

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:

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

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

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

where H is the Hamiltonian for the whole system:

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

(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:

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

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

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

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

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

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

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

and E is the total energy of the system.

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

$$\mu \equiv \frac{m_1m_2}{m_1 + m_2} \quad [5.8]$$

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) Solve by separation of 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: $E = E_R + E_r$. *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* mechanics¹; 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 μ .

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- α ” 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*:

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

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 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 *noncommittal* as to which particle is in which state. There are actually *two* ways to do it:

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

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

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

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 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

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

and we are left with no wave function at all. 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 ψ_a and the other in state ψ_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:

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

Clearly, $P^2 = 1$, and it follows (prove it for yourself) that the eigenvalues of P are ± 1 . 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,

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

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:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm\psi(\mathbf{r}_2, \mathbf{r}_1) \quad (+ \text{ for bosons, } - \text{ for fermions}). \quad [5.14]$$

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.

²It 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 noninteracting³ 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 $K \equiv \pi^2 \hbar^2 / 2ma^2$). 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 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.)

³They 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.