

## Quantum Numbers

### THE QUANTUM MECHANICAL MODEL OF THE ATOM

In 1927, Erwin Schroedinger explored the idea of **matter waves of electrons** and **principles of quantum mechanics** to successfully formulate the **quantum mechanical model** of the atom.

He replaced the concept of electron '**orbits**' by the concept of '**orbitals**'. An '**orbital**' denoted by an appropriate wave function ' $\Psi$ ' is essentially a **wave description** of the motion of the electron in a region around the nucleus.

#### Orbits and Orbitals

The concept of 'orbit' of an electron violates Heisenberg's uncertainty principle. Schroedinger's concept of 'orbital' avoids this violation by defining a **region** around the nucleus where electrons in an atom might be **found without specifying the path followed**.

According to the modern concept, if we do an experiment to 'find' an electron at any given instant, we do so by considering it as a particle. At that instant, its wave description and hence all information regarding its momentum (in the de Broglie sense) is lost. This is in keeping with the uncertainty principle and constitutes the precise difference between the '**orbital**' description and Bohr's '**orbit**' description of electrons in an atom.

#### Can we use this concept of orbital to define its shape and size?

Yes, if we repeatedly try to 'find' the electron at different instants of time, on many identical atoms we will see that the electron is at different points around the nucleus. Some points are more common than others. We refer to the region defined by such points as a region of high probability density (or charge density). You should note that there is always a small but finite probability that the electron is very very far away from the nucleus. Nevertheless, we can define a region around the nucleus where the electron is most likely to be present.

One way to visualise an orbital is to imagine the size and shape of this region of 90% probability as the size and shape of the orbital.

#### Energy of an Orbital - Schroedinger's Wave Equation

An orbital, strictly speaking, does not have any meaning without considering the electron it describes. So when we refer to the energy of an orbital, we mean the energy of the electron represented by the orbital. However, while studying Chemistry, we will very often use the terms 'filled', half-filled' or 'unfilled' orbitals in a sense where orbitals are considered as empty boxes where electrons can come in. Such descriptions become valid since  $\Psi$  is a mathematical eigen function and can always assign an eigen value to it.

Schroedinger formulated an operator  $H$  which could be used to extract information regarding the energy  $E$  of an electron represented by the wave function  $\Psi$ .

According to the relation (known as Schroedinger's wave equation),

$$H\Psi = E\Psi \text{ (} \text{click here} \text{)}$$

The figure below gives an idea of this dependence. Note the crossing of other lines by lines for  $3d$ ,  $4d$  and  $4f$ . We will refer to this while discussing the electronic configurations.

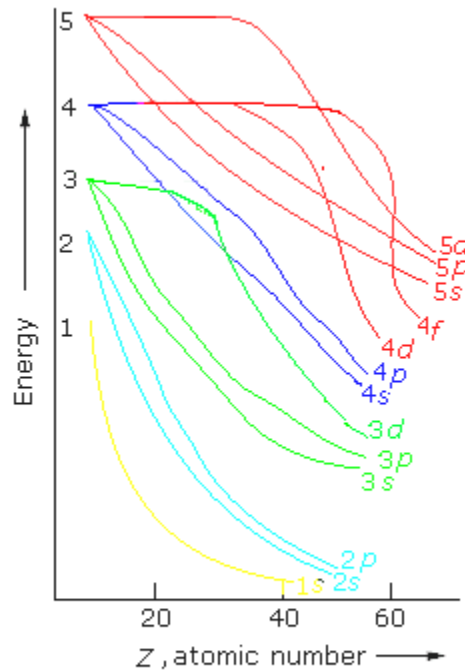


Figure: **Schematic diagram showing variation in orbital energies of neutral atoms as functions of atomic number**

### The Wave Function

Like any function,  $\Psi$  is a function of the coordinates. Since the electrons in an atom are moving in the central electric field of the nucleus with spherical equipotential surfaces, Schrodinger used **spherical polar coordinates**  $(r, \theta, \phi)$  instead of Cartesian coordinates  $(x, y, z)$ . This way he could express  $\Psi$  as a product of the **radial part** of the wave function (related to the 'size' of  $\Psi$ ) and the **angular part** (related to the shape of  $\Psi$ ).

$$\Psi(r, \theta, \phi) = \Psi_{\text{total}} = \Psi_{\text{radial}} \times \Psi_{\text{angular}} = \Psi(r) \times \Psi(\theta, \phi)$$

We shall see later how such a resolution helps us in visualising different aspects of

an orbital.

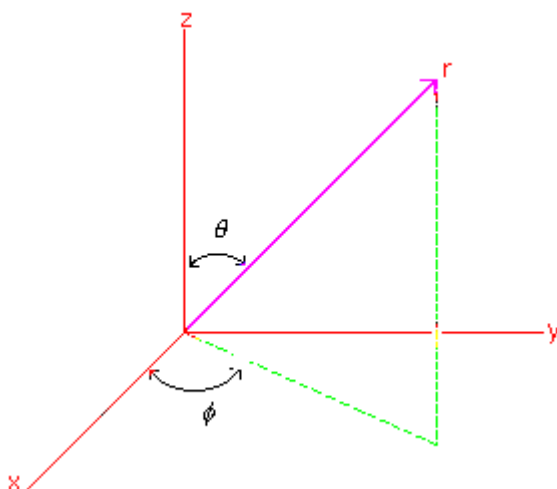


Figure: **The relationship of the spherical polar coordinates  $r$ ,  $\theta$  and  $\phi$  to the Cartesian coordinates  $x$ ,  $y$  and  $z$ . The nucleus is at the origin and the electron is at the end of the radius vector.**

## Quantum Numbers

In Schrodinger's wave equation, the function  $\Psi$  represents all electrons in an atom. **Schrodinger's wave equation is a second degree differential equation.** Its solutions are also equations. In order to get definite solution for an electron in three dimensional space, three quantum conditions namely energy, angular momentum and magnetic moment must be specified which gives rise to three quantum numbers.

1. The principal quantum number  $n$ .
2. The azimuthal quantum number (or the angular momentum quantum number)  $l$ .
3. The magnetic quantum number  $m_l$  or simply  $m$ .

If we specify the values of  $n$ ,  $l$  and  $m_l$  within a given  $\Psi$  for an atom, we can specify a particular orbital of an atom.

For example, if we write  $\Psi = A \sin \frac{n\pi x}{c}$  and specify  $n$ , then we specify all  $\Psi$ 's with quantum number  $n$ .

To specify a particular orbital we have to specify the quantum number  $n, l$  and  $m_l$

$$\Psi = A \sin \frac{n\pi x}{c} \sin \frac{m\pi y}{c} \sin \frac{l\pi z}{c}$$

in

To locate a particular electron in an orbital, we require a fourth quantum condition

arising because of spin of electron  $(\pm \frac{1}{2})$  called spin quantum number  $m_s$  or simply  $s$ . In an atom, **electrons** occupy orbitals, which belong to a **subshell**, which in turn belong to a **shell**. The shell is defined by the value of ' $n$ '. A subshell within this shell is defined by the value of ' $l$ '. An orbital within this subshell is defined by the value of ' $m_l$ ', whereas the value of ' $m_s$ ' defines a particular electron in an orbital (a maximum of two per orbital).

### An analogy

Consider a shoe shop with many racks (shells!). Each rack has several shelves (subshells!) and each shell contains several boxes (orbitals!), each containing a pair of shoes (electrons!). Even when the shopkeeper takes out several shoes for display, each shoe has an address - rack number ( $n$ ), shell number ( $l$ ), box number ( $m_l$ ) and whether it is the right shoe or left shoe ( $s$ ).

### The Significance of the Quantum Number and the Rules Governing their Values

As is apparent from the name, quantum number can have only certain values.

#### 1. Principal quantum number

The principal quantum number ' $n$ ' can have only integral values  $n = 1, 2, 3, 4, \dots \infty$  designating the different **shells** represented by K, L, M, N, etc., respectively.

##### Significance

The value of ' $n$ ' specifies the **size** of the orbital and its **energy**. **Higher values** of  $n$  implies **larger size** and **higher energy**.

#### 2. Azimuthal quantum number

The azimuthal or angular momentum quantum number ' $l$ ' can have only  $n$  values.  $l = 0, 1, 2, 3, 4, \dots (n-1)$  designating different **subshells** within a particular shell ' $n$ '. These subshells are represented by symbols s, p, d, f, g, h ...etc corresponding to  $l = 0, 1, 2, 3, 4, 5$ , etc, respectively.

##### Significance

The number of subshells is restricted by the shell which contains them. Thus for  $n = 1$ , there is only **one** s subshell. The value of  $l$  specifies the **shape** of the orbital, its **angular momentum** and to a small extent, its **energy**.

Orbitals having different values of  $n$  but same value of  $l$  have the same shapes and same angular momenta. They differ, however, in their sizes and energies.

The total value of energy depends on both  $n$  and  $l$ . We will study more about this aspect when we discuss *Aufbau* or 'building up' principle used to determine the electronic configuration of atoms.

The angular momentum of an electron with azimuthal quantum number ' $l$ ' is given by

$$L = \sqrt{l(l+1)} \frac{h}{2\pi}$$

and is a vector quantity. For an orbital in the s subshell, ' $l$ ' = 0. Such an orbital would have an angular momentum zero.

### To determine the orbital angular momentum using the azimuthal quantum number

#### Assignment

Calculate the values of angular momenta for orbital belonging to 'p', 'd' and 'f' subshells.

(Answer:

$$\sqrt{2} \frac{h}{2\pi}, \sqrt{6} \frac{h}{2\pi}, 2\sqrt{3} \frac{h}{2\pi} )$$

(**Note:** Compare these values with Bohr's values of quantised angular momenta)

All orbitals belonging to a particular subshell 'l' have the same magnitude for the angular momentum vector. But their direction corresponding to the orientation of the orbital are different. If we consider the component along any one direction for these vectors, we have  $(2l + 1)$  different values. This leads us to another set of quantum numbers corresponding to the orientation of the orbitals in a subshell.

### 3. Magnetic quantum numbers

The magnetic quantum number ' $m_l$ ' can have only  $(2l + 1)$  values.  $m_l = -l, -(l - 1), -(l - 2), \dots, 0, \dots, (l - 2), (l - 1), +l$  corresponding to the  $(2l + 1)$  orientations of the orbital belonging to a subshell  $l$ .

#### Significance

The number of orbital in a subshell is restricted only by the type of subshell concerned. Thus, for the 's' subshell,  $l = 0$  and there is  $(2l + 1) = 2 \times 0 + 1 = 1$  orbital in it - irrespective of which shell it belongs to. For the 'p', 'd' and 'f' subshells we have  $l = 1, 2$  and  $3$  and the numbers of orbitals are 3, 5 and 7 respectively.

In the 's' subshell there is only one orbital corresponding to  $m_l = 0$

In the 'p' subshell there are three orbitals corresponding to  $m_l = -1, 0$  and  $+1$  (designated by  $p_x, p_y$  and  $p_z$  and not necessarily in one to one correspondence)

#### Assignment

What are the  $m_l$  values of orbitals of 'd', 'y' and 'g' subshells?

The energy of an orbital **does not** depend on its magnetic quantum number. All the orbitals in a subshell 'l' have the same energy and are termed as degenerate orbitals with a  $(2l + 1)$  -fold degeneracy. The orbital in a 'd' subshell is thus five-fold degenerate.

The magnetic quantum of an orbital refers only to its orientation and to one component of its **magnetic moment**. The values say **nothing about their energies**. But they do correspond to the z component of the angular momentum. When a charged particle has an angular momentum, it also has a magnetic moment. An orbital with azimuthal quantum number  $l$  has an angular

momentum  $\sqrt{l(l+1)} \frac{h}{2\pi}$  and a magnetic moment given by  $\mu = \sqrt{l(l+1)}$  BM or Bohr Magnetons.

The z component of the angular momentum is given by  $m_l \frac{h}{2\pi}$  and corresponding magnetic moment would be  $\mu_z = m_l$  BM

Where  $m_l$  can take any one of the allowed  $(2l + 1)$  values. A  $p_z$  orbital oriented along the z-axis is represented by  $m_l = 0$ . This means the z component of the magnetic moment of a  $p_z$  electron will be zero Bohr Magnetons.

$$\text{Bohr Magnetron} = \frac{e\hbar}{4\pi mc}$$

### 4. Spin quantum number

The spin quantum number  $m_s$  can have only two values  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . (Note that in

many texts,  $s$  is used instead of  $m_s$  which is wrong. The value of  $s$  for electron is  $\frac{1}{2}$  and not  $\pm \frac{1}{2}$ .  $m_s$  has values  $\pm \frac{1}{2}$  where  $s$  and  $m_s$  are related in the same way as  $l$  and  $m_l$  are related. We will discuss this while discussing the significance of electron spin).

### Significance

The spin quantum number, in a way, denotes the orientation of a 'spinning' electron (clockwise or anti clockwise) with respect to a given direction e.g. the z-axis.

We can consider the electron as a spinning charged particle. Consequently an electron will have both an angular momentum and a magnetic moment due to its [spin only](#) (in addition to what it has due to the shape of its orbital).

The magnitude of the 'spin only' angular momentum vector of an electron is given

by 
$$\sqrt{s(s+1)} \frac{h}{2\pi} = \frac{\sqrt{3}h}{4\pi}$$
 while there will be  $(2s + 1) = 2$  possible **energetically**

**equivalent orientations.** The values are calculated by substituting  $s = \frac{1}{2}$ . (Note the analogy with calculating orbital angular momentum)

The two orientations correspond to  $\pm s$  (compare with  $m_s = \pm \frac{1}{2}$ ) and refer to the 'spin only' angular momenta components along the z-axis. As in the case of calculating the z component of orbital angular momenta, the values of 'spin only'

angular momenta along the z-axis is given by  $m_s \frac{h}{2\pi}$  or  $\pm \frac{1}{2} \frac{h}{2\pi}$ .  
(Note the extra factor of '2' which was not there while calculating orbital magnetic moment.)

The total magnetic moment, not the 'z' component, due to the spin of an electron

can be calculated from its 'spin only' value  $\sqrt{s(s+1)} \frac{h}{2\pi}$  as  $2\sqrt{s(s+1)}$  BM.

### Calculating 'spin only' magnetic moments

The 'spin only' magnetic moment is given by the formula  $2\sqrt{S(S+1)}$  BM where  $S$  is the total spin due to all the unpaired electrons. If there are  $n$  unpaired electrons in

an atom or ion, the total spin will be  $n \times \frac{1}{2} = \frac{n}{2}$ .

Substituting in the formula above, we have

$$\mu = 2\sqrt{\frac{n}{2}(\frac{n}{2} + 1)} \text{ BM}$$

$$\text{or, } \mu = \sqrt{n(n+2)} \text{ BM}$$

If there is only one unpaired electron, we have

$$\mu = \sqrt{1(1+2)} = \sqrt{3} \text{ BM or } 1.73 \text{ BM}$$

### Assignment

What would be the 'spin only' magnetic moment of a  $\text{Cr}^{3+}$  ion containing three

unpaired electrons?

Answer: 3.87 BM

### Summary of rules governing quantum numbers

The table below displays a summary of what we have learned regarding the rules governing quantum numbers and their significance.

One new aspect refers to calculating the total number of orbitals in a shell. This corresponds to  $n^2$ . How do we reach this formula? We know that the  $n^{\text{th}}$  shell with principal quantum number  $n$  has  $n$  subshells having azimuthal quantum number  $l = 0, 1, 2, \dots, (n - 1)$ , each in turn having  $(2l + 1)$  orbitals. Total number of orbitals in a shell = number of orbitals in  $l = 0$  + number of orbitals in  $l = 1$  + number of orbitals in  $l = 2 + \dots$  to  $n$  terms.

Clearly, this corresponds to the sum of the first  $n$  terms of an arithmetic progression series of odd natural numbers (i.e.  $1 + 3 + 5 + 7 + \dots$  to  $n$  terms) and it works out to  $n^2$  orbitals. Since each orbital can contain two electrons, the possible number of electrons in  $2n^2$ .

This aspect along with a visual display of the subshell wire orbital and electron count is provided in the table which follows:

### Using the rules for quantum numbers

We can now look at a set of four quantum numbers to judge whether they are consistent with the rules governing them and to assign *spdf* notation.

#### Summary of rules governing quantum members and their significance

Quantum number	Denoted by	Represents	Determines	Allowed number	Allowed values	Notation used	Other comments
Principal	$n$	shell of the orbital	a) size of the orbital b) energy of the orbital electron	$\infty$	Integral values 1, 2, 3 ... $\infty$	$n = 1 \Rightarrow K$ $n = 2 \Rightarrow L$ $n = 3 \Rightarrow M$ $n = 4 \Rightarrow N$ etc.	A shell contains $n^2$ orbitals and a maximum of $2n^2$ electrons.
Azimuthal	$l$	subshell of the orbital	a) shape of the orbital b) angular momentum of the orbital electron = $\sqrt{l(l+1)} \frac{h}{2\pi}$ c) minor part of energy of orbital electron	$n$	Integral values 0, 1, 2, 3, ..., $(n - 1)$	$l = 0 \Rightarrow s$ $l = 1 \Rightarrow p$ $l = 2 \Rightarrow d$ $l = 3 \Rightarrow f$ $l = 4 \Rightarrow g$ etc.	A shell contains $(2l + 1)$ degenerate orbitals.
Magnetic	$m_l$	Orbital	a) orientation of	$2l + 1$	Integral values $-l, -l+1, \dots, l-1, l$	For $p$ subshell	An orbital can contain

			orbital  b) one component of the magnetic moment of orbital electron. (about arbitrary axis z) $\mu_z = m_l \text{ BM}$		$-(l - 1), -(l - 2), \dots, 0, \dots, +(l - 2), +(l - 1), +l$	$p_x, p_y, p_z$ . For $d$ subshell $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$	at the most two electrons.
Spin	$m_s$	electron	a) orientation (clockwise or anti clockwise) of spin of electron  b) one component of magnetic moment due to electron spin (about arbitrary axis z) $\mu = m_s \text{ BM}$	2	$+\frac{1}{2}$ and $-\frac{1}{2}$	$\uparrow$ or $\downarrow$	Magnitude of 'spin only' magnetic moment for atom with $n$ unpaired electron = $\sqrt{n(n+2)} \text{ BM}$

### Subshell wise distribution of orbitals and electrons

Principal shell	1st	2nd	3rd	
$n =$	1	2	3	
$l =$	0	0 1	0 1 2	
$m_l =$	0	0 -1 0 +1	0 -1 0 +1 -2 -1 0 +1 +2	
Orbital destination	1s	2s 2p <sub>y</sub> 2p <sub>z</sub> 2p <sub>x</sub>	3s 3p <sub>y</sub> 3p <sub>z</sub> 3p <sub>x</sub> 3d <sub>xy</sub> 3d <sub>yz</sub> 3d <sub>z<sup>2</sup></sub> 3d <sub>xz</sub> 3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	
number of orbitals in subshell	1	1 3	1 3 5	
Total number of orbital = $n^2$	1	4	9	
Total number of electron = $2n^2$	2	8	18	



### Example

Given below are sets of the four quantum numbers for electrons in an atom. Some of them violate the rules for quantum numbers, identify them and explain why they are inconsistent. For the correct sets provide an *spdf* notation.

a)	$n = 2$	$l = 2$	$m_l = +1$	$m_s = +\frac{1}{2}$
b)	$n = 4$	$l = 3$	$m_l = -3$	$m_s = -\frac{1}{2}$
c)	$n = 3$	$l = 2$	$m_l = -1$	$m_s = +\frac{1}{2}$
d)	$n = 5$	$l = 0$	$m_l = 4$	$m_s = -\frac{1}{2}$
e)	$n = 6$	$l = 4$	$m_l = 0$	$m_s = +\frac{1}{2}$
f)	$n = 2$	$l = 1$	$m_l = 0$	$m_s = 1$

a) Incorrect. Maximum value of  $l$  is  $(n - 1)$ .

b) Correct.  $4f$

c) Correct.  $3d$

d) Incorrect. The value of  $m_l$  has to be an integer between  $-l$  and  $+l$  or Zero

e) Correct.  $6g$

f) Incorrect. The value of  $m_s$  can be only  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .

### The Consequences of the Spin of an Electron - Pauli's Exclusion Principle

Elementary particles with non integral values of spin  $s$  are called **Fermions**. Electron and nucleus are examples of Fermions (as against photons which have an integral value of spin and are called Bosons). Fermions obey a principle called Pauli's exclusion principle. (Bosons do not obey this).

According to Pauli's exclusion principle, no two electrons in an atom can have the **same set of all four quantum numbers**. Since a set of the three quantum numbers  $n$ ,  $l$  and  $m_l$  specifies a particular orbital and since there can be only two

values of  $m_s$  i.e.  $\pm \frac{1}{2}$ . An **alternative** statement of Pauli's exclusion principle is simply: **"An orbital cannot have more than two electrons"**.

### The Consequences of the Charge and Spin of an Electron - The Hund's Rule of Maximum Spin Multiplicity

This rule applies to the electron occupancy of degenerate orbitals. It states that **"degenerate orbitals** of a subshell show the maximum multiplicity of spin."

It means that electrons occupy degenerate orbitals of a subshell to provide the maximum possible number of unpaired electrons corresponding to the given number

of electrons belonging to the subshell. In conjunction with Pauli's exclusion principle which forbids more than one electron in an orbital from having the same spin

( $+\frac{1}{2}$  or  $-\frac{1}{2}$ ), we can reframe Hund's rule in terms of two simple statements as follows:

1. Electrons occupy all available degenerate orbitals in a subshell singly before having to pair up.  
(The explanation is easy. All electrons are negatively charged. If two electrons occupy the same orbital, we should expect a decrease in stability due to **electron-electron repulsion**. If the energy required by the second electron to occupy a higher energy vacant orbital is greater than this repulsion energy, then it pairs up with the electron into the lower energy half-filled (single occupancy) orbital. But **if vacant degenerate orbitals are available, then the second electron would prefer to go to the vacant orbital**.)

2. Electrons occupying degenerate orbitals singly have the same value of  $m_s$  ( $+\frac{1}{2}$  or  $-\frac{1}{2}$ ).

The basis for this lies in the quantum mechanical principles. In other words, electrons belonging to different orbitals can exchange places if they have the same spin. This leads to an extra stabilisation. Also, the same spin orientation modifies many electron wave function and repulsion decreases.

## **Physical Meaning of the Wave Function $\psi$ Physical representations of the orbitals**

### **1. Wave description of an orbital**

The wave function  $\psi$  itself has no **physical meaning**. With the values of  $n$ ,  $l$  and  $m_l$  duly substituted, it represents an orbital. As a wave function it has different values of **amplitude** at different points in space around the nucleus of the atom. These values may be positive, zero or negative.

Imagining an orbital mathematically in terms of a wave function  $\psi$  has certain advantages as given below.

a) Since  $\psi$  contains all information about the motion of the electron, we can undertake mathematical operations on  $\psi$  to obtain values of physically significant quantities. For example, in the Schrodinger's wave equation, the energy operator  $H$  is used to extract the value of energy of an orbital.

b) We can mathematically combine different wave functions to develop the combination or mixing of orbitals using the principles of super-position of waves.

### **2. Probability density description of an orbital**

Another way of imagining an orbital is by analysing the properties of  $\psi^2$ , which has a physical meaning. It is a probability density function. The square of the amplitude of the wave function (i.e.  $\psi^2$ ) at different points in space around the nucleus are the values for the probability of finding an electron represented by the orbital, at those points. We can use this description to conceptualise the electron in an atom in two different ways:

a) Electron as a negatively charged cloud, with density of the charge varying from point to point.

b) Electron as a particle, the probability of finding the electron varying from point to point.

Whichever way we conceptualise, we can always visualise the shape and size of an orbital as the region within a boundary surface in space where the electron spends almost 90% of its time.

Such a concept of the orbital helps us visualise various aspects of bonding and shapes and sizes of atoms, ions and molecules.

### Analysis of the 1s Orbital of Hydrogen

We have seen earlier that the wave function  $\psi$  can be expressed as

$$\psi = \psi_{\text{radial}} \times \psi_{\text{angular}} = \psi(r) \times \psi(\theta, \phi)$$

$\psi(r)$  is the radial part of the orbital.

$\psi^2(r)$  gives the probability density due to the radial part for any given point at distance  $r$  from the nucleus.

$4\pi r^2 \psi^2(r)$  gives the [probability density](#) due to the radial part for all points at distance  $r$  from the nucleus.

### Size and shape of the 1s orbital

We can now interpret the significance of the figures below. The distance  $r_B$  corresponds to the radius where the probability of finding the 1s electron is the highest. The distance corresponds to the Bohr radius ( $.529 \text{ \AA}$ ) of the  $n = 1$  orbit for hydrogen.

The radius corresponding to the dotted line, however, implies the radius of a sphere within which the 1s electron spends most of its time (almost 90%). The ratio of the area under the curve inside the dotted box to the total area under the whole curve is the fraction of time the 1s electron spends within this sphere.

In the absence of any angular dependence, thus, this sphere represents both, the size and the shape of the 1s orbital.

The second figure below shows the plot of  $\psi^2$  [not  $4\pi r^2 \psi^2(r)$ ] versus  $r$  and what it means in terms of the shape and size of the 1s orbital.

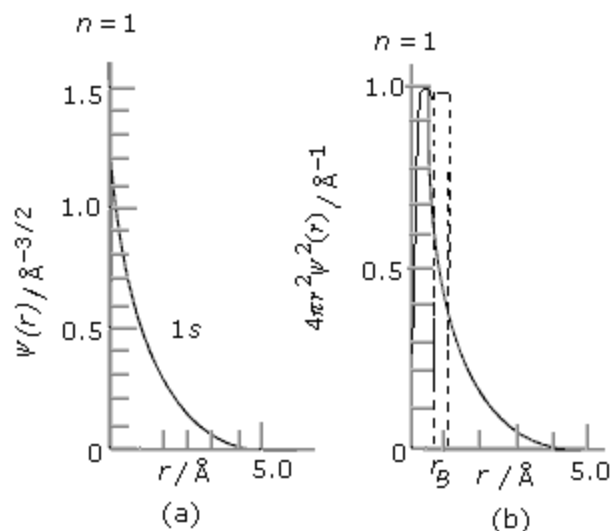


Figure: **The plots of radial wave function  $\psi(r)$ (fig. a) and the radial probability distribution function  $4\pi r^2 \psi^2(r)$  versus  $r$  (fig. b)**

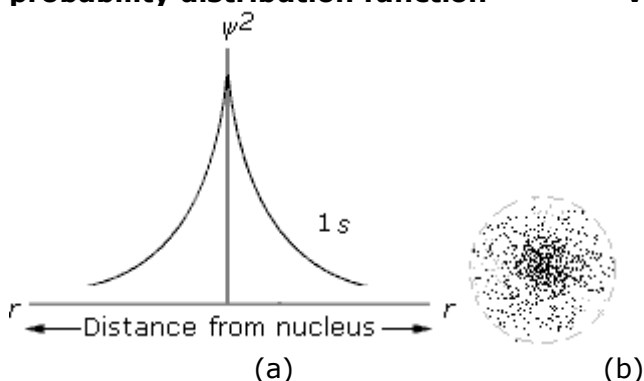


Figure: **(a) plot of  $\psi^2$  versus  $r$  and (b) cloud representation of the probability density distribution 1s electron**

Through the electron cloud depiction of an orbital expresses a lot about the variation of probability density, it is not convenient to use it all the time. Further, while explaining the role of orbitals in phenomena such as hybridisation, bonding, determination of shapes of molecules, etc. such a depiction would be useless. A convenient and useful way to depict the shapes of orbitals is to use the concept of boundary surfaces. (The surface confining the region within which the electron spends a large part of its time. The first figure given below gives such a description of the 1s orbital.)

The second figure is a plot of the boundary surface of the 'angular' part of the **wave function**  $\psi$  for the 1s orbital. Such a representation is useful where the 'sign' and shape of the wave function has to be shown. (Note that this does not depict electrical charge.)

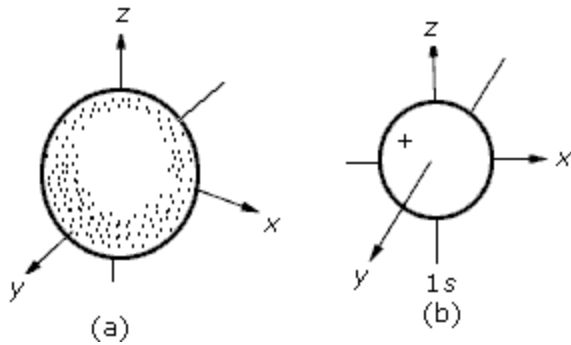


Figure: **(a) Boundary surface description (probability) of the 1s orbital**  
**(b) Boundary surface for the angular part of the wave function  $(\psi, \theta, \phi)$  of the 1s orbital**

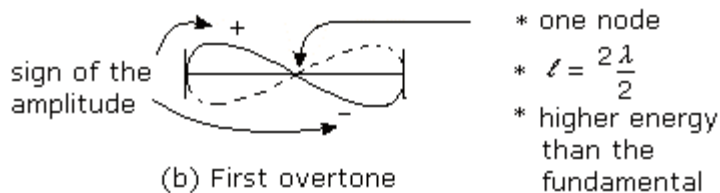
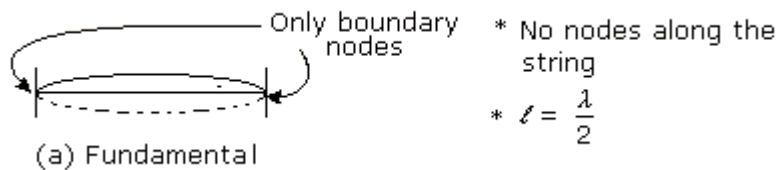
### Nodes - Regions of Zero Electron Density

#### Energy of orbitals in the presence of nodes

From our analogy of vibrating strings and stationary waves, we know that for the **fundamental** frequency we have nodes (amplitude is zero) only in the boundaries at the two ends. As we go to the higher **overtones**, the number of nodes along the string increases. For electron waves too, we have nodes, with higher number of nodes  $\Rightarrow$  (higher frequency  $\Rightarrow$  shorter wavelength  $\Rightarrow$  higher momentum)  $\Rightarrow$  higher energy.

We have also seen this before where the quantum number  $n$  is also the number of standing waves formed when we combine Bohr's model with the de Broglie's relation.

In terms of  $\psi$  and  $\psi^2$  a node would appear for values of  $r, \theta$  and  $\phi$ , where  $\psi = \psi^2 = 0$ .  
**Physically this would mean the surface where the probability of finding the orbital electron is zero.**



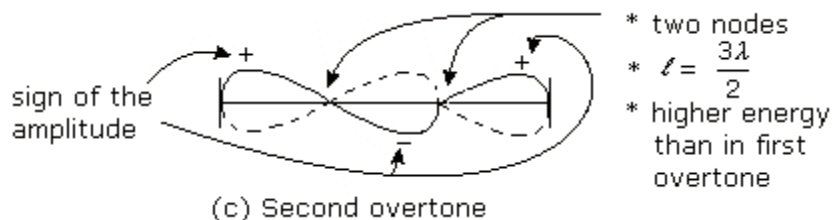


Figure: **Nodes, energies and standing waves on a vibrating string**

### The number and types of nodes

The nodes are surfaces which are the loci of nodal points. The **number of nodes** in an orbital, within a finite distance from the nucleus, depends on its principal quantum number (i.e. its energy) and is **equal to  $(n - 1)$** . **If we also consider the node, which is common to all orbitals, at an infinite distance from the nucleus, the number would be  $n$ .**

There are **two** possible types of nodes as follows:

1. **Angular nodes:** Angular nodes are encountered if we go around the nucleus (i.e. vary  $\theta$  and  $\phi$ ) at a fixed distance (i.e. fixed  $r$ ) from the nucleus. This happens when  $\psi(\theta, \phi) = 0$ . The locus of angular nodes form a planar surface and are therefore also called **planar nodes**.

2. **Radial nodes:** Radial nodes are encountered when we move out radially along a straight line from the nucleus (i.e. vary  $r$ ) at a fixed angle (i.e. fixed  $\theta$  and  $\phi$ ). This happens when  $\psi(r) = 0$ . The locus of radial nodes form a spherical surface and hence are also called spherical nodes.

We thus have a node when **either**  $\psi_{\text{angular}}$  or  $\psi_{\text{radial}}$  becomes zero, since

$$\psi = \psi_{\text{radial}} \times \psi_{\text{angular}}$$

The angular part of the wave function or  $\psi(\theta, \phi)$  as we have already seen depends only on the value of  $l$  (and not on  $n$ ). The **number of angular nodes** is also always equal to the value of  $l$  independently of  $n$ .

### Example

Finding out the number of radial and angular nodes in an orbital.

### Solution

The total number of nodes we have =  $n-1$

The number of angular nodes =  $l$

Hence,

the total number of radial nodes = (total nodes - angular nodes) =  $n - l - 1$   
 (Here we have not considered the spherical radial node at an infinite distance from the nucleus)

### Example

Calculate the total number of nodes at finite distances from the nucleus for the 2s and 2p orbitals. Are they radial nodes or are they angular nodes?

### Solution

#### For the 2s orbital

$$n = 2 \Rightarrow \text{Total number of nodes} = (n - 1) = (2 - 1) = 1$$

$l = 0$  Number of angular nodes = zero.

Hence, **number of radial nodes** (or spherical nodes) is  $n - l - 1 = 1$

Therefore, the 2s orbital has **only one node which is a radial node**.

For the 2p orbital

$$n = 2 \Rightarrow \text{total nodes} = 2 - 1 = 1$$

$$l = 1 \Rightarrow \text{angular nodes} = 1$$

$$\text{Total radial nodes} = 1 - 1 = 0$$

The 2p orbital has **only one node which is an angular node**

### Assignment

Calculate the number of radial nodes and angular nodes in a 4d orbital.

Answer: angular nodes = 2  
 radial nodes = 1  
 total nodes = 3

### The Consequences of Nodes

The types and numbers of nodes in the orbitals of electrons in an atom affects its properties in more than one ways.

#### 1. Penetration of orbitals and nodes

If you compare the  $4\pi r^2 \psi^2(r)$  versus  $r$  plots for say the 3s and 3p you will find that because of the **extra** radial node in the 3s orbitals there is a higher probability density near the nucleus. Thus though both the 3s and 3p electrons can **penetrate** through the 1st and 2nd shell electrons, the 3s electrons penetrate closer to the nucleus.

This fact is primarily responsible for the 3s electrons to have a lower energy than the 3p electrons.

In **general** the penetration of orbitals help us to determine the **relative energies of subshells** in multielectron atoms. We have to be, however, careful not to forget other effects which depend on the atomic number of the atom. The nuclear charge and the presence of inner shell electrons also affect the relative energies of subshells of outer shells since they affect the nature of the radial distribution curves. We have seen this earlier, where the energy of 4s is less than that of 3d **only** for  $Z = 19$  and 20. For  $Z < 19$  and  $Z > 20$  we have  $4s > 3d$  in terms of energy.

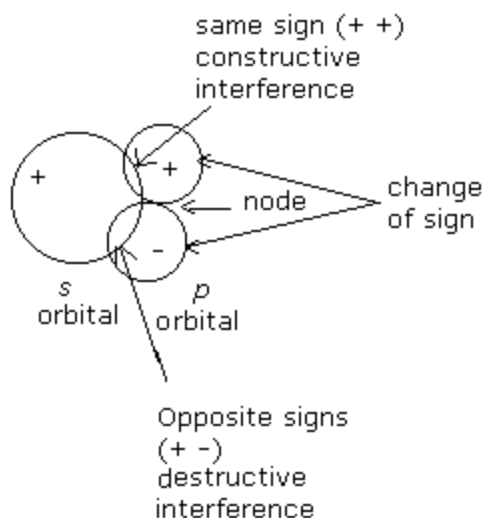
## 2. The number of angular nodes and shielding efficiency

Electrons in the other shell of the atom do not experience the full attraction due to the nucleus because of **shielding** by the inner shell electrons. **But all inner shell electrons do not shield with the same efficiency.** Electrons in orbitals with **angular nodes** at the nucleus naturally have **lower shielding efficiency**. The **larger the number** of angular nodes - the **lower is the shielding** efficiency. Since the number of angular nodes is given by the value of  $l$  **the order of shielding efficacy of different types** of electron orbitals is  $s > p > d > f$

## 3. Nodes and the combination of orbitals

Wherever there is a node, the wave function changes its sign corresponding to the **amplitude** of the orbital concerned. In our future chapter on bonding we will come across situations where we have to combine different orbitals. Such combinations are carried out by applying the principle of superposition of waves (orbitals are after all electron waves) where amplitudes of two waves add (constructive interference) to give higher amplitudes when they are of the same sign. If they are of opposite signs, they interfere destructively to give resultant lower amplitude.

For example, when orbitals of two atoms overlap to produce an orbital with a high amplitude **between the nuclei**, this implies a high electron density between the nuclei. Such a region of high electron density helps to hold together the two nuclei and thus results in the bonding of atoms. If the overlap of the two orbitals involve same 'signs' it would lead to a constructive interference and hence to bonding. If they involve opposite signs, they do not lead to bonding. This explains why there can be only one type of overlap geometry between an s orbital and a p orbital as shown in the figure below.



Net overlap is zero. Thus, no bonding can result from such a geometry of overlap.



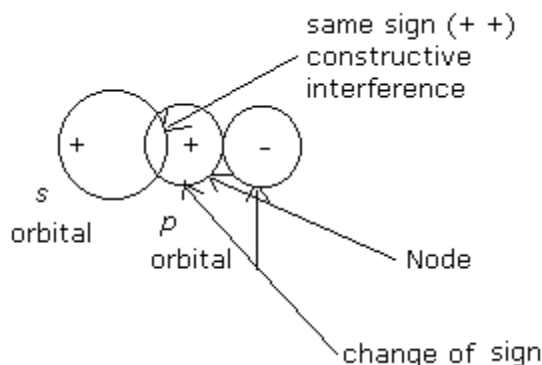


Figure: **Boundary surface diagrams of the angular part showing two possible geometry of  $sp$  overlap of  $s$  and  $p$  orbitals**

Overlap leads to increased value of amplitude between the nuclei. Such a geometry of overlap leads to bonding.

We will learn more about such combinations while studying molecular orbitals in the chapter on bonding.

Another type of **combination of orbitals of the same atom** are involved in what is called **hybridisation**. We can use boundary surface representations of the angular part of  $s$  and  $p$  orbitals (for example) to find out about the shapes of  $sp$  hybridised orbitals. This is shown in the figure below. This also involves the concept of nodes and the change of sign of the amplitude.

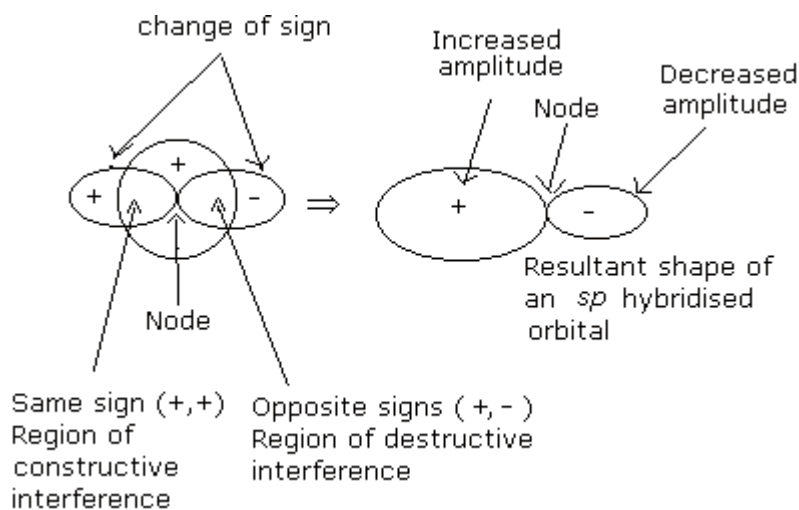


Figure: **Combination of  $s$  and  $p$  orbitals of the same atom using boundary surface diagrams of the angular part of the wave functions**