



UPL UNIVERSITY OF SUSTAINABLE TECHNOLOGY

SRICT-INSTITUTE OF SCIENCE AND RESEARCH (SRICT-ISR)



ATOMIC STRUCTURE

Chemistry-II

❖ TOWARDS QUANTUM MECHANICAL MODEL OF THE ATOM

In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of such a model were:

1. Dual behaviour of matter,
2. Heisenberg uncertainty principle

❖ Dual Behaviour of Matter

The French physicist, de Broglie in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties. This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength, de Broglie, from this analogy, gave the following relation between wavelength (λ) and momentum (p) of a material particle.

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

where m is the mass of the particle, v its velocity and p its momentum. de Broglie's prediction was confirmed experimentally. when it was found that an electron beam undergoes diffraction, a phenomenon characteristic of waves. This fact has been put to use in making an electron microscope, which is based on the wavelike behaviour of electrons just as an ordinary microscope utilises the wave nature of light. An electron microscope is a powerful tool in modern scientific research because it achieves a magnification of about 15 million times. It needs to be noted that according to de Broglie, every object in motion has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can however be detected experimentally. Results obtained from the following problems prove these points qualitatively.

Problem 2.12

What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} ?

Solution

According to de Broglie equation (2.22)

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ Js})}{(0.1 \text{ kg})(10 \text{ m s}^{-1})}$$

$$= 6.626 \times 10^{-34} \text{ m} \quad (\text{J} = \text{kg m}^2 \text{ s}^{-2})$$

Problem 2.13

The mass of an electron is $9.1 \times 10^{-31} \text{ kg}$. If its K.E. is $3.0 \times 10^{-25} \text{ J}$, calculate its wavelength.

Solution

Since K. E. = $\frac{1}{2} mv^2$

$$v = \left(\frac{2 \text{K.E.}}{m} \right)^{1/2} = \left(\frac{2 \times 3.0 \times 10^{-25} \text{ kg m}^2 \text{ s}^{-2}}{9.1 \times 10^{-31} \text{ kg}} \right)^{1/2}$$

$$= 812 \text{ m s}^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ Js}}{(9.1 \times 10^{-31} \text{ kg})(812 \text{ m s}^{-1})}$$

$$= 8967 \times 10^{-10} \text{ m} = 896.7 \text{ nm}$$

Problem 2.14

Calculate the mass of a photon with wavelength 3.6 \AA .

Solution

$$\lambda = 3.6 \text{ \AA} = 3.6 \times 10^{-10} \text{ m}$$

Velocity of photon = velocity of light

$$m = \frac{h}{\lambda v} = \frac{6.626 \times 10^{-34} \text{ Js}}{(3.6 \times 10^{-10} \text{ m})(3 \times 10^8 \text{ m s}^{-1})}$$

$$= 6.135 \times 10^{-29} \text{ kg}$$

❖ Heisenberg's Uncertainty Principle

Werner Heisenberg a German physicist in 1927, stated uncertainty principle which is the consequence of dual behaviour of matter and radiation. **It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.**

Mathematically, it can be given as in equation

$$\Delta x \times \Delta p_x \geq \frac{h}{4\pi}$$

$$\text{OR} \quad \Delta x \times \Delta(mv_x) \geq \frac{h}{4\pi}$$

$$\text{OR} \quad \Delta x \times \Delta v_x \geq \frac{h}{4\pi m}$$

Where Δx is the uncertainty in position and Δp_x (or Δv_x) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [$\Delta(v_x)$ is large]. On the other hand, if the velocity of the electron is known precisely ($\Delta(v_x)$ is small), then the position of the electron will be uncertain (Δx will be large). Thus, if we carry out some physical measurements on the electron's position or velocity, the outcome will always depict a fuzzy or blur picture.

The uncertainty principle can be best understood with the help of an example. Suppose you are asked to measure the thickness of a sheet of paper with an unmarked metrestick. Obviously, the results obtained would be extremely inaccurate and meaningless, In order to obtain any accuracy, you should use an instrument graduated in units smaller than the thickness of a sheet of the paper. Analogously, in order to determine the position of an electron, we must use a meterstick calibrated in units of smaller than the dimensions of electron (keep in mind that an electron is considered as a point charge and is therefore, dimensionless). To observe an electron, we can illuminate it with "light" or electromagnetic radiation. The "light" used must have a wavelength smaller than the] dimensions of an electron. The high momentum photons of such light ($p=h/\lambda$) would change the energy of electrons by collisions. In this process we, no doubt,

would be able to calculate the position of the electron, but we would know very little about the velocity of the electron after the collision.

❖ Significance of Uncertainty Principle

One of the important implications of the Heisenberg Uncertainty Principle is that **it rules out existence of definite paths or trajectories of electrons and other similar particles**. The trajectory of an object is determined by its location and velocity at various moments. If we know where a body is at a particular instant and if we also know its velocity and the forces acting on it at that instant, we can tell where the body would be sometime later. We, therefore, conclude that the position of an object and its velocity fix its trajectory. Since for a sub-atomic object such as an electron, it is not possible simultaneously to determine the position and velocity at any given instant to an arbitrary degree of precision, it is not possible to talk of the trajectory of an electron.

The effect of Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects. This can be seen from the following examples. If uncertainty principle is applied to an object of mass, say about a milligram (10^{-6} kg), then

$$\begin{aligned}\Delta v \cdot \Delta x &= \frac{h}{4\pi \cdot m} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.1416 \times 10^{-6} \text{ kg}} \approx 10^{-28} \text{ m}^2 \text{ s}^{-1}\end{aligned}$$

The value of $\Delta v \Delta x$ obtained is extremely small and is insignificant. Therefore, one may say that **in dealing with milligram-sized or heavier objects, the associated uncertainties are hardly of any real consequence.**

In the case of a microscopic object like an electron on the other hand. $\Delta v \cdot \Delta x$ obtained is much larger and such uncertainties are of real consequence. For example, for an electron whose mass is 9.11×10^{-31} kg., according to Heisenberg uncertainty principle

$$\begin{aligned}\Delta v \cdot \Delta x &= \frac{h}{4\pi m} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.1416 \times 9.11 \times 10^{-31} \text{ kg}} \\ &= 10^{-4} \text{ m}^2 \text{ s}^{-1}\end{aligned}$$

It, therefore, means that if one tries to find the exact location of the electron, say to an uncertainty of only 10^{-8} m , then the uncertainty Δv in velocity would be

$$\frac{10^{-4} \text{ m}^2 \text{ s}^{-1}}{10^{-8} \text{ m}} \approx 10^4 \text{ m s}^{-1}$$

which is so large that the classical picture of electrons moving in Bohr's orbits (fixed) cannot hold good. **It, therefore, means that the precise statements of the position and momentum of electrons have to be replaced by the statements of probability, that the electron has at a given position and momentum. This is what happens in the quantum mechanical model of atom.**

Problem 2.15

A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 \AA . What is the uncertainty involved in the measurement of its velocity?

Solution

$$\Delta x \Delta p = \frac{h}{4\pi} \quad \text{or} \quad \Delta x m \Delta v = \frac{h}{4\pi}$$

$$\Delta v = \frac{h}{4\pi \Delta x m}$$

$$\begin{aligned}\Delta v &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 0.1 \times 10^{-10} \text{ m} \times 9.11 \times 10^{-31} \text{ kg}} \\ &= 0.579 \times 10^7 \text{ m s}^{-1} \quad (1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}) \\ &= 5.79 \times 10^6 \text{ m s}^{-1}\end{aligned}$$

Problem 2.16

A golf ball has a mass of 40 g , and a speed of 45 m/s . If the speed can be measured within accuracy of 2% , calculate the uncertainty in the position.

Solution

The uncertainty in the speed is 2%, i.e.,

$$45 \times \frac{2}{100} = 0.9 \text{ m s}^{-1} .$$

Using the equation (2.22)

$$\begin{aligned} \Delta x &= \frac{h}{4\pi m \Delta v} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 40 \text{g} \times 10^{-3} \text{ kg g}^{-1} (0.9 \text{ m s}^{-1})} \\ &= 1.46 \times 10^{-33} \text{ m} \end{aligned}$$

This is nearly $\sim 10^{18}$ times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

❖ Schrödinger wave Equation

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (**principal quantum number n, azimuthal quantum number l and magnetic quantum number m_l**) arise as a natural consequence in the solution of the Schrödinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals. Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

$$H \psi = E \psi$$

Application of Schrödinger equation to multi-electron atoms presents a difficulty: the Schrödinger equation cannot be solved exactly for a multi-electron

atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later, unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number n , the energies of the orbitals in multi-electron atoms depend on quantum numbers n and l .

❖ Orbitals and Quantum Numbers

A large number of orbitals are possible in an atom. Qualitatively these orbitals can be distinguished by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly shape and orientation mean that there is more probability of finding the electron along certain directions than along others. Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labelled as n , l and m_l .

The principal quantum number ' n ' is a positive integer with value of $n = 1, 2, 3, \dots$. The principal quantum number determines the size and to large extent the energy of the orbital. For hydrogen atom and hydrogen like species (He^+ , Li^{2+} , ... etc.) energy and size of the orbital depends only on ' n '.

The principal quantum number also identifies the **shell**. With the increase in the value of ' n ', the number of allowed orbital increases **are given by ' n^2 '**. All the orbitals of a given value of ' n ' constitute a single shell of atom and are represented by the following letters

$n = 1 \ 2 \ 3 \ 4 \ \dots\dots\dots$
Shell = K L M N $\dots\dots\dots$

Size of an orbital increases with increase of principal quantum number ' n '. In other words the electron will be located away from the nucleus. Since energy is required in shifting away the negatively charged electron from the positively charged nucleus, the energy of the orbital will increase with increase of n .

Azimuthal quantum number. ' l ' is also known as **orbital angular momentum** or **subsidiary quantum number**. It defines the three dimensional shape of the orbital.

For a given value of n , l can have n values ranging from 0 to $n - 1$, that is, for a given value of n , the possible value of l are : $l = 0, 1, 2, \dots, (n-1)$

For example, when $n = 1$, value of l is only 0. For $n = 2$, the possible value of l can be 0 and 1. For $n = 3$, the possible l values are 0, 1 and 2.

Each shell consists of one or more sub-shells or sub-levels. The number of sub-shells in a principal shell is equal to the value of n . For example in the first shell ($n = 1$), there is only one sub-shell which corresponds to $l = 0$. There are two sub-shells ($l = 0, 1$) in the second shell ($n = 2$), three ($l = 0, 1, 2$) in third shell ($n = 3$) and so on. Each sub-shell is assigned an azimuthal quantum number (l). Sub-shells corresponding to different values of l are represented by the following symbols.

Value for l : 0 1 2 3 4 5.....

Notation for: s p d f g h

Sub-shell

Table shows the permissible values of ' l ' for a given principal quantum number and the corresponding sub-shell notation.

n	l	Subshell notation
1	0	1s
2	0	2s
2	1	2p
3	0	3s
3	1	3p
3	2	3d
4	0	4s
4	1	4p
4	2	4d
4	3	4f

Magnetic orbital quantum number. 'm_l' gives information about **the spatial orientation of the orbital with respect to standard set of co-ordinate axis**. For any sub-shell (defined by 'l' value) 2l+1 values of m_l are possible and these values are given by :

$$m_l = -l, -(l-1), -(l-2)\dots 0, 1\dots (l-2), (l-1), l$$

Thus for l = 0, the only permitted value of m_l = 0, [2(0) + 1 = 1, one s orbital]. For l = 1, m_l can be -1, 0 and +1 [2(1) + 1 = 3, three p orbitals]. For l = 2, m_l = -2, -1, 0, +1 and +2, [2(2) + 1 = 5, five d orbitals]. It should be noted that the values of m_l are derived from l and that the value of l are derived from n.

Each orbital in an atom, therefore, is defined by a set of values for n, l and m_l. An orbital described by the quantum numbers n = 2, l = 1, m_l = 0 is an orbital in the p sub-shell of the second shell. The following chart gives the relation between the sub-shell and the number of orbitals associated with it.

Value of l	0	1	2	3	4	5
Subshell notation	s	p	d	f	g	h
number of orbitals	1	3	5	7	9	11

Electron spin 's' : The three quantum numbers labelling an atomic orbital can be used equally well to define its energy, shape and orientation. But all these quantum numbers are not enough to explain the line spectra observed in the case of multi-electron atoms, that is, some of the lines actually occur in doublets (two lines closely spaced), triplets (three lines, closely spaced) etc. This suggests the presence of a few more energy levels than predicted by the three quantum numbers.

In 1925, George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth quantum number known as the **electron spin quantum number (m_s)**. An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun. In other words, an electron has, besides charge and mass, intrinsic spin angular quantum number. Spin angular momentum of the electron — a vector quantity, can have two orientations relative to the chosen axis. These two orientations are distinguished by the spin quantum numbers m_s which can take the values of +½ or -½. These are called the **two spin**

states of the electron and are normally represented by two arrows, \uparrow (spin up) and \downarrow (spin down). Two electrons that have different m_s values (one $+\frac{1}{2}$ and the other $-\frac{1}{2}$) are said to have opposite spins. An orbital cannot hold more than two electrons and these two electrons should have opposite spins. To sum up, the four quantum numbers provide the following information:

i) n defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital.

ii) There are n subshells in the n^{th} shell. l identifies the subshell and determines the shape of the orbital (see section 2.6.2). There are $(2l+1)$ orbitals of each type in a subshell, that is, one s orbital ($l = 0$), three p orbitals ($l = 1$) and five d orbitals ($l = 2$) per subshell. To some extent l also determines the energy of the orbital in a multi-electron atom.

iii) m_l designates the orientation of the orbital. For a given value of l , m_l has $(2l+1)$ values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.

iv) m_s refers to orientation of the spin of the electron.

❖ Shapes of Atomic Orbitals

The orbital wave function or ψ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of corresponding wave functions as a function of r (the distance from the nucleus) are different. gives such plots for $1s$ ($n = 1, l = 0$) and $2s$ ($n = 2, l = 0$) orbitals.

According to the German physicist, Max Born, the square of the wave function (i.e., ψ^2) at a point gives the probability density of the electron at that point. The variation of ψ^2 as a function of r for $1s$ and $2s$ orbitals is given in Here again, you may note that the curves for $1s$ and $2s$ orbitals are different.

It may be noted that for $1s$ orbital the probability density is maximum at the nucleus and it decreases sharply as we move

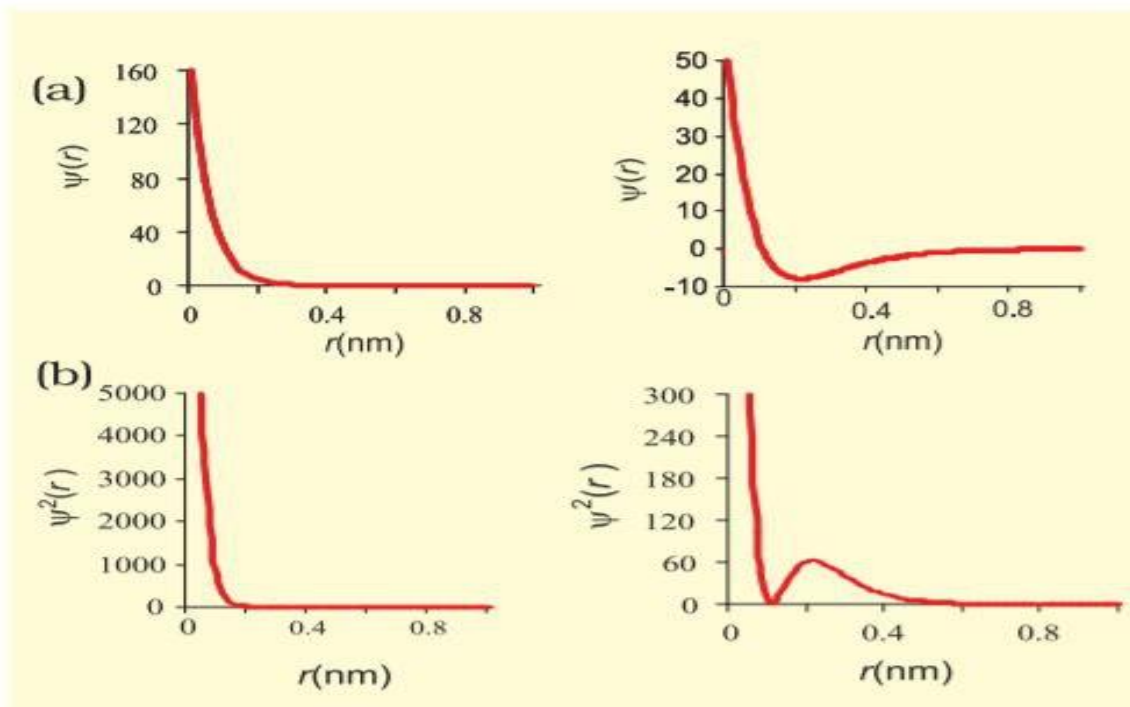


Fig. 2.12 The plots of (a) the orbital wave function $\psi(r)$; (b) the variation of probability density $\psi^2(r)$ as a function of distance r of the electron from the nucleus for 1s and 2s orbitals.

away from it. On the other hand, for 2s orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maxima it decreases again and approaches zero as the value of r increases further. The region where this probability density function reduces to zero is called **nodal surfaces** or simply **nodes**. In general, it has been found that ns -orbital has $(n - 1)$ nodes, that is, number of nodes increases with increase of principal quantum number n . In other words, number of nodes for 2s orbital is one, two for 3s and so on.

These probability density variation can be visualised in terms of charge cloud diagrams [Fig. 2.13(a)]. In these diagrams, the density of the dots in a region represents electron probability density in that region.

Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this

representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of

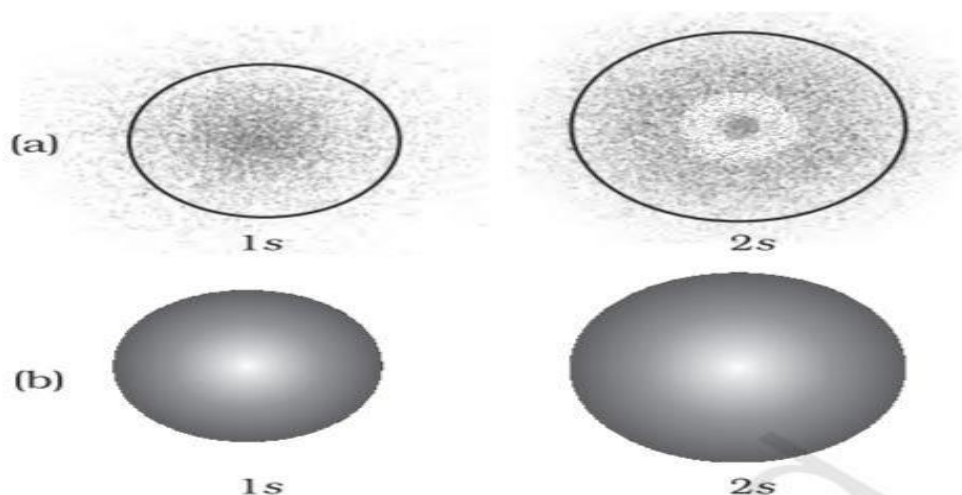


Fig. 2.13 (a) Probability density plots of 1s and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region. (b) Boundary surface diagram for 1s and 2s orbitals.

probability density $|\psi|^2$ is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density* is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%. The boundary surface diagram for 1s and 2s orbitals are given in Fig. 2.13(b). One may ask a question: Why do we not draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is, 100 %? The answer to this question is that the probability density $|\psi|^2$ has always some value, howsoever small it may be, at any finite distance from the nucleus. It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for a s orbital is actually a sphere centred on the nucleus. In two dimensions, this sphere looks like a circle. It encloses a region in which probability of finding the electron is about 90%

Thus we see that 1s and 2s orbitals are spherical in shape. In reality all the s-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in n , that is, $4s > 3s > 2s > 1s$ and the electron is located further away from the nucleus as the principal quantum number increases.

Boundary surface diagrams for three 2p orbitals ($l = 1$) are shown in Fig. 2.14. In these diagrams, the nucleus is at the origin. Here, unlike s-orbitals, the boundary surface diagrams are not spherical. Instead each p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density function is zero on the plane where the two lobes touch each other. The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations $2p_x$, $2p_y$, and $2p_z$. It should be understood, however, that there is no simple relation between the values of m_l ($-1, 0$ and $+1$) and the x, y and z directions. For our purpose, it is sufficient to remember that,

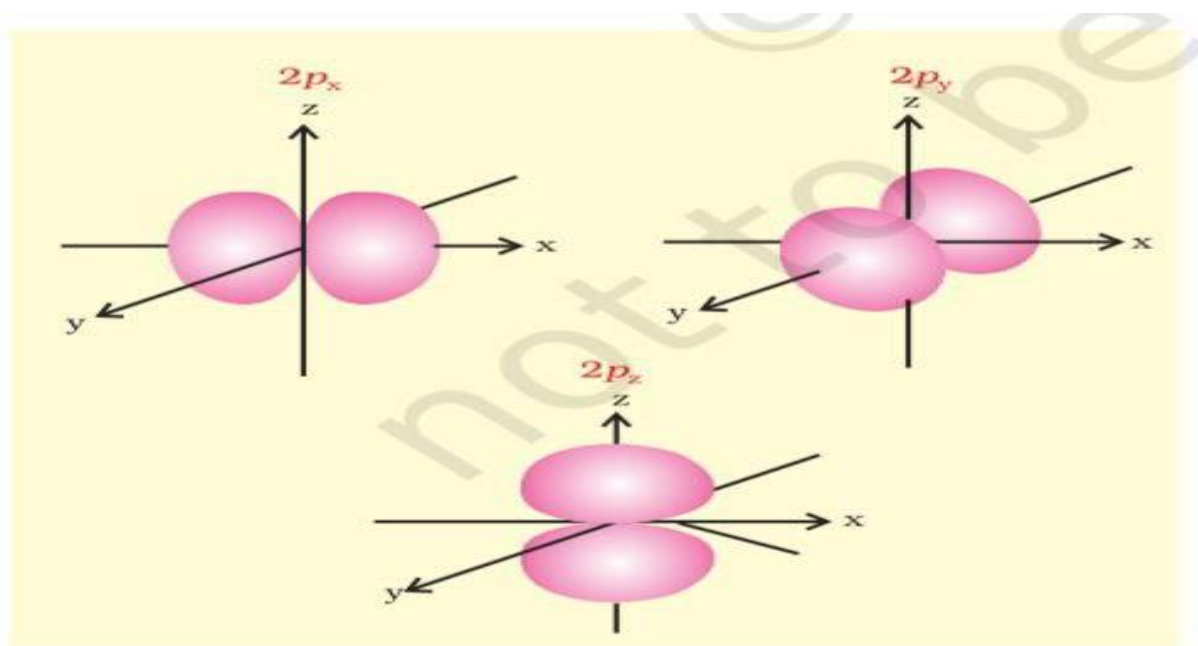


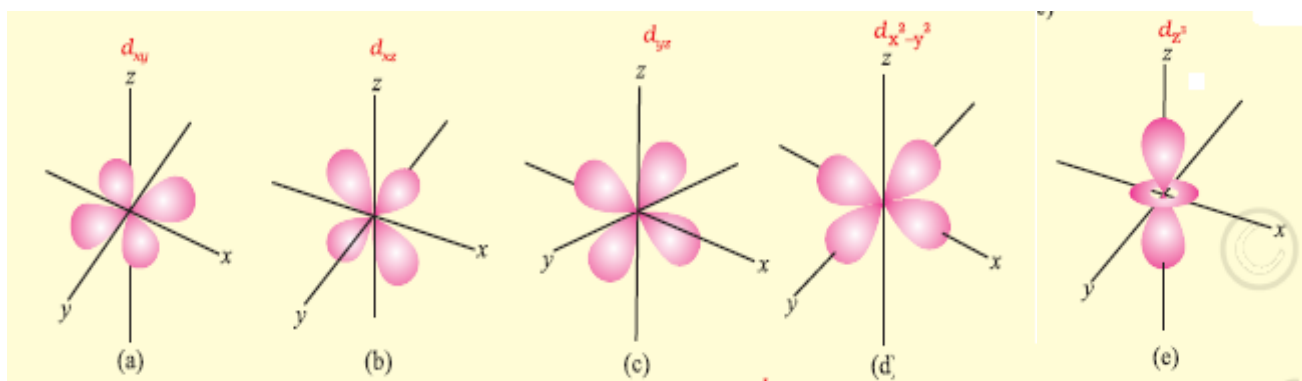
Fig. 2.14 Boundary surface diagrams of the three 2p orbitals.

because there are three possible values of m_l , there are, therefore, three p orbitals whose axes are mutually perpendicular. Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is $4p > 3p > 2p$. Further, like s orbitals, the probability density functions for p-orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases. The number of nodes are given by the $n - 2$, that is number of radial node is 1 for 3p orbital, two for 4p orbital and so on.

For $l = 2$, the orbital is known as d-orbital and the minimum value of principal quantum number (n) has to be 3. As the value of l cannot be greater than $n - 1$. There are five m_l values ($-2, -1, 0, +1$ and $+2$) for $l = 2$ and thus there are five d orbitals. The boundary surface diagram of d orbitals are shown in Fig.

The five d-orbitals are designated as d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ and d_{z^2} . The shapes of the first four d-orbitals are similar to each other, whereas that of the fifth one, d_{z^2} , is different from others, but all five 3d orbitals are equivalent in energy. The d orbitals for which n is greater than 3 (4d, 5d...) also have shapes similar to 3d orbital, but differ in energy and size.

Besides the radial nodes (i.e., probability density function is zero), the probability density functions for the np and nd orbitals are zero at the plane (s), passing through the nucleus (origin). For example, in case of p_z orbital, xy -plane is a nodal plane, in case of d_{xy} orbital, there are two nodal planes passing through the origin and bisecting the xy plane containing z -axis. These are called angular nodes and number of angular nodes are given by ' l ', i.e., one angular node for p orbitals, two angular nodes for 'd' orbitals and so on. The total number of nodes are given by $(n-1)$, i.e., sum of l angular nodes and $(n - l - 1)$ radial nodes.



❖ Filling of Orbitals in Atom

The filling of electrons into the orbitals of different atoms takes place according to the Aufbau principle which is based on the Pauli's exclusion principle, the Hund's rule of maximum multiplicity and the relative energies of the orbitals.

❖ Aufbau Principle

The word 'aufbau' in German means 'building up'. The building up of orbitals means the filling up of orbitals with electrons. The principle states: **In the ground state of the atoms, the orbitals are filled in order of their increasing energies.** In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled.

The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows : $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s...$

The order may be remembered by using the method given in Fig. 2.17. Starting from the top, the direction of the arrows gives the order of filling of orbitals that is starting from right top to bottom left.

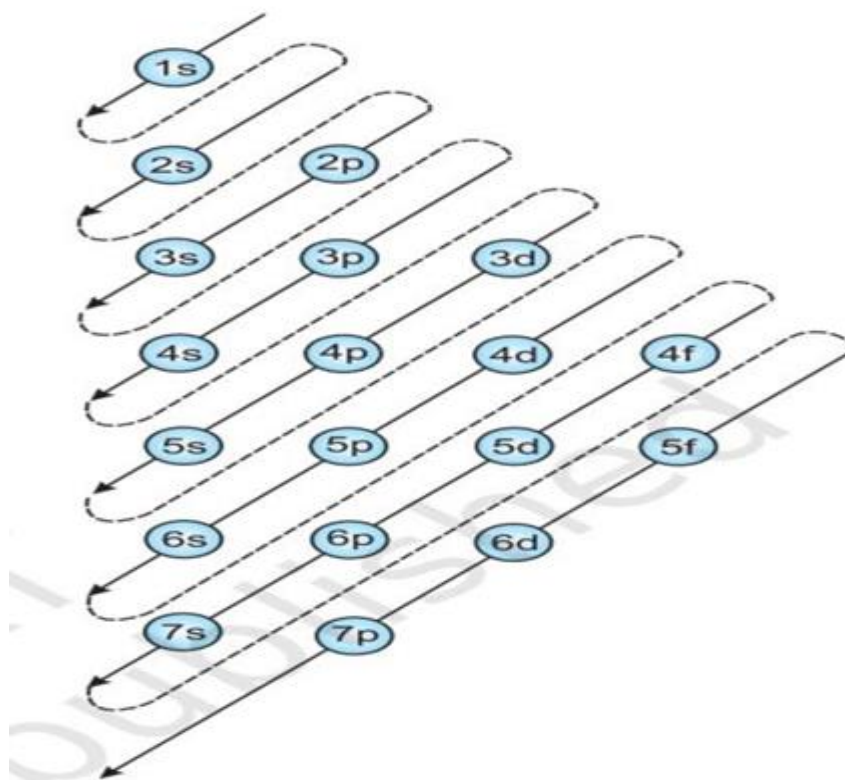


Fig.2.17 Order of filling of orbitals

❖ Pauli Exclusion Principle

The number of electrons to be filled in various orbitals is restricted by the exclusion principle, given by the Austrian scientist Wolfgang Pauli (1926). According to this principle: **No two electrons in an atom can have the same set of four quantum numbers.** Pauli Exclusion Principle can also be stated as: **“Only two electrons may exist in the same orbital and these electrons must have opposite spin.”** This means that the two electrons can have the same value of three quantum numbers n , l and m_l , but must have the opposite spin quantum number. The restriction imposed by Pauli’s exclusion principle on the number of electrons in an orbital helps in calculating the capacity of electrons to be present in any subshell. For example, subshell $1s$ comprises of one orbital and thus the maximum number of electrons present in $1s$ subshell can be two, in p and d subshells, the maximum number of electrons can be 6 and 10 and so on. This can be summed up as: **the maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.**

❖ Hund’s Rule of Maximum Multiplicity

This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called degenerate orbitals). It states: **pairing of electrons in the orbitals belonging to the same subshell (p , d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.**

Since there are three p , five d and seven f orbitals, therefore, the pairing of electrons will start in the p , d and f orbitals with the entry of 4th, 6th and 8th electron, respectively. It has been observed that half-filled and fully filled degenerate set of orbitals acquire extra stability due to their symmetry.

❖ Electronic Configuration of Atoms

The distribution of electrons into orbitals of an atom is called its electronic configuration. If one keeps in mind the basic rules which govern the filling of different atomic orbitals, the electronic configurations of different atoms can be written very easily. The electronic configuration of different atoms can be represented in two ways. For example:

(i) $s^a p^b d^c \dots$ notation

(ii) Orbital diagram



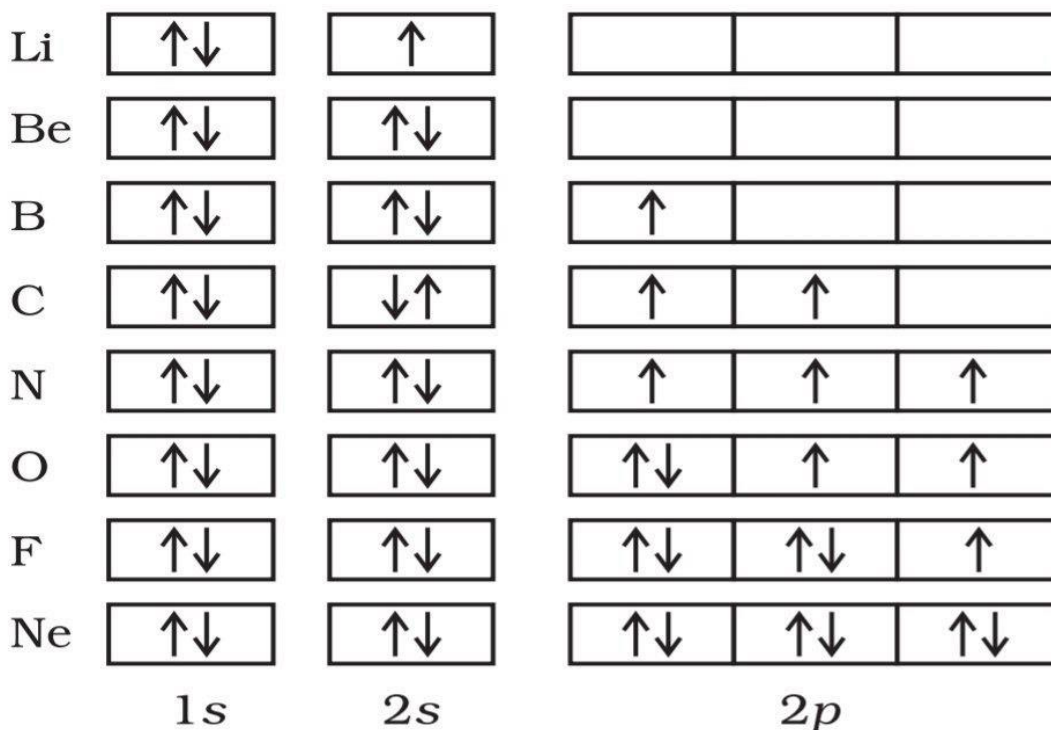
In the first notation, the subshell is represented by the respective letter symbol and the number of electrons present in the subshell is depicted, as the super script, like a, b, c ... etc. The similar subshell represented for different shells is differentiated by writing the principal quantum number before the respective subshell. In the second notation each orbital of the subshell is represented by a box and the electron is represented by an arrow (\uparrow) a positive spin or an arrow (\downarrow) a negative spin. The advantage of second notation over the first is that it represents all the four quantum numbers.

The hydrogen atom has only one electron which goes in the orbital with the lowest energy, namely 1s. The electronic configuration of the hydrogen atom is $1s^1$ meaning that it has one electron in the 1s orbital. The second electron in helium (He) can also occupy the 1s orbital. Its configuration is, therefore, $1s^2$. As mentioned above, the two electrons differ from each other with opposite spin, as can be seen from the orbital diagram.



The third electron of lithium (Li) is not allowed in the 1s orbital because of Pauli Exclusion Principle. It, therefore, takes the next available choice, namely the 2s orbital. The electronic configuration of Li is $1s^2 2s^1$. The 2s orbital can accommodate one more electron. The configuration of beryllium (Be) atom is, therefore, $1s^2 2s^2$.

In the next six elements-boron (B, $1s^2 2s^2 2p^1$), carbon (C, $1s^2 2s^2 2p^2$), nitrogen (N, $1s^2 2s^2 2p^3$), oxygen (O, $1s^2 2s^2 2p^4$), fluorine (F, $1s^2 2s^2 2p^5$) and neon (Ne, $1s^2 2s^2 2p^6$), the 2p orbitals get progressively filled. This process is completed with the neon atom. The orbital picture of these elements can be represented as follows:



The electronic configuration of the elements sodium (Na, $1s^2 2s^2 2p^6 3s^1$) to argon (Ar, $1s^2 2s^2 2p^6 3s^2 3p^6$), follow exactly the same pattern as the elements from lithium to neon with the difference that the 3s and 3p orbitals are getting filled now. This process can be simplified if we represent the total number of electrons in the first two shells by the name of element neon (Ne). The electronic configuration of the elements from sodium to argon can be written as (Na, [Ne] $3s^1$) to (Ar, [Ne] $3s^2 3p^6$). The electrons in the completely filled shells are known as core electrons and the electrons that are added to the electronic shell with the highest principal quantum number are called **valence electrons**.

For example, the electrons in Ne are the core electrons and the electrons from Na to Ar are the valence electrons. In potassium (K) and calcium (Ca), the 4s orbital, being lower in energy than the 3d orbitals, is occupied by one and two electrons respectively.

A new pattern is followed beginning with scandium (Sc). The 3d orbital, being lower in energy than the 4p orbital, is filled first. Consequently, in the next ten elements, scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn), the five 3d orbitals are progressively occupied. We may be puzzled by the fact that chromium and copper have five and ten electrons in 3d orbitals rather than four and nine as their position would have indicated with two-electrons in the 4s orbital. The reason is that fully filled orbitals and half-filled orbitals have extra stability (that is, lower energy). Thus p^3 , p^6 , d^5 , d^{10} , f^7 , f^{14} etc. configurations, which are either half-filled or fully filled, are more stable. Chromium and copper therefore adopt the d^5 and d^{10} configuration.

Table 2.9 Electronic Configurations of the Elements

Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	2	2	6	2	3													
S	16	2	2	6	2	4													
Cl	17	2	2	6	2	5													
Ar	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	2	6	2	6	3	2											
Cr*	24	2	2	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu*	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38	2	2	6	2	6	10	2	6			2							
Y	39	2	2	6	2	6	10	2	6	1		2							
Zr	40	2	2	6	2	6	10	2	6	2		2							
Nb*	41	2	2	6	2	6	10	2	6	4		1							
Mo*	42	2	2	6	2	6	10	2	6	5		1							
Tc	43	2	2	6	2	6	10	2	6	5		2							
Ru*	44	2	2	6	2	6	10	2	6	7		1							
Rh*	45	2	2	6	2	6	10	2	6	8		1							
Pd*	46	2	2	6	2	6	10	2	6	10									
Ag*	47	2	2	6	2	6	10	2	6	10		1							
Cd	48	2	2	6	2	6	10	2	6	10		2							
In	49	2	2	6	2	6	10	2	6	10		2	1						
Sn	50	2	2	6	2	6	10	2	6	10		2	2						
Sb	51	2	2	6	2	6	10	2	6	10		2	3						
Te	52	2	2	6	2	6	10	2	6	10		2	4						
I	53	2	2	6	2	6	10	2	6	10		2	5						
Xe	54	2	2	6	2	6	10	2	6	10		2	6						

* Elements with exceptional electronic configurations

Element Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
Cs 55	2	2	6	2	6	10	2	6	10		2	6			1			
Ba 56	2	2	6	2	6	10	2	6	10		2	6			2			
La* 57	2	2	6	2	6	10	2	6	10		2	6	1		2			
Ce* 58	2	2	6	2	6	10	2	6	10	2	2	6			2			
Pr 59	2	2	6	2	6	10	2	6	10	3	2	6			2			
Nd 60	2	2	6	2	6	10	2	6	10	4	2	6			2			
Pm 61	2	2	6	2	6	10	2	6	10	5	2	6			2			
Sm 62	2	2	6	2	6	10	2	6	10	6	2	6			2			
Eu 63	2	2	6	2	6	10	2	6	10	7	2	6			2			
Gd* 64	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
Tb 65	2	2	6	2	6	10	2	6	10	9	2	6			2			
Dy 66	2	2	6	2	6	10	2	6	10	10	2	6			2			
Ho 67	2	2	6	2	6	10	2	6	10	11	2	6			2			
Er 68	2	2	6	2	6	10	2	6	10	12	2	6			2			
Tm 69	2	2	6	2	6	10	2	6	10	13	2	6			2			
Yb 70	2	2	6	2	6	10	2	6	10	14	2	6			2			
Lu 71	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
Hf 72	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
Ta 73	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
W 74	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
Re 75	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
Os 76	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
Ir 77	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
Pt* 78	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
Au* 79	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
Hg 80	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Tl 81	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
Pb 82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
Bi 83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
Po 84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
At 85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
Rn 86	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
Fr 87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
Ra 88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
Ac 89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
Th 90	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
Pa 91	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
U 92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
Np 93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
Pu 94	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
Am 95	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
Cm 96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
Bk 97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
Cf 98	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
Es 99	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
Fm 100	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
Md 101	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
No 102	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
Lr 103	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
Rf 104	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	2	2
Db 105	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	3	2
Sg 106	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	4	2
Bh 107	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	5	2
Hs 108	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	6	2
Mt 109	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	7	2
Ds 110	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	8	2
Rg** 111	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	10	1

** Elements with atomic number 112 and above have been reported but not yet fully authenticated and named.

❖ Effective nuclear charge

The attractive positive charge of nuclear protons acting on valence electrons.

1. The effective nuclear charge is always less than the total number of protons present in a nucleus due to the shielding effect.
2. Effective nuclear charge is behind all other periodic table tendencies.

The effective nuclear charge may be approximated by the equation:

$$Z_{\text{eff}} = Z - S$$

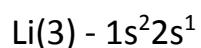
Where Z is the atomic number and S is the number of shielding electrons.

Trends

The periodic table tendency for effective nuclear charge:

1. Increase across a period (due to increasing nuclear charge with no accompanying increase in shielding effect).
2. Decrease down a group (although nuclear charge increases down a group, shielding effect more than counters its effect).

Examples:



- A 2s lithium can have 2 electrons, 1s electrons between itself and the lithium nucleus. So, these 1s electrons shield 2s electrons from the nucleus.
- Measurements indicate the effective nuclear charge experienced by a 2s lithium electron is 0.43 times the charge of the lithium nucleus.