

Symmetric & Antisymmetric Wave Functions

One electron wave functions

In order to specify the wave function of a single electron we need to specify the five quantum numbers

1. n – Principal Quantum Number
2. ℓ – Orbital Quantum Number
3. m_ℓ – Magnetic Quantum Number, the projection of ℓ on the z axis
4. s – Spin, always equal to $\frac{1}{2}$
5. m_s – projection of s on the z axis

The first three quantum numbers define the spatial part of the wave function $\psi(n\ell m_\ell)$, the solution to Schrodinger's Equation. The last two quantum numbers define the spin part of the wave function, although since the spin is always equal to $\frac{1}{2}$ it is sufficient to specify only its projection on the z axis, m_s . The projection can only take on one of two values $+\frac{1}{2}$ (spin up) and $-\frac{1}{2}$ (spin down). The spin portion of the wave function has two forms $\sigma(\uparrow)$ and $\sigma(\downarrow)$.

The total wave function for the electron is the product of the spatial part and the spin part

$$\Psi(n\ell m_\ell m_s) = \psi(n\ell m_\ell) \sigma(m_s)$$

Two electron wave functions

The wave function for two electrons is a combination of two one electron wave functions. However, we have to take into account two properties of electrons

- the electrons in an atom are indistinguishable. If we have two electrons, which we shall arbitrarily label as A and B, and a $n\ell n'\ell'$ configuration then we should have no way of telling which electron is the $n\ell$ electron and which is the $n'\ell'$ electron.
- The electrons are fermions¹. Fermions cannot have the same set of quantum numbers, and must have antisymmetric wave functions. If the labels a and b on the electrons are exchanged then the new wave function must be the same as the original wave function, except for a negative sign.

$$\Psi(A,B) = - \Psi(B,A)$$

If $n=n'$ and $\ell=\ell'$ then the electrons are said to be equivalent. For these electrons the Pauli Exclusion Principle restricts the number of wave functions that can be produced. However if either $n \neq n'$ or $\ell \neq \ell'$ then the Pauli Exclusion Principle is already satisfied and the full set of wave functions is produced. We shall look at the two cases separately.

Non-equivalent electrons

In order to get an antisymmetric wave function we can either

- multiply a symmetric spatial wave function with an antisymmetric spin wave function

¹ Particles whose spin is a half integer.

- multiply an antisymmetric spatial wave function with a symmetric spin wave function

If we try writing the spatial wave function as the product of two one electron spatial wave functions

$$\psi(n\ell n'\ell') = \psi_A(n\ell) \psi_B(n'\ell')$$

the result is not acceptable, it tells us which electron is the $n\ell$ electron and which is the $n'\ell'$ electron. However, linear combinations of this trial form solves the problem

- $\psi_A(n\ell) \psi_B(n'\ell') + \psi_B(n\ell) \psi_A(n'\ell')$ is symmetric. If the labels A and B are switched then the new wave function is the same as the old wave function.
- Similarly, $\psi_A(n\ell) \psi_B(n'\ell') - \psi_B(n\ell) \psi_A(n'\ell')$ is antisymmetric.

(It is common to re-normalize the wave function by dividing by a factor of $\sqrt{2}$ in each of the above expressions. However, this does not affect the argument here, and we shall not include this factor.)

Now turn to the spin wave functions. If both electrons are in the same spin state (either both spin up or both spin down) then we can write two possible two electron spin wave functions

1. $\sigma_A(\uparrow) \sigma_B(\uparrow)$
2. $\sigma_A(\downarrow) \sigma_B(\downarrow)$

both of which are symmetric. However, if they are in opposite spin states (one spin up and the other spin down) then a spin wave function of the form $\sigma_A(\uparrow)\sigma_B(\downarrow)$ is not acceptable, we would know that electron A is the spin up electron and B is the spin down electron. As was the case with the spatial wave functions we will get round the problem by writing linear combinations

3. $\sigma_A(\uparrow) \sigma_B(\downarrow) + \sigma_B(\uparrow) \sigma_A(\downarrow)$, which is symmetric
4. $\sigma_A(\uparrow) \sigma_B(\downarrow) - \sigma_B(\uparrow) \sigma_A(\downarrow)$, which is antisymmetric

Of the four possible acceptable spin wave functions, three are symmetric and one is antisymmetric. The antisymmetric one must have one spin up electron and one spin down electron, such that $M_S = m_{sA} + m_{sB} = 0$. This can only correspond to an atom with $S = 0$, a singlet state.

On the other hand, the three symmetric spin wave functions can have both electrons spin up ($M_S = 1$), one spin up and the other spin down ($M_S = 0$), or both spin down ($M_S = -1$). With these three values of M_S the total spin is $S = 1$, and we have a triplet state.

The excited configurations of helium

The ground configuration of helium is $1s^2$, that is two equivalent electrons (see below). The excited configurations are formed by promoting one these electrons² to form the $1sn\ell$ configuration. Each one of these configurations can form two terms, with $L = \ell$, and $S = 0$ or 1

- $1s2s \rightarrow {}^1S$ and 3S
- $1s2p \rightarrow {}^1P$ and 3P
- $1s3s \rightarrow {}^1S$ and 3S

2 Promoting both electrons is possible but rare

- $1s3p \rightarrow {}^1P$ and 3P
- $1s3d \rightarrow {}^1D$ and 3D
- etc

Equivalent s electrons

With two equivalent electrons the Pauli Exclusion Principle limits the possible wave functions. Since we have $n=n'$, $\ell=\ell'=0$, $m_\ell=m_\ell'=0$, and $s=s'=1/2$ the two electrons cannot have the same values of m_s . We therefore cannot form M_S equal to either +1 or -1, and so the triplet term ($S=1$) does not exist. The ns^2 configuration can only produce a 1S term, with wave function

$$\Psi(ns^2 {}^1S) = \psi_a(ns) \psi_b(ns) [\sigma_a(\uparrow) \sigma_b(\downarrow) - \sigma_a(\downarrow) \sigma_b(\uparrow)]$$

Equivalent electrons with $\ell > 0$

As the value of ℓ increases, or as the number of equivalent electrons increases, the complexity of determining which terms are permitted rises rapidly. For example, if the atom has two non-equivalent p electrons (e. g. the $2p3p$ configuration) there are six allowed terms (see table to right.) However, with two equivalent p electrons (e. g. the $3p^2$ configuration) the number of allowed terms drops to only 3.

Non-equivalent electrons	Equivalent electrons
● ${}^1S, {}^3S$	● 1S
● ${}^1P, {}^3P$	● 3P
● ${}^1D, {}^3D$	● 1D



For other equivalent electron configuration please refer to the literature³.

Energy Terms of Helium

Note that with two equivalent electron, the ground $1s^2$ configuration only gives rise to a singlet term, whereas the excited configurations each give rise to both singlet and triplet terms

1s² ¹S

Schematic diagram of the energy levels of helium

³ See for example, *Introduction to Modern Physics*, 6th ed., by Richtmeyer, Kennard, and Cooper, pages 452 to 455