Exchange Energy

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We have learned that when it comes to Fermionic particles, the full wavefunction must be antisymmetric under exchange of any two particles. For two particles, we have

$$\Psi(x_1, x_2) = -\Psi(x_2, x_1)$$

This has several dramatic effects, one of which is the following, called exchange energy.

Suppose we have two particles which interact via a repulsive force, so that their potential energy is large when the particles are nearby. Quantum mechanically, this means the energy is large when the probability density $|\Psi(x_1, x_2)|^2$ is large for x_1 is close to x_2. For an antisymmetric spatial wavefunction, $\Psi(x_1, x_2) \to 0$ as x_1 approaches x_2, which can be seen by plugging $x_1 = x_2$ into the first equation. The probability density is also small when x_1 is near x_2 therefore. This reflects the tendency of fermionic particles to 'spread out,' which will lead to a lowering of their potential energy.

Here is an example using spin $1/2$ particles in a harmonic oscillator potential. Schematically, we want to consider a situation like

$$\mathbf{H} = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{1}{2}m\omega^2(x_1^2 + x_2^2) + V(|x_1 - x_2|)$$

Generically, the presence of the additional potential V means that we will no longer be able to solve the problem. We can approximate the effects of the interaction by first solving the problem without the interaction and then calculating the expectation value of the interaction energy in the eigenstates of the solvable problem. This will tell us approximately how much the energy of each state shifts due to the potential.

If we erase V, we just have a quantum harmonic oscillator, which we have already solved. The first two wavefunctions are $\phi_0(x) \sim e^{-m\omega x^2/2\hbar}$ and $\phi_1(x) \sim xe^{-m\omega x^2/2\hbar}$ (neglecting some normalization constants). Our particles also have spin, which in this case just acts as another label which goes along for the ride.

A single particle wave function is therefore specified by n and s in $\phi_{ns}(x)$. For notational simplicity, I will write the two values of s and $+$ and $-$ rather than $+1/2$ and $-1/2$. So there are two ground state wave functions $\phi_{0+}(x)$ and $\phi_{0-}(x)$. The dependence on x is the same.

Because the particles are fermionic, their total wave function must be antisymmetric. This leads us to two possibilities: one is that the spatial part is symmetric and the spin part is antisymmetric, the other is that the spatial part is antisymmetric and the spin part is symmetric.

Let us now write the first four states for the two-particle case. The energy is $\epsilon = \hbar\omega(n_1 + n_2 + 1)$ so the lowest energy state has $n_1 = n_2 = 0$. The Pauli exclusion principle states that no two fermions can have the same set of quantum numbers, so if the two electrons have the same n, they must have different spin. Together with the overall antisymmetry of the wavefunction, this determines the ground state to be

$$\Psi_{gs}(x_1, x_2) = \phi_{0+}(x_1)\phi_{0-}(x_2) - \phi_{0+}(x_2)\phi_{0-}(x_1)$$

You should verify that $\Psi \to -\Psi$ if you exchange x_1 and x_2. There is a fourfold degeneracy of the first excited energy level. The states participating are

$$\Psi_1(x_1, x_2) = \phi_{1+}(x_1)\phi_{0+}(x_2) - \phi_{1+}(x_2)\phi_{0+}(x_1)$$
$$\Psi_2(x_1, x_2) = \phi_{1-}(x_1)\phi_{0-}(x_2) - \phi_{1-}(x_2)\phi_{0-}(x_1)$$
$$\Psi_3(x_1, x_2) = \phi_{1+}(x_1)\phi_{0-}(x_2) + \phi_{1-}(x_1)\phi_{0+}(x_2) - \phi_{0+}(x_1)\phi_{1-}(x_2) - \phi_{0-}(x_1)\phi_{1+}(x_2)$$
$$\Psi_4(x_1, x_2) = \phi_{1+}(x_1)\phi_{0-}(x_2) - \phi_{1-}(x_1)\phi_{0+}(x_2) + \phi_{0+}(x_1)\phi_{1-}(x_2) - \phi_{0-}(x_1)\phi_{1+}(x_2)$$

up to some overall normalization constants. The first three wavefunctions have a symmetric spin part, and an antisymmetric spatial part (which you can see by exchanging either the $+$ and $-$ assignments, or the $0, 1$ assignments). The fourth wave function has a symmetric spatial part and an antisymmetric spin part. All four wave functions are overall antisymmetric. When we want to calculate the expectation value of the potential, which does not involve the spin, we will only need the spatial parts

$$\psi_{sym} = \phi_0(x_1)\phi_1(x_2) + \phi_0(x_2)\phi_1(x_2) \qquad \psi_{anti} = \phi_0(x_1)\phi_1(x_2) - \phi_0(x_2)\phi_1(x_2)$$

and the corresponding probability densities $|\psi|^2$. Suppose we consider the two electrons interacting via a repulsive coulomb interaction

$$V(|x_1 - x_2|) = \frac{ke^2}{|x_1 - x_2|}$$

Intuitively, the expectation value of this potential energy should be lower in the state with the antisymmetric wavefunction because the vanishing probability density counteracts the increasing potential energy when x_1 approaches x_2. We can calculate

$$\frac{\int_{-\infty}^{\infty} dx_1 dx_2 \, |\psi_{anti}(x_1, x_2)|^2 \frac{ke^2}{|x_1 - x_2|}}{\int_{-\infty}^{\infty} dx_1 dx_2 \, |\psi_{anti}(x_1, x_2)|^2} = \sqrt{\frac{2m\omega}{\pi\hbar}}$$

Unfortunately for the symmetric wave function, the answer is infinity, which certainly supports the argument but is a bit pathological. The reason is that the denominator in the integrand in this case is free to go to zero without anything in the numerator also vanishing, so the integrand becomes infinite. We can get around this by pretending the electrons have a 'hard core' so that they cannot get closer than some distance d to each other. In that case the maximum value of the potential energy is ke^2/d and now both integrals are finite.

Unfortunately we can no longer evaluate them. However, the situation is not hopeless. Using $|\psi_{sym}|^2 = e^{-m\omega(x_1^2+x_2^2)/\hbar}(x_1+x_2)^2$ and $|\psi_{anti}|^2 = e^{-m\omega(x_1^2+x_2^2)/\hbar}(x_1-x_2)^2$, we can still see that

$$\int dx_1 dx_2 \, \frac{e^{-m\omega(x_1^2+x_2^2)/\hbar}(x_1+x_2)^2}{|x_1-x_2|+d} > \int dx_1 dx_2 \, \frac{e^{-m\omega(x_1^2+x_2^2)/\hbar}(x_1-x_2)^2}{|x_1-x_2|+d}$$

because for any x_1 and x_2, the integrand on the left hand side is larger than that of the right hand side when evaluated either at the same x, or possibly reversing the sign of one of them. So $\langle V \rangle_{anti} < \langle V \rangle_{sym}$, which was what we set out to show.

A different potential energy which does not display this diverging behavior is $V = V_0 e^{-(x_1-x_2)^2/r_0^2}$ which has a maximum value of V_0 and dies off with a characteristic length r_0 as x_1 and x_2 move apart. In this case, both of the integrals are finite and we find (use mathematica to help with the integrals)

$$\langle V \rangle_{anti} = \frac{r_0^3 V_0}{(r_0^2 + \frac{2\hbar}{m\omega})^{3/2}}$$

and

$$\langle V \rangle_{sym} = \frac{r_0 V_0}{\sqrt{r_0^2 + \frac{2\hbar}{m\omega}}}$$

The difference $\Delta\langle V \rangle = \langle V \rangle_{sym} - \langle V \rangle_{anti} = 2r_0 V_0 \hbar \sqrt{\frac{m\omega}{(m\omega r_0^2+2\hbar)^3}}$ which is a positive number. So we have shown that the state with the symmetric spatial wave function has a higher average potential energy.

Now we have understood this effect in both general and specific terms: when the spatial part of the wave function is antisymmetric, it is more 'spread out', leading to a decrease in the potential energy, which is supported by our example calculation. Another perspective on the situation is to look at it from the spin side of things: the symmetric spin state has lower energy than the antisymmetric spin state. This phenomenon is very impotant and leads to many nontrivial effects in condensed matter physics, for example.