

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 ψ_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 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

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

In this case, then,

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

(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,

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

Similarly,

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

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

$$\begin{aligned} \langle x_1 x_2 \rangle &= \frac{1}{2} \left[\int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 \right. \\ &\quad + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \\ &\quad \pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) dx_2 \\ &\quad \left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{2}(\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}) \\
&= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2,
\end{aligned}$$

where

$$\langle x \rangle_{ab} \equiv \int x \psi_a(x)^* \psi_b(x) dx. \quad [5.20]$$

Evidently

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

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

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2|\langle x \rangle_{ab}|^2; \quad [5.22]$$

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 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* 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_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

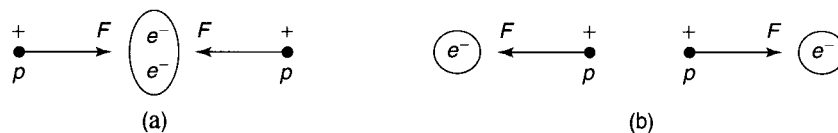


Figure 5.1: Schematic picture of the covalent bond: (a) Symmetric configuration produces attractive force; (b) antisymmetric configuration produces repulsive force.

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 spin⁴:

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

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 *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 ψ_n (Equation 2.24) and the other in state ψ_m orthogonal to ψ_n , calculate $\langle (x_1 - x_2)^2 \rangle$, 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 $\psi_a(x)$, one in state $\psi_b(x)$, and one in state $\psi_c(x)$. Assuming that 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.) *Note:* There's a cute

⁴In 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: $\psi_+(\mathbf{r})\chi_+ + \psi_-(\mathbf{r})\chi_-$.

⁵In 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.