

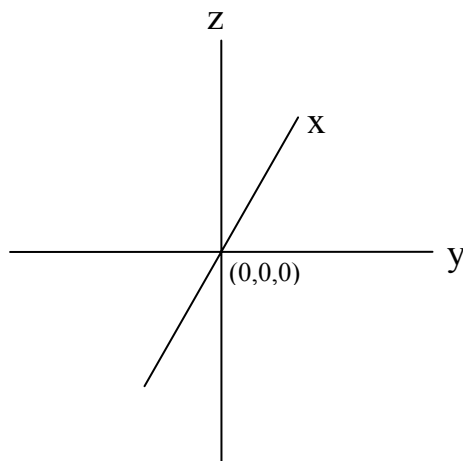
SESSION 6: Spherical Polar Coordinates, Radial & Angular Wavefunctions

Overview: In this session we will look at

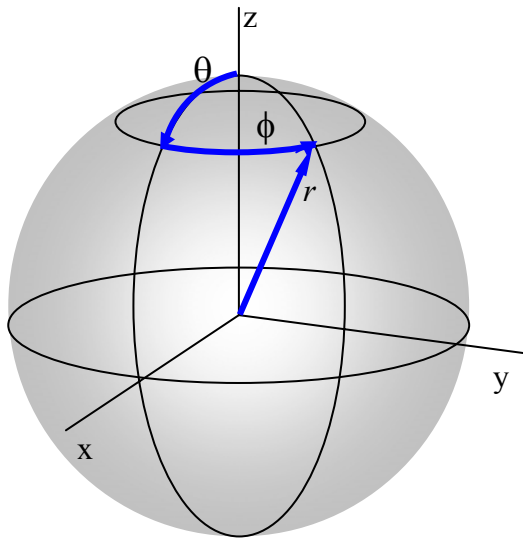
- Cartesian and Spherical Polar Coordinate systems
- the separation of the total wavefunction into radial and angular parts
- information on electron density distribution from hydrogenic radial wavefunctions
- information on orbital shape from hydrogenic angular wavefunctions

Spherical Polar Coordinates

The usual means of expressing the location of a point in three-dimensional space is by using the Cartesian (or x-y-z) Coordinate system. This consists of three mutually perpendicular axes, with the origin (where the three axes intersect) having the coordinates (0,0,0).



In expressing wavefunctions, it is more convenient to use a different type of coordinate system. This new system, Spherical Polar Coordinates, also has three coordinates, namely r , θ and ϕ , one displacement and two angles, as shown in the following diagram:



The position of a mass m moving at a distance (radius) r from the nucleus, is located by the three polar coordinates r , θ and ϕ .

To cover all space:

r is the distance from the nucleus, and has the range $0 \rightarrow \infty$,

θ is the angle that the radius vector makes with the vertical (or z-axis) and has the range $0 \rightarrow \pi$, and

ϕ is the horizontal angle that the radius vector makes with the xz-plane, and has the range $0 \rightarrow 2\pi$.

When a wavefunction ψ , is specified using the spherical polar coordinates, it can be separated into two parts: a radial part R , which is a function of r and an angular part Y , that is a function of θ and ϕ . Thus:

$$\psi(n, \ell, m_\ell) = R(r) \cdot Y(\theta, \phi)$$

sentence taken out The square of the radial wavefunction, $R(r)^2$, gives information about the variation of the electron density with distance, r , from the nucleus. The angular wavefunction, $Y(\theta, \phi)$, gives information about the three-dimensional region of space in which the electron can be found (i.e. the shape of the orbital).

Acceptable angular wavefunctions are specified by the two quantum numbers ℓ and m_ℓ , which come out of solutions of the SWE. Normalized angular wavefunctions are denoted as $Y_{\ell, m_\ell}(\theta, \phi)$ and are called the spherical harmonics.

In the following table there are some examples of Hydrogenic Radial wavefunctions and Spherical Harmonics.

Let us take a closer look at the R_{1S} function. This is a term involving e^{-r} , which means that the value of the function decreases as the value of the parameter r increases. This explains the shape (exponential decrease) of the graph of R_{1S} vs r . The spherical harmonic Y_{1S} does not depend on the value of the angles θ and ϕ , since they do not appear in the expression. This means that Y_{1S} is independent of θ and ϕ and therefore is of spherical symmetry. Hence the 1s orbital is spherical. This is the kind of information that can be obtained by just taking a quick look at $R(r)$ and $Y(\theta, \phi)$. The other spherical harmonics look more complex and one would have to do a three-dimensional plot while varying r , θ and ϕ to get the picture. (Please see your text books for actual diagrams).

Hydrogenic Radial Wavefunctions

<i>Orbital</i>	n	l	$R_{n,l}$
1S	1	0	$2\left(\frac{Z}{a_o}\right)^{3/2} e^{-\frac{1}{2}\rho}$
2S	2	0	$\frac{1}{2(2)^{1/2}}\left(\frac{Z}{a_o}\right)^{3/2}\left(2 - \frac{1}{2}\rho\right)e^{-\rho/4}$
2P	2	1	$\frac{1}{4(6)^{1/2}}\left(\frac{Z}{a_o}\right)^{3/2}\rho e^{-\rho/4}$

(N.B. $\rho = \frac{2Zr}{na_o}$)

Spherical Harmonics

ℓ	m_ℓ	Y_{ℓ, m_ℓ}
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$
1	± 1	$\mp \left(\frac{3}{8\pi}\right)^{1/2} (\sin \theta) e^{\pm i\phi}$

Exercise 7. Use the information in the table above to generate the total wavefunction of the hydrogen 1S state.

Solution

To generate the total wavefunction for the 1S state of hydrogen (ψ_{1S}) where $n = 1$ and $Z = 1$, the radial part is combined with the angular part:

$$\begin{aligned}\psi_{1S} = R_{1S} \cdot Y_{1S} &= 2 \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{1}{2}\rho} \cdot \left(\frac{1}{4\pi}\right)^{1/2} = 2 \left\{ \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{1}{4\pi}\right)^{1/2} \right\} e^{-\frac{1}{2}\rho} \\ &= \left(\frac{1}{\pi a_0^3}\right)^{1/2} \cdot e^{-\frac{r}{a_0}}\end{aligned}$$

SESSION 7: Angular Momentum, Space Quantization and Ionization Enthalpies

Overview: In this session we will look at

- the quantization of orbital angular momentum and its implications
- the importance of the magnetic quantum number in spatial orientation of orbitals within a sub-shell
- the effects of shielding and electron repulsion on the variation of Ionization Enthalpy across a period

Previously we had looked at the different quantum numbers that are used to classify the electrons in an atom. ℓ is known as the orbital angular momentum quantum number. In solving the SWE, ℓ and m_ℓ come out of the angular solutions of ψ and specify the angular momentum (A.M.) of the electron about the nucleus. The magnitude of the angular momentum is given by:

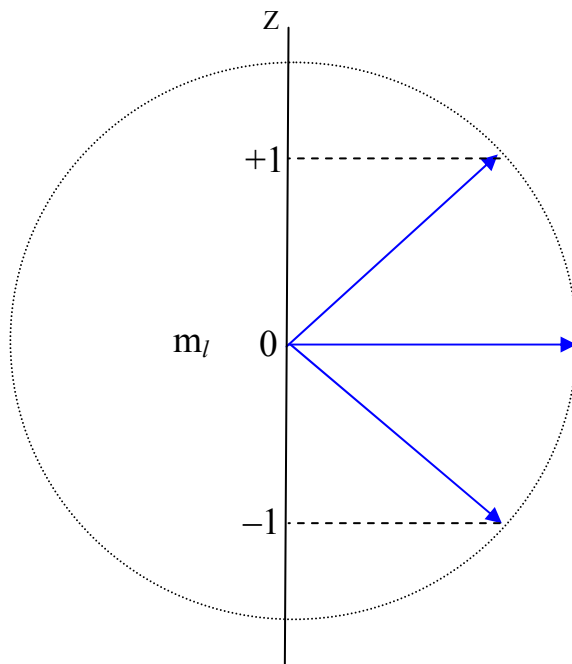
$$\text{A.M.} = \{\ell(\ell + 1)\}^{1/2} \cdot \hbar$$

It should be noted that the magnitude of the angular momentum depends only on the value of ℓ . The magnitude of the A.M. of an electron in the s , p and d orbitals would therefore be 0 , $\sqrt{2} \hbar$ and $\sqrt{6} \hbar$ respectively.

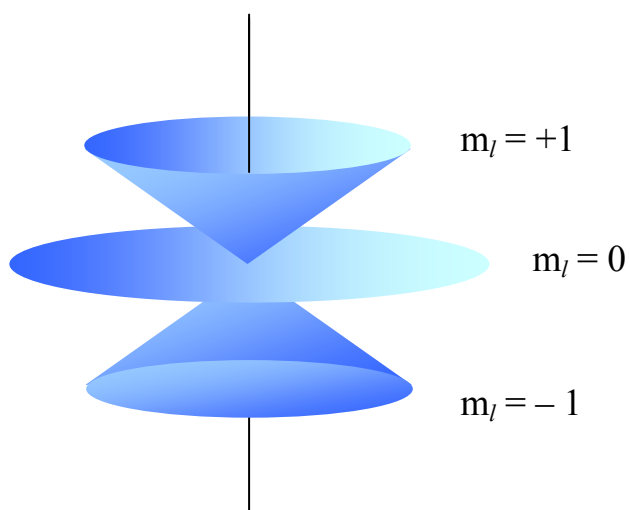
The A.M. is a vector quantity, meaning that it has both magnitude and direction. The A.M. vector is not allowed to have just any arbitrary orientation. Quantum Mechanics states that:

*A rotating body may not take up any arbitrary orientation with respect to some specified axis, which is defined by the direction of an externally applied magnetic or electric field. This is called **space quantization**.*

This means that the electron has to behave in a certain way so that the angular momentum vector, that it generates, does not take up just any arbitrary orientation. For a specified z-axis, the z-component of the A.M. vector, for an electron in an orbital with magnetic quantum number m_ℓ , has a value of $m_\ell \hbar$. For example, if an electron is in a p-orbital, ($\ell = 1$), the angular momentum vector is allowed to have only one of three possible orientations corresponding to z-components of $-1 \hbar$, $0 \hbar$ and $+1 \hbar$ (since the allowed value of $m_\ell = -1, 0, +1$). *This implication is that the orientation of a rotating body is quantized. See diagram:*



The arrows in the diagram indicate the three possible orientations of the angular momentum vector with respect to the z -axis. The vector is also allowed to rotate freely about the z -axis, hence the path described by the two arrows ($m_l = +1, -1$) moving around the z -axis would be of a right-side-up and of an inverted cone, respectively, and the path of the third arrow ($m_l = 0$) would prescribe a horizontal circle (see diagram):

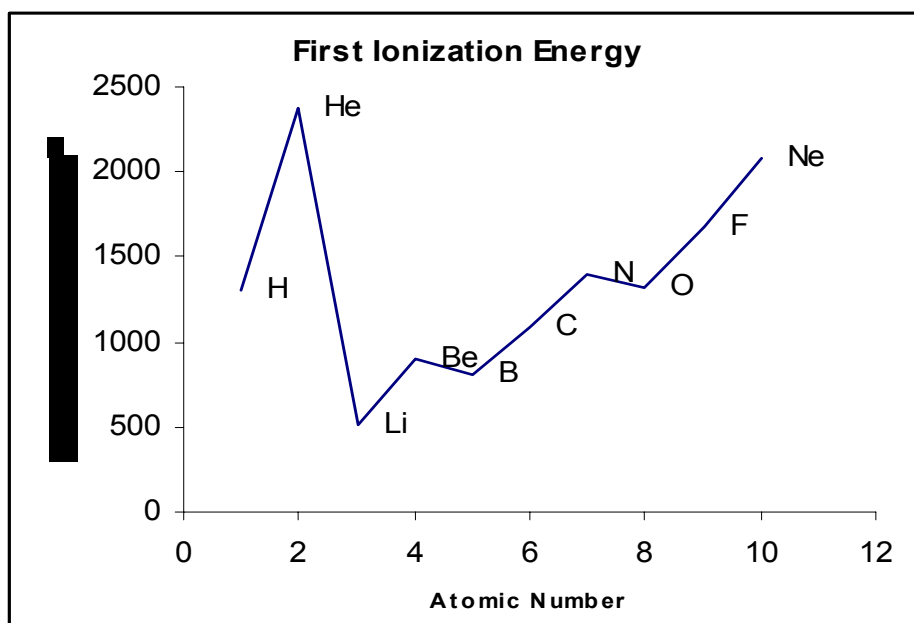


Ionization Enthalpies

The First Ionization enthalpy (ΔH_{ion}) of an atom (element) is defined as the energy that must be supplied to the atom in order to excite the most weakly held electron out of reach of the nucleus.



The trend for the values of ionization energy across a period (from left to right) is for there to be a general increase. However, there are some anomalies along the period which can be explained by the shielding (screening) effect of electrons in inner orbitals and the repulsive energy of electrons in the same orbital. Observe the figure below:



Note that for the period Li – Ne, there is almost a straight line increase for the value of ionization energy. There is, however, a dip at Boron and at Oxygen.

At Lithium, the value is low because the 1S electron density (due to the two 1S electrons) is shielding the outer 2S electron from the full effects of the Li nucleus. This 2s electron feels a reduced attraction from the nucleus because of the shielding and so the electron in the 2S orbital can be removed without much difficulty.

At Beryllium, the nuclear charge has increased by +1 but the electron is being placed into the same 2S orbital. Electrons in the same orbital do not effectively

shield each other from the nucleus. This additional 2S electron will therefore feel an increased attraction from the nucleus and so will be more difficult to remove, hence a higher value of the ionization energy.

At Boron, a slight decrease is observed. This decrease is due to effective shielding of the outer 2P electron from the nucleus by the inner core of 2S electrons. An almost linear increase is observed through to Carbon and Nitrogen as electrons are added to separate p-orbitals as the nuclear charge is increased. The electrons in the p-orbitals do not screen each other and therefore an increase is seen here.

At Oxygen there is a decrease. The fourth p-electron has to be placed into an orbital that is already occupied by a single electron. This electron will experience electron-electron repulsion in the orbital, and this repulsion will make it easier to remove one of these electrons, hence the decrease. An increase is observed to Fluorine and Neon as electron are added to the other p-orbitals.

Summary

You have covered new information about the hydrogen atom (and some of the higher atoms), and in particular, about the behaviour of the electron in the different orbitals on the atom. You now have a more modern view of the atom, and the different theories that are used to assist in explaining its observed properties. The material covered here is very important and will form the foundation for building the other Units. This should also serve as a guide but should not deter you from reading around the topics which are covered within the Unit, as reading will strengthen your knowledge base.

It is desirable that you make full use of the text books that are available, and revise the required material before the tutorial sessions, so that you will be better able to interact with the tutor. If you do this you will find that the tutorials are more beneficial.