CHAPTER 5

IDENTICAL PARTICLES

5.1 TWO-PARTICLE SYSTEMS

For a *single* particle, $\Psi(\mathbf{r}, t)$ is a function of the spatial coordinates, $\mathbf{r}$, and the time, t (we'll ignore spin, for the moment). The state of a *two*-particle system is a function of the coordinates of particle one ($\mathbf{r}_1$), the coordinates of particle two ($\mathbf{r}_2$), and the time:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t).$$ [5.1]

Its time evolution is determined (as always) by the Schrödinger equation:

$$i\hbar\frac{\partial \Psi}{\partial t} = H\Psi,$$ [5.2]

where H is the Hamiltonian for the whole system:

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t)$$ [5.3]

(the subscript on ∇ indicates differentiation with respect to the coordinates of particle 1 or particle 2, as the case may be). The statistical interpretation carries over in the obvious way:

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2$$ [5.4]

is the probability of finding particle 1 in the volume $d^3\mathbf{r}_1$ *and* particle 2 in the volume $d^3\mathbf{r}_2$; evidently Ψ must be normalized in such a way that

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 = 1.$$ [5.5]

For time-independent potentials, we obtain a complete set of solutions by separation of variables:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2)e^{-iEt/\hbar},$$ [5.6]

where the spatial wave function (ψ) satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V\psi = E\psi,$$ [5.7]

and E is the total energy of the system.

∗∗**Problem 5.1** Typically, the interaction potential depends only on the vector $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$ between the two particles. In that case the Schrödinger equation separates, if we change variables from $\mathbf{r}_1$, $\mathbf{r}_2$ to $\mathbf{r}$ and $\mathbf{R} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1 + m_2)$ (the center of mass).

(a) Show that $\mathbf{r}_1 = \mathbf{R} + (\mu/m_1)\mathbf{r}$, $\mathbf{r}_2 = \mathbf{R} - (\mu/m_2)\mathbf{r}$, and $\nabla_1 = (\mu/m_2)\nabla_R + \nabla_r$, $\nabla_2 = (\mu/m_1)\nabla_R - \nabla_r$, where

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2}$$ [5.8]

is the **reduced mass** of the system.

(b) Show that the (time-independent) Schrödinger equation becomes

$$-\frac{\hbar^2}{2(m_1 + m_2)}\nabla_R^2\psi - \frac{\hbar^2}{2\mu}\nabla_r^2\psi + V(\mathbf{r})\psi = E\psi.$$

(c) Separate the variables, letting $\psi(\mathbf{R}, \mathbf{r}) = \psi_R(\mathbf{R})\psi_r(\mathbf{r})$. Note that ψ_R satisfies the one-particle Schrödinger equation, with the *total* mass ($m_1 + m_2$) in place of m, potential zero, and energy E_R, while ψ_r satisfies the one-particle Schrödinger equation with the *reduced* mass in place of m, potential $V(\mathbf{r})$, and energy E_r. The total energy is the sum: $E = E_R + E_r$. What this tells us is that the center of mass moves like a free particle, and the *relative* motion (that is, the motion of particle 2 with respect to particle 1) is the same as if we had a *single* particle with the *reduced* mass, subject to the potential V. Exactly the same decomposition occurs in *classical* mechanics;[1] it reduces the two-body problem to an equivalent one-body problem.

---

[1]See, for example, Jerry B. Marion and Stephen T. Thornton, *Classical Dynamics of Particles and Systems*, 4th ed., Saunders, Fort Worth, TX (1995), Section 8.2.

Problem 5.2 In view of Problem 5.1, we can correct for the motion of the nucleus in hydrogen by simply replacing the electron mass with the reduced mass.

(a) Find (to two significant digits) the percent error in the binding energy of hydrogen (Equation 4.77) introduced by our use of m instead of μ.

(b) Find the separation in wavelength between the red Balmer lines ($n = 3 \rightarrow$ $n = 2$) for hydrogen and deuterium.

(c) Find the binding energy of **positronium** (in which the proton is replaced by a positron—positrons have the same mass as electrons, but opposite charge).

(d) Suppose you wanted to confirm the existence of **muonic hydrogen**, in which the electron is replaced by a muon (same charge, but 206.77 times heavier). Where (i.e., at what wavelength) would you look for the "Lyman-α" line ($n = 2 \rightarrow n = 1$)?

Problem 5.3 Chlorine has two naturally occurring isotopes, Cl^{35} and Cl^{37}. Show that the vibrational spectrum of HCl should consist of closely spaced doublets, with a splitting given by $\Delta \nu = 7.51 \times 10^{-4} \nu$, where ν is the frequency of the emitted photon. *Hint:* Think of it as a harmonic oscillator, with $\omega = \sqrt{k/\mu}$, where μ is the reduced mass (Equation 5.8) and k is presumably the same for both isotopes.

5.1.1 Bosons and Fermions

Suppose particle 1 is in the (one-particle) state $\psi_a(\mathbf{r})$, and particle 2 is in the state $\psi_b(\mathbf{r})$. (Remember: I'm ignoring spin, for the moment.) In that case $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is a simple *product*:[2]

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2). \tag{5.9}$$

Of course, this assumes that we can tell the particles apart—otherwise it wouldn't make any sense to claim that number 1 is in state ψ_a and number 2 is in state ψ_b; all we could say is that *one* of them is in the state ψ_a and the other is in state ψ_b, but we wouldn't know which is which. If we were talking *classical* mechanics this would be a silly objection: You can *always* tell the particles apart, in principle—just

---

[2] It is emphatically *not* true that every two-particle wave function is a product of two one-particle wave functions. There exist so-called **entangled states** that *cannot* be decomposed this way. However: If particle 1 is in state a and particle 2 is in state b, *then* the two-particle state is a product. I know what you're thinking: "How could particle 1 *not* be in *some* state, and particle 2 in some other state?" The classic example is the singlet spin configuration (Equation 4.178)—I can't tell you the state of particle 1 by itself, because it is "entangled" (Schrödinger's lovely word) with the state of particle 2. If 2 is measured, and found to be spin *up*, then 1 is spin *down*, but if 2 is spin *down*, then 1 is spin *up*.

paint one of them red and the other one blue, or stamp identification numbers on them, or hire private detectives to follow them around. But in quantum mechanics the situation is fundamentally different: You can't paint an electron red, or pin a label on it, and a detective's observations will inevitably and unpredictably alter its state, raising doubts as to whether the two had perhaps switched places. The fact is, all electrons are *utterly identical*, in a way that no two classical objects can ever be. It's not just that *we* don't happen to know which electron is which; *God* doesn't know which is which, because there is *no such thing* as "this" electron, or "that" electron; all we can legitimately speak about is "an" electron.

Quantum mechanics neatly accommodates the existence of particles that are *indistinguishable in principle*: We simply construct a wave function that is *noncommittal* as to which particle is in which state. There are actually *two* ways to do it:

$$\psi_\pm(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)]. \qquad [5.10]$$

Thus the theory admits two kinds of identical particles: **bosons**, for which we use the plus sign, and **fermions**, for which we use the minus sign. Photons and mesons are bosons; protons and electrons are fermions. It so happens that

$$\left\{ \begin{array}{l} \text{all particles with } integer \text{ spin are bosons, and} \\ \text{all particles with } half\,integer \text{ spin are fermions.} \end{array} \right. \qquad [5.11]$$

This connection between **spin and statistics** (as we shall see, bosons and fermions have quite different statistical properties) can be *proved* in *relativistic* quantum mechanics; in the nonrelativistic theory it is taken as an axiom.[3]

It follows, in particular, that *two identical fermions* (for example, two electrons) *cannot occupy the same state*. For if $\psi_a = \psi_b$, then

$$\psi_-(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) - \psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] = 0,$$

and we are left with no wave function at all.[4] This is the famous **Pauli exclusion principle**. It is not (as you may have been led to believe) a weird ad hoc assumption applying only to electrons, but rather a consequence of the rules for constructing two-particle wave functions, applying to *all* identical fermions.

I assumed, for the sake of argument, that one particle was in the state ψ_a and the other in state ψ_b, but there is a more general (and more sophisticated)

---

[3]It seems bizarre that *relativity* should have anything to do with it, and there has been a lot of discussion recently as to whether it might be possible to prove the spin-statistics connection in other (simpler) ways. See, for example, Robert C. Hilborn, *Am. J. Phys.* **63**, 298 (1995); Ian Duck and E. C. G. Sudarshan, *Pauli and the Spin-Statistics Theorem*, World Scientific, Singapore (1997).

[4]I'm still leaving out the spin, don't forget—if this bothers you (after all, a spinless fermion is a contradiction in terms), assume they're in the *same* spin state. I'll incorporate spin explicitly in a moment.

way to formulate the problem. Let us define the **exchange operator**, P, which interchanges the two particles:

$$Pf(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1). \qquad [5.12]$$

Clearly, $P^2 = 1$, and it follows (prove it for yourself) that the eigenvalues of P are ± 1. Now, if the two particles are identical, the Hamiltonian must treat them the same: $m_1 = m_2$ and $V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_2, \mathbf{r}_1)$. It follows that P and H are compatible observables,

$$[P, H] = 0, \qquad [5.13]$$

and hence we can find a complete set of functions that are simultaneous eigenstates of both. That is to say, we can find solutions to the Schrödinger equation that are either symmetric (eigenvalue $+1$) or antisymmetric (eigenvalue -1) under exchange:

$$\boxed{\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm \psi(\mathbf{r}_2, \mathbf{r}_1).} \qquad [5.14]$$

Moreover, if a system starts out in such a state, it will remain in such a state. The *new* law (I'll call it the **symmetrization requirement**) is that for identical particles the wave function is not merely *allowed*, but *required* to satisfy Equation 5.14, with the plus sign for bosons, and the minus sign for fermions.[5] This is the *general* statement, of which Equation 5.10 is a special case.

Example 5.1 Suppose we have two noninteracting—they pass right through one another ... never mind how you would set this up in practice!—particles, both of mass m, in the infinite square well (Section 2.2). The one-particle states are

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right), \quad E_n = n^2 K$$

(where $K = \pi^2\hbar^2/2ma^2$, for convenience). If the particles are *distinguishable*, with #1 in state n_1 and #2 in state n_2, the composite wave function is a simple product:

$$\psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2), \quad E_{n_1 n_2} = (n_1^2 + n_2^2)K.$$

---

[5]It is sometimes suggested that the symmetrization requirement (Equation 5.14) is *forced* by the fact that P and H commute. This is false: It is perfectly possible to imagine a system of two *distinguishable* particles (say, an electron and a positron) for which the Hamiltonian is symmetric, and yet there is no requirement that the wave function be symmetric (or antisymmetric). But *identical* particles *have* to occupy symmetric or antisymmetric states, and this is a completely *new fundamental law*—on a par, logically, with Schrödinger's equation and the statistical interpretation. Of course, there didn't *have* to be any such things as identical particles; it could have been that every single particle in nature was distinguishable from every other one. Quantum mechanics allows *for* the *possibility* of identical particles, and nature (being lazy) seized the opportunity. (But I'm not complaining—this makes matters enormously simpler!)

For example, the ground state is

$$\psi_{11} = \frac{2}{a} \sin(\pi x_1/a) \sin(\pi x_2/a), \quad E_{11} = 2K;$$

the first excited state is doubly degenerate:

$$\psi_{12} = \frac{2}{a} \sin(\pi x_1/a) \sin(2\pi x_2/a), \quad E_{12} = 5K,$$

$$\psi_{21} = \frac{2}{a} \sin(2\pi x_1/a) \sin(\pi x_2/a), \quad E_{21} = 5K;$$

and so on. If the two particles are identical *bosons*, the ground state is unchanged, but the first excited state is *nondegenerate*:

$$\frac{\sqrt{2}}{a} \left[\sin(\pi x_1/a) \sin(2\pi x_2/a) + \sin(2\pi x_1/a) \sin(\pi x_2/a) \right]$$

(still with energy $5K$). And if the particles are identical *fermions*, there is *no* state with energy $2K$; the ground state is

$$\frac{\sqrt{2}}{a} \left[\sin(\pi x_1/a) \sin(2\pi x_2/a) - \sin(2\pi x_1/a) \sin(\pi x_2/a) \right],$$

and its energy is $5K$.

---

*Problem 5.4

(a) If ψ_a and ψ_b are orthogonal, and both normalized, what is the constant A in Equation 5.10?

(b) If $\psi_a = \psi_b$ (and it is normalized), what is A? (This case, of course, occurs only for bosons.)

Problem 5.5

(a) Write down the Hamiltonian for two noninteracting identical particles in the infinite square well. Verify that the fermion ground state given in Example 5.1 is an eigenfunction of H, with the appropriate eigenvalue.

(b) Find the next two excited states (beyond the ones in Example 5.1)—wave functions and energies—for each of the three cases (distinguishable, identical bosons, identical fermions).

5.1.2 Exchange Forces

To give you some sense of what the symmetrization requirement actually *does*, I'm going to work out a simple one-dimensional example. Suppose one particle is in state $\psi_a(x)$, and the other is in state $\psi_b(x)$, and these two states are orthogonal and normalized. If the two particles are distinguishable, and number 1 is the one in state ψ_a, then the combined wave function is

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2);$$ [5.15]

if they are identical bosons, the composite wave function is (see Problem 5.4 for the normalization)

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)];$$ [5.16]

and if they are identical fermions, it is

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)].$$ [5.17]

Let's calculate the expectation value of the square of the separation distance between the two particles,

$$\langle(x_1 - x_2)^2\rangle = \langle x_1^2\rangle + \langle x_2^2\rangle - 2\langle x_1 x_2\rangle.$$ [5.18]

Case 1: Distinguishable particles. For the wavefunction in Equation 5.15,

$$\langle x_1^2\rangle = \int x_1^2 |\psi_a(x_1)|^2 \, dx_1 \int |\psi_b(x_2)|^2 \, dx_2 = \langle x^2\rangle_a$$

(the expectation value of x^2 in the one-particle state ψ_a),

$$\langle x_2^2\rangle = \int |\psi_a(x_1)|^2 \, dx_1 \int x_2^2 |\psi_b(x_2)|^2 \, dx_2 = \langle x^2\rangle_b,$$

and

$$\langle x_1 x_2\rangle = \int x_1 |\psi_a(x_1)|^2 \, dx_1 \int x_2 |\psi_b(x_2)|^2 \, dx_2 = \langle x\rangle_a\langle x\rangle_b.$$

In this case, then,

$$\langle(x_1 - x_2)^2\rangle_d = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b.$$ [5.19]

(Incidentally, the answer would, of course, be the same if particle 1 had been in state ψ_b, and particle 2 in state ψ_a.)

Case 2: Identical particles. For the wave functions in Equations 5.16 and 5.17,

$$\langle x_1^2 \rangle = \frac{1}{2}\left[\int x_1^2 |\psi_a(x_1)|^2\, dx_1 \int |\psi_b(x_2)|^2\, dx_2 \right.$$

$$+ \int x_1^2 |\psi_b(x_1)|^2\, dx_1 \int |\psi_a(x_2)|^2\, dx_2$$

$$\pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1)\, dx_1 \int \psi_b(x_2)^* \psi_a(x_2)\, dx_2$$

$$\left. \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1)\, dx_1 \int \psi_a(x_2)^* \psi_b(x_2)\, dx_2 \right]$$

$$= \frac{1}{2}\left[\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0 \right] = \frac{1}{2}\left(\langle x^2 \rangle_a + \langle x^2 \rangle_b \right).$$

Similarly,

$$\langle x_2^2 \rangle = \frac{1}{2}\left(\langle x^2 \rangle_b + \langle x^2 \rangle_a \right).$$

(Naturally, $\langle x_2^2 \rangle = \langle x_1^2 \rangle$, since you can't tell them apart.) But

$$\langle x_1 x_2 \rangle = \frac{1}{2}\left[\int x_1 |\psi_a(x_1)|^2\, dx_1 \int x_2 |\psi_b(x_2)|^2\, dx_2 \right.$$

$$+ \int x_1 |\psi_b(x_1)|^2\, dx_1 \int x_2 |\psi_a(x_2)|^2\, dx_2$$

$$\pm \int x_1 \psi_a(x_1)^* \psi_b(x_1)\, dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2)\, dx_2$$

$$\left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1)\, dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2)\, dx_2 \right]$$

$$= \frac{1}{2}\left(\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab} \right)$$

$$= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2,$$

where

$$\langle x \rangle_{ab} \equiv \int x \psi_a(x)^* \psi_b(x)\, dx. \tag{5.20}$$

Evidently

$$\langle (x_1 - x_2)^2 \rangle_\pm = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2|\langle x \rangle_{ab}|^2. \tag{5.21}$$

Comparing Equations 5.19 and 5.21, we see that the difference resides in the final term:

$$\langle (\Delta x)^2 \rangle_\pm = \langle (\Delta x)^2 \rangle_d \mp 2|\langle x \rangle_{ab}|^2. \tag{5.22}$$
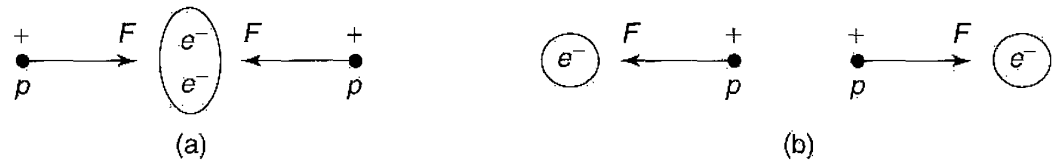
FIGURE 5.1: Schematic picture of the covalent bond: (a) Symmetric configuration produces attractive force. (b) Antisymmetric configuration produces repulsive force.

Identical bosons (the upper signs) tend to be somewhat closer together, and identical fermions (the lower signs) somewhat farther apart, than distinguishable particles in the same two states. Notice that $(x)_{ab}$ vanishes unless the two wave functions actually overlap [if $\psi_a(x)$ is zero wherever $\psi_b(x)$ is nonzero, the integral in Equation 5.20 is zero]. So if ψ_a represents an electron in an atom in Chicago, and ψ_b represents an electron in an atom in Seattle, it's not going to make any difference whether you antisymmetrize the wave function or not. As a *practical* matter, therefore, it's okay to pretend that electrons with nonoverlapping wave functions are distinguishable. (Indeed, this is the only thing that allows physicists and chemists to proceed at *all*, for in *principle* every electron in the universe is linked to every other one, via the antisymmetrization of their wave functions, and if this really *mattered*, you wouldn't be able to talk about any *one* unless you were prepared to deal with them *all*!)

The *interesting* case is when there *is* some overlap of the wave functions. The system behaves as though there were a "force of attraction" between identical bosons, pulling them closer together, and a "force of repulsion" between identical fermions, pushing them apart (remember that we are for the moment ignoring spin). We call it an **exchange force**, although it's not really a force at all—no physical agency is pushing on the particles; rather, it is a purely *geometrical* consequence of the symmetrization requirement. It is also a strictly quantum mechanical phenomenon, with no classical counterpart. Nevertheless, it has profound consequences. Consider, for example, the hydrogen molecule (H_2). Roughly speaking, the ground state consists of one electron in the atomic ground state (Equation 4.80) centered on nucleus 1, and one electron in the atomic ground state centered at nucleus 2. If electrons were *bosons*, the symmetrization requirement (or, if you like, the "exchange force") would tend to concentrate the electrons toward the middle, between the two protons (Figure 5.1(a)), and the resulting accumulation of negative charge would attract the protons inward, accounting for the **covalent bond**.[6] Unfortunately, electrons *aren't* bosons, they're fermions, and this means that the concentration of negative charge should actually be shifted to the wings (Figure 5.1(b)), tearing the molecule apart!

---

[6]A covalent bond occurs when shared electrons congregate between the nuclei, pulling the atoms together. It need not involve *two* electrons—in Section 7.3 we'll encounter a covalent bond with just *one* electron.

But wait! We have been ignoring *spin*. The *complete* state of the electron includes not only its position wave function, but also a spinor, describing the orientation of its spin:[7]

$$\psi(\mathbf{r})\chi(\mathbf{s}).$$ [5.23]

When we put together the two-electron state, it is the *whole works*, not just the spatial part, that has to be antisymmetric with respect to exchange. Now, a glance back at the composite spin states (Equations 4.177 and 4.178) reveals that the singlet combination is antisymmetric (and hence would have to be joined with a *symmetric* spatial function), whereas the three triplet states are all symmetric (and would require an *antisymmetric* spatial function). Evidently, then, the singlet state should lead to *bonding*, and the triplet to *anti*bonding. Sure enough, the chemists tell us that covalent bonding requires the two electrons to occupy the singlet state, with total spin zero.[8]

---

*Problem 5.6 Imagine two noninteracting particles, each of mass m, in the infinite square well. If one is in the state ψ_n (Equation 2.28), and the other in state ψ_l ($l \neq n$), calculate $\langle (x_1 - x_2)^2 \rangle$, assuming (a) they are distinguishable particles, (b) they are identical bosons, and (c) they are identical fermions.

Problem 5.7 Suppose you had *three* particles, one in state $\psi_a(x)$, one in state $\psi_b(x)$, and one in state $\psi_c(x)$. Assuming ψ_a, ψ_b, and ψ_c are orthonormal, construct the three-particle states (analogous to Equations 5.15, 5.16, and 5.17) representing (a) distinguishable particles, (b) identical bosons, and (c) identical fermions. Keep in mind that (b) must be completely symmetric, under interchange of *any* pair of particles, and (c) must be completely *anti*symmetric, in the same sense. *Comment:* There's a cute trick for constructing completely antisymmetric wave functions: Form the **Slater determinant**, whose first row is $\psi_a(x_1)$, $\psi_b(x_1)$, $\psi_c(x_1)$, etc., whose second row is $\psi_a(x_2)$, $\psi_b(x_2)$, $\psi_c(x_2)$, etc., and so on (this device works for any number of particles).

5.2 ATOMS

A neutral atom, of atomic number Z, consists of a heavy nucleus, with electric charge Ze, surrounded by Z electrons (mass m and charge $-e$). The Hamiltonian

---

[7] In the absence of coupling between spin and position, we are free to assume that the state is *separable* in its spin and spatial coordinates. This just says that the probability of getting spin up is independent of the *location* of the particle. In the *presence* of coupling, the general state would take the form of a linear combination: $\psi_+(\mathbf{r})\chi_+ + \psi_-(\mathbf{r})\chi_-$, as in Problem 4.55.

[8] In casual language, it is often said that the electrons are "oppositely aligned" (one with spin up, and the other with spin down). This is something of an oversimplification, since the same could be said of the $m = 0$ triplet state. The precise statement is that they are in the singlet configuration.

for this system is[9]

$$H = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right\} + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^{Z} \frac{e^2}{|r_j - r_k|}. \qquad [5.24]$$

The term in curly brackets represents the kinetic plus potential energy of the jth electron, in the electric field of the nucleus; the second sum (which runs over all values of j and k except $j = k$) is the potential energy associated with the mutual repulsion of the electrons (the factor of 1/2 in front corrects for the fact that the summation counts each pair twice). The problem is to solve Schrödinger's equation,

$$H\psi = E\psi, \qquad [5.25]$$

for the wave function $\psi(r_1, r_2, \ldots, r_Z)$. Because electrons are identical fermions, however, not all solutions are acceptable: only those for which the complete state (position and spin),

$$\psi(r_1, r_2, \ldots, r_Z)\chi(s_1, s_2, \ldots, s_Z), \qquad [5.26]$$

is antisymmetric with respect to interchange of any two electrons. In particular, no two electrons can occupy the same state.

Unfortunately, the Schrödinger equation with Hamiltonian in Equation 5.24 cannot be solved exactly (at any rate, it *hasn't* been), except for the very simplest case, $Z = 1$ (hydrogen). In practice, one must resort to elaborate approximation methods. Some of these we shall explore in Part II; for now I plan only to sketch some qualitative features of the solutions, obtained by neglecting the electron repulsion term altogether. In Section 5.2.1 we'll study the ground state and excited states of helium, and in Section 5.2.2 we'll examine the ground states of higher atoms.

Problem 5.8 Suppose you could find a solution $(\psi(r_1, r_2, \ldots, r_Z))$ to the Schrödinger equation (Equation 5.25), for the Hamiltonian in Equation 5.24. Describe how you would construct from it a completely symmetric function and a completely antisymmetric function, which also satisfy the Schrödinger equation, with the same energy.

---

[9]I'm assuming the nucleus is *stationary*. The trick of accounting for nuclear motion by using the reduced mass (Problem 5.1) works only for the *two*-body problem; fortunately, the nucleus is so much more massive than the electrons that the correction is extremely small even in the case of hydrogen (see Problem 5.2(a)), and it is smaller still for the heavier atoms. There are more interesting effects, due to magnetic interactions associated with electron spin, relativistic corrections, and the finite size of the nucleus. We'll look into these in later chapters, but all of them are minute corrections to the "purely coulombic" atom described by Equation 5.24.

5.2.1 Helium

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

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

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 trouble. If we simply *ignore* it, the Schrödinger equation separates, and the solutions can be written as products of *hydrogen* wave functions:

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

only with half the Bohr radius (Equation 4.72), and four times the Bohr energies (Equation 4.70)—if you don't see why, refer back to Problem 4.16. The total energy would be

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

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

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

(see Equation 4.80), and its energy would be

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

Because ψ_0 is a symmetric function, the spin state has to be *antisymmetric*, so the ground state of helium should be 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 5.11).

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

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

[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 5.9—but it is not our present concern.] We can construct 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).
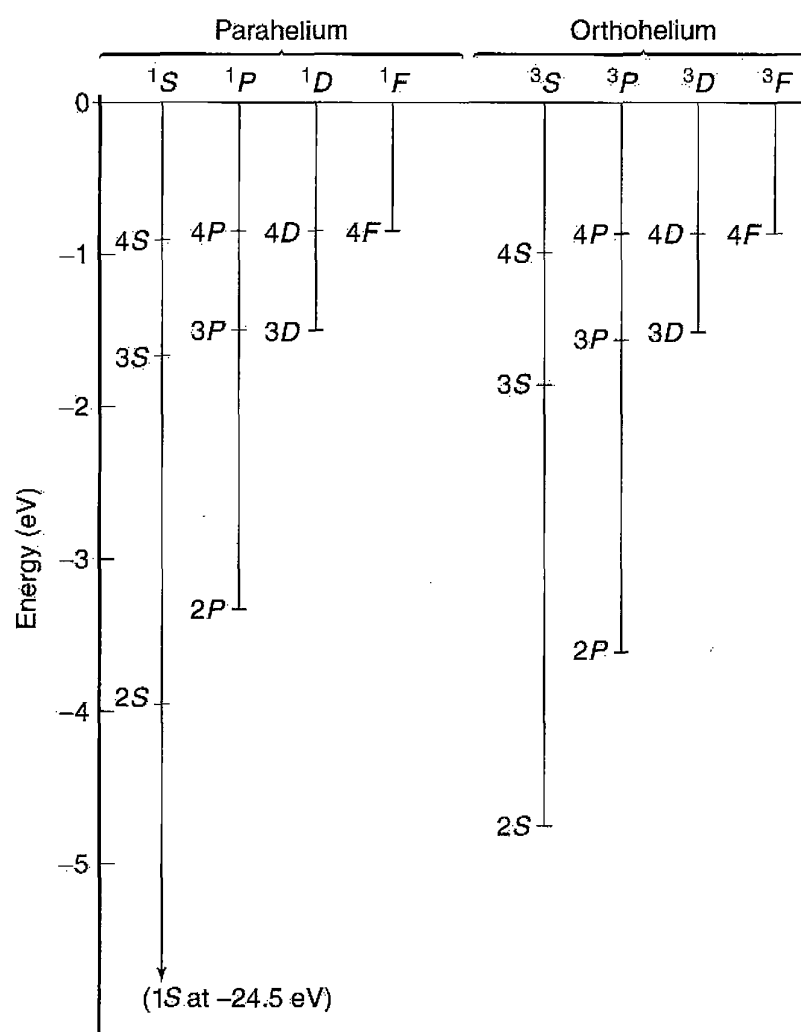

FIGURE 5.2: Energy level diagram for helium (the notation is explained in Section 5.2.2). Note that parahelium energies are uniformly higher than their orthohelium counterparts. The numerical values on the vertical scale are relative to the ground state of ionized helium (He^+): $4 \times (-13.6)$ eV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

Problem 5.9

(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 5.10 Discuss (qualitatively) the energy level scheme for helium if (a) electrons were identical bosons, and (b) if electrons were distinguishable particles (but with the same mass and charge). Pretend these "electrons" still have spin 1/2, so the spin configurations are the singlet and the triplet.

∗∗Problem 5.11

(a) Calculate $\langle (1/|\mathbf{r}_1 - \mathbf{r}_2|) \rangle$ for the state ψ_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 θ_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 ∞. *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. (Of course, we're still working with an approximate wave function, so don't expect *perfect* agreement.)

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 2 electrons, the $n = 2$ shell holds 8, $n = 3$ takes 18, and in general the nth shell can accommodate $2n^2$ 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, and the farther out it 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 I refer you to any book on atomic physics.[10]

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 imagination, because it now continues alphabetically (g, h, i, but skip j—just to be utterly perverse, k, l, etc.).[11] The state of a particular electron is represented by the pair nl, with n (the number) giving the shell, and l (the letter)

---

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

[11]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).

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, known as **Hund's Rules** (see Problem 5.13) 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.[12]

∗Problem 5.12

(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.

---

[12]After krypton—element 36—the situation gets more complicated (fine structure starts to play a significant role in the ordering of the states) so it is not for want of space that the table terminates there.

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

**Problem 5.13

(a) **Hund's first rule** says that, consistent with the Pauli principle, the state with the highest total spin (S) will have the lowest energy. What would this predict in the case of the excited states of helium?

(b) **Hund's second rule** says that, for a given spin, the state with the highest total orbital angular momentum (L), consistent with overall antisymmetrization, will have the lowest energy. Why doesn't carbon have $L = 2$? *Hint:* Note that the "top of the ladder" ($M_L = L$) is symmetric.

(c) **Hund's third 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 Problem 5.12(b).

(d) Use Hund's rules, together with the fact that a symmetric spin state must go with an antisymmetric position state (and vice versa) to resolve the carbon and nitrogen ambiguities in Problem 5.12(b). *Hint:* Always go to the "top of the ladder" to figure out the symmetry of a state.

Problem 5.14 The ground state of dysprosium (element 66, in the 6th row of the Periodic Table) is listed as $^5 I_8$. What are the total spin, total orbital, and grand total angular momentum quantum numbers? Suggest a likely electron configuration for dysprosium.

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 "solidity," and provide illuminating

insight into the remarkable electrical properties of conductors, semi-conductors, 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:

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

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

$$-\frac{\hbar^2}{2m}\frac{d^2 X}{dx^2} = E_x X; \qquad -\frac{\hbar^2}{2m}\frac{d^2 Y}{dy^2} = E_y Y; \qquad -\frac{\hbar^2}{2m}\frac{d^2 Z}{dz^2} = E_z Z,$$

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

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

we obtain the general solutions

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x), \qquad Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y),$$

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

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 that

$$k_x l_x = n_x \pi, \qquad k_y l_y = n_y \pi, \qquad k_z l_z = n_z \pi, \qquad [5.36]$$

where each n is a positive integer:

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

The (normalized) wave functions are

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

and the allowed energies are

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

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

If you imagine a three-dimensional space, with axes k_x, k_y, k_z, and planes drawn in at $k_x = (\pi/l_x)$, $(2\pi/l_x)$, $(3\pi/l_x)$, ..., at $k_y = (\pi/l_y)$, $(2\pi/l_y)$, $(3\pi/l_y)$, ..., and at $k_z = (\pi/l_z)$, $(2\pi/l_z)$, $(3\pi/l_z)$, ..., each intersection point represents
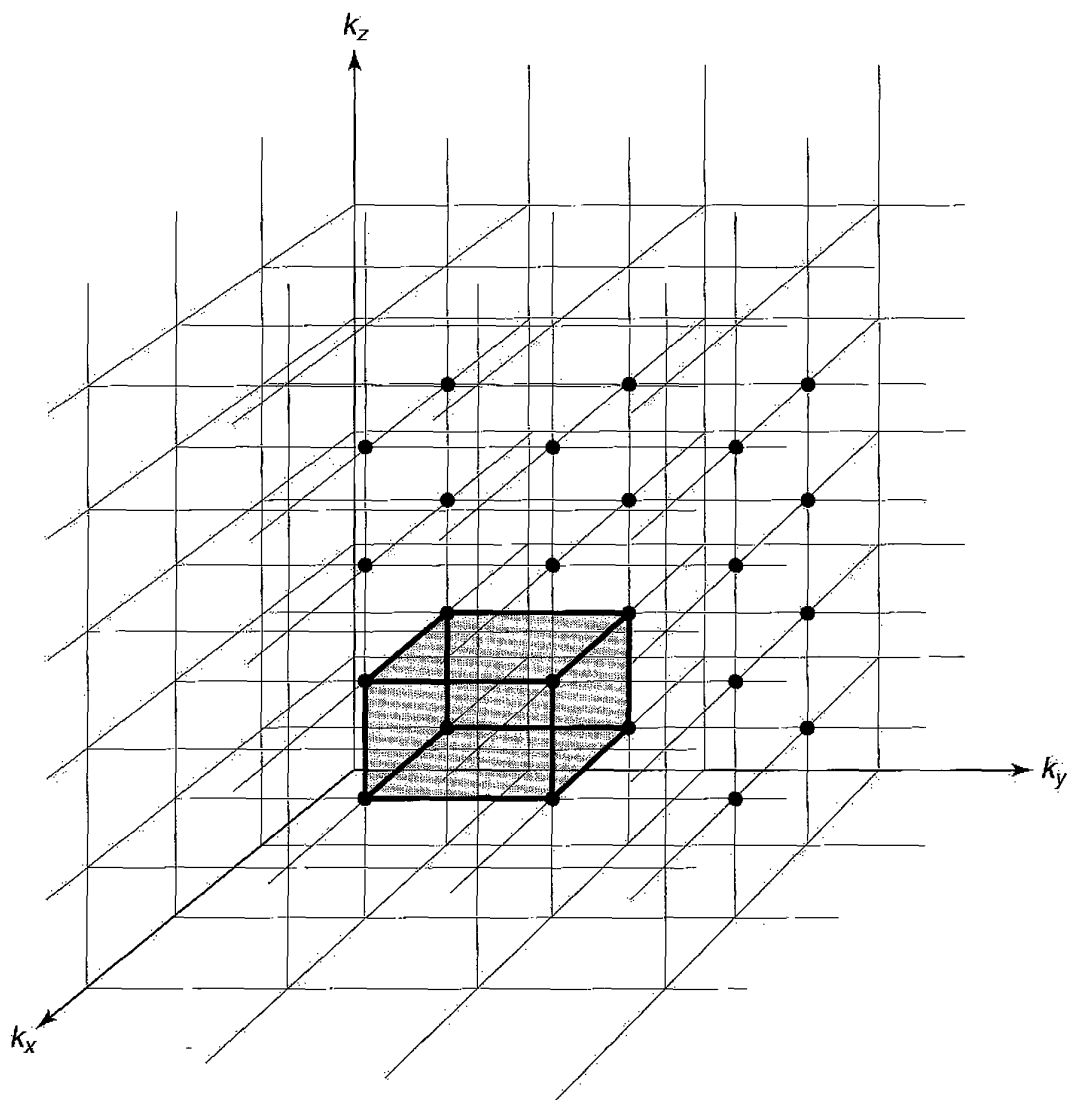

FIGURE 5.3:   Free electron gas. Each intersection on the grid represents a stationary state. Shading indicates one "block"; there is one state for every block.

a distinct (one-particle) stationary state (Figure 5.3). Each block in this grid, and hence also each state, occupies a volume

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V} \qquad [5.40]$$

of "k-space," where $V = l_x l_y l_z$ is the volume of the object itself. 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—whereas q is a small number—1 or 2, typically.) If electrons were bosons (or distinguishable particles), they would all settle down to the ground state, ψ_{111}.[13] 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,[14] whose radius, k_F, is determined by the fact that each pair of electrons requires a volume π^3/V (Equation 5.40):

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

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 corresponding energy is called the **Fermi energy**, E_F; 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

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

---

[13]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 5.16(c)), typical solids are still "cold," in this sense, far above room temperature.

[14]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.
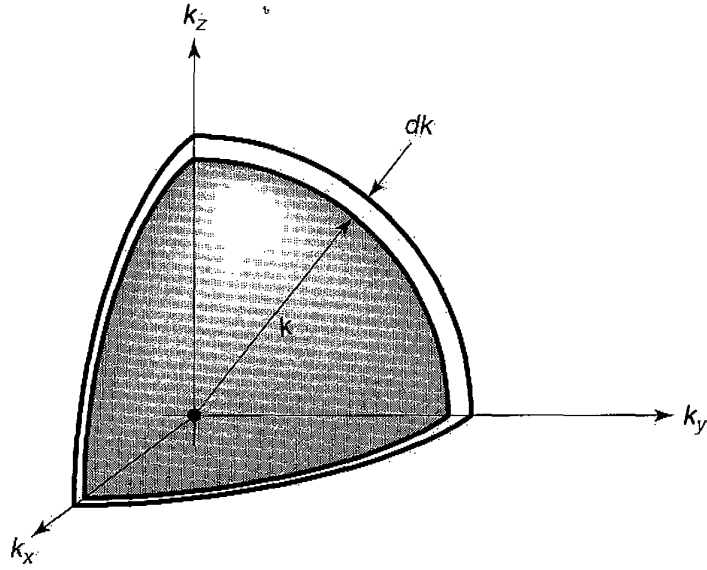
FIGURE 5.4:   One octant of a spherical shell in k-space.

so the number of electron states in the shell is

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

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

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

and hence the total energy is

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

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

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

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, having 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**, though "exclusion pressure" might be a better term.[15]

Problem 5.15 Find the average energy per free electron (E_{tot}/Nq), as a fraction of the Fermi energy. *Answer:* $(3/5)E_F$.

Problem 5.16 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? *Hint:* Set $E_F = (1/2)mv^2$. Is it safe to assume the electrons in copper are nonrelativistic?

(c) At what temperature would the characteristic thermal energy ($k_B T$, where k_B is the Boltzmann constant and T is the Kelvin temperature) equal the Fermi energy, for copper? *Comment:* 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 lowest accessible state. Since the melting point of copper is 1356 K, solid copper is *always* cold.

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

Problem 5.17 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 5.16(d) to estimate the bulk modulus of copper. *Comment:* The observed value is 13.4×10^{10} N/m^2, but don't expect perfect agreement—after all, we're

---

[15]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.

neglecting all electron-nucleus and electron-electron forces! Actually, it is rather surprising that this calculation comes as close as it *does*.

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 model: a one-dimensional **Dirac comb**, consisting of evenly spaced delta function spikes (Figure 5.5).[16] But first I need to introduce a powerful theorem that vastly simplifies the analysis of periodic potentials.

A periodic potential is one that repeats itself after some fixed distance a:

$$V(x + a) = V(x).$$

[5.47]

Bloch's theorem tells us that for such a potential the solutions to the Schrödinger equation,

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

[5.48]

can be taken to satisfy the condition

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

[5.49]

for some constant K (by "constant" I mean that it is independent of x; it may well depend on E).
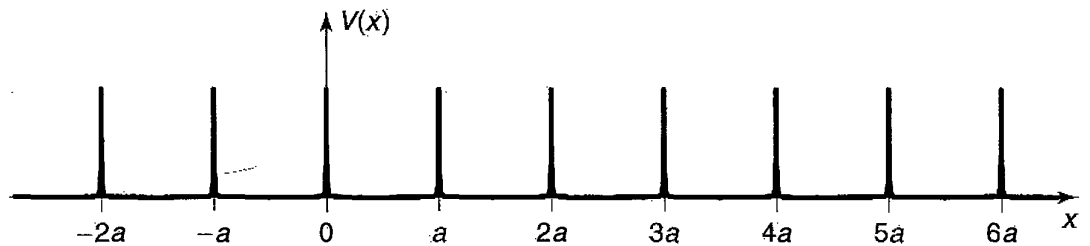

FIGURE 5.5:   The Dirac comb, Equation 5.57.

---

[16]It would be more natural to let the delta functions go *down*, so as to represent the attractive force of the nuclei. But then there would be negative energy solutions as well as positive energy solutions, and that makes the calculations more cumbersome (see Problem 5.20). Since all we're trying to do here is explore the consequences of periodicity, it is simpler to adopt this less plausible shape; if it comforts you, think of the nuclei as residing at $\pm a/2$, $\pm 3a/2$, $\pm 5a/2$, ...

Proof: Let D be the "displacement" operator:

$$Df(x) = f(x + a).$$ [5.50]

For a periodic potential (Equation 5.47), D commutes with the Hamiltonian:

$$[D, H] = 0,$$ [5.51]

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

$$\psi(x + a) = \lambda\psi(x).$$ [5.52]

Now, λ 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); like any nonzero complex number, it can be expressed as an exponential:

$$\lambda = e^{iKa},$$ [5.53]

for some constant K. QED

At this stage Equation 5.53 is just a strange way to write the eigenvalue λ, 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:

$$|\psi(x + a)|^2 = |\psi(x)|^2,$$ [5.54]

as one would certainly expect.[17]

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

$$\psi(x + Na) = \psi(x).$$ [5.55]

It follows (from Equation 5.49) that

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

---

[17]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.

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

$$K = \frac{2\pi n}{Na}, \quad (n = 0, \pm 1, \pm 2, \ldots).$$ [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 $0 \le x < a$); recursive application of Equation 5.49 generates the solution everywhere else.

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

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

(In Figure 5.5 you must imagine that the x-axis has been "wrapped around," so the Nth spike 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[18] used a repeating *rectangular* pattern, and many authors still prefer that one.[19] 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

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

as usual.

The general solution is

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

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

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

---

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

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

At $x = 0$, ψ must be continuous, so

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

its derivative suffers a discontinuity proportional to the strength of the delta function (Equation 2.125, with the sign of α switched, since these are spikes instead of wells):

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

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

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

Substituting this into Equation 5.62, and cancelling 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

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

This is the fundamental result, from which all else follows. For the Kronig-Penney potential (see footnote 18), 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

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

so the right side of Equation 5.64 can be written as

$$f(z) \equiv \cos(z) + \beta\frac{\sin(z)}{z}.$$ [5.66]

The constant β is a dimensionless measure of the "strength" of the delta function. In Figure 5.6 I have plotted $f(z)$, for the case $\beta = 10$. 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 $|\cos(Ka)|$, of course, cannot be greater than 1. These **gaps** represent *forbidden* energies; they are separated by **bands** of *allowed* energies. Within a given band, virtually any energy is allowed, since according to Equation 5.56 $Ka = 2\pi n/N$, where N is a huge number, 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
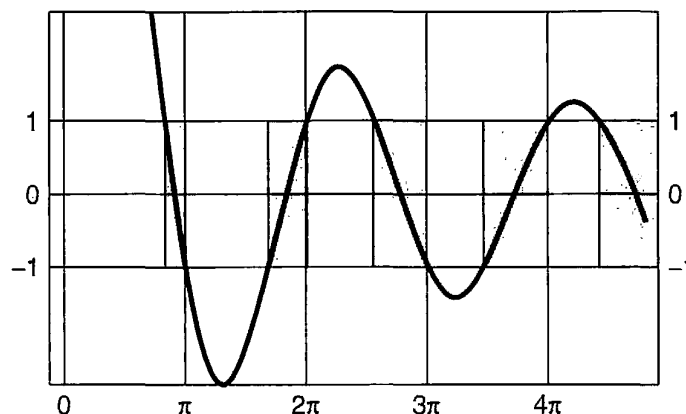
FIGURE 5.6: Graph of $f(z)$ (Equation 5.66) for $\beta = 10$, showing allowed bands (shaded) separated by forbidden gaps (where $|f(z)| > 1$).
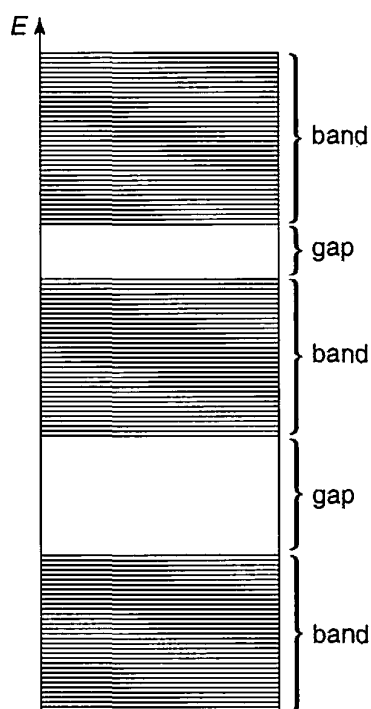

FIGURE 5.7: The allowed energies for a periodic potential form essentially continuous bands.

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 states in each band, 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 the Pauli exclusion principle, only two electrons can occupy a given spatial state, so if $q = 1$, they will half fill 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 the ground state. (In three dimensions, and with more realistic potentials, the band structure may

be more complicated, but the *existence* of allowed 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.

Problem 5.18

(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

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

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

(b) There is an exception: At the top of a band, where z is an integer multiple of π (Figure 5.6), (a) yields $\psi(x) = 0$. Find the correct wave function for this case. Note what happens to ψ at each delta function.

Problem 5.19 Find the energy at the bottom of the first allowed band, for the case $\beta = 10$, correct to three significant digits. For the sake of argument, assume $\alpha/a = 1$ eV.

****Problem 5.20** Suppose we use delta function *wells*, instead of *spikes* (i.e., switch the sign of α in Equation 5.57). Analyze this case, constructing the analog to Figure 5.6. This requires no new calculation, for the positive energy solutions (except that β is now negative; use $\beta = -1.5$ for the graph), but you *do* need to work out the negative energy solutions (let $\kappa \equiv \sqrt{-2mE}/\hbar$ and $z \equiv -\kappa a$, for $E < 0$). How many states are there in the first allowed band?

Problem 5.21 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 allowed 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 particle, selected at random, would be found to have the 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 of a system in thermal equilibrium. The only new twist introduced by quantum mechanics has to do with *how we count the distinct states* (it's actually *easier* than in the classical theory, because the states are generally discrete), 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 An 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 2.27), where n_A, n_B, and n_C are positive integers. Now suppose, for the sake of argument, that $E = 363(\pi^2\hbar^2/2ma^2)$, which is to say,

$$n_A^2 + n_B^2 + n_C^2 = 363. \qquad [5.68]$$

There are, as it happens, 13 combinations of three positive integers, the sum of whose squares is 363: All three could be 11, two could be 13 and one 5

(which occurs in three permutations), one could be 19 and two 1 (again, three permutations), or one could be 17, one 7, and one 5 (six permutations). Thus (n_A, n_B, n_C) is one of the following:

$$(11, 11, 11).$$

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

$$(1, 1, 19), \quad (1. 19. 1), \quad (19, 1. 1).$$

$$(5, 7, 17), \quad (5, 17, 7), \quad (7, 5, 17), \quad (7, 17, 5), \quad (17, 5, 7), \quad (17, 7, 5).$$

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[20] 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 ψ_n. The collection of all occupation numbers for a given 3-particle state we will call the **configuration**. If all three are in ψ_{11}, the configuration is

$$(0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 3, 0, 0, 0, 0, 0, 0, 0, \ldots). \tag{5.69}$$

(i.e., $N_{11} = 3$, all others zero). If two are in ψ_{13} and one is in ψ_5, the configuration is

$$(0, 0, 0, 0, 1, 0, 0, 0, 0, 0, 0, 0, 2, 0, 0, 0, 0, \ldots), \tag{5.70}$$

(i.e., $N_5 = 1$, $N_{13} = 2$, all others zero). If two are in ψ_1 and one is in ψ_{19}, the configuration is

$$(2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, \ldots), \tag{5.71}$$

(i.e., $N_1 = 2$, $N_{19} = 1$, all others zero). And if there is one particle in ψ_5, one in ψ_7, and one in ψ_{17}, the configuration is

$$(0, 0, 0, 0, 1, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, 0, \ldots). \tag{5.72}$$

(i.e., $N_5 = N_7 = N_{17} = 1$, all others zero.) Of these, the last is the *most probable* configuration, because it can be achieved in six different ways, whereas the middle two occur three ways, and the first only one.

---

[20]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.

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? The only way you can get E_1 is if it's in the third configuration (Equation 5.71); the chances of the system being in that configuration are 3 in 13, and in that configuration the probability of getting E_1 is 2/3, so $P_1 = (3/13) \times (2/3) = 2/13$. You could get E_5 either from configuration 2 (Equation 5.70)—chances 3 in 13—with probability 1/3, or from configuration 4 (Equation 5.72)—chances 6 in 13—with probability 1/3, so $P_5 = (3/13) \times (1/3) + (6/13) \times (1/3) = 3/13$. You can only get E_7 from configuration 4: $P_7 = (6/13) \times (1/3) = 2/13$. Likewise, E_{11} comes only from the first configuration (Equation 5.69)—chances 1 in 13—with probability 1: $P_{11} = (1/13)$. Similarly, $P_{13} = (3/13) \times (2/3) = 2/13$, $P_{17} = (6/13) \times (1/3) = 2/13$, and $P_{19} = (3/13) \times (1/3) = 1/13$. As a check, note that

$$P_1 + P_5 + P_7 + P_{11} + P_{13} + P_{17} + P_{19} = \frac{2}{13} + \frac{3}{13} + \frac{2}{13} + \frac{1}{13} + \frac{2}{13} + \frac{2}{13} + \frac{1}{13} = 1.$$

That's when the particles are distinguishable. If in fact they are *identical fermions*, the antisymmetrization requirement (leaving aside spin, for simplicity—or assuming they are all in the *same* spin state, if you prefer) excludes the first three configurations (which assign two—or, worse still, three—particles to the same state), and there is just *one* state in the fourth configuration (see Problem 5.22(a)). For identical fermions, then, $P_5 = P_7 = P_{17} = 1/3$ (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 in each configuration (see Problem 5.22(b)), so $P_1 = (1/4) \times (2/3) = 1/6$, $P_5 = (1/4) \times (1/3) + (1/4) \times (1/3) = 1/6$, $P_7 = (1/4) \times (1/3) = 1/12$, $P_{11} = (1/4) \times (1) = 1/4$, $P_{13} = (1/4) \times (2/3) = 1/6$, $P_{17} = (1/4) \times (1/3) = 1/12$, and $P_{19} = (1/4) \times (1/3) = 1/12$. 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, $N_5 = N_7 = N_{17} = 1$, 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:[21] *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 $P_5 = P_7 = P_{17} = 1/3$ 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.

---

[21] This is an astonishing and counterintuitive fact about the statistics of large numbers. For a good discussion see Ralph Baierlein, *Thermal Physics*. Cambridge U.P. (1999). Section 2.1.

*Problem 5.22

(a) Construct the completely antisymmetric wave function $\psi(x_A, x_B, x_C)$ for three identical fermions, one in the state ψ_5, one in the state ψ_7, and one in the state ψ_{17}.

(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 ψ_{11}, (ii) if two are in state ψ_1 and one is in state ψ_{19}, and (iii) if one is in the state ψ_5, one in the state ψ_7, and one in the state ψ_{17}.

---

*Problem 5.23 Suppose you had three (noninteracting) particles, in thermal equilibrium, in a one-dimensional harmonic oscillator potential, 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 we did 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, ..., with degeneracies $d_1, d_2, d_3, ...$ (i.e., there are d_n distinct one-particle states with energy E_n). Suppose we put N particles (all with the same mass) into this potential; we are interested in the configuration $(N_1, N_2, N_3, ...)$, 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, $Q(N_1, N_2, N_3, ...)$, depends on whether the particles are distinguishable, identical fermions, or identical bosons, so we'll treat the three cases separately.[22]

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"?

---

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

Answer: the **binomial coefficient**, "N choose N_1,"

$$\binom{N}{N_1} \equiv \frac{N!}{N_1!(N - N_1)!}.$$ [5.73]

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

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

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 29th draw; so we divide by $N_1!$, confirming Equation 5.73. 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:

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

and so on. It follows that

$$Q(N_1, N_2, N_3, \ldots)$$

$$= \frac{N!d_1^{N_1}}{N_1!(N - N_1)!} \frac{(N - N_1)!d_2^{N_2}}{N_2!(N - N_1 - N_2)!} \frac{(N - N_1 - N_2)!d_3^{N_3}}{N_3!(N - N_1 - N_2 - N_3)!} \cdots$$

$$= N!\frac{d_1^{N_1} d_2^{N_2} d_3^{N_3} \cdots}{N_1!N_2!N_3!\ldots} = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}.$$ [5.74]

(You should pause right now and *check* this result, for the example in Section 5.4.1— see Problem 5.24.)

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 are 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 nth bin,[23] so

$$Q(N_1, N_2, N_3, \ldots) = \prod_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n - N_n)!}.$$ [5.75]

(Check it for the example in Section 5.4.1—see Problem 5.24.)

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 are occupied, but this time there is no restriction on the number of particles that can share the same one-particle state. For the nth bin, the question becomes: How many different ways can we assign N_n identical particles to d_n different slots? There are many tricks to solve this combinatorial problem; an especially clever method is as follows: 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 change the state. Likewise, the crosses are all equivalent—permuting them ($(d_n - 1)!$ ways) changes nothing. So there are in fact

$$\frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!} = \binom{N_n + d_n - 1}{N_n}$$ [5.76]

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

$$Q(N_1, N_2, N_3, \ldots) = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}$$ [5.77]

(Check it for the Example in Section 5.4.1—see Problem 5.24.)

∗Problem 5.24 Check Equations 5.74, 5.75, and 5.77, for the example in Section 5.4.1.

∗∗Problem 5.25 Obtain Equation 5.76 by induction. The combinatorial question is this: How many different ways can you put N identical balls into d baskets (never

---

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

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.

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

$$\sum_{n=1}^{\infty} N_n = N,$$
[5.78]

and

$$\sum_{n=1}^{\infty} N_n E_n = E.$$
[5.79]

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**.[24] We introduce the new function

$$G(x_1, x_2, x_3, \ldots, \lambda_1, \lambda_2, \ldots) \equiv F + \lambda_1 f_1 + \lambda_2 f_2 + \cdots,$$
[5.80]

and set *all* its derivatives equal to zero:

$$\frac{\partial G}{\partial x_n} = 0; \quad \frac{\partial G}{\partial \lambda_n} = 0.$$
[5.81]

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

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

---

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

where α and β are the Lagrange multipliers. Setting the derivatives with respect to α and β equal to zero merely reproduces the constraints (Equations 5.78 and 5.79); 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 5.74, and we have

$$G = \ln(N!) + \sum_{n=1}^{\infty} [N_n \ln(d_n) - \ln(N_n!)]$$

$$+ \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right].$$

[5.83]

Assuming the relevant occupation numbers (N_n) are large, we can invoke **Stirling's approximation**:[25]

$$\ln(z!) \approx z \ln(z) - z \quad \text{for } z \gg 1,$$

[5.84]

to write

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

$$+ \ln(N!) + \alpha N + \beta E.$$

[5.85]

It follows that

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

[5.86]

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

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

[5.87]

If the particles are *identical fermions*, then Q is given by Equation 5.75, and we have

$$G = \sum_{n=1}^{\infty} \{\ln(d_n!) - \ln(N_n!) - \ln[(d_n - N_n)!]\}$$

$$+ \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right].$$

[5.88]

---

[25]Stirling's approximation can be improved by including more terms in the **Stirling series**, but the first two will suffice for our purposes. See George Arfken and Hans-Jurgen Weber, *Mathematical Methods for Physicists*, 5th ed., Academic Press, Orlando (2000), Section 10.3. If the relevant occupation numbers are *not* large—as in 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.

This time we must assume not only that N_n is large, but also that $d_n \gg N_n$,[26] so that Stirling's approximation applies to both terms. In that case

$$G \approx \sum_{n=1}^{\infty} \left[\ln(d_n!) - N_n \ln(N_n) + N_n - (d_n - N_n) \ln(d_n - N_n) \right.$$

$$\left. + (d_n - N_n) - \alpha N_n - \beta E_n N_n \right] + \alpha N + \beta E, \qquad [5.89]$$

so

$$\frac{\partial G}{\partial N_n} = -\ln(N_n) + \ln(d_n - N_n) - \alpha - \beta E_n. \qquad [5.90]$$

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

$$N_n = \frac{d_n}{e^{(\alpha + \beta E_n)} + 1}. \qquad [5.91]$$

Finally, if the particles are *identical bosons*, then Q is given by Equation 5.77, and we have

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

$$+ \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]. \qquad [5.92]$$

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

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

$$+ N_n - \ln[(d_n - 1)!] - \alpha N_n - \beta E_n N_n \} + \alpha N + \beta E, \qquad [5.93]$$

so

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

---

[26]In *one* dimension the energies are nondegenerate (see Problem 2.45), 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 $z = 0$.

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

$$N_n = \frac{d_n - 1}{e^{(\alpha + \beta E_n)} - 1}.$$ [5.95]

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

Problem 5.26 Use the method of Lagrange multipliers to find the rectangle of largest area, with sides parallel to the axes, that can be inscribed in the ellipse $(x/a)^2 + (y/b)^2 = 1$. What is that maximum area?

Problem 5.27

(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 α and β

The parameters α and β 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 5.87, 5.91, and 5.95) back into the constraints (Equations 5.78 and 5.79). 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 an **ideal gas**—a large number of noninteracting particles, all with the same mass, in the three dimensional infinite square well. This will motivate the physical interpretation of α and β.

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

$$E_k = \frac{\hbar^2}{2m} k^2,$$ [5.96]

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 $\mathbf{k}$ as a continuous variable, with one state (or, for spin s, $2s + 1$ states) per volume π^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

$$d_k = \frac{1}{8} \frac{4\pi k^2 \, dk}{(\pi^3/V)} = \frac{V}{2\pi^2} k^2 \, dk. \qquad [5.97]$$

For distinguishable particles (Equation 5.87), the first constraint (Equation 5.78) becomes

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

so

$$e^{-\alpha} = \frac{N}{V} \left(\frac{2\pi\beta\hbar^2}{m}\right)^{3/2}. \qquad [5.98]$$

The second constraint (Equation 5.79) says

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

or, putting in Equation 5.98 for $e^{-\alpha}$:

$$E = \frac{3N}{2\beta}. \qquad [5.99]$$

(If you include the spin factor, $2s + 1$, in Equation 5.97, it cancels out at this point, so Equation 5.99 is correct for all spins.)

This result (Equation 5.99) is reminiscent of the classical formula for the average kinetic energy of an atom at temperature T:[27]

$$\frac{E}{N} = \frac{3}{2} k_B T, \qquad [5.100]$$

where k_B is the Boltzmann constant. This suggests that β is related to the *temperature*:

$$\beta = \frac{1}{k_B T}. \qquad [5.101]$$

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 β. The argument is sketched in many books,[28] but I shall not reproduce it here—I will simply adopt Equation 5.101 as the *definition* of T.

---

[27]See, for example, David Halliday, Robert Resnick, and Jearl Walker. *Fundamentals of Physics*. 5th ed., Wiley, New York (1997). Section 20-5.

[28]See, for example, Yariv (footnote 22), Section 15.4.

It is customary to replace α (which, as is clear from the special case of Equation 5.98, is a function of T) by the so-called **chemical potential**,

$$\mu(T) \equiv -\alpha k_B T,$$ [5.102]

and rewrite Equations 5.87, 5.91, and 5.95 as formulas for the *most probable number of particles in a particular (one-particle) state with energy* ϵ (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):

$$n(\epsilon) = \begin{cases} e^{-(\epsilon-\mu)/k_B T} & \text{MAXWELL-BOLTZMANN} \\[2mm] \dfrac{1}{e^{(\epsilon-\mu)/k_B T} + 1} & \text{FERMI-DIRAC} \\[2mm] \dfrac{1}{e^{(\epsilon-\mu)/k_B T} - 1} & \text{BOSE-EINSTEIN} \end{cases}$$ [5.103]

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 $T \rightarrow 0$:

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

so

$$n(\epsilon) \rightarrow \begin{cases} 1, & \text{if } \epsilon < \mu(0), \\ 0, & \text{if } \epsilon > \mu(0). \end{cases}$$ [5.104]

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:

$$\mu(0) = E_F.$$ [5.105]

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

Returning now to the special case of an ideal gas, for distinguishable particles we found that the total energy at temperature T is (Equation 5.99)

$$E = \frac{3}{2} N k_B T.$$ [5.106]
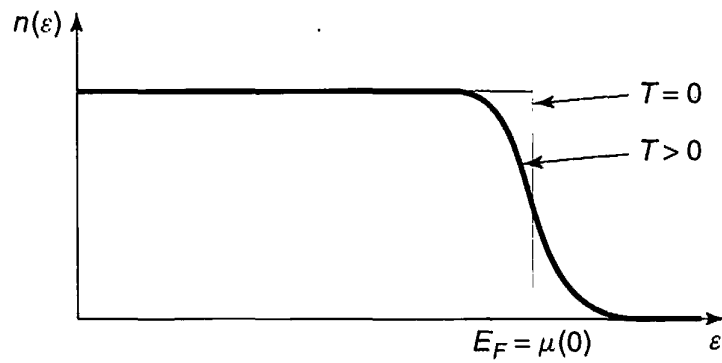
FIGURE 5.8:   Fermi-Dirac distribution for $T = 0$ and for T somewhat above zero.

while (from Equation 5.98) the chemical potential is

$$\mu(T) = k_B T \left[\ln\left(\frac{N}{V}\right) + \frac{3}{2} \ln\left(\frac{2\pi\hbar^2}{mk_B T}\right) \right].$$ [5.107]

I would *like* to work out the corresponding formulas for an ideal gas of identical fermions and bosons, using Equations 5.91 and 5.95 in place of Equation 5.87. The first constraint (Equation 5.78) becomes

$$N = \frac{V}{2\pi^2} \int_0^\infty \frac{k^2}{e^{[(\hbar^2 k^2/2m)-\mu]/k_B T} \pm 1} dk,$$ [5.108]

(with the plus sign for fermions and minus for bosons), and the second constraint (Equation 5.79) reads

$$E = \frac{V}{2\pi^2} \frac{\hbar^2}{2m} \int_0^\infty \frac{k^4}{e^{[(\hbar^2 k^2/2m)-\mu]/k_B T} \pm 1} dk.$$ [5.109]

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, these integrals cannot be evaluated in terms of elementary functions, and I shall leave it for you to explore the matter further (see Problems 5.28 and 5.29).

Problem 5.28 Evaluate the integrals (Equations 5.108 and 5.109) 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 5.108 and 5.109, to account for the spin degeneracy.)

***Problem 5.29

(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, $\mu(T) < 0$ for all T. Show that in this case $\mu(T)$ monotonically increases as T decreases, assuming N and V are held constant. *Hint:* Study Equation 5.108, 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. Below the critical temperature, the particles crowd into the ground state, and the calculational device of replacing the discrete sum (Equation 5.78) by a continuous integral (Equation 5.108) loses its validity.[29] *Hint:*

$$\int_0^\infty \frac{x^{s-1}}{e^x - 1}\, dx = \Gamma(s)\zeta(s), \qquad\qquad [5.110]$$

where Γ is Euler's **gamma function** and ζ 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. *Comment:* 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 footnote 29.

5.4.5 The Blackbody Spectrum

Photons (quanta of the electromagnetic field) are identical bosons with spin 1, but they are very special, 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 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).

---

[29] See F. Mandl. *Statistical Physics*, Wiley, London (1971). Section 11.5.

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 5.78) does not apply. We can take account of this by simply setting $\alpha \to 0$, in Equation 5.82 and everything that follows. Thus the most probable occupation number, for photons, is (Equation 5.95):

$$N_\omega = \frac{d_k}{e^{\hbar\omega/k_B T} - 1}.$$ [5.111]

For free photons in a box of volume V, d_k is given by Equation 5.97,[30] multiplied by 2 for spin (item 3), and expressed in terms of ω instead of k (item 2):

$$d_k = \frac{V}{\pi^2 c^3}\omega^2\, d\omega.$$ [5.112]

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

$$\boxed{\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3 \left(e^{\hbar\omega/k_B T} - 1\right)}.}$$ [5.113]

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

Problem 5.30

(a) Use Equation 5.113 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 $\overline{\rho}(\lambda)$.

(b) Derive the **Wien displacement law** for the wavelength at which the blackbody energy density is a maximum:

$$\lambda_{\max} = \frac{2.90 \times 10^{-3}\ \text{mK}}{T}.$$ [5.114]

Hint: 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.

---

[30]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 5.36.
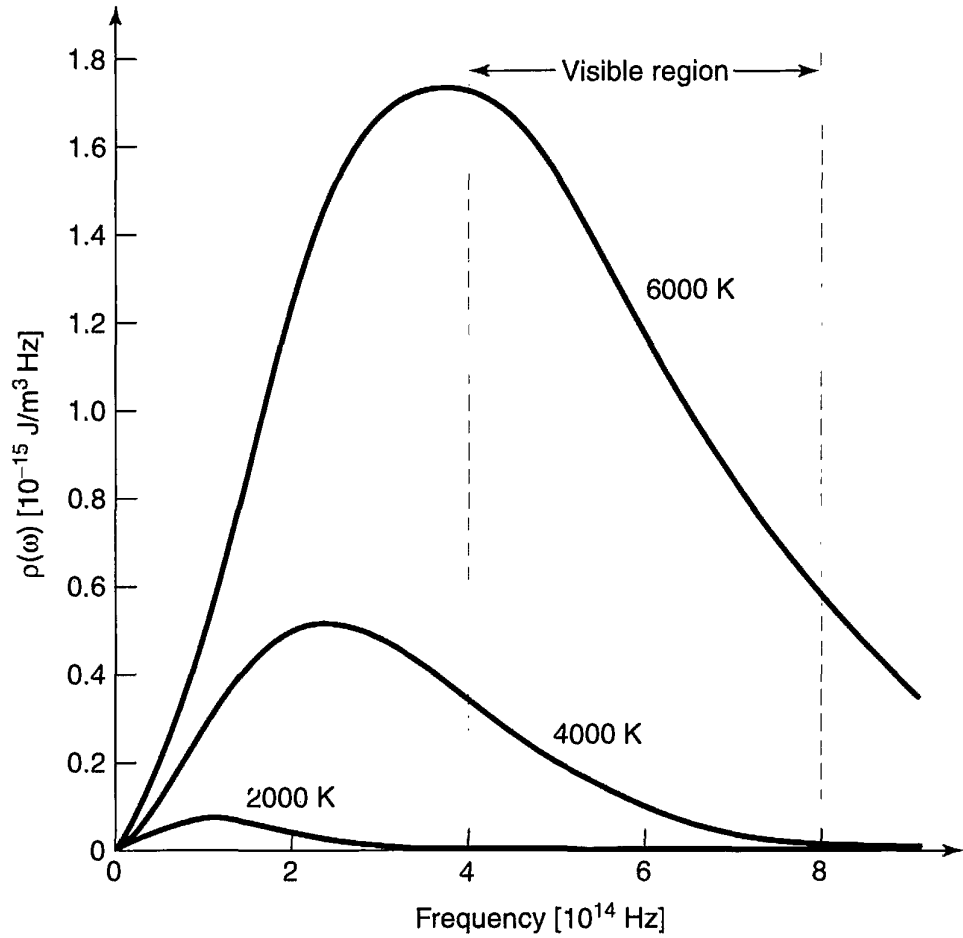
FIGURE 5.9: Planck's formula for the blackbody spectrum, Equation 5.113.

Problem 5.31 Derive the **Stefan-Boltzmann formula** for the *total* energy density in blackbody radiation:

$$\frac{E}{V} = \left(\frac{\pi^2 k_B^4}{15 \hbar^3 c^3} \right) T^4 = \left(7.57 \times 10^{-16} \ \mathrm{Jm^{-3}K^{-4}} \right) T^4. \qquad [5.115]$$

Hint: Use Equation 5.110 to evaluate the integral. Note that $\zeta(4) = \pi^4/90$.

FURTHER PROBLEMS FOR CHAPTER 5

Problem 5.32 Imagine two noninteracting particles, each of mass m, in the one-dimensional harmonic oscillator potential (Equation 2.43). If one is in the ground state, and the other is in the first excited state, calculate $\langle (x_1 - x_2)^2 \rangle$, assuming (a) they are distinguishable particles, (b) they are identical bosons, and (c) they are

identical fermions. Ignore spin (if this bothers you, just assume they are both in the same spin state).

Problem 5.33 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, (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 5.34 Calculate the Fermi energy for noninteracting electrons in a *two*-dimensional infinite square well. Let σ be the number of free electrons per unit area.

***Problem 5.35 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:*

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

(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:* $R = 7.6 \times 10^{25} N^{-1/3}$ m.

(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 5.36).

***Problem 5.36** 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 $\hbar^2 k^2/2m$ in Equation 5.44 by the ultra-relativistic expression, $\hbar ck$, and calculate E_{tot} in this regime.

(b) Repeat parts (a) and (b) of Problem 5.35 for the ultra-relativistic 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:* 2.04×10^{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 5.35). 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 a neutron star nonrelativistically?

***Problem 5.37**

(a) Find the chemical potential and the total energy for distinguishable particles in the three dimensional harmonic oscillator potential (Problem 4.38). *Hint:* The sums in Equations 5.78 and 5.79 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,**

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n,$$ [5.116]

you can get

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

and similar results for higher derivatives. *Answer:*

$$E = \frac{3}{2}N\hbar\omega \left(\frac{1 + e^{-\hbar\omega/k_B T}}{1 - e^{-\hbar\omega/k_B T}} \right).$$ [5.117]

(b) Discuss the limiting case $k_B T \ll \hbar\omega$.

(c) Discuss the classical limit, $k_B T \gg \hbar\omega$, in the light of the **equipartition theorem**.[31] How many **degrees of freedom** does a particle in the three dimensional harmonic oscillator possess?

---

[31] See, for example, Halliday and Resnick (footnote 27), Section 20-9.