{J} \rangle. \qquad [6.74]$$

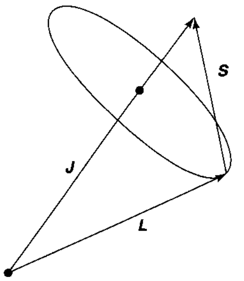

Figure 6.10: In the presence of spin-orbit coupling, **L** and **S** are not separately conserved; they precess about the fixed total angular momentum, **J**.

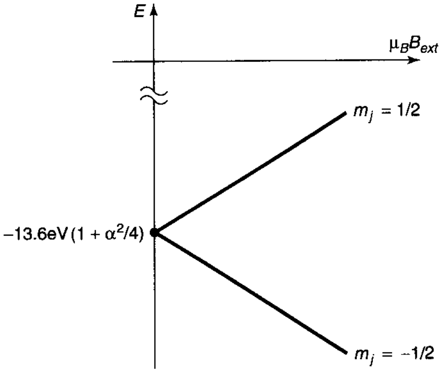

**Figure 6.11:** Weak-field Zeeman splitting of the ground state; the upper line ($m_j = 1/2$) has slope 1, the lower line ($m_j = -1/2$) has slope $-1$

The term in square brackets is known as the **Landé g-factor**, $g_J$.

We may as well choose the $z$-axis to lie along $\mathbf{B}_{\text{ext}}$; then

$$E^1_Z = \mu_B g_J B_{\text{ext}} m_j, \qquad [6.75]$$

where

$$\mu_B \equiv \frac{e\hbar}{2m} = 5.788 \times 10^{-5}\ \text{eV/T} \qquad [6.76]$$

is the so-called **Bohr magneton**. The *total* energy is the sum of the fine-structure part (Equation 6.66) and the Zeeman contribution (Equation 6.75). For example, the ground state ($n = 1, l = 0,\ j = 1/2$, and therefore $g_J = 2$) splits into two levels:

$$-\ 13.6\ \text{eV}(1 + \alpha^2/4) \pm \mu_B B_{\text{ext}}, \qquad [6.77]$$

with the plus sign for $m_j = 1/2$, and minus for $m_j = -1/2$. These energies are plotted (as functions of $B_{\text{ext}}$) in Figure 6.11.

***Problem 6.19** Consider the (eight) $n = 2$ states, $|2\ l\ j\ m_j\rangle$. Find the energy of each state, under weak-field Zeeman splitting, and construct a diagram like Figure 6.11 to show how the energies evolve as $B_{\text{ext}}$ increases. Label each line clearly, and indicate its slope.

### 6.4.2 Strong-Field Zeeman Effect

If $B_{\text{ext}} \gg B_{\text{int}}$, the Zeeman effect dominates[13]; with $B_{\text{ext}}$ in the $z$ direction, the "good" quantum numbers are now $n, l, m_l$, and $m_s$ (but not $j$ and $m_j$ because—in the presence of the external torque—the total angular momentum is not conserved, whereas $L_z$ and

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[13] In this regime the Zeeman effect is also known as the **Paschen-Back effect**.

$S_z$ are). The Zeeman Hamiltonian is

$$H'_Z = \frac{e}{2m} B_{\text{ext}}(L_z + 2S_z),$$

and the "unperturbed" energies are

$$E_{nm_l m_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{\text{ext}}(m_l + 2m_s). \qquad [6.78]$$

In first-order perturbation theory, the fine-structure correction to these levels is

$$E^1_{\text{fs}} = \langle n\, l\, m_l\, m_s | (H'_r + H'_{so}) | n\, l\, m_l\, m_s \rangle. \qquad [6.79]$$

The relativistic contribution is the same as before (Equation 6.56); for the spin-orbit term (Equation 6.60) we need

$$\langle \mathbf{S} \cdot \mathbf{L} \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle = \hbar^2 m_l m_s \qquad [6.80]$$

(note that $\langle S_x \rangle = \langle S_y \rangle = \langle L_x \rangle = \langle L_y \rangle = 0$ for eigenstates of $S_z$ and $L_z$). Putting all this together (Problem 6.20), we conclude that

$$E^1_{\text{fs}} = \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left\{ \frac{3}{4n} - \left[ \frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right] \right\}. \qquad [6.81]$$

(The term in square brackets is indeterminate for $l = 0$; its correct value in this case is 1—see Problem 6.22.) The *total* energy is the sum of the Zeeman part (Equation 6.78) and the fine-structure contribution (Equation 6.81).

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**Problem 6.20** Starting with Equation 6.79 and using Equations 6.56, 6.60, 6.63, and 6.80, derive Equation 6.81.

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****Problem 6.21** Consider the eight $n = 2$ states, $|2\, l\, m_l\, m_s\rangle$. Find the energy of each state, under strong-field Zeeman splitting. (Express your answers as the sum of three terms, as in Equation 6.77: the Bohr energy; the fine structure, proportional to $\alpha^2$; and the Zeeman contribution, proportional to $\mu_B B_{\text{ext}}$.) If you ignore fine structure altogether, how many distinct levels are there, and what are their degeneracies?

---

**Problem 6.22** If $l = 0$, then $j = s$, $m_j = m_s$, and the "good" states are the same ($|n\, m_s\rangle$) for weak *and* strong fields. Determine $E^1_Z$ (from Equation 6.71) and the fine structure energies (Equation 6.66), and write down the general result for the $l = 0$ Zeeman effect—*regardless* of the strength of the field. Show that the strong-field formula (Equation 6.81) reproduces this result, provided that we interpret the indeterminate term in square brackets as 1.

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### 6.4.3 Intermediate-Field Zeeman Effect

In the intermediate regime, neither $H'_Z$ nor $H'_{\text{fs}}$ dominates, and we must treat the two on an equal footing, as perturbations to the Bohr Hamiltonian (Equation 6.41):

$$H' = H'_Z + H'_{\text{fs}}. \tag{6.82}$$

I'll confine my attention here to the case $n = 2$ and choose as the basis for degenerate perturbation theory the states characterized by $l$, $j$, and $m_j$.[14] Using the Clebsch-Gordan coefficients (Problem 4.45 or Table 4.7) to express $|j\, m_j\rangle$ as a linear combination of $|l\, m_l\rangle|s\, m_s\rangle$, we have

$$l=0\left\{\begin{array}{lllll} \psi_1 & \equiv & \left|\frac{1}{2}\,\frac{1}{2}\right\rangle & = & |0\,0\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle, \\ \psi_2 & \equiv & \left|\frac{1}{2}\,\frac{-1}{2}\right\rangle & = & |0\,0\rangle\left|\frac{1}{2}\,\frac{-1}{2}\right\rangle, \end{array}\right.$$

$$l=1\left\{\begin{array}{lllllll} \psi_3 & \equiv & \left|\frac{3}{2}\,\frac{3}{2}\right\rangle & = & |1\,1\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle, & & \\ \psi_4 & \equiv & \left|\frac{3}{2}\,\frac{-3}{2}\right\rangle & = & |1\,-1\rangle\left|\frac{1}{2}\,\frac{-1}{2}\right\rangle, & & \\ \psi_5 & \equiv & \left|\frac{3}{2}\,\frac{1}{2}\right\rangle & = & \sqrt{2/3}|1\,0\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle & + & \sqrt{1/3}|1\,1\rangle\left|\frac{1}{2}\,\frac{-1}{2}\right\rangle, \\ \psi_6 & \equiv & \left|\frac{1}{2}\,\frac{1}{2}\right\rangle & = & -\sqrt{1/3}|1\,0\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle & + & \sqrt{2/3}|1\,1\rangle\left|\frac{1}{2}\,\frac{-1}{2}\right\rangle, \\ \psi_7 & \equiv & \left|\frac{3}{2}\,\frac{-1}{2}\right\rangle & = & \sqrt{1/3}|1\,-1\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle & + & \sqrt{2/3}|1\,0\rangle\left|\frac{1}{2}\,\frac{-1}{2}\right\rangle, \\ \psi_8 & \equiv & \left|\frac{1}{2}\,\frac{-1}{2}\right\rangle & = & -\sqrt{2/3}|1\,-1\rangle\left|\frac{1}{2}\,\frac{1}{2}\right\rangle & + & \sqrt{1/3}|1\,0\rangle\left|\frac{1}{2}\,\frac{-1}{2}\right\rangle. \end{array}\right.$$

In this basis the nonzero matrix elements of $H'_{\text{fs}}$ are all on the diagonal, and given by Equation 6.65; $H'_Z$ has four off-diagonal elements, and the complete matrix $-W$ is (see Problem 6.23)

$$\begin{pmatrix} 5\gamma-\beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5\gamma+\beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma-2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma+2\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma-\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma-\frac{1}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \gamma+\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma+\frac{1}{3}\beta \end{pmatrix}$$

where

$$\gamma \equiv (\alpha/8)^2 13.6\ \text{eV} \quad \text{and} \quad \beta \equiv \mu_B B_{\text{ext}}.$$

The first four eigenvalues are displayed along the diagonal; it remains only to find the eigenvalues of the two 2 × 2 blocks. The characteristic equation for the first is

$$\lambda^2 + \lambda(6\gamma - \beta) + (5\gamma^2 - \frac{11}{3}\gamma\beta) = 0,$$

---

[14] You can use $l$, $m_l$, $m_s$ states if you prefer—this makes the matrix elements of $H'_Z$ easier but those of $H'_{\text{fs}}$ more difficult; the $W$-matrix will be more complicated, but its eigenvalues (which are independent of basis) are the same either way.

**Table 6.2:** Energy levels for the $n = 2$ states of hydrogen, with fine structure and Zeeman splitting.

$$\begin{aligned}
\epsilon_1 &= E_2 - 5\gamma + \beta \\
\epsilon_2 &= E_2 - 5\gamma - \beta \\
\epsilon_3 &= E_2 - \gamma + 2\beta \\
\epsilon_4 &= E_2 - \gamma - 2\beta \\
\epsilon_5 &= E_2 - 3\gamma + \beta/2 + \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4} \\
\epsilon_6 &= E_2 - 3\gamma + \beta/2 - \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4} \\
\epsilon_7 &= E_2 - 3\gamma - \beta/2 + \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4} \\
\epsilon_8 &= E_2 - 3\gamma - \beta/2 - \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}
\end{aligned}$$

and the quadratic formula gives the eigenvalues:

$$\lambda_\pm = -3\gamma + (\beta/2) \pm \sqrt{4\gamma^2 + (2/3)\gamma\beta + (\beta^2/4)}. \qquad [6.83]$$

The eigenvalues of the second block are the same, but with the sign of $\beta$ reversed. The eight energies are listed in Table 6.2, and plotted against $B_{\text{ext}}$ in Figure 6.12. In the zero-field limit ($\beta = 0$) they reduce to the fine-structure values; for weak fields ($\beta \ll \gamma$) they reproduce what you got in Problem 6.19; for strong fields ($\beta \gg \gamma$) we recover the results of Problem 6.21 (note the convergence to five distinct energy levels, at very high fields, as predicted in Problem 6.21).

**Problem 6.23** Work out the matrix elements of $H'_Z$ and $H'_{\text{fs}}$, and construct the $W$-matrix given in the text, for $n = 2$.

*****Problem 6.24** Analyze the Zeeman effect for the $n = 3$ states of hydrogen in the weak, strong, and intermediate field regimes. Construct a table of energies (analogous

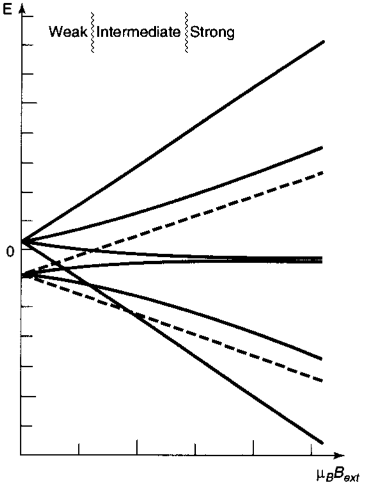

**Figure 6.12:** Zeeman splitting of the $n = 2$ states of hydrogen in the weak, intermediate, and strong field regimes.

to Table 6.2), plot them as functions of the external field (as in Figure 6.12), and check that the intermediate-field results reduce properly in the two limiting cases.

## 6.5 HYPERFINE SPLITTING

The proton itself constitutes a magnetic dipole, though its dipole moment is much smaller than the electron's because of the mass in the denominator (Equation 6.59):

$$\boldsymbol{\mu}_p = \frac{ge}{2m_p}\mathbf{S}_p, \quad \boldsymbol{\mu}_e = -\frac{e}{m_e}\mathbf{S}_e. \qquad [6.84]$$

(The proton is a composite structure, made up of three quarks, and its gyromagnetic ratio is not as simple as the electron's—hence the $g$-factor,[15] whose measured value is 5.59 as opposed to 2.00 for the electron.) According to classical electrodynamics, a dipole $\boldsymbol{\mu}$ sets up a magnetic field[16]

$$\mathbf{B} = \frac{\mu_0}{4\pi r^3}[3(\boldsymbol{\mu}\cdot\hat{r})\hat{r} - \boldsymbol{\mu}] + \frac{2\mu_0}{3}\boldsymbol{\mu}\delta^3(\mathbf{r}). \qquad [6.85]$$

So the Hamiltonian (Equation 6.57) of the electron, in the magnetic field due to the proton's magnetic dipole moment, is

$$H'_{\text{hf}} = \frac{\mu_0 ge^2}{8\pi m_p m_e}\frac{[3(\mathbf{S}_p\cdot\hat{r})(\mathbf{S}_e\cdot\hat{r}) - \mathbf{S}_p\cdot\mathbf{S}_e]}{r^3} + \frac{\mu_0 ge^2}{3m_p m_e}\mathbf{S}_p\cdot\mathbf{S}_e\delta^3(\mathbf{r}). \qquad [6.86]$$

According to perturbation theory, the first-order correction to the energy (Equation 6.9) is the expectation value of the perturbing Hamiltonian:

$$E^1_{\text{hf}} = \frac{\mu_0 ge^2}{8\pi m_p m_e}\left\langle\frac{3(\mathbf{S}_p\cdot\hat{r})(\mathbf{S}_e\cdot\hat{r}) - \mathbf{S}_p\cdot\mathbf{S}_e}{r^3}\right\rangle$$

$$+ \frac{\mu_0 ge^2}{3m_p m_e}\langle\mathbf{S}_p\cdot\mathbf{S}_e\rangle|\psi(0)|^2. \qquad [6.87]$$

In the ground state (or any other state for which $l = 0$) the wave function is spherically symmetrical, and the first expectation value vanishes (see Problem 6.25). Meanwhile, from Equation 4.80 we find that $|\psi_{100}(0)|^2 = 1/(\pi a^3)$, so

$$E^1_{\text{hf}} = \frac{\mu_0 ge^2}{3\pi m_p m_e a^3}\langle\mathbf{S}_p\cdot\mathbf{S}_e\rangle, \qquad [6.88]$$

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[15] The Landé $g$-factor, in Equation 6.74, plays a similar role in the proportionality between the electron's *total* magnetic moment ($\boldsymbol{\mu}_l + \boldsymbol{\mu}_s$) and its total angular momentum $\mathbf{J}$.

[16] If you are unfamiliar with the delta function term in Equation 6.85, you can derive it by treating the dipole as a spinning charged spherical shell, in the limit as the radius goes to zero and the charge goes to infinity (with $\boldsymbol{\mu}$ held constant). See D. J. Griffiths, *Am. J. Phys.* **50**, 698 (1982).

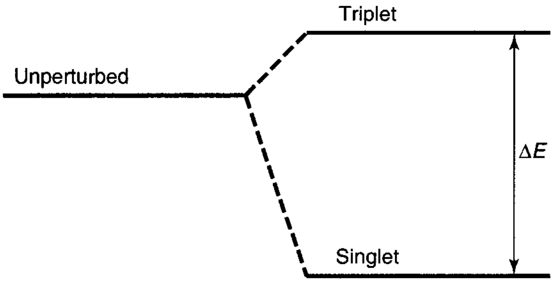

**Figure 6.13:** Hyperfine splitting in the ground state of hydrogen.

in the ground state. This is called **spin-spin coupling** because it involves the dot product of two spins (contrast spin-orbit coupling, which involves $\mathbf{S} \cdot \mathbf{L}$).

In the presence of spin-spin coupling, the individual spin angular momenta are no longer conserved; the "good" states are eigenvectors of the *total* spin,

$$\mathbf{S} \equiv \mathbf{S}_e + \mathbf{S}_p. \qquad [6.89]$$

As before, we square this out to get

$$\mathbf{S}_p \cdot \mathbf{S}_e = \frac{1}{2}(S^2 - S_e^2 - S_p^2). \qquad [6.90]$$

But the electron and proton both have spin 1/2, so $S_e^2 = S_p^2 = (3/4)\hbar^2$. In the triplet state (spins "parallel") the total spin is 1, and hence $S^2 = 2\hbar^2$; in the singlet state the total spin is 0, and $S^2 = 0$. Thus

$$E_{\text{hf}}^1 = \frac{4g\hbar^4}{3m_p m_e^2 c^2 a^4} \begin{cases} +1/4, & \text{(triplet);} \\ -3/4, & \text{(singlet).} \end{cases} \qquad [6.91]$$

Spin-spin coupling breaks the spin degeneracy of the ground state, lifting the triplet configuration and depressing the singlet (see Figure 6.13).
The energy gap is evidently

$$\Delta E = \frac{4g\hbar^4}{3m_p m_e^2 c^2 a^4} = 5.88 \times 10^{-6} \text{eV}. \qquad [6.92]$$

The frequency of the photon emitted in a transition from the triplet to the singlet state is

$$\nu = \frac{\Delta E}{h} = 1420 \text{ MHz}, \qquad [6.93]$$

and the corresponding wavelength is $c/\nu = 21$ cm, which falls in the microwave region. This famous "21-centimeter line" is among the most pervasive and ubiquitous forms of radiation in the universe.

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**Problem 6.25** Let **a** and **b** be two constant vectors. Show that

$$\int (\mathbf{a}\cdot\hat{r})(\mathbf{b}\cdot\hat{r})\sin\theta\, d\theta\, d\phi = \frac{4\pi}{3}(\mathbf{a}\cdot\mathbf{b}). \qquad [6.94$$

The integration is over the usual range: $0 < \theta < \pi$, $0 < \phi < 2\pi$. Use this result to demonstrate that

$$\left\langle \frac{3(\mathbf{S}_p\cdot\hat{r})(\mathbf{S}_e\cdot\hat{r}) - \mathbf{S}_p\cdot\mathbf{S}_e}{r^3} \right\rangle = 0,$$

for states with $l = 0$. *Hint*: $\hat{r} = \sin\theta\cos\phi\hat{\imath} + \sin\theta\sin\phi\hat{\jmath} + \cos\theta\hat{k}$.

---

**Problem 6.26** By appropriate modification of the hydrogen formula, determine the hyperfine splitting in the ground state of (a) muonic hydrogen (in which a muon—same charge and $g$-factor as the electron, but 207 times the mass—substitutes for the electron), (b) positronium (in which a positron—same mass and $g$-factor as the electron, but opposite charge—substitutes for the proton), and (c) muonium (in which an antimuon—same mass and $g$-factor as a muon, but opposite charge—substitutes for the proton). *Hint*: Don't forget to use the reduced mass (Problem 5.1) in calculating the "Bohr radius" of these exotic "atoms.". Incidentally, the answer you get for positronium ($4.85 \times 10^{-4}$ eV) is quite far from the experimental value ($8.41 \times 10^{-4}$ eV); the large discrepancy is due to pair annihilation ($e^+ + e^- \rightarrow \gamma + \gamma$), which contributes an extra $(3/4)\Delta E$ and does not occur (of course) in ordinary hydrogen. muonic hydrogen, or muonium. See Griffiths (footnote 16) for further details.

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## FURTHER PROBLEMS FOR CHAPTER 6

****Problem 6.27** Suppose the Hamiltonian $H$, for a particular quantum system. is a function of some parameter $\lambda$; let $E_n(\lambda)$ and $\psi_n(\lambda)$ be the eigenvalues and eigenfunctions of $H(\lambda)$. The **Feynman-Hellmann theorem** states that

$$\frac{\partial E_n}{\partial \lambda} = \langle \psi_n | \frac{\partial H}{\partial \lambda} | \psi_n \rangle \qquad [6.95]$$

(assuming either that $E_n$ is nondegenerate, or—if degenerate—that the $\psi_n$'s are the "good" linear combinations of the degenerate eigenfunctions).

**(a)** Prove the Feynman-Hellmann theorem. *Hint*: Use Equation 6.9.

**(b)** Apply it to the one-dimensional harmonic oscillator, (i) using $\lambda = \omega$ (this yields a formula for the expectation value of $V$), (ii) using $\lambda = \hbar$ (this yields $\langle T \rangle$), and (iii) using $\lambda = m$ (this yields a relation between $\langle T \rangle$ and $\langle V \rangle$). Compare your answers to Problem 2.37 and the virial theorem predictions (Problem 3.53).

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****Problem 6.28** The Feynman-Hellmann theorem (Problem 6.27) can be used to determine the expectation values of $1/r$ and $1/r^2$ for hydrogen.[17] The effective Hamiltonian for the radial wave functions is (Equation 4.53)

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r},$$

and the eigenvalues (expressed in terms of $l$)[18] are (Equation 4.70)

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2(j_{\max}+l+1)^2}.$$

**(a)** Use $\lambda = e$ in the Feynman-Hellmann theorem to obtain $\langle 1/r\rangle$. Check your result against Equation 6.54.

**(b)** Use $\lambda = l$ to obtain $\langle 1/r^2\rangle$. Check your answer with Equation 6.55.

---

*****Problem 6.29** Prove **Kramers' relation**:

$$\frac{s+1}{n^2}\langle r^s\rangle - (2s+1)a\langle r^{s-1}\rangle + \frac{s}{4}[(2l+1)^2 - s^2]a^2\langle r^{s-2}\rangle = 0, \qquad [6.96]$$

which relates the expectation values of $r$ to three different powers ($s$, $s-1$, and $s-2$), for an electron in the state $\psi_{nlm}$ of hydrogen. *Hint*: Rewrite the radial equation (Equation 4.53) in the form

$$u'' = \left[\frac{l(l+1)}{r^2} - \frac{2}{ar} + \frac{1}{n^2a^2}\right]u,$$

and use it to express $\int(ur^su'')dr$ in terms of $\langle r^s\rangle$, $\langle r^{s-1}\rangle$, and $\langle r^{s-2}\rangle$. Then use integration by parts to reduce the second derivative. Show that $\int(ur^su')dr = -(s/2)\langle r^{s-1}\rangle$, and $\int(u'r^su')dr = -[2/(s+1)]\int(u''r^{s+1}u')dr$. Take it from there.

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**Problem 6.30**

**(a)** Plug $s = 0$, $s = 1$, $s = 2$, and $s = 3$ into Kramers' relation (Equation 6.96) to obtain formulas for $\langle r^{-1}\rangle$, $\langle r\rangle$, $\langle r^2\rangle$, and $\langle r^3\rangle$. Note that you could continue indefinitely, to find *any* positive power.

**(b)** In the *other* direction, however, you hit a snag. Put in $s = -1$, and show that all you get is a relation between $\langle r^{-2}\rangle$ and $\langle r^{-3}\rangle$.

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[17] C. Sánchez del Rio, *Am. J. Phys.*, **50**, 556 (1982); H. S. Valk, *Am. J. Phys.*, **54**, 921 (1986).

[18] In part (b) we treat $l$ as a continuous variable; $n$ becomes a function of $l$, according to Equation 4.67, because $j_{\max}$, which must be an integer, is fixed. To avoid confusion, I have eliminated $n$, to reveal the dependence on $l$ explicitly.

**(c)** But if you can get $\langle r^{-2}\rangle$ by some *other* means, you can apply the Kramers' relation to obtain the rest of the negative powers. Use Equation 6.55 (which is derived in Problem 6.28) to determine $\langle r^{-3}\rangle$, and check your answer against Equation 6.63.

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******Problem 6.31** When an atom is placed in a uniform external electric field $\mathbf{E}_{\text{ext}}$, the energy levels are shifted—a phenomenon known as the **Stark effect**. In this problem we analyze the Stark effect for the $n = 1$ and $n = 2$ states of hydrogen. Let the field point in the $z$ direction, so the potential energy of the electron is

$$H'_S = -eE_{\text{ext}}z = -eE_{\text{ext}}r\cos\theta.$$

Treat this as a perturbation on the Bohr Hamiltonian (Equation 6.41); spin is irrelevant to this problem, so ignore it.

**(a)** Show that the ground-state energy is not affected by this perturbation, in first order.

**(b)** The first excited state is fourfold degenerate: $\psi_{200}, \psi_{211}, \psi_{210}, \psi_{21-1}$. Using degenerate perturbation theory, determine the first-order corrections to the energy. Into how many levels does $E_2$ split?

**(c)** What are the "good" wave functions for part (b)? Find the expectation value of the electric dipole moment ($\mathbf{p}_e = -e\mathbf{r}$), in each of these "good" states. Notice that the results are independent of the applied field—evidently hydrogen in its first excited state can carry a *permanent* electric dipole moment.

*Hint*: There are a lot of integrals in this problem, but almost all of them are zero. So study each one carefully before you do any calculations: If the $\phi$ integral vanishes, there's not much point in doing the $r$ and $\theta$ integrals! *Partial answer*: $W_{13} = W_{31} = 3eaE_{\text{ext}}$; all other elements are zero.

---

******Problem 6.32** Consider the Stark effect (Problem 6.31) for the $n = 3$ states of hydrogen. There are initially nine degenerate states, $\psi_{3lm}$ (neglecting spin, of course), and we turn on an electric field in the $z$ direction.

**(a)** Construct the $9 \times 9$ matrix representing the perturbing Hamiltonian. *Partial answer*: $\langle 3\,0\,0|z|3\,1\,0\rangle = -3\sqrt{6}a$, $\langle 3\,1\,0|z|3\,2\,0\rangle = -3\sqrt{3}a$, $\langle 3\,1\,\pm1|z|3\,2\,\pm1\rangle = -(9/2)a$.

**(b)** Find the eigenvalues and their degeneracies.

---

**Problem 6.33** Calculate the wavelength, in centimeters, of the photon emitted under a hyperfine transition in the ground state ($n = 1$) of **deuterium**. Deuterium is "heavy" hydrogen, with an extra neutron in the nucleus. The proton and neutron bind together to form a **deuteron**, with spin 1 and magnetic moment

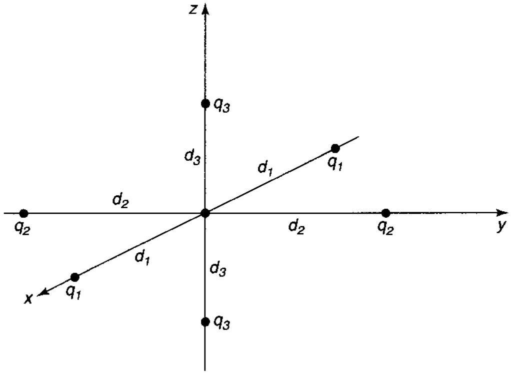

**Figure 6.14:** Hydrogen atom surrounded by six point charges (crude model for a crystal lattice); Problem 6.34.

$$\boldsymbol{\mu}_d = \frac{g_d e}{2m_d}\mathbf{S}_d;$$

the deuteron $g$-factor is 1.71.

---

∗∗∗**Problem 6.34** In a crystal, the electric field of neighboring ions perturbs the energy levels of an atom. As a crude model, imagine that a hydrogen atom is surrounded by three pairs of point charges, as shown in Figure 6.14.
(Spin is irrelevant to this problem, so ignore it.)

**(a)** Assuming that $r \ll d_1$, $r \ll d_2$, and $r \ll d_3$, show that

$$H' = V_0 + 3(\beta_1 x^2 + \beta_2 y^2 + \beta_3 z^2) - (\beta_1 + \beta_2 + \beta_3)r^2,$$

where

$$\beta_i \equiv -\frac{e}{4\pi\epsilon_0}\frac{q_i}{d_i^3}, \quad \text{and } V_0 = 2(\beta_1 d_1^2 + \beta_2 d_2^2 + \beta_3 d_3^2).$$

**(b)** Find the lowest-order correction to the ground-state energy.

**(c)** Calculate the first-order corrections to the energy of the first excited states ($n = 2$). Into how many levels does this fourfold degenerate system split, (i) in the case of **cubic symmetry**, $\beta_1 = \beta_2 = \beta_3$; (ii) in the case of **orthorhombic symmetry**, $\beta_1 = \beta_2 \neq \beta_3$; (iii) in the general case of **tetragonal symmetry** (all three different)?

## CHAPTER 7

# THE VARIATIONAL PRINCIPLE

## 7.1 THEORY

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:**

$$\boxed{E_g \leq \langle\psi|H|\psi\rangle \equiv \langle H\rangle.} \qquad [7.1]$$

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[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 $\psi$ is normalized,

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

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

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

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,

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

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

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

Now

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

where, in this case,

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

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

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

According to the theorem, this exceeds $E_g$ *for any* $b$; to get the *tightest* bound let's *minimize* $\langle H\rangle$ with respect to $b$:

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

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

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

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 2.48). 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 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 2.109): $E_g = -m\alpha^2/2\hbar^2$. 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,

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

and we know that this exceeds $E_g$ 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

$$\langle H\rangle_{\min} = -\frac{m\alpha^2}{\pi\hbar^2}, \qquad [7.9]$$

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

---

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

---

**Example 3.** Find an upper bound on the ground-state energy of the one-dimensional infinite square well (Equation 2.15), using the "triangular" trial wave function (Figure 7.1)[2]:

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

where $A$ is determined by normalization:

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

In this case

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

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

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

and hence

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

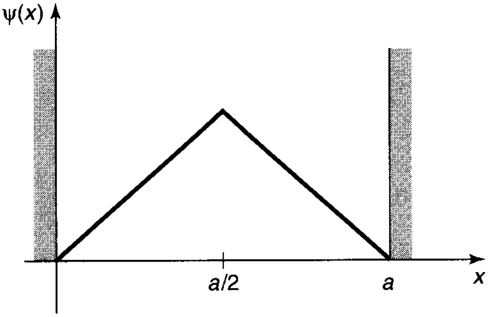

**Figure 7.1:** Triangular trial wave function for the infinite square well (Equation 7.10).

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[2] There is no point in trying a function (such as the gaussian) that extends outside the well, because you'll get $\langle V \rangle = \infty$, and Equation 7.1 tells you nothing.

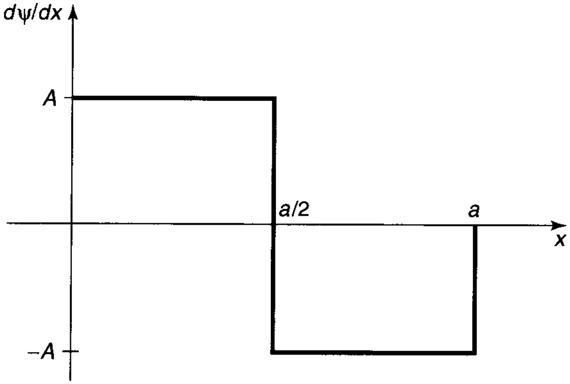

**Figure 7.2:** Derivative of the wave function in Figure 7.1.

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 trail function (Equation 7.10). (This time $a$ is an adjustable parameter.)

---

---

### 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 $\psi$ is orthogonal to $\psi_g$, 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

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

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:

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

This is the number we would like to reproduce theoretically.

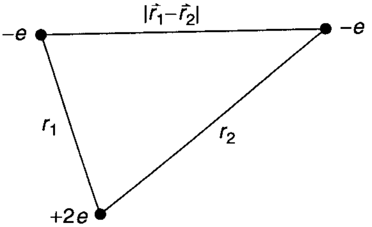

**Figure 7.3:** The helium atom.

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 $\psi_0$ 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 $n$th Bohr energy; recall that for a nucleus with atomic number $Z$, $E_n \rightarrow Z^2E_n$ 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 $E_g$.

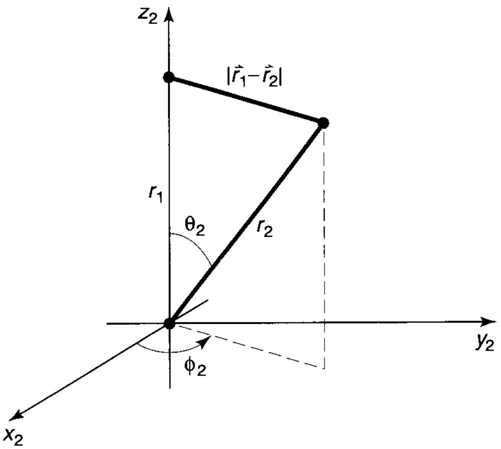

**Figure 7.4:** Choice of coordinates for the $\mathbf{r}_2$ integral (Equation 7.20).

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,

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

and hence

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

The $\phi_2$ integral is trivial $(2\pi)$; the $\theta_2$ integral is

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

$$= \frac{1}{r_1r_2}\left(\sqrt{r_1^2 + r_2^2 + 2r_1r_2} - \sqrt{r_1^2 + r_2^2 - 2r_1r_2}\right)$$

$$= \frac{1}{r_1r_2}\left[(r_1 + r_2) - |r_1 - r_2|\right] = \begin{cases} 2/r_1, & \text{if } r_2 < r_1, \\ 2/r_2, & \text{if } r_2 > r_1. \end{cases} \qquad [7.23]$$

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 ($4\pi$), 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 $\psi_0$ (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 $\psi_{100}$ (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, $\text{He}^+$, with a single electron orbitting the nucleus; then subtract the two energies.

***Problem 7.7** Apply the techniques of this Section to the $\text{H}^-$ and $\text{Li}^+$ 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 $\text{H}^-$ 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

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

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,[7] 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.[8]

## 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). 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

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

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),

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

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

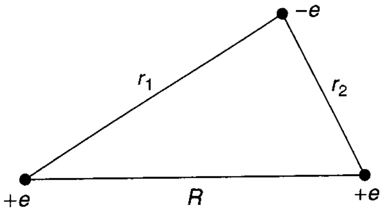

**Figure 7.5:** The hydrogen molecule ion, $H_2^+$.

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[7] Robert N. Hill, *J. Math. Phys.* **18**, 2316 (1977).

[8] 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

$$\psi = A\left[\psi_g(r_1) + \psi_g(r_2)\right]. \qquad [7.37]$$

(Quantum chemists call this the **LCAO** technique, because we are expressing the *molecular* wave function as a *l*inear *c*ombination of *a*tomic *o*rbitals.)

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

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

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

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

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

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

and therefore

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

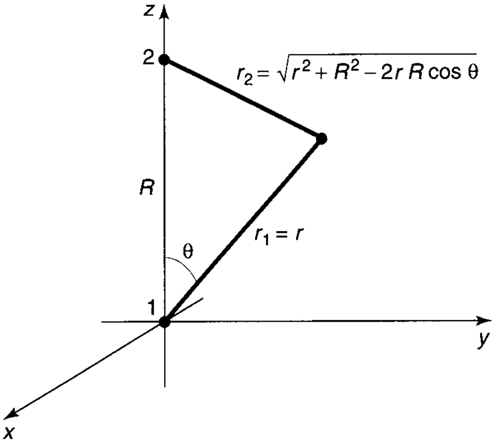

**Figure 7.6:** Coordinates for the calculation of $I$ (Equation 7.39).

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

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

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

The $r$ integral is now straightforward:

$$I = \frac{2}{a^2R}\Big[-e^{-R/a}\int_0^{\infty}(r+R+a)e^{-2r/a}r\,dr + e^{-R/a}\int_0^{R}(R-r+a)r\,dr$$

$$+e^{R/a}\int_R^{\infty}(r-R+a)e^{-2r/a}r\,dr\Big].$$

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

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

$I$ 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 $R \to 0$, and to 0 as $R \to \infty$). In terms of $I$, the normalization factor (Equation 7.38) is

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

Next we must calculate the expectation value of $H$ in the trial state $\psi$. Noting that

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_1}\right)\psi_g(r_1) = E_1\psi_g(r_1)$$

(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

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

$$= E_1\psi - A\left(\frac{e^2}{4\pi\epsilon_0}\right)\left[\frac{1}{r_2}\psi_g(r_1) + \frac{1}{r_1}\psi_g(r_2)\right].$$

It follows that

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

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

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

and the **exchange integral**,

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

The results (see Problem 7.8) are

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

and

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

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

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

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:

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

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

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

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.

---

$*$**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):

$$\psi = A[\psi_g(r_1) - \psi_g(r_2)]. \tag{7.52}$$

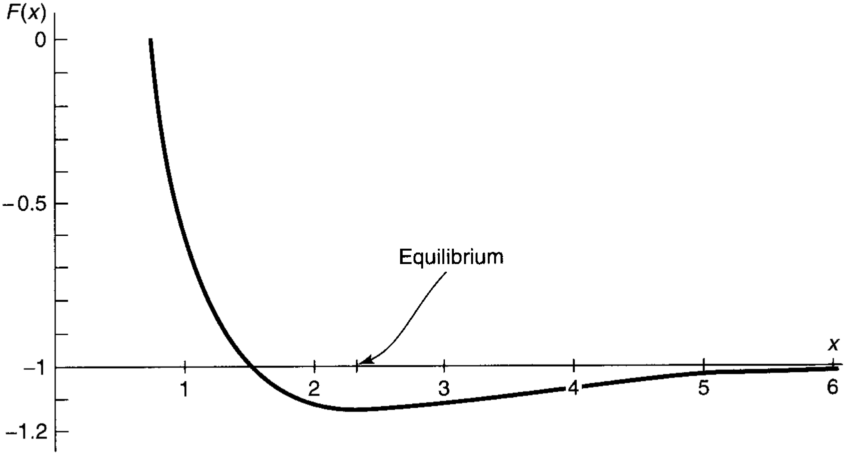

**Figure 7.7:** Plot of the function $F(x)$, Equation 7.51, showing existence of a bound state.

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

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

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.

---

*****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.

---

## FURTHER PROBLEMS FOR CHAPTER 7

**Problem 7.11** 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 7.12** If the photon had a nonzero mass ($m_\gamma \neq 0$), the Coulomb potential would be replaced by a **Yukawa potential**, of the form

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

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 7.13** Suppose you're given a quantum system whose Hamiltonian $H_0$ admits just two eigenstates, $\psi_a$ (with energy $E_a$), and $\psi_b$ (with energy $E_b$). They are orthogonal, normalized, and nondegenerate (assume $E_a$ is the smaller of the two). Now we turn on a perturbation $H'$, with the following matrix elements:

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

**(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

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

where $\phi$ is an adjustable parameter. (Note that writing the linear combination in this way guarantees that $\psi$ is normalized.)

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

---

**Problem 7.14** As an explicit example of the method developed in Problem 7.13, consider an electron at rest in a uniform magnetic field $\mathbf{B} = B_z\hat{k}$, for which the Hamiltonian is (Equation 4.158):

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

The eigenspinors, $\chi_a$ and $\chi_b$, 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:

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

**(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 7.13(b), find the new ground-state energy, in second-order perturbation theory.

**(c)** Using your result in Problem 7.13(c), find the variational principle bound on the ground-state energy.

---

*****Problem 7.15** Although the Schrödinger equation for helium itself cannot be solved exactly, there exist "helium like" systems that do admit exact solutions. A simple example[9] is "rubber-band helium", in which the Coulomb forces are replaced by Hooke's law forces:

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

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

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

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

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

**(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 7.16** 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

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[9] For a more sophisticated model, see R. Crandall, R. Whitnell, and R. Bettega, *Am. J. Phys.* **52**. 438 (1984).

of a bound state for the negative hydrogen ion. Chandrasekhar[10] used a trial wave function of the form

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

where

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

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 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 7.17** 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 "brute force" method is to heat the particles 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.[11]

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[10] S. Chandrasekhar, *Astrophys. J.* **100**, 176 (1944).

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

## CHAPTER 8

# THE WKB APPROXIMATION

The **WKB** (Wentzel, Kramers, Brillouin)[1] method is a technique for obtaining approximate solutions to the time-independent Schrödinger equation in one dimension (the same basic idea can be applied to many other differential equations, and to the radial part of the Schrödinger equation in three dimensions). It is particularly useful in calculating bound-state energies and tunneling rates through potential barriers.

The essential idea is as follows: Imagine a particle of energy $E$ moving through a region where the potential $V(x)$ is *constant.* If $E > V$, the wave function is of the form

$$\psi(x) = Ae^{\pm ikx}, \quad \text{with} \quad k \equiv \sqrt{2m(E-V)}/\hbar.$$

The plus sign indicates that the particle is traveling to the right, and the minus sign means it is going to the left (the general solution, of course, is a linear combination of the two). The wave function is oscillatory, with constant wavelength $\lambda = 2\pi/k$ and constant amplitude $A$. Now suppose that $V(x)$ is *not* constant, but varies rather slowly in comparison to $\lambda$, so that over a region containing many full wavelengths the potential is *essentially* constant. Then it is reasonable to suppose that $\psi$ remains *practically* sinusoidal, except that the wavelength and the amplitude change slowly with $x$. This is the inspiration behind the WKB approximation. In effect, it identifies two different levels of $x$-dependence: rapid oscillations, *modulated* by gradual variation in amplitude and wavelength.

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[1] In Holland it's KWB, in France it's BWK, and in England it's JWKB (for Jeffreys).

By the same token, if $E < V$ (and $V$ is constant), then $\psi$ is exponential:

$$\psi(x) = Ae^{\pm\kappa x}, \quad \text{with} \quad \kappa \equiv \sqrt{2m(V-E)}/\hbar.$$

And if $V(x)$ is *not* constant, but varies slowly in comparison with $1/\kappa$, the solution remains *practically* exponential, except that $A$ and $\kappa$ are now slowly varying functions of $x$.

Now, there is one place where this whole program is bound to fail, and that is in the immediate vicinity of a classical **turning point**, where $E \approx V$. For here $\lambda$ (or $1/\kappa$) goes to infinity, and $V(x)$ can hardly be said to vary "slowly" in comparison. As we shall see, a proper handling of the turning points is the most difficult aspect of the WKB approximation, though the final results are simple to state and easy to implement.

## 8.1 THE "CLASSICAL" REGION

The Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi,$$

can be rewritten in the following way:

$$\frac{d^2\psi}{dx^2} = -\frac{p^2}{\hbar^2}\psi, \qquad [8.1]$$

where

$$p(x) \equiv \sqrt{2m[E - V(x)]} \qquad [8.2]$$

is the classical formula for the momentum of a particle with total energy $E$ and potential energy $V(x)$. For the moment, I'll assume that $E > V(x)$, so that $p(x)$ is *real*; we call this the "classical" region, for obvious reasons—classically the particle is *confined* to this range of $x$ (see Figure 8.1). In general, $\psi$ is some complex function; we can express it in terms of its *amplitude*, $A(x)$, and its *phase*, $\phi(x)$—both of which are *real*:

$$\psi(x) = A(x)e^{i\phi(x)}. \qquad [8.3]$$

Using a prime to denote the derivative with respect to $x$, we find

$$\frac{d\psi}{dx} = (A' + iA\phi')e^{i\phi},$$

and

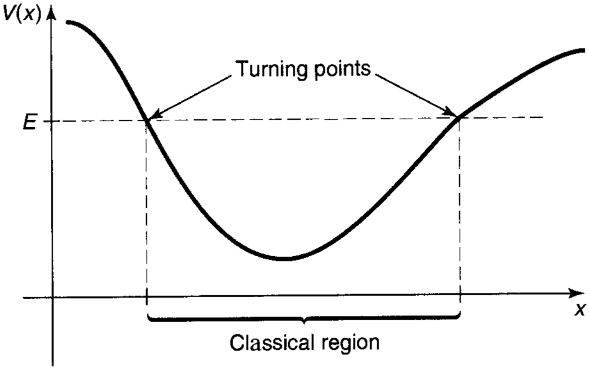

**Figure 8.1:** Classically, the particle is confined to the region where $E \geq V(x)$.

$$\frac{d^2\psi}{dx^2} = [A'' + 2iA'\phi' + iA\phi'' - A(\phi')^2]. \qquad [8.4]$$

Putting this into Equation 8.1,

$$A'' + 2iA'\phi' + iA\phi'' - A(\phi')^2 = -\frac{p^2}{\hbar^2}A. \qquad [8.5]$$

This is equivalent to two *real* equations, one for the real part and one for the imaginary part:

$$A'' - A(\phi')^2 = -\frac{p^2}{\hbar^2}A, \quad \text{or} \quad A'' = A\left[(\phi')^2 - \frac{p^2}{\hbar^2}\right], \qquad [8.6]$$

and

$$2A'\phi' + A\phi'' = 0, \quad \text{or} \quad \left(A^2\phi'\right)' = 0. \qquad [8.7]$$

Equations 8.6 and 8.7 are entirely equivalent to the original Schrödinger equation. The second one is easily solved:

$$A^2\phi' = C^2, \quad \text{or} \quad A = \frac{C}{\sqrt{\phi'}}, \qquad [8.8]$$

where $C$ is a (real) constant. The first one (Equation 8.6) cannot be solved in general—so here comes the approximation: *We assume that the amplitude $A$ varies slowly*, so that the $A''$ term is negligible. (More precisely, we assume that $A''/A$ is much less than both $(\phi')^2$ and $p^2/\hbar^2$.) In that case we can drop the left side of Equation 8.6, and we are left with

$$(\phi')^2 = \frac{p^2}{\hbar^2}, \quad \text{or} \quad \frac{d\phi}{dx} = \pm\frac{p}{\hbar},$$

and therefore

$$\phi(x) = \pm\frac{1}{\hbar}\int p(x)\,dx. \qquad [8.9]$$

(I'll write this as an *indefinite* integral, for now—any constant of integration can be absorbed into $C$, which thereby becomes complex.) It follows, then, that

$$\boxed{\psi(x) \cong \frac{C}{\sqrt{p(x)}}e^{\pm\frac{i}{\hbar}\int p(x)\,dx},} \qquad [8.10]$$

and the general (approximate) solution will be a linear combination of two such terms, one with each sign.

Notice that

$$|\psi(x)|^2 \cong \frac{|C|^2}{p(x)}, \qquad [8.11]$$

which says that the probability of finding the particle at point $x$ is inversely proportional to its (classical) momentum (and hence its velocity) at that point. This is exactly what you would expect—the particle doesn't spend long in the places where it is moving rapidly, so the probability of getting caught there is small. In fact, the WKB approximation is sometimes *derived* by starting with this "semiclassical" observation, instead of by dropping the $A''$ term in the differential equation. The latter approach is cleaner mathematically, but the former offers a more plausible physical rationale.

---

**Example: Potential well with two vertical walls.** Suppose we have an infinite square well with a bumpy bottom (Figure 8.2):

$$V(x) = \begin{cases} \text{some specified function}, & \text{if } 0 < x < a, \\ \infty, & \text{otherwise}. \end{cases} \qquad [8.12]$$

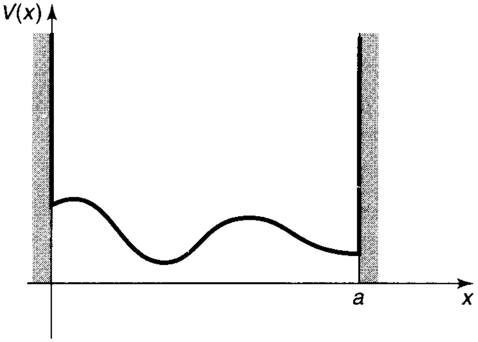

**Figure 8.2:** Infinite square well with a bumpy bottom.

Inside the well [assuming $E > V(x)$ throughout] we have

$$\psi(x) \cong \frac{1}{\sqrt{p(x)}}\left[C_+ e^{i\phi(x)} + C_- e^{-i\phi(x)}\right],$$

or, more conveniently,

$$\psi(x) \cong \frac{1}{\sqrt{p(x)}}\left[C_1 \sin\phi(x) + C_2 \cos\phi(x)\right], \qquad [8.13]$$

where (exploiting the freedom noted earlier to impose a convenient lower limit on the integral)

$$\phi(x) = \frac{1}{\hbar}\int_0^x p(x')\,dx'. \qquad [8.14]$$

Now $\psi(x)$ must go to zero at $x = 0$, so, since $\phi(0) = 0$, $C_2 = 0$. Also, $\psi(x)$ goes to zero at $x = a$, so

$$\phi(a) = n\pi \quad (n = 1, 2, 3 \ldots). \qquad [8.15]$$

Conclusion:

$$\boxed{\int_0^a p(x)\,dx = n\pi\hbar.} \qquad [8.16]$$

This quantization condition is our main result; it determines the (approximate) allowed energies.

For instance, if the well has a *flat* bottom [$V(x) = 0$], then $p(x) = \sqrt{2mE}$ (a constant), and Equation 8.16 says $pa = n\pi\hbar$, or

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2},$$

which are precisely the energy levels of the original infinite square well (Equation 2.23). In this case the WKB approximation yields the *exact* answer (the amplitude of the true wave function is *constant*, so dropping $A''$ cost us nothing).

---

***Problem 8.1** Use the WKB approximation to find the allowed energies ($E_n$) of an infinite square well with a "shelf", of height $V_0$, extending half-way across (see Figure 6.3):

$$V(x) = \begin{cases} V_0, & \text{if } 0 < x < a/2, \\ 0, & \text{if } a/2 < x < a, \\ \infty, & \text{otherwise.} \end{cases}$$

Express your answer in terms of $V_0$ and $E_n^0 \equiv (n\pi\hbar)^2/2ma^2$ (the $n$th allowed energy for the "unperturbed" infinite square well, with *no* shelf). Assume that $E_1^0 > V_0$, but do *not* assume that $E_n \gg V_0$. Compare your result with what we got in Section 6.1.2, using first-order perturbation theory. Note that they are in agreement if either $V_0$ is very small (the perturbation theory regime) or $n$ is very large (the semiclassical WKB regime).

---

****Problem 8.2** An illuminating alternative derivation of the WKB formula (Equation 8.10) is based on an expansion in powers of $\hbar$. Motivated by the free particle wave function, $\psi = A\exp(\pm ipx/\hbar)$, we write

$$\psi(x) = e^{if(x)/\hbar},$$

where $f(x)$ is some *complex* function. (Note that there is no loss of generality here—*any* nonzero function can be written in this way.)

**(a)** Put this into Schrödinger's equation (in the form of Equation 8.1), and show that

$$i\hbar f'' - (f')^2 + p^2 = 0.$$

**(b)** Write $f(x)$ as a power series in $\hbar$:

$$f(x) = f_0(x) + \hbar f_1(x) + \hbar^2 f_2(x) + \cdots,$$

and, collecting like powers of $\hbar$, show that

$$(f_0')^2 = p^2, \quad if_0'' = 2f_0'f_1', \quad if_1'' = 2f_0'f_2' + (f_1')^2, \quad \text{etc.}$$

**(c)** Solve for $f_0(x)$ and $f_1(x)$, and show that—to first order in $\hbar$—you recover Equation 8.10.

*Note*: The logarithm of a negative number is defined by $\ln(-z) = \ln(z) + in\pi$, where $n$ is an odd integer. If this formula is new to you, try exponentiating both sides, and you'll see where it comes from.

## 8.2 TUNNELING

So far, I have assumed that $E > V$, so that $p(x)$ is real. But we can easily write down the corresponding result in the *non*classical region ($E < V$)—it's the same as before (Equation 8.10), only now $p(x)$ is *imaginary*[2]:

$$\boxed{\psi(x) \cong \frac{C}{\sqrt{|p(x)|}} e^{\pm\frac{1}{\hbar}\int |p(x)|\,dx}.} \tag{8.17}$$

Consider, for example, the problem of scattering from a rectangular barrier with a bumpy top (Figure 8.3). To the left of the barrier ($x < 0$),

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \tag{8.18}$$

where $A$ is the incident amplitude, $B$ is the reflected amplitude, and $k \equiv \sqrt{2mE}/\hbar$ (see Section 2.7). To the right of the barrier ($x > a$),

$$\psi(x) = Fe^{ikx}; \tag{8.19}$$

$F$ is the transmitted amplitude, and the tunneling probability is

$$T = \frac{|F|^2}{|A|^2}. \tag{8.20}$$

In the tunneling region ($0 \leq x \leq a$), the WKB approximation gives

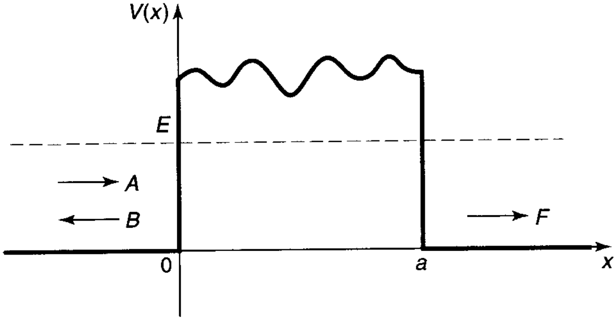

**Figure 8.3:** Scattering from a rectangular barrier with a bumpy top.

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[2] In this case the wave function is *real*, and the analogs to Equations 8.6 and 8.7 do not follow *necessarily* from Equation 8.5, although they are still *sufficient*. If this bothers you, study the alternative derivation in Problem 8.2.

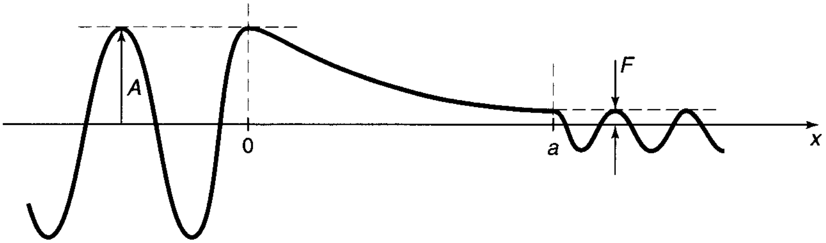

**Figure 8.4:** Qualitative structure of the wave function, for scattering from a high, broad barrier.

$$\psi(x) \cong \frac{C}{\sqrt{|p(x)|}} e^{\frac{1}{\hbar}\int_0^x |p(x')|\,dx'} + \frac{D}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_0^x |p(x')|\,dx'}. \tag{8.21}$$

But if the barrier is very high and/or very wide (which is to say, if the probability of tunneling is small), then the coefficient of the exponentially *increasing* term ($C$) must be small (in fact, it would be *zero* if the barrier were *infinitely* broad), and the wave function looks something like[3] Figure 8.4. The relative amplitudes of the incident and transmitted waves are determined essentially by the total decrease of the exponential over the nonclassical region:

$$\frac{|F|}{|A|} \sim e^{-\frac{1}{\hbar}\int_0^a |p(x')|\,dx'},$$

so that

$$\boxed{T \cong e^{-2\gamma}, \quad \text{with} \quad \gamma \equiv \frac{1}{\hbar}\int_0^a |p(x)|\,dx.} \tag{8.22}$$

---

**Example: Gamow's theory of alpha decay.** In 1928, George Gamow (and, independently, Condon and Gurney) used this result to provide the first theoretical account of alpha decay (the spontaneous emission of an alpha particle—two protons and two neutrons—by certain radioactive nuclei). Since the alpha particle carries a positive charge ($2e$), it will be electrically repelled by the leftover nucleus (charge $Ze$) as soon as it gets far enough away to escape the nuclear binding force. Gamow pictured the potential energy curve for the alpha particle as a finite square well (representing the attractive nuclear force), extending out to $r_1$ (the radius of the nucleus), joined to a repulsive Coulombic tail (Figure 8.5). If $E$ is the energy of the emitted alpha particle, the outer turning point ($r_2$) is determined by

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[3] This heuristic argument can be made more rigorous—see Problem 8.10.

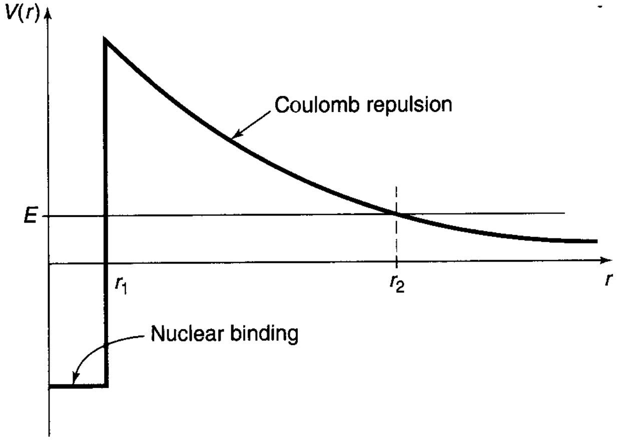

**Figure 8.5:** Gamow's model for the potential energy of an alpha particle in a radioactive nucleus.

$$\frac{1}{4\pi\epsilon_0}\frac{2Ze^2}{r_2} = E. \qquad [8.23]$$

The exponent $\gamma$ (Equation 8.22) is evidently[4]

$$\gamma = \frac{1}{\hbar}\int_{r_1}^{r_2}\sqrt{2m\left(\frac{1}{4\pi\epsilon_0}\frac{2Ze^2}{r} - E\right)}\,dr = \frac{\sqrt{2mE}}{\hbar}\int_{r_1}^{r_2}\sqrt{\frac{r_2}{r} - 1}\,dr$$

$$= \frac{\sqrt{2mE}}{\hbar}\left[r_2\cos^{-1}\sqrt{r_1/r_2} - \sqrt{r_1(r_2 - r_1)}\right]. \qquad [8.24]$$

Typically, $r_1 \ll r_2$, and we can simplify this result. The argument of the inverse cosine is close to zero, so the angle itself is close to $\pi/2$. Call it $\theta = (\pi/2) - \epsilon$; then

$$\cos\theta = \cos(\pi/2)\cos\epsilon + \sin(\pi/2)\sin\epsilon \cong \sin\epsilon \cong \epsilon,$$

and hence

$$\cos^{-1}\sqrt{\frac{r_1}{r_2}} \cong \frac{\pi}{2} - \sqrt{\frac{r_1}{r_2}}.$$

---

[4] In this case the potential does not drop to zero on both sides of the barrier (moreover, this is really a three-dimensional problem), but the essential inspiration, contained in Equation 8.22, is all we really need.

Thus

$$\gamma \cong \frac{\sqrt{2mE}}{\hbar}\left[\frac{\pi}{2}r_2 - 2\sqrt{r_1 r_2}\right] = K_1\frac{Z}{\sqrt{E}} - K_2\sqrt{Zr_1}, \qquad [8.25]$$

where

$$K_1 \equiv \left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{\pi\sqrt{2m}}{\hbar} = 1.980\,\mathrm{MeV}^{1/2}, \qquad [8.26]$$

and

$$K_2 \equiv \left(\frac{e^2}{4\pi\epsilon_0}\right)^{1/2}\frac{4\sqrt{m}}{\hbar} = 1.485\,\mathrm{fm}^{-1/2}. \qquad [8.27]$$

(One fermi, fm, is $10^{-15}$ m, which is about the size of a typical nucleus.)

If we imagine the alpha particle rattling around inside the nucleus, with an average velocity $v$, the average time between "collisions" with the "wall" is about $2r_1/v$, and hence the *frequency* of collisions is $v/2r_1$. The probability of escape at each collision is $e^{-2\gamma}$, so the probability of emission, per unit time, is $(v/2r_1)e^{-2\gamma}$, and hence the **lifetime** of the parent nucleus is about

$$\tau = \frac{2r_1}{v}e^{2\gamma}. \qquad [8.28]$$

Unfortunately, we don't know $v$—but it hardly matters, for the exponential factor varies over a *fantastic* range (25 orders of magnitude) as we go from one radioactive nucleus to another; relative to this the variation in $v$ is pretty insignificant. In particular, if you plot the *logarithm* of the experimentally measured lifetime against $1/\sqrt{E}$ (related to $\gamma$ by Equation 8.25), the result is a beautiful straight line (Figure 8.6), confirming that the lifetime of an alpha emitter is governed by the difficulty of penetrating the Coulomb barrier.

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∗**Problem 8.3** Use Equation 8.22 to calculate the approximate transmission probability for a particle of energy $E$ that encounters a finite square barrier of height $V_0 > E$ and width $2a$. Compare the exact result (Prob. 2.32) in the WKB regime $T \ll 1$.

---

∗∗**Problem 8.4** Calculate the lifetimes of $U^{238}$ and $Po^{212}$, using Equation 8.28, with Equation 8.25 for $\gamma$. *Hint*: The density of nuclear matter is relatively constant (i.e., the same for all nuclei), so $(r_1)^3$ is proportional to $A$ (the number of neutrons plus protons). Empirically,

$$r_1 \cong (1.07\ \mathrm{fm})A^{1/3}. \qquad [8.29]$$

The energy of the emitted alpha particle is determined by Einstein's formula ($E = mc^2$):

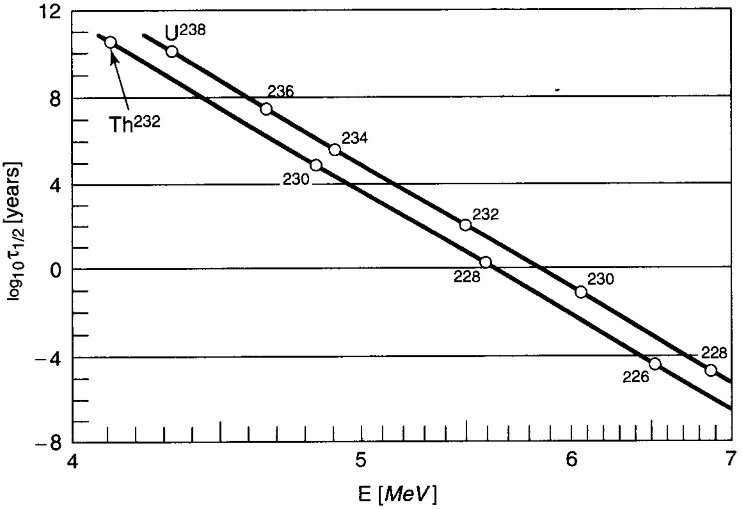

**Figure 8.6:** Graph of the logarithm of the lifetime versus $1/\sqrt{E}$, for several alpha emitters. From David Park, *Introduction to the Quantum Theory*, 3rd ed. (New York: McGraw-Hill, 1992). (See acknowledgment in Preface.)

$$E = m_p c^2 - m_d c^2 - m_\alpha c^2, \qquad [8.30]$$

where $m_p$ is the mass of the parent nucleus, $m_d$ is the mass of the daughter nucleus, and $m_\alpha$ is the mass of the alpha particle (which is to say, the $He^4$ nucleus). To figure out what the daughter nucleus is, note that the alpha particle carries off two protons and two neutrons, so $Z$ decreases by 2 and $A$ by 4. Look up the relevant nuclear masses. To estimate $v$, use $E = (1/2)m_\alpha v^2$; this ignores the (negative) potential energy inside the nucleus, and surely *underestimates* $v$, but it's about the best we can do at this stage. Incidentally, the experimental lifetimes are $6 \times 10^9$ years and 0.5 $\mu$s, respectively.

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## 8.3 THE CONNECTION FORMULAS

In the discussion so far I have assumed that the "walls" of the potential well (or the barrier) are *vertical*, so that the "exterior" solution is simple and the boundary conditions trivial. As it turns out, our main results (Equations 8.16 and 8.22) are reasonably accurate even when the edges are not so abrupt (indeed, in Gamow's theory they were applied to just such a case). Nevertheless, it is of some interest to study more closely what happens to the wave function at a turning point ($E = V$), where the "classical" region joins the "nonclassical" region and the WKB approximation itself breaks down. In this section I'll treat the bound-state problem (Figure 8.1); you get to do the scattering problem for yourself (Problem 8.10).[5]

For simplicity, let's shift the axes over so that the right-hand turning point occurs at $x = 0$ (Figure 8.7). In the WKB approximation, we have

$$\psi(x) \cong \begin{cases} \frac{1}{\sqrt{p(x)}}\left[Be^{\frac{i}{\hbar}\int_x^0 p(x')\,dx'} + Ce^{-\frac{i}{\hbar}\int_x^0 p(x')\,dx'}\right], & \text{if } x < 0, \\ \frac{1}{\sqrt{|p(x)|}}De^{-\frac{1}{\hbar}\int_0^x |p(x')|\,dx'}, & \text{if } x > 0. \end{cases} \qquad [8.31]$$

[Assuming that $V(x)$ remains greater than $E$ for *all* $x > 0$, we can exclude the positive exponent in this region, because it blows up as $x \to \infty$.] Our task is to join the two solutions at the boundary. But there is a serious difficulty here: In the WKB approximation, $\psi$ goes to *infinity* at the turning point, where $p(x) \to 0$. The *true* wave function, of course, has no such wild behavior—as anticipated, the WKB method simply fails in the vicinity of a turning point. And yet, it is precisely the boundary conditions at the turning points that determine the allowed energies. What we need to do, then, is *splice* the two WKB solutions together, using a "patching" wave function that straddles the turning point.

Since we only need the patching wave function ($\psi_p$) in the neighborhood of the origin, we'll *approximate the potential by a straight line*:

$$V(x) \cong E + V'(0)x, \qquad [8.32]$$

and solve the Schrödinger for this linearized $V$:

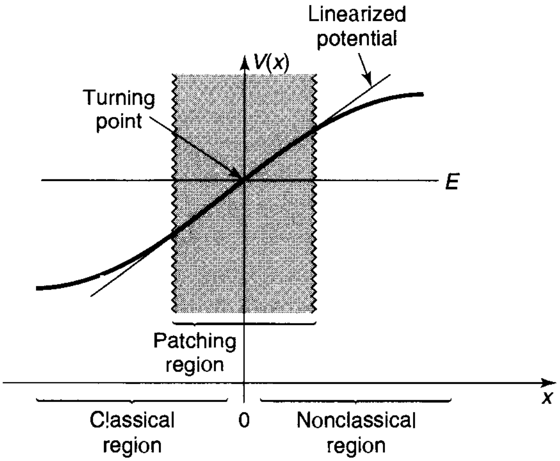

**Figure 8.7:** Enlarged view of the right-hand turning point.

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[5] *Warning:* The following argument is quite technical, and you may wish to skip it on a first reading.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_p}{dx^2}+(E+V'(0)x)\psi_p=E\psi_p,$$

or

$$\frac{d^2\psi_p}{dx^2}=\alpha^3x\psi_p, \tag{8.33}$$

where

$$\alpha\equiv\left[\frac{2m}{\hbar^2}V'(0)\right]^{1/3}. \tag{8.34}$$

The $\alpha$'s can be absorbed into the independent variable by defining

$$z\equiv\alpha x, \tag{8.35}$$

so that

$$\frac{d^2\psi_p}{dz^2}=z\psi_p. \tag{8.36}$$

This is **Airy's equation**, and the solutions are called **Airy functions**.[6] Since the Airy equation is a second-order differential equation, there are two linearly independent

**Table 8.1:** Some properties of the Airy functions.

| | |
|---|---|
| *Differential Equation:* | $\frac{d^2y}{dz^2}=zy.$ |
| *Solutions:* | Linear combinations of Airy Functions, $Ai(z)$ and $Bi(z)$. |
| *Integral Representation:* | $Ai(z)=\frac{1}{\pi}\int_0^\infty\cos\left(\frac{s^3}{3}+sz\right)ds$<br>$Bi(z)=\frac{1}{\pi}\int_0^\infty\left[e^{-\frac{s^3}{3}+sz}+\sin\left(\frac{s^3}{3}+sz\right)\right]ds$ |
| *Asymptotic Forms:* | |
| $\left.\begin{array}{l}Ai(z)\sim\frac{1}{2\sqrt{\pi}\,z^{1/4}}e^{-\frac{2}{3}z^{3/2}}\\ Bi(z)\sim\frac{1}{\sqrt{\pi}\,z^{1/4}}e^{\frac{2}{3}z^{3/2}}\end{array}\right\}z\gg 0$ | $\left.\begin{array}{l}Ai(z)\sim\frac{1}{\sqrt{\pi}(-z)^{1/4}}\sin\left[\frac{2}{3}(-z)^{3/2}+\frac{\pi}{4}\right]\\ Bi(z)\sim\frac{1}{\sqrt{\pi}(-z)^{1/4}}\cos\left[\frac{2}{3}(-z)^{3/2}+\frac{\pi}{4}\right]\end{array}\right\}z\ll 0$ |

---

[6] *Classically*, a linear potential means a constant force, and hence a constant acceleration—the simplest nontrivial motion possible, and the *starting* point for elementary mechanics. It is ironic that the same potential in *quantum* mechanics gives rise to unfamiliar transcendental functions, and plays only a peripheral role in the theory.

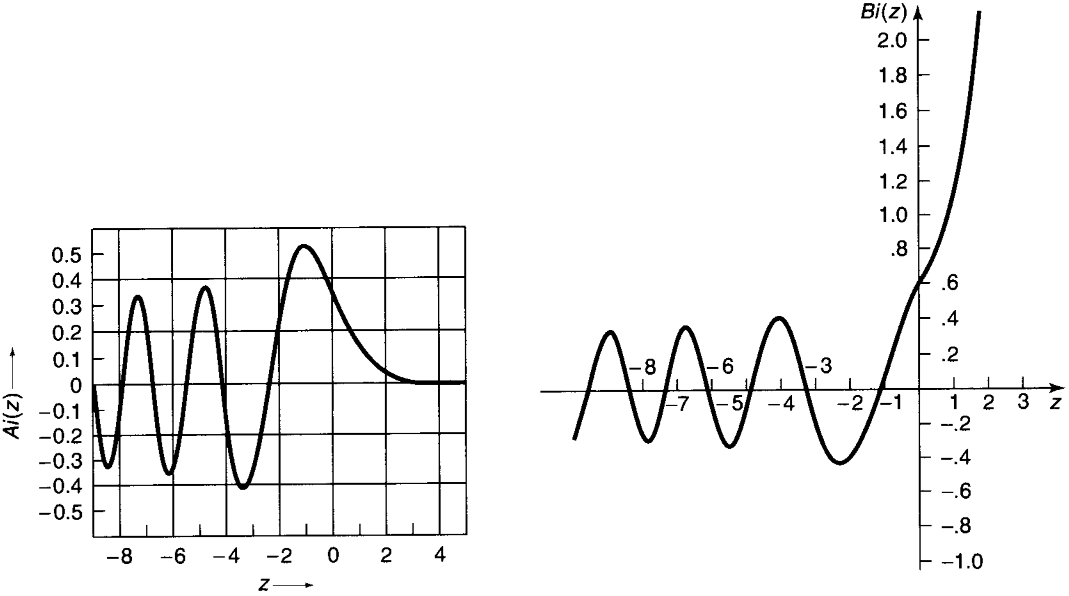

**Figure 8.8:** Graph of the Airy functions.

Airy functions, $Ai(z)$ and $Bi(z)$; the general solution is a linear combination of these. $Ai$ and $Bi$ are related to Bessel functions of order 1/3; some of their properties are listed in Table 8.1 and they are plotted in Figure 8.8. Evidently the patching wave function is

$$\psi_p(x) = aAi(\alpha x) + bBi(\alpha x), \qquad [8.37]$$

for appropriate constants $a$ and $b$.

Now $\psi_p$ is the (approximate) wave function in the neighborhood of the origin; our job is to match it to the WKB solutions in the overlap regions on either side (see Figure 8.9). These overlap zones are close enough to the turning point that the linearized potential is reasonably accurate (so that $\psi_p$ is a good approximation to the true wave function), and yet far enough away from the turning point that the WKB approximation is reliable.[7] In the overlap regions Equation 8.32 holds, and therefore (in the notation of Equation 8.34)

$$p(x) \cong \sqrt{2m(E - E - V'(0)x)} = \hbar\alpha^{3/2}\sqrt{-x}. \qquad [8.38]$$

In particular, in overlap region 2,

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[7] This is a delicate double constraint, and it is possible to concoct potentials so pathological that no such overlap region exists. However, in practical applications this seldom occurs. See Problem 8.8.

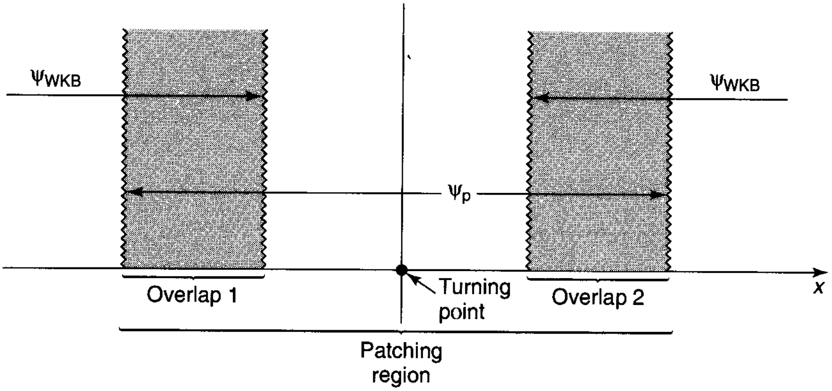

**Figure 8.9:** Patching region and the two overlap zones.

$$\int_0^x |p(x')|\, dx' \cong \hbar\alpha^{3/2} \int_0^x \sqrt{x'}\, dx' = \frac{2}{3}\hbar(\alpha x)^{3/2},$$

and therefore the WKB wave function (Equation 8.31) can be written as

$$\psi(x) \cong \frac{D}{\sqrt{\hbar}\alpha^{3/4}x^{1/4}} e^{-\frac{2}{3}(\alpha x)^{3/2}}. \qquad [8.39]$$

Meanwhile, using the large-$z$ asymptotic forms[8] of the Airy functions (from Table 8.1), the patching wave function (Equation 8.37) in overlap region 2 becomes

$$\psi_p(x) \cong \frac{a}{2\sqrt{\pi}(\alpha x)^{1/4}} e^{-\frac{2}{3}(\alpha x)^{3/2}} + \frac{b}{\sqrt{\pi}(\alpha x)^{1/4}} e^{\frac{2}{3}(\alpha x)^{3/2}}. \qquad [8.40]$$

Comparing the two solutions, we see that

$$a = \sqrt{\frac{4\pi}{\alpha\hbar}}\, D, \quad \text{and} \quad b = 0. \qquad [8.41]$$

Now we go back and repeat the procedure for overlap region 1. Once again, $p(x)$ is given by Equation 8.38, but this time $x$ is *negative*, so

$$\int_x^0 p(x')\, dx' \cong \frac{2}{3}\hbar(-\alpha x)^{3/2} \qquad [8.42]$$

and the WKB wave function (Equation 8.31) is

---

[8] At first glance it seems absurd to use a *large-z* approximation in this region, which after all is supposed to be reasonably close to the turning point at $z = 0$ (so that the linear approximation to the potential is valid). But notice that the argument here is $\alpha x$, and if you study the matter carefully (see Problem 8.8) you will find that there *is* (typically) a region in which $\alpha x$ is large, but at the same time it is reasonable to approximate $V(x)$ by a straight line.

$$\psi(x) \cong \frac{1}{\sqrt{\hbar}\alpha^{3/4}(-x)^{1/4}}\left[Be^{i\frac{2}{3}(-\alpha x)^{3/2}} + Ce^{-i\frac{2}{3}(-\alpha x)^{3/2}}\right]. \qquad [8.43]$$

Meanwhile, using the asymptotic form of the Airy function for large *negative* $z$ (Table 8.1), the patching function (Equation 8.37, with $b = 0$) reads

$$\psi_p(x) \cong \frac{a}{\sqrt{\pi}(-\alpha x)^{1/4}} \sin\left[\frac{2}{3}(-\alpha x)^{3/2} + \frac{\pi}{4}\right]$$

$$= \frac{a}{\sqrt{\pi}(-\alpha x)^{1/4}}\frac{1}{2i}\left[e^{i\pi/4}e^{i\frac{2}{3}(-\alpha x)^{3/2}} - e^{-i\pi/4}e^{-i\frac{2}{3}(-\alpha x)^{3/2}}\right]. \qquad [8.44]$$

Comparing the WKB and patching wave functions in overlap region 1, we find

$$\frac{a}{2i\sqrt{\pi}}e^{i\pi/4} = \frac{B}{\sqrt{\hbar\alpha}} \quad \text{and} \quad \frac{-a}{2i\sqrt{\pi}}e^{-i\pi/4} = \frac{C}{\sqrt{\hbar\alpha}},$$

or, putting in Equation 8.41 for $a$,

$$B = -ie^{i\pi/4}D, \quad \text{and} \quad C = ie^{-i\pi/4}D. \qquad [8.45]$$

These are the so-called **connection formulas**, joining the WKB solutions at either side of the turning point. We're done with the patching wave function now—its only purpose was to bridge the gap. Expressing everything in terms of the one normalization constant $D$, and shifting the turning point back from the origin to an arbitrary point $x_2$, the WKB wave function (Equation 8.31) becomes

$$\psi(x) \cong \begin{cases} \frac{2D}{\sqrt{p(x)}}\sin\left[\frac{1}{\hbar}\int_x^{x_2} p(x')\,dx' + \frac{\pi}{4}\right], & \text{if } x < x_2; \\ \frac{D}{\sqrt{|p(x)|}}e^{-\frac{1}{\hbar}\int_{x_2}^{x}|p(x')|\,dx'}, & \text{if } x > x_2. \end{cases} \qquad [8.46]$$

**Example: Potential well with one vertical wall.** Imagine a potential well that has one vertical side (at $x = 0$) and one sloping side (Figure 8.10). In this case $\psi(0) = 0$, so Equation 8.46 says

$$\frac{1}{\hbar}\int_0^{x_2} p(x)\,dx + \frac{\pi}{4} = n\pi, \quad (n = 1, 2, 3, \ldots),$$

or

$$\boxed{\int_0^{x_2} p(x)\,dx = \left(n - \frac{1}{4}\right)\pi\hbar.} \qquad [8.47]$$

For instance, consider the "half-harmonic oscillator",

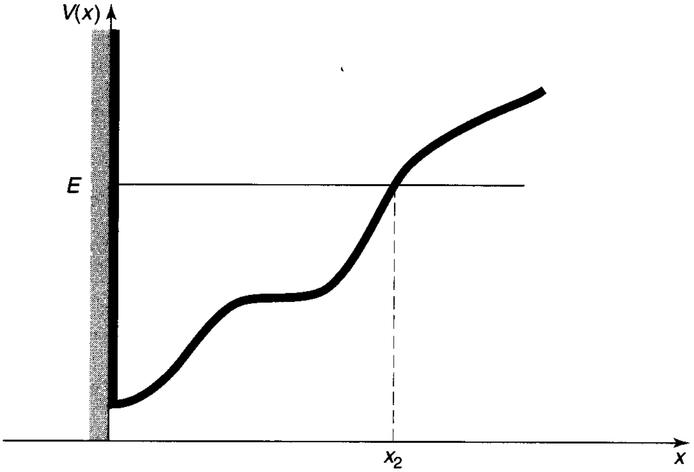

**Figure 8.10:** Potential well with one vertical wall.

$$V(x) = \begin{cases} \frac{1}{2}m\omega^2x^2, & \text{if } x > 0, \\ 0, & \text{otherwise.} \end{cases} \qquad [8.48]$$

In this case

$$p(x) = \sqrt{2m[E - (1/2)m\omega^2x^2]} = m\omega\sqrt{x_2^2 - x^2},$$

where

$$x_2 = \frac{1}{\omega}\sqrt{\frac{2E}{m}}$$

is the turning point. So

$$\int_0^{x_2} p(x)\,dx = m\omega\int_0^{x_2}\sqrt{x_2^2 - x^2}\,dx = \frac{\pi}{4}m\omega x_2^2 = \frac{\pi E}{2\omega},$$

and the quantization condition Equation 8.47 yields

$$E_n = \left(2n - \frac{1}{2}\right)\hbar\omega = \left(\frac{3}{2}, \frac{7}{2}, \frac{11}{2}, \ldots\right)\hbar\omega. \qquad [8.49]$$

In this particular case the WKB approximation actually delivers the *exact* allowed energies (which are precisely the *odd* energies of the *full* harmonic oscillator—see Problem 2.38).

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**Example: Potential well with no vertical walls.** Equation 8.46 connects the WKB wave functions at a turning point where the potential slopes *upward*

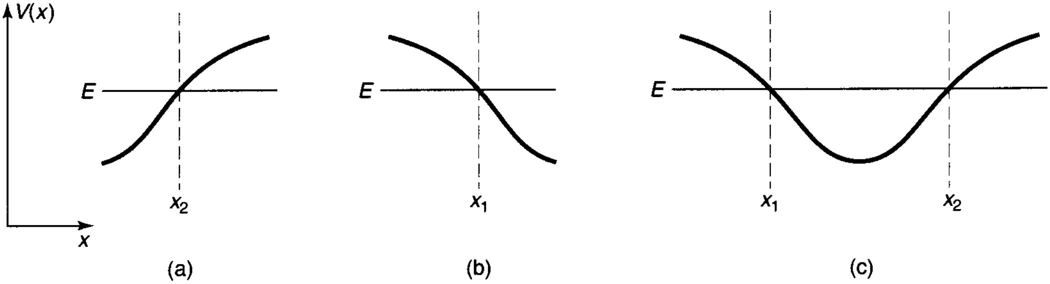

**Figure 8.11:** Upward-sloping and downward-sloping turning points.

(Figure 8.11a); the same reasoning, applied to a *downward*-sloping turning point (Figure 8.11b), yields (Problem 8.9)

$$\psi(x) \cong \begin{cases} \dfrac{D'}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_x^{x_1} |p(x')|\,dx'}, & \text{if } x < x_1; \\ \dfrac{2D'}{\sqrt{p(x)}} \sin\left[\dfrac{1}{\hbar}\displaystyle\int_{x_1}^{x} p(x')\,dx' + \dfrac{\pi}{4}\right], & \text{if } x > x_1. \end{cases} \qquad [8.50]$$

In particular, if we're talking about a potential *well* (Figure 8.11c), the wave function in the "interior" region ($x_1 < x < x_2$) can be written *either* as

$$\psi(x) \cong \frac{2D}{\sqrt{p(x)}} \sin\theta_2(x), \quad \text{where} \quad \theta_2(x) \equiv \frac{1}{\hbar}\int_x^{x_2} p(x')\,dx' + \frac{\pi}{4}$$

(Equation 8.46), *or* as

$$\psi(x) \cong \frac{-2D'}{\sqrt{p(x)}} \sin\theta_1(x), \quad \text{where} \quad \theta_1(x) \equiv -\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' - \frac{\pi}{4}$$

(Equation 8.50). Evidently the arguments of the sine functions must be equal, modulo $\pi$:[9] $\theta_2 = \theta_1 + n\pi$, from which it follows that

$$\boxed{\int_{x_1}^{x_2} p(x)\,dx = \left(n - \frac{1}{2}\right)\pi\hbar, \quad \text{with} \quad n = 1,\ 2,\ 3, \ldots} \qquad [8.51]$$

This quantization condition determines the allowed energies for the "typical" case of a potential well with two sloping sides. Notice that it differs from the formulas

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[9] *Not* $2\pi$—an overall minus sign can be absorbed into the normalization factors $D$ and $D'$.

for two vertical walls (Equation 8.16) or one vertical wall (Equation 8.47) only in the number that is subtracted from $n$ (0, 1/4, or 1/2). Since the WKB approximation works best in the semiclassical (large $n$) regime, the distinction is more in appearance than in substance. In any event, the result is extraordinarily powerful, for it enables us to calculate (approximate) allowed energies *without ever solving the Schrödinger equation*, by simply evaluating one integral. The wave function itself has dropped out of sight.

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****Problem 8.5** Consider the quantum mechanical analog to the classical problem of a ball (mass $m$) bouncing elastically on the floor.

**(a)** What is the potential energy, as a function of height $x$ above the floor? (For negative $x$, the potential is *infinite*—the ball can't get there at all.)

**(b)** Solve the Schrödinger equation for this potential, expressing your answer in terms of the appropriate Airy function [note that $Bi(z)$ blows up for large $z$, and hence does not yield a normalizable wave function]. Don't bother to normalize $\psi(x)$.

**(c)** Using $g = 9.80$ m/s$^2$ and $m = 0.100$ kg, find the first four allowed energies, in Joules, correct to three significant digits. *Hint*: see Milton Abromowitz and Irene A. Stegun, *Handbook of Mathematical Functions* (New York: Dover 1970), page 478; the notation is defined on page 450.

**(d)** What is the ground state energy, in eV, of an *electron* in this gravitational field? How high off the ground is this electron, on the average? *Hint*: Use the virial theorem to determine $\langle x \rangle$.

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***Problem 8.6** Analyze the bouncing ball (Problem 8.5) using the WKB approximation.

**(a)** Find the allowed energies $E_n$ in terms of $m$, $g$, and $\hbar$.

**(b)** Now put in the particular values given in Problem 8.5(c), and compare the WKB approximation to the first four energies with the "exact" results.

**(c)** About how large would the quantum number $n$ have to be to give the ball an average height of, say, 1 meter above the ground?

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***Problem 8.7** Use the WKB approximation to find the allowed energies of the harmonic oscillator.

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**Problem 8.8** Consider a particle of mass $m$ in the $n$th stationary state of the harmonic oscillator (angular frequency $\omega$).

**(a)** Find the turning point $x_2$.

**(b)** How far ($d$) could you go *above* the turning point before the error in the linearized potential (Equation 8.32, but with the turning point at $x_2$) reaches 1%? That is, if

$$\frac{V(x_2+d)-V_{\text{lin}}(x_2+d)}{V(x_2)} = 0.01,$$

what is $d$?

**(c)** The asymptotic form of $Ai(z)$ is accurate to 1% as long as $z \geq 5$. For the $d$ in part (b), determine the smallest $n$ such that $\alpha d \geq 5$. (For any $n$ larger than this, there exists an overlap region in which the linearized potential is good to 1% *and* the large-$z$ form of the Airy function is good to 1%.)

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$**$**Problem 8.9** Derive the connection formulas at a downward-sloping turning point, and confirm Equation 8.50.

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$***$**Problem 8.10** Use appropriate connection formulas to analyse the problem of scattering from a barrier with sloping walls (Figure 8.12). Begin by writing the WKB wave function in the form

$$\psi(x) \cong \begin{cases} \frac{1}{\sqrt{p(x)}}\left[Ae^{\frac{i}{\hbar}\int_x^{x_1} p(x')\,dx'} + Be^{-\frac{i}{\hbar}\int_x^{x_1} p(x')\,dx'}\right], & (x < x_1); \\ \frac{1}{\sqrt{|p(x)|}}\left[Ce^{\frac{1}{\hbar}\int_{x_1}^{x} |p(x')|\,dx'} + De^{-\frac{1}{\hbar}\int_{x_1}^{x} |p(x')|\,dx'}\right], & (x_1 < x < x_2); \\ \frac{1}{\sqrt{p(x)}}\left[Fe^{\frac{i}{\hbar}\int_{x_2}^{x} p(x')\,dx'}\right], & (x > x_2). \end{cases} \qquad [8.52]$$

Do *not* assume $C = 0$. Calculate the tunneling probability, $T = |F|^2/|A|^2$, and show that your result reduces to Equation 8.22 in the case of a broad, high barrier.

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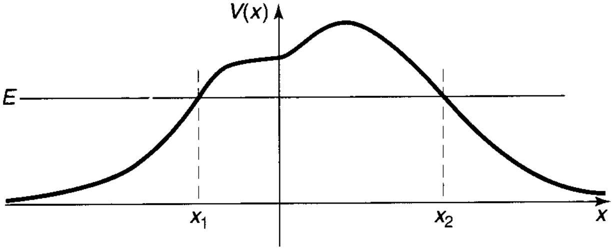

**Figure 8.12:** Barrier with sloping walls.

## FURTHER PROBLEMS FOR CHAPTER 8

****Problem 8.11** Use the WKB approximation to find the allowed energies of the general power-law potential:

$$V(x) = \alpha |x|^{\nu},$$

where $\nu$ is a positive number. Check your result for the case $\nu = 2$. *Answer:*

$$E_n = \alpha \left[ (n - 1/2)\hbar \sqrt{\frac{\pi}{2m\alpha}} \frac{\Gamma\left(\frac{1}{\nu} + \frac{3}{2}\right)}{\Gamma\left(\frac{1}{\nu} + 1\right)} \right]^{\left(\frac{2\nu}{\nu+2}\right)}. \qquad [8.53]$$

****Problem 8.12** Use the WKB approximation to find the bound-state energy for the potential in Problem 2.48. Compare the exact answer. *Answer:*

$$-[(9/8) - (1/\sqrt{2})]\hbar^2 a^2/m.$$

**Problem 8.13** For spherically symmetrical potentials, we can apply the WKB approximation to the radial equation, (Equation 4.37). In the case $l = 0$, it is reasonable[10] to use Equation 8.47 in the form

$$\int_0^{r_0} p(r)\, dr = (n - 1/4)\pi\hbar, \qquad [8.54]$$

where $r_0$ is the turning point (in effect, we treat $r = 0$ as an infinite wall). Apply this formula to estimate the allowed energies of a particle in the logarithmic potential

$$V(r) = V_0 \ln(r/a)$$

(for constants $V_0$ and $a$). Treat only the case $l = 0$. Show that the spacing between the levels is independent of mass. *Partial answer:*

$$E_{n+1} - E_n = V_0 \ln\left(\frac{n + 3/4}{n - 1/4}\right).$$

****Problem 8.14** Use the WKB approximation in the form

$$\int_{r_1}^{r_2} p(r)\, dr = (n - 1/2)\pi\hbar \qquad [8.55]$$

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[10] Application of the WKB approximation to the radial equation raises some delicate and subtle problems, which I will not go into here. The classic paper on the subject is R. Langer, *Phys. Rev.* **51**, 669 (1937).