CHAPTER 5

IDENTICAL PARTICLES

5.1 TWO-PARTICLE SYSTEMS

For a single particle, the wave function $\Psi(\mathbf{r}, t)$ is a function of the spatial coordinates $\mathbf{r}$ and the time $t$ (we’ll ignore spin for the moment). The wave function for 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:

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

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

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

where $H$ is the Hamiltonian for the whole system:

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

(the subscript on $\nabla$ 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:

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 \; d^3\mathbf{r}_2$$  \hfill [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 $\Psi$ must be normalized in such a way that

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 \; d^3\mathbf{r}_2 = 1.$$  \hfill [5.5]
For time-independent potentials, we obtain a complete set of solutions by separation of variables:

\[ \Psi(r_1, r_2, t) = \psi(r_1, r_2)e^{-iE_1t}/\hbar, \]  

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

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

and \( E \) is the total energy of the system.

**Problem 5.1** Typically, the interaction potential depends only on the vector \( \mathbf{r} \equiv r_1 - r_2 \) separating the two particles. In that case the Schrödinger equation separates, if we change variables from \( r_1, \ r_2 \) to \( \mathbf{r}, \mathbf{R} \equiv (m_1r_1 + m_2r_2)/(m_1 + m_2) \), (the center of mass).

(a) Show that \( r_1 = R + (\mu/m_1)r, \ r_2 = R - (\mu/m_2)r, \) and \( \nabla_1 = (\mu/m_2)\nabla_R - \nabla_r, \) where

\[ \mu \equiv \frac{m_1m_2}{m_1 + m_2} \]

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) Solve by separation of variables, letting \( \psi(\mathbf{R}, \mathbf{r}) = \psi_R(\mathbf{R})\psi_r(\mathbf{r}) \). Note that \( \psi_R \) 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 \( \psi_r \) 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: \( E = E_R + E_r \). Note: 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 separation occurs in classical mechanics; it reduces the two-body problem to an equivalent one-body problem.

**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 \( \mu \).

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1See, for example, Jerry Marion, Classical Dynamics, 2nd ed. (New York: Academic Press 1970). Section 8.2.
(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-\(\alpha\)” line 
\( n = 2 \rightarrow n = 1 \)?

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 
\( \psi_b(\mathbf{r}) \). In that case \( \psi(\mathbf{r}_1, \mathbf{r}_2) \) is a simple product:

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

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 \( \psi_a \) and number 2 is in state \( \psi_b \); all 
we could say is that one of them is in the state \( \psi_a \) and the other is in state \( \psi_b \), but 
we wouldn’t know which is which. If we were talking about classical mechanics this 
would be a silly objection: You can always tell the particles apart, in principle—just 
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 the 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 is 
not merely 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 noncom-
mittal as to which particle is in which state. There are actually two ways to do it:

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

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

\[
\begin{align*}
&\text{all particles with integer spin are bosons, and} \\
&\text{all particles with half-integer spin are fermions.} \tag{5.11}
\end{align*}
\]
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 must be taken as an axiom.

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

\[
\psi_-(r_1, r_2) = \Phi[\psi_a(r_1)\psi_a(r_2) - \psi_a(r_1)\psi_a(r_2)] = 0,
\]

and we are left with no wave function at all. This is the famous Pauli exclusion principle. It is not (as you may have been led to believe) a bizarre 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 \( \psi_a \) and the other in state \( \psi_b \), but there is a more general (and more sophisticated) way to formulate the problem. Let us define the exchange operator \( P \) which interchanges the two particles:

\[
P f(r_1, r_2) = f(r_2, r_1).
\]  \[5.12\]

Clearly, \( P^2 = 1 \), and it follows (prove it for yourself) that the eigenvalues of \( P \) are \( \pm 1 \). If the two particles are identical, the Hamiltonian must treat them the same: \( m_1 = m_2 \) and \( V(r_1, r_2) = V(r_2, r_1) \). It follows that \( P \) and \( H \) are compatible observables,

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

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:

\[
\psi(r_1, r_2) = \pm \psi(r_2, r_1) \quad (+ \text{ for bosons, } - \text{ for fermions}).
\]  \[5.14\]

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.\(^2\) This is the general statement of which Equation 5.10 is a special case.

\(^2\)It is sometimes suggested that the symmetrization requirement (Equation 5.14) is nothing new—that it 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 clearly 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!)
Example. Suppose we have two noninteracting\(^3\) 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 \(K = \pi^2 \hbar^2 / 2ma^2\)). If the particles are distinguishable, the composite wave functions are simple products:

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

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:

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

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

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

and its energy is \(5K\).

*Problem 5.3*

(a) If \(\psi_a\) and \(\psi_b\) 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.)

\(^3\)They pass right through one another—never mind how you would set this up in practice! I’ll ignore spin—if this bothers you (after all, a spinless fermion is a contradiction in terms), assume they’re in the same spin state.
Problem 5.4

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

(b) Find the next two excited states (beyond the ones given in the example)—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 $\psi_a$, then the combined wave function is

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

if they are identical bosons, the composite wave function is (see Problem 5.3 for the normalization)

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

and if they are identical fermions, it is

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

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

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

Case 1: Distinguishable particles. For the wave function in Equation 5.15.

we have

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

(the expectation value of $x^2$ in the one-particle state $\psi_a$),

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

\[ \langle x_1 x_2 \rangle = \int x_1 |\psi(x_1)|^2 \, dx_1 \int x_2 |\psi(x_2)|^2 \, dx_2 = \langle x \rangle_a \langle x \rangle_b. \]

In this case, then,

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

(Incidentally, the answer would—of course—be the same if particle 1 had been in state $\psi_a$, and particle 2 in state $\psi_b$.)

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

\[
\langle x_1^2 \rangle = \frac{1}{2} \left[ \int x_1^2 |\psi_a(x_1)|^2 \, dx_1 \int |\psi_b(x_2)|^2 \, dx_2 
+ \int x_1^2 |\psi_b(x_1)|^2 \, dx_1 \int |\psi_a(x_2)|^2 \, dx_2 
\pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) \, dx_1 \int \psi_b(x_2)^* \psi_a(x_2) \, dx_2 
\pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) \, dx_1 \int \psi_a(x_2)^* \psi_b(x_2) \, dx_2 \right] 
= \frac{1}{2} \left[ \langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0 \right] = \frac{1}{2} \left( \langle x^2 \rangle_a + \langle x^2 \rangle_b \right).
\]

Similarly,

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

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

\[
\langle x_1 x_2 \rangle = \frac{1}{2} \left[ \int x_1 |\psi_a(x_1)|^2 \, dx_1 \int x_2 |\psi_b(x_2)|^2 \, dx_2 
+ \int x_1 |\psi_b(x_1)|^2 \, dx_1 \int x_2 |\psi_a(x_2)|^2 \, dx_2 
\pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) \, dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) \, dx_2 
\pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) \, dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) \, dx_2 \right]
\]
\[ \langle x \rangle_{ab} = \frac{1}{2} \left( \langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab} \right) \]

where

\[ \langle x \rangle_{ab} = \int x \psi_a(x)^* \psi_b(x) \, dx. \]  \hspace{1cm} [5.20]

Evidently

\[ \langle (x_1 - x_2) \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2. \]  \hspace{1cm} [5.21]

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

\[ \langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_a \mp 2 |\langle x \rangle_{ab}|^2; \]  \hspace{1cm} [5.22]

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 \( \langle x \rangle_{ab} \) 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 itself zero]. So if \( \psi_a \) represents an electron in an atom in Chicago and \( \psi_b \) 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 electron until 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. 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\textsubscript{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 5.1a), and the resulting accumulation of negative charge would attract the protons inward, accounting for the covalent bond that holds
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![Figure 5.1: Schematic picture of the covalent bond: (a) Symmetric configuration produces attractive force; (b) antisymmetric configuration produces repulsive force.](image)

the molecule together. 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 5.1b), tearing the molecule apart!

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:

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

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 antibonding. Sure enough, the chemists tell us that covalent bonding requires the two electrons to occupy the singlet state, with total spin zero.\(^5\)

**Problem 5.5** Imagine two noninteracting particles, each of mass \( m \), in the infinite square well. If one is in the state \( \psi_\alpha \) (Equation 2.24) and the other in state \( \psi_\beta \), orthogonal to \( \psi_\alpha \), calculate \( (x_1 - x_2)^2 \), assuming that (a) they are distinguishable particles, (b) they are identical bosons, and (c) they are identical fermions.

**Problem 5.6** Suppose you had three particles, one in state \( \psi_\alpha(x) \), one in state \( \psi_\beta(x) \), and one in state \( \psi_{\pi}(x) \). Assuming that \( \psi_\alpha, \psi_\beta, \) and \( \psi_{\pi} \) 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. \( \text{i.e.,} \) Note: There’s a cute

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\(^4\)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: \( \psi_\uparrow(\mathbf{r}) \chi_\uparrow + \psi_\downarrow(\mathbf{r}) \chi_\downarrow \).

\(^5\)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.
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 for this system is

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

The term in curly brackets represents the kinetic plus potential energy of the \( j \)th 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.

\[ H \psi = E \psi, \tag{5.25} \]

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),

\[ \psi(r_1, r_2, \ldots, r_Z) \chi(s_1, s_2, \ldots, s_Z), \tag{5.26} \]

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 the 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 of the 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.

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6I’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—hydrogen; fortunately, the nucleus is so much more massive than the electrons that the correction is extremely small even in that case (see Problem 5.2a), 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.
Problem 5.7 Suppose you could find a solution $\psi(r_1, r_2, \ldots, r_Z)$ to the Schrödinger (Equation 5.25) for the Hamiltonian in Equation 5.24. Describe how you could construct from it a completely symmetric function and a completely antisymmetric function, which also satisfy the Schrödinger equation, with the same energy.

5.2.1 Helium

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

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

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

$$\psi(r_1, r_2) = \psi_{nlm}(r_1)\psi_{n'r'm'}(r_2), \quad [5.28]$$

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

$$E = 4(E_n + E_n'), \quad [5.29]$$

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

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

(see Equation 4.80), and its energy would be

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

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

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

$$\psi_{nlm}\psi_{100}. \quad [5.32]$$
[If you try to put both electrons in excited states, one immediately drops to the ground state, releasing enough energy to knock the other one into the continuum (E > 0), leaving you with a helium ion (He⁺) and a free electron. This is an interesting system in its own right—see Problem 5.8—but it is not our present concern.] We can construct from this both symmetric and antisymmetric combinations, in the usual way (Equation 5.10); the former go with the antisymmetric spin configuration (the singlet), and they are called \textit{parahelium}, while the latter require a symmetric spin configuration (the triplet), and they are known as \textit{orthohelium}. The ground state is necessarily parahelium; the excited states come in both forms. Because the symmetric spatial state brings the electrons closer together (as we discovered in Section 5.1.2), we expect a higher interaction energy in parahelium, and indeed it is experimentally confirmed that the parahelium states have somewhat higher energy than their orthohelium counterparts (see Figure 5.2).

**Problem 5.8**

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

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

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

**Problem 5.10**

(a) Calculate \((1/|\mathbf{r}_1 - \mathbf{r}_2|)\) for the state \( \psi_0 \) (Equation 5.30). \textit{Hint:} Do the \( d^3r_2 \) integral first, using spherical coordinates and setting the polar axis along \( \mathbf{r}_1 \), so that

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

The \( \theta_2 \) integral is easy, but be careful to take the \textit{positive} root. You’ll have to break the \( r_2 \) integral into two pieces, one ranging from 0 to \( r_1 \), the other from \( r_1 \) to \( \infty \). \textit{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. \textit{Note:} Of course, we’re still working with an approximate wave function, so don’t expect \textit{perfect} agreement.
Figure 5.2: Energy level diagram for helium (the notation is explained in Section 5.2.2). Note that parahelium energies are uniformly higher than their orthohelium counterparts. The numerical values on the vertical scale are relative to the ground state of ionized helium (He⁺): $4 \times (-13.6 \text{ eV}) = -54.4 \text{ eV}$; to get the total energy of the state, subtract 54.4 eV.

5.2.2 The Periodic Table

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

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

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

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

---

\(^7\)See, for example, U. Fano and L. Fano, Basic Physics of Atoms and Molecules (New York: John Wiley & Sons, 1959), Chapter 18, or the classic by G. Herzberg, Atomic Spectra and Atomic Structure (New York: Dover, 1944).
imagination, because the list just continues alphabetically \((g, h, i, \text{ etc.})\). The state of a particular electron is represented by the pair \(nl\), with \(n\) (the number) giving the shell and \(l\) (the letter) specifying the orbital angular momentum; the magnetic quantum number \(m\) is not listed, but an exponent is used to indicate the number of electrons that occupy the state in question. Thus the configuration

\[
(1s)^2(2s)^2(2p)^2
\]

[5.33]

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

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

\[
\frac{2S+1}{L} J
\]

[5.34]

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

### Problem 5.11

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

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

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

\(^9\)See, for example, Stephen Gasiorowicz, Quantum Physics (New York: John Wiley & Sons, 1974), Chapters 18 and 19.
**Table 5.1:** Ground-state electron configurations for the first four rows of the Periodic Table.

<table>
<thead>
<tr>
<th>Z</th>
<th>Element</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>(1s) 2S(_{1/2})</td>
</tr>
<tr>
<td>2</td>
<td>He</td>
<td>(1s)(^2) 1S(_0)</td>
</tr>
<tr>
<td>3</td>
<td>Li</td>
<td>(He) (2s) 2S(_{1/2})</td>
</tr>
<tr>
<td>4</td>
<td>Be</td>
<td>(He)(2s)(^2) 1S(_0)</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>(He)(2s)(^2)(2p)(^2) 2P(_{1/2})</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>(He)(2s)(^2)(2p)(^2) 3P(_0)</td>
</tr>
<tr>
<td>7</td>
<td>N</td>
<td>(He)(2s)(^2)(2p)(^3) 4S(_{1/2})</td>
</tr>
<tr>
<td>8</td>
<td>O</td>
<td>(He)(2s)(^2)(2p)(^4) 3P(_2)</td>
</tr>
<tr>
<td>9</td>
<td>F</td>
<td>(He)(2s)(^2)(2p)(^5) 2P(_{1/2})</td>
</tr>
<tr>
<td>10</td>
<td>Ne</td>
<td>(He)(2s)(^2)(2p)(^6) 1S(_0)</td>
</tr>
<tr>
<td>11</td>
<td>Na</td>
<td>(Ne)(3s) 2S(_{1/2})</td>
</tr>
<tr>
<td>12</td>
<td>Mg</td>
<td>(Ne)(3s)(^2) 1S(_0)</td>
</tr>
<tr>
<td>13</td>
<td>Al</td>
<td>(Ne)(3s)(^2)(3p)(^2) 2P(_{1/2})</td>
</tr>
<tr>
<td>14</td>
<td>Si</td>
<td>(Ne)(3s)(^2)(3p)(^2) 3P(_0)</td>
</tr>
<tr>
<td>15</td>
<td>P</td>
<td>(Ne)(3s)(^2)(3p)(^3) 4S(_{1/2})</td>
</tr>
<tr>
<td>16</td>
<td>S</td>
<td>(Ne)(3s)(^2)(3p)(^4) 3P(_2)</td>
</tr>
<tr>
<td>17</td>
<td>Cl</td>
<td>(Ne)(3s)(^2)(3p)(^5) 2P(_{1/2})</td>
</tr>
<tr>
<td>18</td>
<td>Ar</td>
<td>(Ne)(3s)(^2)(3p)(^6) 1S(_0)</td>
</tr>
<tr>
<td>19</td>
<td>K</td>
<td>(Ar)(4s) 2S(_{1/2})</td>
</tr>
<tr>
<td>20</td>
<td>Ca</td>
<td>(Ar)(4s)(^2) 1S(_0)</td>
</tr>
<tr>
<td>21</td>
<td>Sc</td>
<td>(Ar)(4s)(^3)(3d)(^3) 2D(_{3/2})</td>
</tr>
<tr>
<td>22</td>
<td>Ti</td>
<td>(Ar)(4s)(^3)(3d)(^2) 3F(_3)</td>
</tr>
<tr>
<td>23</td>
<td>V</td>
<td>(Ar)(4s)(^3)(3d)(^3) 4F(_5/2)</td>
</tr>
<tr>
<td>24</td>
<td>Cr</td>
<td>(Ar)(4s)(3d)(^2) 5D(_5)</td>
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<tr>
<td>25</td>
<td>Mn</td>
<td>(Ar)(4s)(^3)(3d)(^5) 6S(_{1/2})</td>
</tr>
<tr>
<td>26</td>
<td>Fe</td>
<td>(Ar)(4s)(^3)(3d)(^6) 5D(_4)</td>
</tr>
<tr>
<td>27</td>
<td>Co</td>
<td>(Ar)(4s)(^3)(3d)(^7) 4F(_{9/2})</td>
</tr>
<tr>
<td>28</td>
<td>Ni</td>
<td>(Ar)(4s)(^3)(3d)(^8) 3F(_4)</td>
</tr>
<tr>
<td>29</td>
<td>Cu</td>
<td>(Ar)(4s)(3d)(^{10}) 2S(_{1/2})</td>
</tr>
<tr>
<td>30</td>
<td>Zn</td>
<td>(Ar)(4s)(^3)(3d)(^{10}) 1S(_0)</td>
</tr>
<tr>
<td>31</td>
<td>Ga</td>
<td>(Ar)(4s)(^3)(3d)(^{10})(4p)(^2) 2P(_{1/2})</td>
</tr>
<tr>
<td>32</td>
<td>Ge</td>
<td>(Ar)(4s)(^3)(3d)(^{10})(4p)(^2) 3F(_0)</td>
</tr>
<tr>
<td>33</td>
<td>As</td>
<td>(Ar)(4s)(^3)(3d)(^{10})(4p)(^3) 4S(_{1/2})</td>
</tr>
<tr>
<td>34</td>
<td>Se</td>
<td>(Ar)(4s)(^3)(3d)(^{10})(4p)(^4) 3P(_2)</td>
</tr>
<tr>
<td>35</td>
<td>Br</td>
<td>(Ar)(4s)(^3)(3d)(^{10})(4p)(^5) 2P(_{1/2})</td>
</tr>
<tr>
<td>36</td>
<td>Kr</td>
<td>(Ar)(4s)(^3)(3d)(^{10})(4p)(^6) 1S(_0)</td>
</tr>
</tbody>
</table>

(c) **Hund's first rule** says that, all other things being equal, the state with the highest total spin will have the lowest energy. What would this predict in the case of the excited states of helium?
(d) Hund’s second rule says that if a subshell \((n, l)\) is no more than half filled, then the lowest energy level has \(J = |L - S|\); if it is more than half filled, then \(J = L + S\) has the lowest energy. Use this to resolve the boron ambiguity in (b).

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

Problem 5.12 The ground state of dysprosium (element 66, in the sixth row of the Periodic Table) is listed as \(^{3}I_{6}\). 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 the “solidity” of solids, and provide illuminating insight into the remarkable electrical properties of conductors, semiconductors, and insulators.

5.3.1 The Free Electron Gas

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

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

The Schrödinger equation,

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