

Module 1 : Atomic Structure

Lecture 6 : Multi-Electron Atoms

Objectives

In this lecture you will learn the following

- Pauli exclusion principle and the aufbau principle.
- Electronic configuration of atoms.
- Schrödinger equation for atomic orbitals.
- Radial electron distribution in atoms.

Introduction

As the number of electrons becomes greater than one and as the nuclear charge also increases, the electronic energy levels will change from those corresponding to the hydrogen atom to those corresponding to the atom which is being studied. Before outlining how these levels are determined, we shall describe two principles which help in understanding atomic structure. These are the Pauli exclusion principle (which is rigorously valid in all situations) and the aufbau principle ('aufbau' means 'building up' in German). Consider two orbital energy level diagrams as shown below

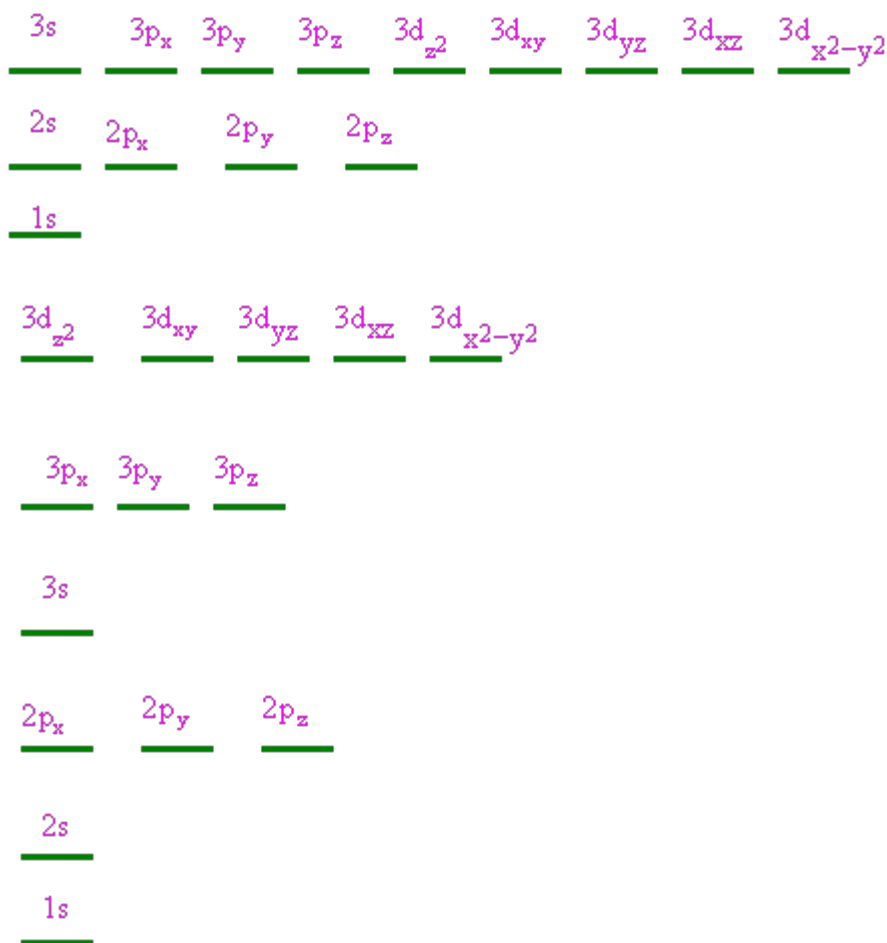


Figure 6.1 Orbital energy levels of: a) hydrogen atom and b) atoms with more than one electron.

We have seen that in the case of H-atom, many of these levels are degenerate e.g. (2s, 2p_x, 2p_y and 2p_z) . In addition to the three quantum numbers n, l and m_l, there is a fourth one, m_s associated with the spin. The

electron spin is commonly represented by an arrow. An arrow pointing up represents $m_s = +\frac{1}{2}$ and an arrow pointing down represents $m_s = -\frac{1}{2}$. The meaning of $m_s = +\frac{1}{2}$ is that an electron with this quantum number has a spin angular momentum of $\frac{1}{2} \hbar$ in a given direction. (Usually the direction of an applied magnetic field). In atoms with nuclear charge greater than 1 and having more than one electron, the degeneracy of s, p, d, f is removed and this is shown in fig 6.1 (b)

6.3 Aufbau Principle

The aufbau principle deals with the filling up of electrons in energy levels. The relative order of various levels has to be known to begin with. We fill the orbitals (with two electrons of opposite spins in each orbital) from the lowest to the highest so that the atoms have maximum stability. The electronic configuration of atoms can be constructed by using these two principles, together with Hund's rule. Related to the spin multiplicity or degeneracy of orbitals.

In a nitrogen atom, there are seven electrons. The first two can be placed in the 1s orbital, the second two in 2s and the next three are placed in $2p_x$, $2p_y$ and $2p_z$ orbitals. They are not placed such that two are in $2p_x$ and one in $2p_y$ because the pairing in $2p_x$ (which takes up some energy) will reduce the spin multiplicity. By avoiding pairing, atoms attain higher spin multiplicity and a lower total energy.

Spin pairing is

The two electrons will have opposite spins.

It is the pairing in the same space that cause, repulsion and hence increase in energy.

6.4 Atomic Structure and the Periodic Table

It would be nice if the problem of atoms containing more than one electron can be solved exactly like the hydrogen atom. Such a solution would give a complete understanding of charge densities and the electronic spectra of many electron atoms. Although such a solution has eluded the chemist all along, a very good (though not exact) description of electronic structure of atoms has been given in terms of atomic orbitals and orbital energies. Let us first outline the description in terms of atomic orbitals.

Next to hydrogen in the periodic table is helium. The second electron is also placed in the 1s orbital, giving the electronic configuration for $1s^2$. The second electron has a spin which is "opposite" to that of the first electron. Although this antiparallel pairing of spins has an energy cost, this is much less than the energy of $1s^1 2s^1$ where the second electron is in the higher 2s level. When one electron is in 1s and another in 2s, their spins need not be paired. Does this violate the Pauli exclusion principle?

The third atom is Li. The first two electrons are placed in 1s giving the configuration $1s^2$. The third one may be placed in 2s or 2p. The charge densities in 2s and 2p orbitals are distinct. An electron in a 2s orbital has a much greater probability of being found "near" the nucleus as the 2s orbital has a non zero value at the nucleus (see Fig 5.1). A 2p electron has a far smaller probability of being found near the nucleus because of its node in the nuclear plane. Therefore a 2s electron experiences a larger effective nuclear charge than a 2p electron. The energy of a 2s electron is lower than that of a 2p electron and the electronic configuration of Li is $1s^2 2s^1$ and not $1s^2 2p^1$. The latter has a higher energy and corresponds to an excited state. The degeneracy of 2s and 2p which was found in the H-atom is removed in Li. The 2p electron in Li is said to be more screened from the nuclear charge than a 2s electron.

We can continue this "filling" up of orbitals: Be ($1s^2 2s^2$), B ($1s^2 2s^2 2p^1$), C ($1s^2 2s^2 2p^2$) and N ($1s^2 2s^2 2p^3$). The p electrons in C and N occupy distinct orbitals $2p_x$, $2p_y$ and $2p_z$ and avoid electron pairing. This is in conformity with the Hund's rule, according to which states of atoms with maximum multiplicity (large value of total spin obtained by avoiding spin pairing) will be favoured. When two spins are paired, the total spin = $\frac{1}{2} - \frac{1}{2} = 0$. When spins are unpaired, the total spin = $n/2$ where n = number of unpaired electrons.

This pattern of filling continues until we reach the configuration $1s^2 2s^2 2p^6 3s^2 3p^6$. We may expect to fill 3d

next. But at this stage 4s is lower in energy than 3d, and the 4s subshell gets filled first, giving the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, which is for Ca. After Ca, the 3d which was so far unfilled gets filled. This 3d series is the series of the first set of transition elements. The orbital energies are a function of atomic number and the variation of orbital energies with atomic number is shown in figure 6.2.

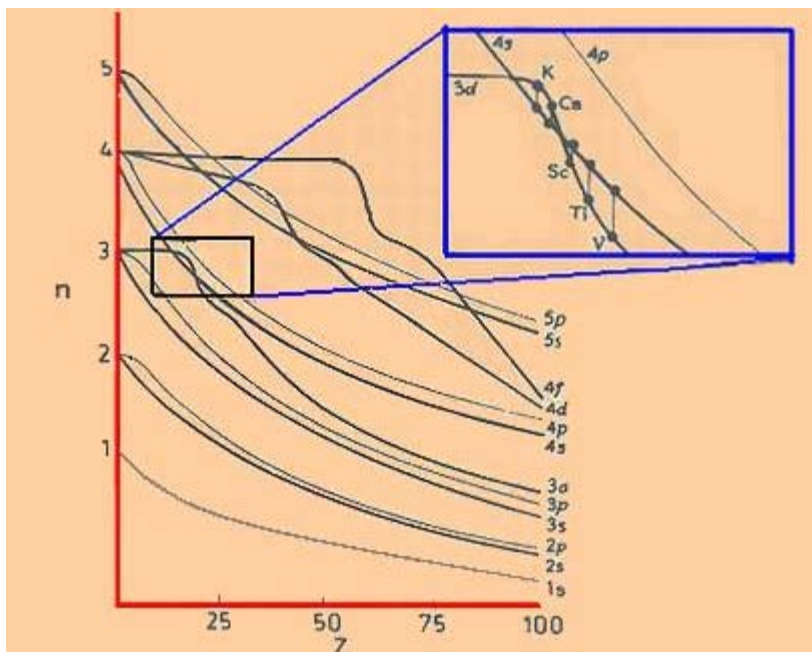


Figure 6.2 Orbital energy levels as a function of atomic numbers.

As the nuclear charge increases, the electrons, on the average are drawn closer to the nucleus and the orbital energies decrease with increasing nuclear charge. The order of filling the orbitals is $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p \dots$ when the energy levels of two orbitals are very close (of the order of a few kJ/ mol, the filling order can change and whenever possible a larger number of unpaired electrons are favoured.

6.5 Wavefunctions and orbitals:

For a multielectron atom such as He, Li, etc. the Schrödinger equation may be written as $H \Psi = E \Psi$ where H is the operator representing the kinetic and potential energies of all the particles and Ψ and E are the wavefunction and energy respectively. For a helium atom, keeping the nucleus fixed (this is not a bad approximation since the nuclei are much heavier than the electrons) H can be written as

$$H = -\frac{h^2}{2m} \nabla_1^2 - \frac{h^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi \epsilon_0 r_1} - \frac{2e^2}{4\pi \epsilon_0 r_2} + \frac{2e^2}{4\pi \epsilon_0 r_{12}} \quad (6.1)$$

The first two terms correspond to the kinetic energy of electrons 1 and 2, the third and fourth are the interaction energies of the two electrons with the He nucleus and the last term is the electron - electron

repulsion. Here

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$$

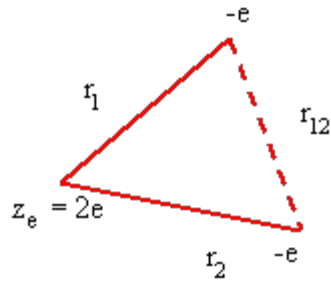


Figure 6.3 The coordinates of the two electrons in He atom

The solution of equation (6.1) is the wavefunction $\Psi = \Psi(1,2)$ or $\Psi(r_1, r_2) = \Psi(x_1, y_1, z_1, x_2, y_2, z_2)$. This is a function of six variables and is difficult to handle. A good way to approximate this is to write it as

$$\Psi(r_1, r_2) = \phi_1(r_1) \cdot \phi_2(r_2), \quad (6.2)$$

which is a product of orbitals $\phi_1(r_1)$ depending on the coordinate of the first electron and $\phi_2(r_2)$, which depends on the coordinates of the second electron. Wavefunctions refer to the solutions of the Schrödinger equation while orbitals refer to the function of the coordinates of a single electron and are the solutions to an approximate or an effective equation which is described below.

6.6 Schrödinger Equation for an Atomic Orbital

In the equation for an orbital, we want to reduce the number of variables from many (in a multi-electronic case) to one. This is done by assuming that each electron moves in an average field created by all the other electrons. For example, one of the electrons in He, say electron 1 may be thought of moving in a field of the nucleus plus the average field created by the second electron.

$$\left[-\frac{\hbar^2}{8\pi^2m} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} + V_{\text{eff}}(r_1) \right] \phi_1(r_1) = E_1 \phi_1(r_1) \quad (6.3)$$

The three terms in the left refer to the kinetic energy, electron nuclear attraction energy and the effective field on electron 1 due to electron 2 and E_1 is the orbital energy. The effective field at r_1 is obtained by averaging the energy between electron 1 at r_1 and electron 2 at r_2 by allowing the second electron at r_2 to cover the whole space

$$V_{\text{eff}}(r_1) = \int_{\text{all volume}} \frac{e^2}{4\pi\epsilon_0 r_{12}} dx_2 dy_2 dz_2. \quad (6.4)$$

By the same analogy, electron 2 moves in an average field created by electron 1. These equations for electron

1 and electron 2 are solved iteratively starting with assumed formulae for $\phi_1(r_1)$ and $\phi_2(r_2)$ and the iterations (repeated solutions) are stopped when the average field created by electron 1 on electron 2 is consistent with the average field created by electron 2 on electron 1. These orbitals are called self-consistent orbitals. This method is referred to as the self-consistent field (SCF) method and forms a very important method for studying atomic and molecular structure.

6.7 Electron Densities: Li atom

From the orbitals, wavefunctions can be constructed using equation (6.2). The square of the wavefunction gives the probability of finding electrons in the corresponding volume elements. $|\psi(r_1, r_2)|^2 d\tau_1 d\tau_2$ gives the probability of finding electron 1 in volume element $d\tau_1$ at r_1 and electron 2 in volume element $d\tau_2$ at r_2 . Since atoms are spherically symmetrical, it is better to consider the radial probability density $4\pi r^2 |\psi(r)|^2$ where $|\psi(r)|^2$ is the probability density of finding any one electron at r . The plot for lithium atom is shown below.

Figure 6.3 Radial probability distribution in Li atom

The Lithium atom has a configuration $1s^2 2s^1$. The 1s electrons lie closer to the nucleus than the 2s electrons. The inner orbitals are held more "tightly" and the outer electrons are more diffuse. The reason is not difficult to find! The outer electrons experience much smaller effective charge due to the shielding of the nuclear charge by the inner or "core" electrons. The radial probability density (radial charge density, $e 4\pi r^2 |\psi(r)|^2$) also gives an indication about the size of an atom. For Li, we notice that the charge density has become very small beyond 3 Å. This implies that radius of Li, is 3 Å. When the outer electron is removed from Li, we get Li^+ with an electronic configuration $1s^2$. The charge density beyond 1 Å would not appear in the scale in figure 6.3 (as the outer electron has been removed) and the Li^+ will have a radius less than 1 Å. The experimental radii of Li and

Li^+ are 3.04 Å and 0.68 Å. The agreement is fairly good. In fact the full charge density curve can be obtained from the scattering experiments on atoms.

6.8 Electron Distributions in Na

Fig 6.4 shows the radial electron densities for various orbitals of the sodium atom. The ground state electronic configuration is $1s^2 2s^2 2p^6 3s^1$. The first shell 1s is held very close to the nucleus (within 0.3 Å). This is closer than the case for Li atom because of the higher nuclear charge of Na. The second shell (2s and 2p) cover the range from 0.3 Å to 1.2 Å and the 3s shell extends from about 1.2 Å to 3 Å. Notice that each shell has a region of peak electron density, which rises sharply initially from a small value and again decays to zero slowly (actually exponentially, as is true for all orbitals). If the outer electron from Na is removed, we get Na^+ .

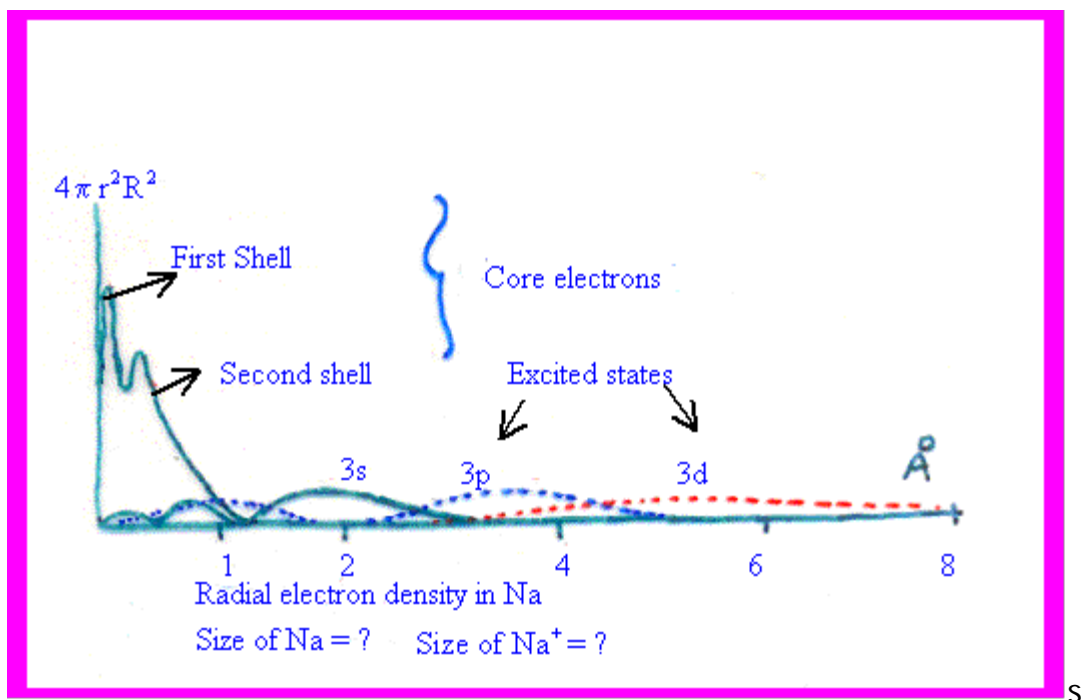


Figure 6.4 Electron density in Na atom

The experimental radii of Na and Na^+ are 3.72 Å and 0.97 Å which match reasonably with the sketch. The larger experimental value raises the possibility of 3p and 3d also contributing indirectly to the atomic size. This turns out to be true. While obtaining an average field, "instantaneous" correlations or interactions between electrons were neglected. Inclusion of instantaneous (or simultaneous) correlations can be done by including the contributions of excited "orbitals". If 3p and 3d of Na are occupied, they would correspond to the excited states of the atom.

Using the methodology of this chapter (and further improvements in it), the charge densities and energy level diagrams of all the atoms in the periodic table can be constructed. When we deal with higher atomic numbers, other interactions such as the spin-orbital interaction (interaction between spin and orbital angular momenta), hyperfine interactions (interaction of electron spin with the nuclear spin) and relativistic effects (when electron velocities approach that of the velocity of light) come into play and these have been studied in detail.

6.9 Exercises

6.1) The ionization energy (IE) of an atom is defined as the minimum energy required to ionize the atom $A \rightarrow A^+ + e$, $I.E = E(A^+) - E(A)$. Look up the ionization energies of atoms hydrogen to argon and explain the trend in their values using the ideas developed in this lecture.

6.2) What is the electronic configuration of atoms with atomic numbers 19, 24, 29, 42, 64 and 103?

6.3) Write the electronic Schrödinger equation for Li and Be atoms.

6.4) Electrons and other microscopic objects are not distinguishable from each other, ie, it is not correct to label the first electron as 1 and the second one as 2. For spin 1/2 particles such as an electron, the total wavefunction is antisymmetric, ie, it changes sign when the electron labels 1 and 2 are interchanged. A correct wavefunction for He is

$$\Psi(1, 2) = \phi_1(r_1) \phi_2(r_2) - \phi_1(r_2) \phi_2(r_1). \text{ Verify that}$$

$$\Psi(1, 2) = -\Psi(2, 1). \text{ Construct antisymmetric functions for } \Psi(1, 2, 3)$$

6.5) The nuclear charge on H is 1. For He, each electron does not experience the full nuclear charge of 2 because this nuclear charge is screened by the second electron. Using the Bohr like formula,

$I.E = Z_{\text{eff}}^2 (I.E)_H / n^2$, calculate the effective nuclear charge for He and Li^+ . Here, $(I.E)_H$ = ionization energy of H = 13.6 eV, or 1.313×10^6 J/mol, n = the principal quantum number of the electron and Z_{eff} = effective nuclear charge. The ionization energies of He and Li^+ are 2.372 and 7.3 MJ/mol respectively ($1 \text{ MJ} = 10^6 \text{ J}$).

The screening of the nuclear charge by other electrons is given by the screening constant, S which is defined by $Z_{\text{eff}} = Z - S$. Calculate Z_{eff} for He and Li^+ .

6.6) Distinguish between probability density and electron density.

Recap

In this lecture you have learnt the following

Summary

In this chapter, we have considered the structure of many electron atoms. Electronic configuration, electronic charge density and the energy level diagram are the main features of atomic structures. The full wave function for an atom would involve the coordinates of all the electrons and that is difficult to deal with. It cannot be even plotted in a 3 dimensional graph! A convenient option is to use atomic orbitals, which describe the behavior of an electron in the field of the nucleus and the average field due to all the other electrons. The Schrödinger equation for an orbital of He has been given and this can be easily generalized for other atoms. Atomic charge densities show the detailed charge distribution of electrons around the nucleus. The examples of Na and Li have been considered. Since atoms are spherically symmetrical, the radial probability distributions have been shown.