Chapter 12

Multiple Particle States

12.1 Indistinguishable Particles

Every electron is exactly the same as every other electron. Thus, all electrons are indistinguishable. This means that if you have a state with two electrons, you can swap the two electrons and it cannot change anything physically observable from that state.

To make this concrete, suppose the state $|\psi\rangle$ is a state with two electrons. Let's define $|\psi'\rangle$ as the state with those two electrons swapped. Then, the expectation value of any operator must be the same for these two different states:

$$\left\langle \psi \middle| \hat{\mathcal{O}} \middle| \psi \right\rangle = \left\langle \psi' \middle| \hat{\mathcal{O}} \middle| \psi' \right\rangle$$

Also, the *probability* for any measurement of any observable to be made must be the same for the two states. That is, if $\langle\phi|$ is an eigenstate of a given observable, then

$$|\langle \phi \,|\, \psi \rangle|^2 = |\langle \phi \,|\, \psi' \rangle|^2$$

If you think about it, however, this does *not* mean that the two states must be identical! However, they must be close enough such that *anything physically observable from the state* must be identical. Below, we will introduce the *exchange operator* as a way of quantifying the effect of identical particles on quantum states.

12.2 Notating Multiple Particle States

Before we go further, we need to refine our notation so that we can keep track of two different particles. We can construct a two-particle state by putting together two states for each individual particle with:

$$|\psi_1\rangle \otimes |\phi_2\rangle$$

The $\otimes$ operator indicates that we're putting these two states together to form a composite state. It's sometimes called a "direct product", but it's not really all that much like multiplication. Really, it just means that we're making some composed state that combines particle 1 in state $|\psi\rangle$ and particle 2 in state $|\phi\rangle$. The subscript indicates which particle we're talking about; the rest of the stuff inside the ket indicates the state of that particular particle.

For simplicity, we will often omit the $\otimes$ symbol in the "direct product", and just write the two states next to each other, e.g.

$$|\psi_1\rangle\,|\phi_2\rangle$$

Again, this does not mean that we're multiplying two ket vectors, which is something we can't do. Instead, it means that we're *composing* the states. If these were spin states, we would *not* represent this with two column vectors. Instead, we'd represent it with a *single* four-row column vector; the first two rows have the column vector representation of whatever state the first particle is in, and the second two rows have the column vector representation of whatever state the second particle is in.

If an operator operates on this state, it only affects the state for the particle it is an operator for. That is, if "spin-z for particle 2" is the observable we're talking about, then the operator $\hat{S}_{z2}$ only operates on (in this example) the state $|\phi_2\rangle$. Indeed, you can treat $|\phi_1\rangle$ as if it were a constant:

$$\hat{S}_{z2}\;|\psi_1\rangle\,|\phi_2\rangle \;=\; |\psi_1\rangle\;\hat{S}_{z2}\;|\phi_2\rangle$$

As an example, suppose that particle 1 is in the state $|{+z}\rangle$ and particle 2 is in the state $|{-z}\rangle$. If we apply the $\hat{S}_{z2}$ operator to this state, we get:

$$\begin{aligned}\hat{S}_{z2}\;|{+z_1}\rangle\,|{-z_2}\rangle &= |{+z_1}\rangle\;\hat{S}_{z2}\;|{-z_2}\rangle \\ &= |{+z_1}\rangle\left(\frac{-\hbar}{2}\right)|{-z_2}\rangle \\ &= \left(-\frac{\hbar}{2}\right)|{+z_1}\rangle\,|{-z_2}\rangle\end{aligned}$$

Here, we have taken advantage of the fact that $|{-z_2}\rangle$ is an eigenstate of $\hat{S}_{z2}$, and replaced the action of the operator with a simple multiplication by the eigenvalue.

There will be some operators (e.g. the forthcoming exchange operator) that don't operate on just one of the two particles, but on both at the same time.

Similarly, with inner products, bra versions of a state only "stick" to ket versions of a state on the straight side of the bra-ket notation if they are states for the same particle. Thus, suppose we had a composite state:

$$|\xi\rangle = |\psi_1\rangle\,|\phi_2\rangle$$

The corresponding bra vector is:

$$\langle\xi| = \langle\psi_1|\,\langle\phi_2|$$

Normalization of this state is then expressed as:

$$\begin{aligned}\langle\xi\,|\,\xi\rangle &= (\langle\psi_1|\,\langle\phi_2|)\ (|\psi_1\rangle\,|\phi_2\rangle) \\ &= \langle\psi_1\,|\,\psi_1\rangle\ \langle\phi_2\,|\,\phi_2\rangle \\ &= 1\end{aligned}$$

We've rearranged states here a bit. We moved the $|\psi_1\rangle$ from after the $\langle\phi_2|$ to before it. This should make you a little nervous; we've seen that with matrices and other things that aren't simple numbers, multiplication is not necessarily commutative. However, again, in this case, when it comes to inner products, a state for a *different* particle can be treated as a constant with respect to inner products for the first particle. As such, it's entirely legitimate to move $|\psi_1\rangle$ into, out of, and through inner products on particle 2 (at least in the case of the simple composed states we're talking about here).

12.3 The Exchange Operator

The exchange operator, notated here by $\hat{P}_{12}$, just exchanges particle 1 for particle 2. In order to satisfy the conditions described in Section 12.1, a state composed of two *indistinguishable* particles (e.g. two electrons) must be an eigenstate of the exchange operator. Suppose that $|\xi\rangle$ is such a state. This means that

$$\hat{P}_{12}\ |\xi\rangle = c\ |\xi\rangle$$

where c is the eigenvalue. Suppose that we apply the exchange operator twice. What will happen? We should get back to the original state! We've just swapped the two particles back. Let's apply this twice:

$$\begin{aligned}\hat{P}_{12}\,\hat{P}_{12}\ |\xi\rangle &= \hat{P}_{12}\ (c\ |\xi\rangle) \\ &= c\,\hat{P}_{12}\ |\xi\rangle \\ &= c^2\ |\xi\rangle\end{aligned}$$

If the result of applying this exchange operator twice must be the state we started with, then we must have $c^2 = 1$. This is regular old fashioned squaring, not taking the absolute square. That $c^2 = 1$ means that there are only two possibilities for the eigenvalue of the exchange operator working on a state of two indistinguishable particles: $c = 1$ or $c = -1$.

12.4 Fermions and Bosons

In quantum mechanics, there are two kinds of particles. **Fermions** are particles that are *antisymmetric* under the exchange operator; that is, if $|\xi\rangle$ is a two-particle state for two indistinguishable fermions, $\hat{P}_{12}\,|\xi\rangle = -\,|\xi\rangle$. **Bosons** are particles that are *symmetric* under the exchange operator; that is, if $|\xi\rangle$ is a two-particle state for two indistinguishable bosons, $\hat{P}_{12}\,|\xi\rangle = |\xi\rangle$. This is summarized below:

$$\hat{P}_{12}\,|\xi\rangle \;=\; \begin{cases} \;\;\,|\xi\rangle & \text{for a two-boson state} \\[1em] -\,|\xi\rangle & \text{for a two-fermion state} \end{cases}$$

Which particles are which? Particles that have half-integral spin— which includes the spin-1/2 electrons we've been talking about all this time— are fermions. Other fermions include protons, neutrons, quarks, and neutrinos. Particles with integral spin are bosons. Bosons include photons, pions, and the force carriers for the weak and strong nuclear forces.

How do you create a two-fermion state with a total z component of angular momentum equal to zero? The most obvious first thing to guess is just to assign each particle angular momentum in a different direction, so that they cancel:

$$|\xi\rangle \;=\; |{+z_1}\rangle\,|{-z_2}\rangle$$

However, this state doesn't work! Why not? Consider the operation of the exchange operator on it:

$$\hat{P}_{12}\;|{+z_1}\rangle\,|{-z_2}\rangle \;=\; |{+z_2}\rangle\,|{-z_1}\rangle$$

We started with particle one having positive z-spin and particle 2 having negative z-spin. After the exchange, it's the other way around. However, this isn't the same state, nor is it a constant times the original state. On other words, this state is not an eigenstate of the exchange operator. Therefore, it's not a valid quantum state if particle 1 and particle 2 are indistinguishable particles (e.g. if they're two electrons).

A valid two-fermion spin state with total angular momentum zero would be:

$$|\xi\rangle \;=\; \frac{1}{\sqrt{2}}\,|{+z_1}\rangle\,|{-z_2}\rangle \;-\; \frac{1}{\sqrt{2}}\,|{+z_2}\rangle\,|{-z_1}\rangle$$

To verify that this works, let's try the exchange operator on this state:

$$\begin{aligned}\hat{P}_{12}\,|\xi\rangle &= \hat{P}_{12}\left(\tfrac{1}{\sqrt{2}}\,|{+z_1}\rangle\,|{-z_2}\rangle \;-\; \tfrac{1}{\sqrt{2}}\,|{+z_2}\rangle\,|{-z_1}\rangle\right)\\ &= \tfrac{1}{\sqrt{2}}\,\hat{P}_{12}\,|{+z_1}\rangle\,|{-z_2}\rangle \;-\; \tfrac{2}{\sqrt{2}}\,\hat{P}_{12}\,|{+z_2}\rangle\,|{-z_1}\rangle\\ &= \tfrac{1}{\sqrt{2}}\,|{+z_2}\rangle\,|{-z_1}\rangle \;-\; \tfrac{1}{\sqrt{2}}\,|{+z_1}\rangle\,|{-z_2}\rangle\\ &= -\,|\xi\rangle\end{aligned}$$

Sure enough, this state is an eigenstate of the exchange operator. What's more, the eigenvalue is -1, which is required for fermions. (If you're wondering about why we mess about with all of the $1/\sqrt{2}$ coefficients, we do that so that $|\xi\rangle$ is properly normalized. You can verify that this is the case, and indeed doing so would be good practice in doing algebra with bra and ket vector representations of multiple particle states.)

12.5 The Pauli Exclusion Principle

The Pauli Exclusion Principle states that no two fermions may occupy the same quantum state. This principle is absolutely crucial to life as we know it; without it, we would not have the Periodic Table of chemistry, nor would we have a lot of the rest of the structure of matter. This doesn't mean, however, that only one electron in the Universe is allowed to have positive z spin! Obviously, we have many more than two electrons in the Universe. However, if you have a quantum state, such as an energy level in an atom, where you can put electrons, you can only put *two* electrons into that energy level. Why two, and not one? Because of electron spin; as long as the two electrons have opposite spin (or, more precisely, are in a combined spin state with spin angular momentum zero such that they are antisymmetric under exchange), then you can put two electrons into the same state. It *is* possible to have two electrons with the same spin, so long as something else is different about their quantum states. So, for example, you could have two electrons with the same spin if they were in different orbitals in an atom.

Why can't you put more than one fermion in the same state? Because it's impossible to construct an antisymmetric state vector two fermions in the same state. Suppose you have a state $|\psi\rangle$, and you want to put two fermions into it. We know that the state:

$$|\psi_1\rangle\,|\psi_2\rangle$$

won't work, because the exchange operator working on it just produces the same state back, not the negative of the same state:

$$\hat{P}_{12}\,|\psi_1\rangle\,|\psi_2\rangle \;=\; |\psi_2\rangle\,|\psi_1\rangle \;=\; |\psi_1\rangle\,|\psi_2\rangle$$

This is an eigenvalue of the exchange operator, which is good, but the eigenvalue is +1. This would work for bosons; indeed, because of this, you can put as many bosons as you want all into the same state. However, for fermions, the eigenvalue of the exchange operator working on the two-particle state needs to be −1. If we try to construct an antisymmetric wave vector with both of these electrons in the same state:

$$\frac{1}{\sqrt{2}}\left|\psi_1\right\rangle\left|\psi_2\right\rangle \; - \; \frac{1}{\sqrt{2}}\left|\psi_2\right\rangle\left|\psi_1\right\rangle$$

we just end up with 0, which isn't a state at all. Thus, if you have two indistinguishable fermions, there *must* be something different about their states; you can't put more than one fermion into a single quantum state.

12.6 Entangled Particles

When two particles' quantum state is a combined quantum state, we say that those two particles are *entangled*. Most of the time we encounter such states, we don't worry about it too much. The two electrons in the ground state of Helium have entangled states, because they are indistinguishable particles. You can't talk about the state of one electron without talking about the state of another.

Entangled quantum states become more interesting when you separate the two particles. Suppose that there is some sort of reaction that produces two electrons that have a total spin angular momentum of zero. We've seen before that the state of these two electrons is then:

$$\frac{1}{\sqrt{2}}\left|+z_1\right\rangle\left|-z_2\right\rangle \; - \; \frac{1}{\sqrt{2}}\left|+z_2\right\rangle\left|-z_1\right\rangle$$

Although the total z angular momentum of this combined state is 0, a definite value, the angular momentum of an individual electron is *not* in a definite state. Now suppose that you separate these two electrons; it may be that the reaction that produces them sends them shooting off in two directions, which for discussion purposes we shall call "left" and "right".

Now let's suppose that somebody far off to the left detects the left electron and measures its z-spin. This measurement will collapse the wave function of the left electron, putting it into a state of definite z spin. However, because it's a combined state for the two electrons, you can't collapse the wave function of just one of them; you have to collapse the entire state all at once. Therefore, if somebody measures the z spin of the left electron, the wave function of the right electron *also* collapses at that moment, even if nobody has made a measurement on it. If the left observer measures that the left electron is spin up, then anybody off to the right *will* observe that the right electron is spin down; the right electron is no longer in an indefinite state, even though nothing was done to it.

This behavior of entangled particles is what Einstein referred to as "spooky action at a distance". (citation needed.) Not only was he disturbed by the stochastic nature of quantum mechanics, he was also bothered by what *seemed* to be communication faster than the speed of light. Does some sort of signal traverse from one electron to the other electron in order to communicate the fact that their mutual wave function has collapsed? Together with two other physicists, Podolsky and Rosen, Einstein argued that this behavior indicated that quantum theory had to be incomplete. In 1935, they published a paper describing what is now known as the "EPR Paradox" (Einstein et al., 1935). If quantum mechanics is indeed incomplete, then there would need to be some sort of "local hidden variable" that tells a particle which way its wave function *should* collapse when that particle is measured. This variable is "hidden" because it is not accounted for in quantum mechanics. In the early 1960's, physicist John Bell proposed experiments that would test the EPR paradox by being able to tell the difference between the standard predictions of quantum mechanics and the predictions of a theory that had some sort of local hidden variables (citation needed). Experiments performed since then have shown that in fact standard quantum mechanics does predict the correct results, and that therefore there are no local hidden variables. The fact is that, somehow, the wave function of an electron can collapse when another electron is measured— and that other electron may, at least in principle even if this is not realizable in practice, be light-years away. This raises philosophical issues associated with the interpretation of quantum mechanics, but also indicates that quantum mechanics remains a very robust theory.