

Hartree approximation

An approximate method for many-electron atoms was first proposed by Hartree. In this method the atomic wave function is a product of one-electron wave functions. This is an extension of what we have seen for helium.

$$\Psi(r_1, r_2, r_3 \dots r_N) = \phi_1(r_1)\phi_2(r_2)\phi_3(r_3) \dots \phi_N(r_N)$$

In this equation the r_i are the positional coordinates and a spin coordinate for each electron $r_i = (x_i, y_i, z_i, m_i)$. As we have seen for the hydrogen atom, spherical polar coordinates work better than Cartesian coordinates. The spin coordinate can be spin up α or spin down β .

Spin and the Pauli Exclusion Principle

The solutions to the Schrodinger equation explain the one Electron atom adequately. However, in order to move beyond a one electron atom we must introduce the concept of electron spin. The word spin arises from the fact that an electron has an apparent magnetic moment. It acts like a spinning charge. Because of the property of spin electrons populate the orbitals in pairs.

The rigorous statement of this idea is that the total wave function must be anti-symmetric with respect to electron exchange. Electrons are a member of the class of particles known as fermions. They have a half integer spin ($s = \frac{1}{2}$). No two fermions may occupy the same energy state.

Spin and Spatial Wavefunctions

We focus on He and the two-electron situation since that is both the first and simplest case where electron spin must be included. The wave function for the two electrons can be written as,

$$\Psi_{\text{total}} = \Psi_{\text{spatial}} \Psi_{\text{spin}}$$

We have already considered how the spatial wave function can arise from a product of hydrogen-like wave functions for each electron (Hartree approximation). The spin part of the wave function consists of single electron wave functions that we will call a and b , for spin-up and spin-down, respectively. The wave function must be antisymmetric with respect to electron exchange. Since there are two parts to the wave function, the antisymmetry can arise either from the spin part or the spatial part.

Symmetric and anti-symmetric wavefunctions

There are 4 possible spin states for a two-electron system. These are:

$$\alpha(1)\alpha(2), \beta(1)\beta(2), \alpha(1)\beta(2), \beta(1)\alpha(2)$$

However, only the first two are symmetric or anti-symmetric to electron exchange (which corresponds to exchanging 1 and 2). The last two need to be rewritten as:

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

The first three are symmetric, whereas the last one is anti-symmetric.

The spatial wave function

Say one of the electrons in the helium atom is excited to the 2s state. In this case, its spatial wavefunction will have to be either anti-symmetric (requiring a symmetric spin wavefunction):

$$\Psi_{\text{spatial}} = \psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)$$

Or symmetric (requiring an anti-symmetric spin wavefunction):

$$\Psi_{\text{spatial}} = \psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)\psi_{1s}(2)$$

Singlet and triplet states

For anti-symmetric spatial wave function, we see that there are three symmetric spin wave functions.

$$\Psi_{1,0} = \{\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)\} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\Psi_{1,1} = \{\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)\} \alpha(1)\alpha(2)$$

$$\Psi_{1,-1} = \{\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)\} \beta(1)\beta(2)$$

This set of wave functions corresponds to a triplet state, i.e. it has a spin multiplicity of 3. The other possible combination

$$\Psi_{0,0} = \{\psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)\psi_{1s}(2)\} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

is the singlet state.

Beyond Hydrogen: The Aufbau Principle

In a conceptual way we can imagine using the H atom as model for all atoms. We can populate the hydrogenic orbitals with electrons to create the atoms of the periodic table.

This is not formally correct since we must confront the fact of electron-electron repulsion. However, we can speak of orbital occupancy in this approximation by building up the atoms.

The German word “aufbau” means building up and it refers to this treatment. Thus, we can imagine helium having two electrons in the 1s orbital or a configuration of $1s^2$. Then

We have

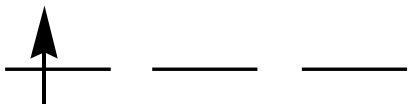
Li: $1s^2 2s$ Be: $1s^2 2s^2$ B: $1s^2 2s^2 2p$ C: $1s^2 2s^2 2p^2$

And so on.

Hund's rule

As we populate the p orbitals we must account for the spin pairing energy. The spin pairing energy is minimized by keeping the unpaired electrons at a maximum as shown below:

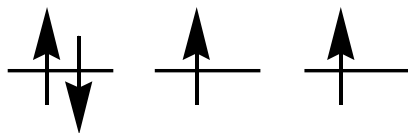
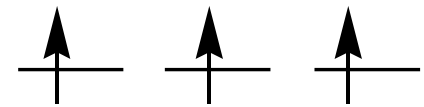
1 electron



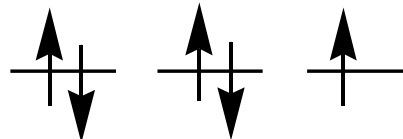
2 electrons



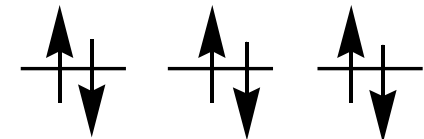
3 electrons



4 electrons



5 electrons



6 electrons

Hund's rule states that the most stable configuration will be the one with the greatest spin multiplicity.

Spin and orbital angular momenta for atoms

The orbital degeneracy is $2\ell + 1$

The spin multiplicity is defined as $2s + 1$.

For N electrons the total value of the angular momentum will be the sum of the individual electronic momenta. The total orbital angular momentum is:

$$L = \ell_1 + \ell_2 + \ell_3 + \dots$$

and the total spin momentum is:

$$S = s_1 + s_2 + s_3 + \dots$$

Term Symbols

The angular momenta result from the configurations possible for the atom. There are actually many configurations possible so it is convenient to summarize the information in a term symbol, which describes the orbital, spin and total angular momentum state of the atom. Term symbols have the form:

$$2S+1L_J$$