orbit) and 2/1 (elliptical orbit). For the principal quantum number $n = 3$, n/k may have values 3/3 (circular), 3/2 (ellipse) and 3/1 (narrower ellipse).

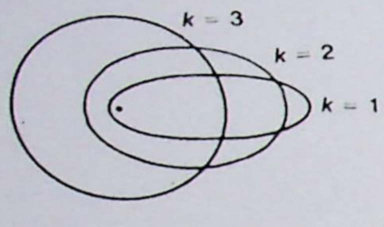

Figure 1.5 Bohr–Sommerfield orbits when $n = 3$.

The presence of these extra orbits, which have slightly different energies from each other, accounts for the extra lines in the spectrum revealed under high resolution. The original quantum number k has now been replaced by a new quantum number l, where $l = k - 1$. Thus for

$n = 1 \quad l = 0$

$n = 2 \quad l = 0$ or 1

$n = 3 \quad l = 0$ or 1 or 2

$n = 4 \quad l = 0$ or 1 or 2 or 3

This explained why some of the spectral lines are split into two, three, four or more lines. In addition some spectral lines are split still further into two lines (a doublet). This is explained by assuming that an electron spins on its axis in either a clockwise or an anticlockwise direction. Energy is quantized, and the value of the spin angular momentum was first considered to be $m_s \cdot h/2\pi$, where m_s is the spin quantum number with values of $\pm\frac{1}{2}$. (Quantum mechanics has since shown the exact expression to be $\sqrt{s(s+1)} \cdot h/2\pi$, where s is either the spin quantum number or the resultant of several spins.)

Zeeman showed that if atoms were placed in a strong magnetic field additional lines appeared on the spectrum. This is because elliptical orbits can only take up certain orientations with respect to the external field, rather than precessing freely. Each of these orientations is associated with a fourth quantum number m which can have values of l, $(l - 1), \ldots 0 \ldots (-l + 1), -l$.

Thus a single line in the normal spectrum will appear as $(2l + 1)$ lines if a magnetic field is applied.

Thus in order to explain the spectrum of the hydrogen atom, four quantum numbers are needed, as shown in Table 1.2. The spectra of other atoms may be explained in a similar manner.

THE DUAL NATURE OF ELECTRONS – PARTICLES OR WAVES

The planetary theory of atomic structure put forward by Rutherford and Bohr describes the atom as a central nucleus surrounded by electrons in

Table 1.2 The four main quantum numbers

	Symbol	Values
Principal quantum number	n	1, 2, 3 . . .
Azimuthal or subsidiary quantum number	l	0, 1, . . . $(n - 1)$
Magnetic quantum number*	m	$-l, \ldots 0, \ldots +l$
Spin quantum number	m_s	$\pm\frac{1}{2}$

certain orbits. The electron is thus considered as a particle. In the 1920s it was shown that moving particles such as electrons behaved in some ways as waves. This is an important concept in explaining the electronic structure of atoms.

For some time light has been considered as either particles or waves. Certain materials such as potassium emit electrons when irradiated with visible light, or in some cases with ultraviolet light. This is called the photoelectric effect. It is explained by light travelling as particles called photons. If a photon collides with an electron, it can transfer its energy to the electron. If the energy of the photon is sufficiently large it can remove the electron from the surface of the metal. However, the phenomena of diffraction and interference of light can only be explained by assuming that light behaves as waves. In 1924, de Brogie postulated that the same dual character existed with electrons – sometimes they are considered as particles, and at other times it is more convenient to consider them as waves. Experimental evidence for the wave nature of electrons was obtained when diffraction rings were observed photographically when a stream of electrons was passed through a thin metal foil. Electron diffraction has now become a useful tool in determining molecular structure, particularly of gases. Wave mechanics is a means of studying the build-up of electron shells in atoms, and the shape of orbitals occupied by the electrons.

THE HEISENBERG UNCERTAINTY PRINCIPLE

Calculations on the Bohr model of an atom require precise information about the position of an electron and its velocity. It is difficult to measure both quantities accurately at the same time. An electron is too small to see and may only be observed if perturbed. For example, we could hit the electron with another particle such as a photon or an electron, or we could apply an electric or magnetic force to the electron. This will inevitably change the position of the electron, or its velocity and direction. Heisenberg stated that the more precisely we can define the position of an electron, the less certainly we are able to define its velocity, and vice versa. If Δx is the uncertainty in defining the position and Δv the uncertainty in the velocity, the uncertainty principle may be expressed mathematically as:

$$\Delta x \,.\, \Delta v \geqslant \frac{h}{4\pi}$$

where h = Planck's constant = 6.6262×10^{-34} J s. This implies that it is impossible to know both the position and the velocity exactly.

The concept of an electron following a definite orbit, where its position and velocity are known exactly, must therefore be replaced by the probability of finding an electron in a particular position, or in a particular volume of space. The Schrödinger wave equation provides a satisfactory description of an atom in these terms. Solutions to the wave equation are called wave functions and given the symbol ψ. The probability of finding an electron at a point in space whose coordinates are x, y and z is $\psi^2(x, y, z)$.

THE SCHRÖDINGER WAVE EQUATION

For a standing wave (such as a vibrating string) of wavelength λ, whose amplitude at any point along x may be described by a function $f(x)$, it can be shown that:

$$\frac{d^2f(x)}{dx^2} = -\frac{4\pi^2}{\lambda_2} f(x)$$

If an electron is considered as a wave which moves in only one dimension then:

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi$$

An electron may move in three directions x, y and z so this becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \psi$$

Using the symbol ∇ instead of the three partial differentials, this is shortened to

$$\nabla^2\psi = -\frac{4\pi^2}{\lambda^2} \psi$$

The de Broglie relationship states that

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

(where h is Planck's constant, m is the mass of an electron and v its velocity); hence:

$$\nabla^2\psi = -\frac{4\pi^2 m^2 v^2}{h^2} \psi$$

or

$$\nabla^2\psi + \frac{4\pi^2 m^2 v^2}{h^2} \psi = 0 \qquad (1.5)$$

However, the total energy of the system E is made up of the kinetic energy K plus the potential energy V

$$E = K + V$$

so

$$K = E - V$$

But the kinetic energy $= \frac{1}{2}mv^2$ so

$$\tfrac{1}{2}mv^2 = E - V$$

and

$$v^2 = \frac{2}{m}(E - V)$$

Substituting for v^2 in equation (1.5) gives the well-known form of the Schrödinger equation

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

Acceptable solutions to the wave equation, that is solutions which are physically possible, must have certain properties:

1. ψ must be continuous.
2. ψ must be finite.
3. ψ must be single valued.
4. The probability of finding the electron over all the space from plus infinity to minus infinity must be equal to one.

The probability of finding an electron at a point x, y, z is ψ^2, so

$$\int_{-\infty}^{+\infty} \psi^2\, dx\, dy\, dz = 1$$

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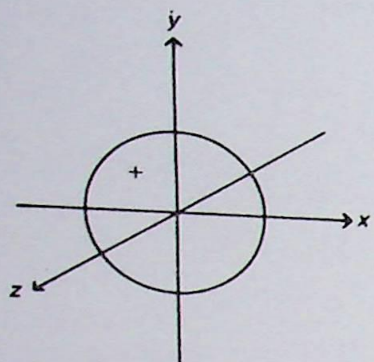
Several wave functions called ψ_1, ψ_2, ψ_3 . . . will satisfy these conditions to the wave equation, and each of these has a corresponding energy E_1, E_2, E_3. . . . Each of these wave functions ψ_1, ψ_2, etc. is called an *orbital*, by analogy with the *orbits* in the Bohr theory. In a hydrogen atom, the single electron normally occupies the lowest of the energy levels E_1. This is called the ground state. The corresponding wave function ψ_1 describes the orbital, that is the volume in space where there is a high probability of finding the electron.

For a given type of atom, there are a number of solutions to the wave equation which are acceptable, and each orbital may be described uniquely by a set of three quantum numbers, n, l and m. (These are the same quantum numbers – principal, subsidiary and magnetic – as were used in the Bohr theory).

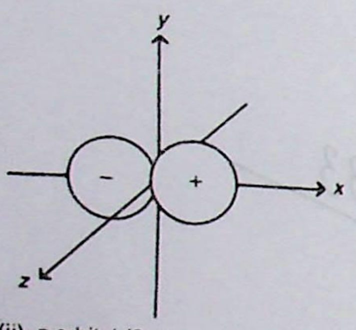
The subsidiary quantum number l describes the shape of the orbital occupied by the electron. l may have values 0, 1, 2 or 3. When $l = 0$, the orbital is spherical and is called an *s* orbital; when $l = 1$, the orbital is dumb-bell shaped and is called a *p* orbital; when $l = 2$, the orbital is double dumb-bell shaped and is called a *d* orbital; and when $l = 3$ a more complicated *f* orbital is formed (see Figure 1.6). The letters *s*, *p*, *d* and *f* come from the spectroscopic terms *s*harp, *p*rincipal, *d*iffuse and *f*undamental, which were used to describe the lines in the atomic spectra.

Examination of a list of all the allowed solutions to the wave equation shows that the orbitals fall into groups.

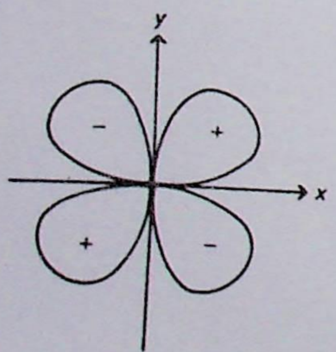
In the first group of solutions the value of the wave function ψ, and



(i) *s* orbital (1*s*)

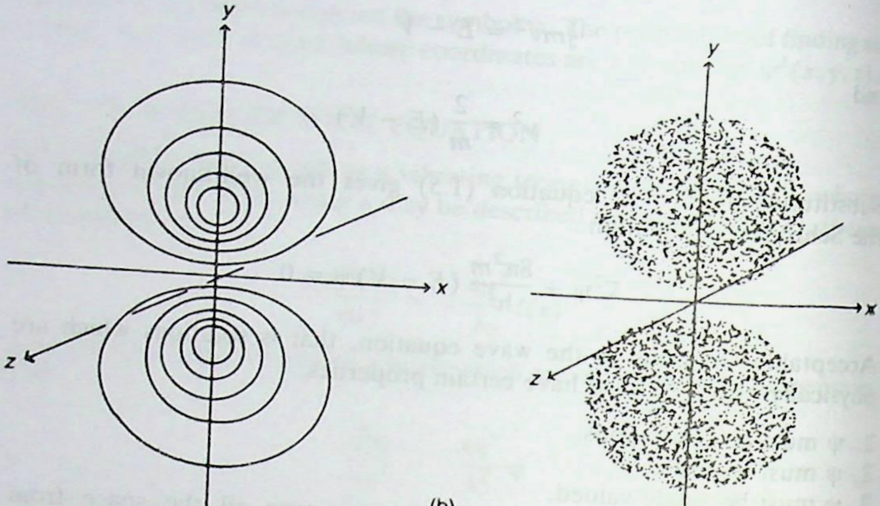


(ii) *p* orbital (2p_x)



(iii) *d* orbital (3d_{xy})

(a)



(b)

Figure 1.6 (a) Wave functions ψ for *s*, *p* and *d* atomic orbitals. (Note that the + and − signs refer to symmetry, not charge.) (b) Different ways of representing ψ^2 for a 2*p* orbital (as a contour diagram or as a 90% boundary surface).

hence the probability of finding the electron ψ^2, depends only on the distance *r* from the nucleus, and is the same in all directions.

$$\psi = f(r)$$

This leads to a spherical orbital, and occurs when the subsidiary quantum number *l* is zero. These are called *s* orbitals. When $l = 0$, the magnetic quantum number $m = 0$, so there is only one such orbital for each value of *n*.

In the second group of solutions to the wave equation, ψ depends both on the distance from the nucleus, and on the direction in space (*x*, *y* or *z*). Orbitals of this kind occur when the subsidiary quantum number $l = 1$. These are called *p* orbitals and there are three possible values of the magnetic quantum number ($m = -1, 0$ and $+1$). There are therefore three orbitals which are identical in energy, shape and size, which differ only in their direction in space. These three solutions to the wave equation may be written

$$\psi_x = f(r) \,.\, f(x)$$
$$\psi_y = f(r) \,.\, f(y)$$
$$\psi_z = f(r) \,.\, f(z)$$

Orbitals that are identical in energy are termed degenerate, and thus three degenerate *p* orbitals occur for each of the values of $n = 2, 3, 4 \ldots$.

The third group of solutions to the wave equation depend on the

Table 1.3 Atomic orbitals

Principal quantum number n	Subsidiary quantum number l	Magnetic quantum numbers m	Symbol
1	0	0	1*s* (one orbital)
2	0	0	2*s* (one orbital)
2	1	−1, 0, +1	2*p* (three orbitals)
3	0	0	3*s* (one orbital)
3	1	−1, 0, +1	3*p* (three orbitals)
3	2	−2, −1, 0, +1, +2	3*d* (five orbitals)
4	0	0	4*s* (one orbital)
4	1	−1, 0, +1	4*p* (three orbitals)
4	2	−2, −1, 0, +1, +2	4*d* (five orbitals)
4	3	−3, −2, −1, 0, +1, +2, −3	4*f* (seven orbitals)

distance from the nucleus r and also on two directions in space, for example

$$\psi = \mathrm{f}(r) \, . \, \mathrm{f}(x) \, . \, \mathrm{f}(y)$$

This group of orbitals has $l = 2$, and these are called *d* orbitals. There are five solutions corresponding to $m = -2, -1, 0, +1$ and $+2$, and these are all equal in energy. Thus five degenerate *d* orbitals occur for each of the values of $n = 3, 4, 5 \ldots$.

A further set of solutions occurs when $l = 3$, and these are called *f* orbitals. There are seven values of m: $-3, -2, -1, 0, +1, +2$ and $+3$, and seven degenerate *f* orbitals are formed when $n = 4, 5, 6 \ldots$.

RADIAL AND ANGULAR FUNCTIONS

The Schrödinger equation can be solved completely for the hydrogen atom, and for related ions which have only one electron such as He^+ and Li^{2+}. For other atoms only approximate solutions can be obtained. For most calculations, it is simpler to solve the wave equation if the cartesian coordinates x, y and z are converted into polar coordinates r, θ and ϕ. The coordinates of the point A measured from the origin are x, y, and z in cartesian coordinates, and r, θ and ϕ in polar coordinates. It can be seen from Figure 1.7 that the two sets of coordinates are related by the following expressions:

$$z = r \cos\theta$$

$$y = r \sin\theta \sin\phi$$

$$x = r \sin\theta \cos\phi$$

The Schrödinger equation is usually written:

$$\nabla^2\psi + \frac{8\pi^2 m}{\mathrm{h}^2}(E - V)\psi = 0$$

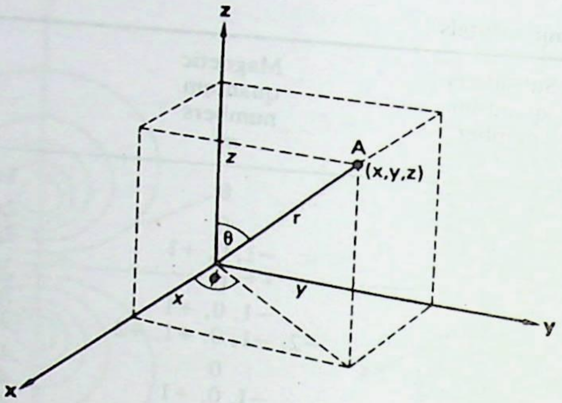


Figure 1.7 The relationship between cartesian and polar coordinates.

where

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$$

Changing to polar coordinates, $\nabla^2\psi$ becomes

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\phi^2} + \frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$

The solution of this is of the form

$$\psi = R(r)\,.\,\Theta(\theta)\,.\,\Phi(\phi) \tag{1.6}$$

$R(r)$ is a function that depends on the distance from the nucleus, which in turn depends on the quantum numbers n and l

$\Theta(\theta)$ is a function of θ, which depends on the quantum numbers l and m

$\Phi(\phi)$ is a function of ϕ, which depends only on the quantum number m

Equation (1.6) may be rewritten

$$\psi = R(r)_{nl}\cdot A_{ml}$$

This splits the wave function into two parts which can be solved separately:

1. $R(r)$ the radial function, which depends on the quantum numbers n and l.
2. A_{ml} the total angular wave function, which depends on the quantum numbers m and l.

The radial function R has no physical meaning, but R^2 gives the probability of finding the electron in a small volume dv near the point at which R is measured. For a given value of r the number of small volumes is $4\pi r^2$, so the probability of the electron being at a distance r from the nucleus is $4\pi r^2R^2$. This is called the radial distribution function. Graphs of the

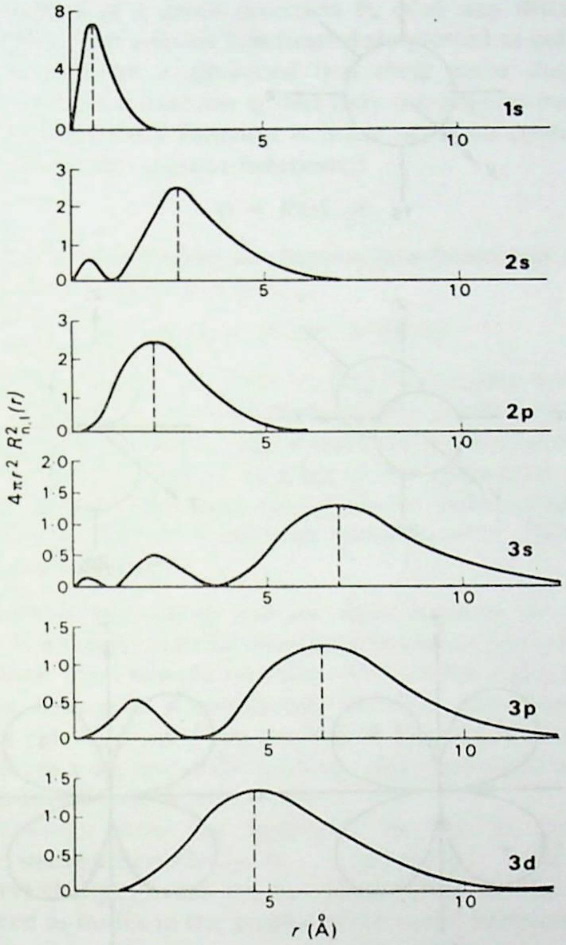


Figure 1.8 Radial distribution functions for various orbitals in the hydrogen atom.

radial distribution function for hydrogen plotted against r are shown in Figure 1.8.

These diagrams show that the probability is zero at the nucleus (as $r = 0$), and by examining the plots for $1s$, $2s$ and $3s$ that the most probable distance increases markedly as the principal quantum number increases. Furthermore, by comparing the plots for $2s$ and $2p$, or $3s$, $3p$ and $3d$ it can be seen that the most probable radius decreases slightly as the subsidiary quantum number increases. All the s orbitals except the first one ($1s$) have a shell-like structure, rather like an onion or a hailstone, consisting of concentric layers of electron density. Similarly, all but the first p orbitals ($2p$) and the first d orbitals ($3d$) have a shell structure.

The angular function A depends only on the direction, and is independent of the distance from the nucleus (r). Thus A^2 is the probability of