Pauli principle and multielectron wavefunctions

Since electrons are identical, the total wavefunction for a group of electrons in the same atom must either **not change** (e.g. be symmetric) under the exchange of any 2 electrons or **change sign** (e.g. be antisymmetric) under the exchange of any 2 electrons. (Note that in general we write the combined wavefunction for several electrons as a sum of products of the different orbitals and spin-states for each electron.) For example, a symmetric wavefunction for 2 electrons might look like this:

$$\phi_T^S(1,2) = \phi_\alpha(1)\phi_\beta(2) + \phi_\alpha(2)\phi_\beta(1) \tag{1}$$

where ϕ_α and ϕ_β correspond to the spatial AND spin state for a given orbital. Note that if we exchange electrons 1 and 2 the wavefunction does not change (the two terms just switch). Also note that we can write ϕ_α as a product of a spatial orbital $\phi_A(r)$ and a spin-part χ_A, e.g.

$$\phi_\alpha(1) = \phi_A(r_1)\chi_A(1) \tag{2}$$

where ϕ corresponds to the spatial wavefunction and χ corresponds to the spin part of the wavefunction. Similarly, we can write $\phi_\beta(1) = \phi_B(r_1)\chi_B(1)$ as the product of a spatial part and a spin part. Note that for a single electron the spin-part of the wavefunction corresponds either to spin-up ($\uparrow$) or spin-down ($\downarrow$).

However, since the only thing that we can measure is the probability (e.g. the square of the wavefunction) there is another possibility:

$$\phi_T^A(1,2) = \phi_\alpha(1)\phi_\beta(2) - \phi_\alpha(2)\phi_\beta(1) \tag{3}$$

This corresponds to an antisymmetric wavefunction, e.g. the wavefunction changes sign when we exchange the 2 electrons. However, since the probability density depends only on the square of the wavefunction such an antisymmetric wavefunction is also acceptable for a pair of identical electrons.

The Pauli principle states that for fermions (e.g. particles with spin 1/2, 3/2 etc.) the TOTAL wavefunction (including spin and spatial part) must be antisymmetric under the exchange of any two particles. Note that this implies that for 2 electrons the total wavefunction may be written according to Eq. 3 above. This also implies that if we have two electrons in the exact same state ϕ_α (including both spin and spatial orbital), e.g. if $\phi_\alpha = \phi_\beta$ or $\alpha = \beta$ then $\phi_T = 0$. In other words, it implies that no two electrons can have the same set of all quantum numbers, e.g. be in the same state α.

Another way to write the total wave function shown in (3) for two electrons is as the product of a spatial part and a spin part. There are two ways in which the total wavefunction can be antisymmetric: (1) either the spatial part can be symmetric and the spin part can be antisymmetric OR (2) the spatial part can be symmetric and the spin part can be antisymmetric. So for two electrons (fermions) we can either write,

$$\phi_T(1,2) = [\phi_A(r_1)\phi_B(r_2) + \phi_A(r_2)\phi_B(r_1)]\;[\chi_A(1)\chi_B(2) - \chi_A(2)\chi_B(1)] \tag{4}$$

or we can write,

$$\phi_T(1,2) = [\phi_A(r_1)\phi_B(r_2) - \phi_A(r_2)\phi_B(r_1)]\;[\chi_A(1)\chi_B(2) + \chi_A(2)\chi_B(1)] \tag{5}$$

In the first case (4) the spatial part is symmetric but the spin part is antisymmetric. In the second case the spatial part is antisymmetric but the spin part is symmetric.

Now, let's consider the spin wave functions for two electrons in two different orbitals ϕ_A and ϕ_B. Since $s_1 = s_2 = 1/2$, then either $S = 0$ or $S = 1$. $S = 0$ corresponds to a singlet state ${}^1S$ while $S = 1$ corresponds to a triplet state ${}^3S$. For the singlet $S = 0$ state it turns out that the spin wave function may be written:

$$\chi(1,2)_{singlet} = \uparrow_1\downarrow_2 - \uparrow_2\downarrow_1 \tag{6}$$

In contrast, for the 3 triplet ($S = 1$) states one has,

$$\chi(1,2)^{M_S=1}_{triplet} = \uparrow_1\uparrow_2 \tag{7}$$

$$\chi(1,2)^{M_S=0}_{triplet} = \uparrow_1\downarrow_2 + \uparrow_2\downarrow_1 \tag{8}$$

$$\chi(1,2)^{M_S=-1}_{triplet} = \downarrow_1\downarrow_2 \tag{9}$$

Notice that the singlet spin-state is antisymmetric which implies that the spatial wave function for the two electrons must be symmetric, e.g.

$$\psi^{S=0}_{singlet}(1,2) = [\phi_A(r_1)\phi_B(r_2) + \phi_A(r_2)\phi_B(r_1)]\chi(1,2)_{singlet} \tag{10}$$

In contrast all the triplet ($S = 1$) spin-states are symmetric which implies that the spatial wave function must be antisymmetric, e.g.

$$\psi^{S=1}_{triplet}(1,2) = [\phi_A(r_1)\phi_B(r_2) - \phi_A(r_2)\phi_B(r_1)]\chi(1,2)_{triplet} \tag{11}$$

Eq. 11 implies that for the $S = 1$ state the probability of finding two electrons in the same position r is zero, since $\phi_A(r_1 = r)\phi_B(r_2 = r) - \phi_A(r_2 = r)\phi_B(r_1 = r) = 0$. This gives an explanation for Hund's rule, e.g. for why the $S = 1$ state has a lower energy than the $S = 0$ state. The reason is that for the $S = 1$ state the probability of the two electrons being near each other (e.g. that $r_1 = r_2 = r$) is zero, which implies that the Coulomb repulsion energy of the electrons is reduced. This reduction in the Coulomb repulsion energy for the $S = 1$ state explains why, for the same pair of spatial orbitals ϕ_A and ϕ_B, it has a lower energy than the $S = 0$ state.

In general, if we have an atom with N electrons, with each electron in a different quantum state ψ_{α_i} then the total wavefunction can be written as,

$$\psi_T(1, 2, ...N) = \frac{1}{\sqrt{N!}} \sum_P Sign(P)\ \psi_{\alpha_1}(P1)\psi_{\alpha_2}(P2)\psi_{\alpha_3}(P3)....\psi_{\alpha_N}(PN) \tag{12}$$

where the sum is over all $N!$ possible permutations P of $1...N$. Note that Sign(P) is +1 if P is an even permutation (even number of exchanges) and -1 if P is an odd permutation. This is sometimes called a Slater determinant.