

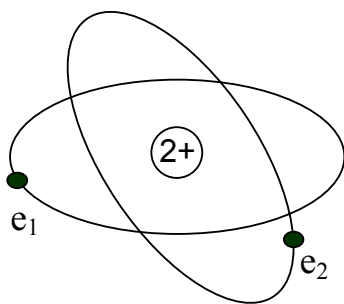
SESSION 5: The Electronic Structure of Higher Atoms

Overview: In this session we will:

- apply the information gained in studying hydrogen to derive the electronic configuration of higher atoms
- define and apply the Orbital Approximation to helium
- define and apply the Pauli Exclusion Principle
- define and apply Hund's Rule

Helium: The Orbital Approximation

The Helium atom consists of a nucleus (with 2 protons) and 2 electrons moving about it.



The wavefunction ψ_{He} , which describes this system, must allow for simultaneous measurements of the positions of both electrons. ψ_{He} must tell the probability of finding e_1 in volume element $d\tau_1$ and e_2 in volume element $d\tau_2$, where

$$d\tau_1 (= dx_1 \cdot dy_1 \cdot dz_1)$$

and

$$d\tau_2 (= dx_2 \cdot dy_2 \cdot dz_2)$$

have the dimensions given in parentheses.

The probability P , of finding e_1 in volume element $d\tau_1$ and e_2 in volume element $d\tau_2$ is,

$$P = \psi_{\text{He}}^2 \cdot d\tau_1 \cdot d\tau_2,$$

where ψ_{He} is now a function of six coordinates.

If electrons did not repel each other then each would behave as if the other was absent (i.e. Hydrogen-like) and could be represented by separate hydrogen-like wavefunctions, ψ_1 and ψ_2 , but this is NOT THE CASE.

The **orbital approximation** can be stated thus:

An electron in a many electron atom will feel the effect of, the averaged charge of the nucleus and all other electrons present in the atom.

In this approximation it is assumed that each electron resides in its own orbital and the total wavefunction,

$$\psi = \psi(1).\psi(2)...$$

where $\psi(1)$ is the wavefunction for electron 1 and $\psi(2)$ is the wavefunction for electron 2 and, so on, where each individual orbital is hydrogen-like but where the nuclear charges are modified (to obtain an effective nuclear charge) by the presence of all other electrons in the atom.

Let us now take a step-by-step application of the orbital approximation to the ground state Helium atom:

- (i) There are two electrons, e_1 and e_2 , and a nucleus with a $2+$ charge.
- (ii) Imagine that e_1 is stationary at some location in the atom.
- (iii) Let e_2 move freely about and generate an electron charge cloud.
- (iv) This cloud of charge will be symmetrically distributed about the nucleus.
- (v) Take the average of this charge cloud (in (iv) above) and the nuclear charge – this will give an effective nuclear charge centred on the nucleus.
- (vi) e_1 will now feel the effect of this effective nuclear charge centred on the nucleus.
- (vii) The result of this approximation is a hydrogen-like wave function for e_1 .

If this is repeated, where e_2 is now stationary and e_1 is allowed to generate a charge cloud, then a similar result is obtained where a hydrogen-like wavefunction is the solution for e_2 .

These two resulting ground-state, hydrogen-like wavefunctions must be of the 1S type (i.e. ψ_{1S}) since the ground state of hydrogen is 1S. This solution is claiming that both electrons in the ground state helium atom reside in the 1S orbital, and therefore the configuration of the ground state helium atom is

$$\text{He} = (1s)^2 \quad (\text{i.e. } \psi_{\text{He}} = \psi_{1S} \psi_{1S})$$

Quantum mechanical calculations may be performed to determine the energy of the ground-state helium atom having the $(1s)^2$ configuration. This calculated value is in very good agreement with experimental values and confirms the ground state configuration of the He atom.

This orbital approximation, as the name suggests, is only approximate, but it is a useful model for discussing the properties of atoms, and is the starting point for more sophisticated descriptions of atomic structure.

You must recognize that this is a very simplified approach and if it is used without modification on the Lithium atom then the predicted theoretical result would be a ground-state configuration of $(1s)^3$, a configuration that gives a predicted energy which is much less than the experimental value. This points to the fact that the third electron cannot therefore reside in the 1s orbital, but has to find other suitable 'accommodation' in another orbital of higher energy.

The question now arises, "Where can the third electron in Li find suitable 'accommodation'?" This takes us to the *Pauli Exclusion Principle*.

The Pauli Exclusion Principle

The capacity of an orbital to hold electrons is limited. One can consider an orbital ψ , as being subdivided into two *spin-orbitals* (ψ_α and ψ_β , one for each spin).

$$\psi = \psi_\alpha \cdot \psi_\beta,$$

The Pauli Principle: only one electron can occupy a given spin orbital.

The third electron in Lithium must then seek an orbital of higher energy, which must be the **2s** or the **2p**. In hydrogen, the **2s** and the **2p** are degenerate since it is a one-electron system (without electronic interaction). This is not so for multi-electron atoms.

This outer electron in helium does not see the full charge, Z , of the nucleus, due to screening from the other electrons. It can be considered to experience an *effective nuclear charge* Z^* , also located at the nucleus. The question is "Will the electron go to the **2s** or to the **2p**?" If the electron density distribution diagrams are reviewed, it will be clear that an electron in the **2s** orbital spends more time near to the nucleus (which is more energetically favourable and therefore more stable) than an electron in the **2p** orbital. The more energetically favourable ground-state configuration of Lithium is

$$\text{Li} = (1s)^2(2s)^1 \quad [\text{i.e. } \psi_{\text{Li}} = (\psi_{1s})^2 \cdot \psi_{2s}]$$

(where $(\psi_{1s})^2$ signifies a doubly occupied orbital, and not the square of the wavefunction).

Atoms Be – Ne: Hund's Rule

By extrapolation, the configuration of the **Beryllium** atom can be reasoned to be,

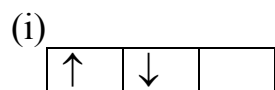
$$\text{Be} = (1s)^2(2s)^2 \quad [\text{i.e. } \psi_{\text{Be}} = (\psi_{1s})^2 \cdot (\psi_{2s})^2]$$

and that of **Boron** to be,

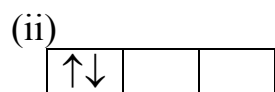
$$\text{B} = (1s)^2(2s)^2(2p)^1 \quad [\text{i.e. } \psi_{\text{B}} = (\psi_{1s})^2 \cdot (\psi_{2s})^2 \cdot (\psi_{2p})]$$

where the electron in the **2p** can reside in any one of the three available and degenerate **2p** orbitals.

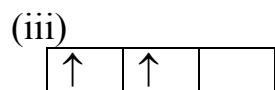
When we come to **Carbon**, there are several available options for the second electron to be placed in the **2p** orbital set. These options are as follows:



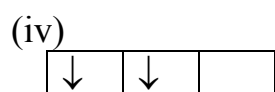
The electrons, with opposite spins, are placed in two different sub-orbitals.



Both electrons, with opposite spins, are placed in the same sub-orbital.



The electrons, with the same spin, are placed in two different sub-orbitals.



The electrons, with the same spin, but with the opposite orientation as in (iii), are placed in two different sub-orbitals.

Hund's Rule will assist us in deciding which of these configuration(s) is(are) the most stable.

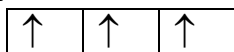
Rule: Other things being equal, the lowest (most stable) energy state is that in which the maximum number of electrons have parallel (same) spins.

Hund's Rule points to options (iii) and (iv) as being the most stable of the four. It is to be noted that, pairs of electrons with parallel (same) spins have their motions correlated so as to keep them as far apart as possible. This means that the electrons would have less interaction with each other, when compared to the case where the electrons are of opposite spins. It should be noted that electrons being of the same electric charge (i.e. both negatively charged) do not want to be in the same region of space and would want to interact as little as possible.

This means that for the carbon atom, options (i) and (ii) would be of higher energy, and therefore less stable, than options (iii) and (iv). This is because in (i) and (ii) the actual repulsion of the two p-electrons is greater.

The p-orbital configurations for the other atoms in the period are therefore, by extrapolation:

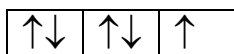
Nitrogen



Oxygen



Fluorine



Neon

