Identical Particles

Suppose you have a system of two particles: particle #1 an particle #2. The overall wave function will be $\psi(\vec{r}_1,\ \vec{r}_2)$ where $\vec{r}_1$ is the position of particle #1 and $\vec{r}_2$ is the position of particle #2. But this assumes that you can tell the two particles apart. What if you can't? It turns out that, in quantum mechanics, identical particles are always indistinguishable. This means that you can never tell one electron from another. Indistinguishable particles require that the probability density does not change if we 'switch' the labels of the two particles, meaning that $|\psi(\vec{r}_1,\ \vec{r}_2)|^2 = |\psi(\vec{r}_2,\ \vec{r}_1)|^2$. There are two ways for this to happen.

If $\psi(\vec{r}_2,\ \vec{r}_1) = \psi(\vec{r}_1,\ \vec{r}_2)$ we say that the particles are symmetric under exchange. Particles that behave this way are called bosons. If $\psi(\vec{r}_2,\ \vec{r}_1) = -\psi(\vec{r}_1,\ \vec{r}_2)$ we say that the particles are antisymmetric under exchange. Particles that behave this way are called fermions. It turns out that particles with integer spin are bosons, while those with half-integer spin are fermions.

So suppose that we have two particles of the same mass, one in single particle state $\psi_1(x)$ and the other in single particle state $\psi_2(x)$. What is the overall wave function? If the particles are distinguishable the overall wave unction is $\psi(x_1,\ x_2) = \psi_1(x_1)\psi_2(x_2)$, indicating that we can distinguish that particle #1 is in state ψ_1. If the two particles are identical bosons then the overall wave function is $\psi(x_1,\ x_2) = \frac{1}{\sqrt{2}}[\psi_1(x_1)\psi_2(x_2) + \psi_2(x_1)\psi_1(x_2)]$. In this wave function we know that one particle is in state ψ_1 and other is in state ψ_2, but we don't know which is which and the overall wave function is symmetric under exchange. If the two particles are identical fermions then the overall wave function is $\psi(x_1,\ x_2) = \frac{1}{\sqrt{2}}[\psi_1(x_1)\psi_2(x_2) - \psi_2(x_1)\psi_1(x_2)]$. This wave function is antisymmetric under exchange.

As a note, everything in the previous paragraph and our next example ignores spin. We sometimes preface problems of this sort by

saying something like "spinless non-interacting fermions" but of course a fermion can't be spinless. We'll cover the changes induced by spin later, but for now we will just accept the concept of a spinless fermion, or if you would prefer just assume that this refers to fermions with the same spin (up or down for example).

In the case of identical fermions, if you try to place two particles (with the same spin) in the same wave function the minus sign in the antisymmetrization leads to, for example $\psi(x_1,\ x_2) = \frac{1}{\sqrt{2}}[\psi_1(x_1)\psi_1(x_2) - \psi_1(x_1)\psi_1(x_2)] = 0$. The wave function goes to zero everywhere and is no longer normalizable. This is an example of the Pauli exclusion principle: two identical fermions can not occupy the same quantum state.

As an example, we will consider two non-interacting, spinless particles of the same mass in the same 1D infinite square well potential of with a. If one particle is in state $\psi_{n_1}(x)$ and the other is in the state $\psi_{n_2}(x)$ Then the energy will be $K(n_1^2+n_2^2)$ where $K \equiv \frac{\pi^2\hbar^2}{2ma^2}$. The lowest energy state should be $\psi_1(x_1)\psi_1(x_2)$: both particles in the ground state for a total energy of $2K$. This is in fact the non-degenerate ground state in the case where the particles are either distinguishable or identical bosons (this state is symmetric under exchange). However, this state is NOT allowed for identical fermions due to the Pauli exclusion principle. The next highest energy will be when one particle is in the ground state ψ_1 and the other is in the first excited state ψ_2; this will have energy $5K$. For distinguishable particles this will be two-fold degenerate: $\psi_1(x_1)\psi_2(x_2)$ and $\psi_2(x_1)\psi_1(x_2)$. This state is non-degenerate for both identical bosons and identical fermions, with symmetric combination $\psi(x_1,\ x_2) = \frac{1}{\sqrt{2}}[\psi_1(x_1)\psi_2(x_2) + \psi_2(x_1)\psi_1(x_2)]$ for bosons and the antisymmetric combination $\psi(x_1,\ x_2) = \frac{1}{\sqrt{2}}[\psi_1(x_1)\psi_2(x_2) - \psi_2(x_1)\psi_1(x_2)]$ for fermions.

Energy	Distinguishable Particles		Identical Bosons		Identical Fermions	
$2K$	1	state $\psi_1\psi_1$	1	state $\psi_1\psi_1$	0	
$5K$	2	$\psi_1\psi_2$ and $\psi_2\psi_1$	1	$\frac{1}{\sqrt{2}}[\psi_1\psi_2+\psi_2\psi_1]$	1	$\frac{1}{\sqrt{2}}[\psi_1\psi_2-\psi_2\psi_1]$
$8K$	1	state $\psi_2\psi_2$	1	state $\psi_2\psi_2$	0	
$10K$	2	$\psi_1\psi_3$ and $\psi_3\psi_1$	1	$\frac{1}{\sqrt{2}}[\psi_1\psi_3+\psi_3\psi_1]$	1	$\frac{1}{\sqrt{2}}[\psi_1\psi_3-\psi_3\psi_1]$

At this point, it is worth it to talk about degeneracy. In the above table I say that the $E = 5K$ state is two-fold degenerate for distinguishable particles with states $\psi_1(x_1)\psi_2(x_2)$ and $\psi_2(x_1)\psi_1(x_2)$. That is a perfectly valid answer. But any linear combination of those two will also be an energy eigenstate with the same energy. So if we wanted, we could have instead said that two states were $\frac{1}{\sqrt{2}}[\psi_1(x_1)\psi_2(x_2)+\psi_2(x_1)\psi_1(x_2)]$ and $\frac{1}{\sqrt{2}}[\psi_1(x_1)\psi_2(x_2)-\psi_2(x_1)\psi_1(x_2)]$. That would have been equally valid: those two states are orthogonal and have the right energy, and for distinguishable particle we don't need to worry about exchange symmetry. As always: if you have N-fold degeneracy then you can construct a basis of N distinct states (distinct meaning mutually orthogonal) that have that same eigenvalue. But the set of states is not unique: there will always be an infinite number of ways of constructing the states and these ways are all equally valid.

Exchange Forces

Suppose we have two spinless non-interacting particles. One particle is in state $\psi_a(x)$ while the other is in state $\psi_b(x)$ where these two states are normalized and orthogonal. We already know how to construct the overall wave functions:
Distinguishable particles - $\psi_d(x_1,\ x_2) = \psi_a(x_1)\psi_b(x_2)$
Identical bosons - $\psi_b(x_1,\ x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2)+\psi_b(x_1)\psi_a(x_2)]$
Identical fermions - $\psi_f(x_1,\ x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2)-\psi_b(x_1)\psi_a(x_2)]$

Now let us calculate $\langle(x_1-x_2)^2\rangle$: the expectation value of the square of the distance between the two particles. Working out the solution it

becomes clear that the answers are:
Distinguishable particles - $\langle(\Delta x)^2\rangle_d = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b$
Identical bosons - $\langle(\Delta x)^2\rangle_b = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b - 2|\langle x\rangle_{ab}|^2$
Identical fermions - $\langle(\Delta x)^2\rangle_f = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b + 2|\langle x\rangle_{ab}|^2$

In these equations we short-hand integrals as $\langle x^2\rangle_a = \int \psi_a^* x^2 \psi_a \, dx$: the expectation value of x^2 for the one-particle state $\psi_a(x)$, etc. The remaining term is defined as

$$\langle x\rangle_{ab} \equiv \int \psi_a^* x \psi_b \, dx$$

and it is this term that causes the difference between the two cases.

What we see is that the average particle separation is smaller when the overall wave function is symmetric under exchange compared to distinguishable particles. And the average particle separation is larger when the overall wave function is antisymmetric under exchange compared to distinguishable particles. It is as if there were an 'exchange force' pushing the particles closer together or farther apart. But this is not a real force - these are non-interacting particles after all.

Spin and the Generalized Symmetrization Principle

So far we have been working on examples where we ignored spin. This is odd - after all there is no such thing as a spinless fermion. Now we bring spin into the story. The two particle state is now $\psi(\vec{r}_1,\ \vec{r}_2)\chi(1,\ 2)$ where $\chi(1,\ 2)$ refers to the spin state of particles #1 and #2. It is this FULL state that determines exchange symmetry. Therefore, fermions being antisymmetric under exchange implies that $\psi(\vec{r}_2,\ \vec{r}_1)\chi(2,\ 1) = -\psi(\vec{r}_1,\ \vec{r}_2)\chi(1,\ 2)$: swapping the labels on our particles yields an overall minus sign to the quantum state.

Suppose that you have two identical spin-$\frac{1}{2}$ fermions (such as electrons). One electron is in state ψ_a and the other in ψ_b. The two particles can exist in a spatially symmetric wave function and the (antisymmetric) singlet spin state:

$$\frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) + \psi_a(x_2)\psi_b(x_1)]|0\ 0\rangle$$

or they can exist in a spatially antisymmetric wave function and a (symmetric) triplet spin state:

$$\frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) - \psi_a(x_2)\psi_b(x_1)]|1\ \ m = -1,\ 0,\ \text{or}\ +1\rangle$$

with this later option being three-fold degenerate.

No let us consider a harder problem. Suppose that you have <u>three</u> identical non-interacting spin-$\frac{1}{2}$ fermions placed in the same 1D simple harmonic oscillator potential. The energies will be $\hbar\omega(n_1+n_2+n_2+\frac{3}{2})$ where the three indices can each be a non-negative integer. However there is no allowed state with $E = \frac{3}{2}\hbar\omega$: by the Pauli exclusion principle you can't put all three spin-$\frac{1}{2}$ particles into the single-particle ground state $\psi_0(x)$. Therefore the ground state energy of the three particle system will by $\frac{5}{2}\hbar\omega$ with two particles in ψ_0 with opposite spins (or more

accurately in the singlet spin state) and the third particle in ψ_1. This ground state will be two-fold degenerate because the particle in ψ_1 can be either spin up or spin down. But of course the actual states must be fully antisymmetric under exchange of any two particles. And in this case we can't write them as a spatially symmetric wave function multiplied by an antisymmetric spin part because it is not possible to write a completely antisymmetric combination of three spin-1/2 particles. Therefore the actual two states for the degenerate ground state are $|\psi_{001}\uparrow\downarrow\uparrow|$ and $|\psi_{001}\uparrow\downarrow\downarrow|$ where I'm trying to denote the Slater determinates:

$$|\psi_{001}\uparrow\downarrow\uparrow| = \begin{vmatrix} \psi_0(x_1)|\uparrow_1\rangle & \psi_0(x_1)|\downarrow_1\rangle & \psi_1(x_1)|\uparrow_1\rangle \\ \psi_0(x_2)|\uparrow_2\rangle & \psi_0(x_2)|\downarrow_2\rangle & \psi_1(x_2)|\uparrow_2\rangle \\ \psi_0(x_3)|\uparrow_3\rangle & \psi_0(x_3)|\downarrow_3\rangle & \psi_1(x_3)|\uparrow_3\rangle \end{vmatrix}$$

which IS in fact fully antisymmetric (You'll use a Slater determinant in the homework).

The first excited state will have $n_1 + n_2 + n_3 = 2$. One way to do this is with two particles in the ground state and the third particle in ψ_2, which I call ψ_{002}. This has a degeneracy of two because the third particle (in ψ_2) could be either spin up or spin down. We could also achieve $n_1 + n_2 + n_3 = 2$ with two particles in ψ_1 and the third particle in ψ_0, or ψ_{110}. The two particles in ψ_1 will necessarily be in a singlet due to Pauli exclusion, but the third particle in ψ_0 can be either spin up or spin down so this also has a degeneracy of 2. Adding these together the first excited state has a degeneracy of four.

The second excited state will have $n_1 + n_2 + n_3 = 3$. Note that $n_1 = n_2 = n_3 = 1$ is NOT ALLOWED by Pauli exclusion so there will not be any ψ_{111} states. The two allowed possibilities will be ψ_{003} (two particles in ψ_0 and the third in ψ_3) and ψ_{012} (one in ψ_0, one in ψ_1, and one in ψ_2). For ψ_{003} the two particles in ψ_0 will have to be in a

singlet, but the particle in ψ_3 can be either spin up or spin down which yields a degeneracy of 2. For ψ_{012} we do not need to worry about Pauli exclusion since each particle is in a different spatial stationary state. Therefore each of the three particles can be either spin up or spin down, yielding a $2^3 = 8$ fold degeneracy for the ψ_{012} states. Adding 2+8 gives a total degeneracy of 10 for the $E = \frac{9}{2}\hbar\omega$ second excited state.

The third excited state will have $n_1 + n_2 + n_3 = 4$. There are four ways to achieve this: ψ_{004}, ψ_{112}, ψ_{220}, and ψ_{013}. The first three of these each feature two particles in the same one-particle stationary state, necessarily in the singlet state. Each of these is two-fold degenerate because the third particle can be either spin up or spin down. For the ψ_{013} states there is no Pauli exclusion to worry about so each spin can be either up or down, giving a degeneracy of 8. Adding 2+2+2+8 gives a total degeneracy of 14 for the $E = \frac{11}{2}\hbar\omega$ third excited state.

Energy	Degeneracy	States
$\frac{5}{2}\hbar\omega$	2	$\lvert\psi_{001}\uparrow\downarrow\uparrow\rangle$ and $\lvert\psi_{001}\uparrow\downarrow\downarrow\rangle$
$\frac{7}{2}\hbar\omega$	4	$\lvert\psi_{002}\uparrow\downarrow\uparrow\rangle$, $\lvert\psi_{002}\uparrow\downarrow\downarrow\rangle$, $\lvert\psi_{110}\uparrow\downarrow\uparrow\rangle$, $\lvert\psi_{110}\uparrow\downarrow\downarrow\rangle$
$\frac{9}{2}\hbar\omega$	10	$\lvert\psi_{003}\uparrow\downarrow\uparrow\rangle$, $\lvert\psi_{003}\uparrow\downarrow\downarrow\rangle$, $\lvert\psi_{012}\uparrow\uparrow\uparrow\rangle$, $\lvert\psi_{012}\uparrow\uparrow\downarrow\rangle$, $\lvert\psi_{012}\uparrow\downarrow\uparrow\rangle$, $\lvert\psi_{012}\uparrow\downarrow\downarrow\rangle$, $\lvert\psi_{012}\downarrow\uparrow\uparrow\rangle$, $\lvert\psi_{012}\downarrow\uparrow\downarrow\rangle$, $\lvert\psi_{012}\downarrow\downarrow\uparrow\rangle$, $\lvert\psi_{012}\downarrow\downarrow\downarrow\rangle$
$\frac{11}{2}\hbar\omega$	14	$\lvert\psi_{112}\uparrow\downarrow\uparrow\rangle$, $\lvert\psi_{112}\uparrow\downarrow\downarrow\rangle$, $\lvert\psi_{004}\uparrow\downarrow\uparrow\rangle$, $\lvert\psi_{004}\uparrow\downarrow\downarrow\rangle$, $\lvert\psi_{220}\uparrow\downarrow\uparrow\rangle$, $\lvert\psi_{220}\uparrow\downarrow\downarrow\rangle$ $\lvert\psi_{013}\uparrow\uparrow\uparrow\rangle$, $\lvert\psi_{013}\uparrow\uparrow\downarrow\rangle$, $\lvert\psi_{013}\uparrow\downarrow\uparrow\rangle$, $\lvert\psi_{013}\uparrow\downarrow\downarrow\rangle$, $\lvert\psi_{013}\downarrow\uparrow\uparrow\rangle$, $\lvert\psi_{013}\downarrow\uparrow\downarrow\rangle$, $\lvert\psi_{013}\downarrow\downarrow\uparrow\rangle$, $\lvert\psi_{013}\downarrow\downarrow\downarrow\rangle$,

So far we have taken the symmetrization/antisymmetrization re-

quirements for bosons/fermions to be a given. We can show why this must be the case. First we define $\hat{P}$ as the exchange operator. This operator exchanges two particles, by switching our labels for them: $\hat{P}|(1,\ 2)\rangle = |(2,\ 1)\rangle$. If you apply $\hat{P}$ twice you switch the particles back to where they started. This means that $\hat{P}^2 = \hat{1}$ (the identity operator). Because applying $\hat{P}$ twice gives the identity operator, $\hat{P}$ can only have the eigenvalues of $+1$ and -1. Bosons have the eigenvalue $+1$ and fermions have the eigenvalue -1.

Further, if the two particles are identical then the Hamiltonian must treat them the same. Therefore $[\hat{H},\ \hat{P}] = 0$ and thus $\dfrac{d\langle\hat{P}\rangle}{dt} = 0$. If the system starts out either symmetric or antisymmetric it will remain that way forever.

Helium and other Atoms

After Hydrogen, the next simplest atoms in Helium. Helium consists of electrons and a nucleus with two protons (and two neutrons in the most common isotope). The Hamiltonian becomes:

$$\hat{H} = \left\{ -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

which is two Hydrogen-like Hamiltonians (with the nucleus charge doubled) plus an electron-electron Coulomb repulsion term.

If we simply ignored the Coulomb repulsion term the ground state would be the product of two hydrogen ground state, but with the Bohr radius halved and each energy quadrupled: $\psi(\vec{r}_1,\, \vec{r}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)$ with energy $8 \cdot (-13.6 \text{ eV}) = -108.8$ eV. The actual ground state has been measured to have an energy of -79.0 eV, with this difference caused by the Coulomb repulsion. This is still a spatially symmetric wave function, so the two electrons must be in the (antisymmetric, singly degenerate) singlet configuration.

The excited states are more interesting. The first excited state is when one electron is roughly $\psi_{100}\psi_{200}$ (not exactly because Coulomb repulsion changes the wave functions, but this is close): one electron in the hydrogen-like ground state and the other is in the $n = 2$, $l = 0$ state. (Note in real hydrogen this is degenerate with $n = 2$, $l = 1$. But in helium those are no longer degenerate.)

The first excited state comes in two types called orthohelium and parahelium. Parahelium has a spatially symmetric wave function and a singlet spin state. It is therefore nondegenerate. Orthohelium has a spatially antisymmetric wave function and a triplet spin state; it has a degeneracy. Parahelium states are a slightly higher energy than orthohelium states. The spatially symmetric states lead to the electrons being closer together, which leads to higher Coulomb repulsion

energy. Orthohelium states, with a spatially antisymmetric wave function, have the electrons on average a bit farther apart. This lead to a lower potential energy and therefore a lower overall energy.

As more electrons are added, further atoms become more complex. The angular momentum state of an atom or ion is often represented by its term symbol: ${}^{2S+1}L_J$ where $2S+1$ and J are represented by numbers while L is represented by a letter. These letters are S ($L = 0$), P ($L = 1$), D ($L = 2$), F ($L = 3$), G ($L = 4$), ... (continuing alphabetically but skipping J, P, and S). Therefore ${}^4F_{3/2}$ is the term symbol for $S = 3/2$, $L = 3$, $J = 3/2$, etc. Determining the appropriate term symbol for a given atom or ion usually means applying Hund's Rules:

- Hund's 1^{st} rule: The lowest energy state will be that with the highest total spin (S), consistent with Pauli exclusion. This means that electrons placed into an orbital will point in the same direction (usually chosen to be spin up) until the orbital is half filled, and only then will further electrons be spin down.
- Hund's 2^{nd} rule: After applying the first rule, the lowest energy state will be that with the highest possible orbital angular momentum L.
- Hund's 3^{rd} rule: If a $(n,\ l)$ orbital is no more than half-filled then $J = |L - S|$. If it is more than half filled then $J = L + S$. (If it is exactly half-filled then the second rule implies that $L = 0$ so these two formulas give the same answer.)