8.5: The Pauli Exclusion Principle

One explanation as to why the differences between the term symbols that arise from a p^2 configuration relative to a pp configuration is the **Pauli Exclusion principle**. The usual statement of the Pauli Exclusion Principle is that no two electrons in an atom can have the same set of four quantum numbers n, l, m_l and m_s. Another explanation is to simply announce that

Electrons are Fermions!

This approach is useful if you happen to know the properties of Fermions, but does not provide much insight if you do not.

A **Fermion** is a particle with half-integral spin. An obvious example (according to the statement above) is an electron which has $\boldsymbol{s} = \frac{1}{2}$. Other examples include protons and neutrons and fluorine-19 nuclei (all with $\boldsymbol{I} = \frac{1}{2}$), aluminum-27 nuclei ($\boldsymbol{I} = \frac{5}{2}$) etc. Fermions have the property that the total wavefunction of a system containing two equivalent fermions must change sign if the two particles are exchanged.

The other type of particle is called a **Boson**. This is a particle with integral spin. Examples of bosons include deuterium nuclei or nitrogen-14 nuclei (both with $\boldsymbol{I} = 1$) or helium-4 nuclei ($\boldsymbol{I} = 0$). A system containing two equivalent bosons must have a wavefunction that does not change sign for the exchange of two equivalent bosons.

$$\Psi(1,2) = -\Psi(2,1) \qquad \text{(for fermions)}$$
$$\Psi(1,2) = \Psi(2,1) \qquad \text{(for bosons)}$$

In order to explore the properties of these types of particles, it is useful to define an operator that exchanges two equivalent particles (1 and 2).

$$\hat{O}\Psi(1,2) = \Psi(2,1)$$
$$\hat{O}\psi_m(1)\psi_n(2) = \psi_m(2)\psi_n(1)$$

In the limit that spin and orbital wavefunctions are separable (the total wavefunction can be expressed as the product of a spin function and an orbital function)

$$\Psi_{tot} = \psi_{orbital}\psi_{spin}$$

both the spin and orbital functions must be eigenfunctions of the electron exchange operator. We shall explore the properties of this operation on spin wavefunction to explore the difference between single and triplet spin wavefunctions as derived from a pp pr p^2 configuration.

Consider how the microstates shown in Table 1 behave under the exchange operation.

$$\hat{O}\Psi_1 = \hat{O}\alpha(1)\alpha(2) = \alpha(2)\alpha(1) = \Psi_1$$
$$\hat{O}\Psi_2 = \hat{O}\alpha(1)\beta(2) = \alpha(2)\beta(1) = \Psi_3$$
$$\hat{O}\Psi_3 = \hat{O}\beta(1)\alpha(2) = \beta(2)\alpha(1) = \Psi_2$$
$$\hat{O}\Psi_4 = \hat{O}\beta(1)\beta(2) = \beta(2)\beta(1) = \Psi_4$$

Wavefunctions Ψ_1 and Ψ_4 are eigenfunctions of $\hat{O}$. Wavefunctions Ψ_2 and Ψ_3 are not eigenfunctions of $\hat{O}$, but they are clearly related to one another through the electron exchange operation as the operation converts one into the other. The relationship suggests that linear combinations of Ψ_2 and Ψ_3 can be taken in order to construct spin wavefunctions that are eigenfunctions of $\hat{O}$. One linear combination is symmetric (eigenvalue = +1) and the other is be antisymmetric (eigenvalue = -1). The correct, normalized linear combinations are as follows.

$$\Psi_s = \frac{1}{\sqrt{2}}(\Psi_2 + \Psi_3) = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2))$$
$$\Psi_a = \frac{1}{\sqrt{2}}(\Psi_2 - \Psi_3) = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

Under the electron exchange operator, these linear combinations behave as follows.

$$\hat{O}\Psi_s = \hat{O}\left[\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\beta(1)\alpha(2))\right] = \frac{1}{\sqrt{2}}(\alpha(2)\beta(1)+\beta(2)\alpha(1)) = \Psi_s$$

$$\hat{O}\Psi_a = \hat{O}\left[\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\beta(1)\alpha(2))\right] = \frac{1}{\sqrt{2}}(\alpha(2)\beta(1)-\beta(2)\alpha(1)) = -\Psi_a$$

So Ψ_s is symmetric with respect to electron interchange and Ψ_a is antisymmetric with respect to electron interchange. Noting that Ψ_1 and Ψ_4 are natural symmetric eigenfunctions of the exchange operator, it is easy to group the spin wavefunctions into triplet and singlet components according to symmetry with respect to the operator $\hat{O}$. The summary of these results is shown in the table below.

		Wavefunction		S	M_S
Triplet	Symmetric	Ψ_1	$\alpha(1)\alpha(2)$	1	+1
		Ψ_s	$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\beta(1)\alpha(2))$		0
		Ψ_4	$\beta(1)\beta(2)$		-1
Singlet	Antisymmetric	Ψ_a	$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\beta(1)\alpha(2))$	0	0

It can be seen that there are three components of the triplet spin wavefunction and only one component to the singlet function, as implied by the names “triplet” and “singlet.” More importantly, it is clear that to generate the ground state wavefunction for the atom, one *must* include contributions from paired electron spin functions (Ψ_s). So the statement of Hund’s rule that maximizing the number of electrons with the same value of m_s attains the lowest energy state is clearly incorrect, as it excludes the necessary component with $M_S = 0$.

For equivalent electrons (electrons in the same subshell, or the p^2 case) the symmetric spin wavefunction set (the triplet functions) must take antisymmetric orbital function (P). The singlet spin function, which is antisymmetric to electron exchange, must take a symmetric orbital function (D or S.) As such, the three term symbols generated are ^1D, ^3P and ^1S. If the electrons are not equivalent, as is the case in a pp configuration, all combinations of the triplet and singlet spin functions with D, P and S orbital functions are possible and the resulting terms are ^3D, ^3P, ^3S, ^1D, ^1P and ^1S.

The ^3D, ^1P and ^3S functions are not possible in the p^2 case, as these would require microstates that are either duplicates of other microstates, or microstates that involve two electrons in the same orbital with the same value of m_s. The latter is a clear violation of the Pauli Exclusion Principle since both electrons would then have the same values of n, l, m_l and m_s.