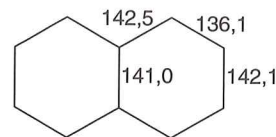


- (i) Find two resonance forms which have no charge separation which are also important in the description of the molecule.
- (ii) With the help of these resonance structures provide a rationale for the differences in bond lengths measured experimentally for this molecule.



- 1.6 (i) Give a Lewis structure for cyanamine H_2NCN which does not place formal charges on the atoms. What is the spatial geometry for this structure?
- (ii) Generate another Lewis structure by delocalizing the lone pair on the amino group. What is the geometry associated with this structure?
- (iii) Experimentally it is found that the amino group is slightly pyramidal and the inversion barrier very small. Explain this result.
- 1.7 Collect together all the molecules with the formula $\text{H}_4\text{C}_2\text{O}$ in which the octet rule is satisfied at each atom.
- (i) Give the Lewis structure and the geometries of the two molecules containing the $\text{C}-\text{C}-\text{O}$ unit.
- (ii) Do the same for a cyclic molecule.
- (iii) Give a structure for the molecule containing the $\text{C}-\text{O}-\text{C}$ unit. Show that one cannot be written without charge separation. Complete the description of the molecule knowing that the two CO bonds are equal.
- 1.8 (i) Show that there exists for the carbon monoxide molecule (CO); (a) A Lewis structure where the octet rule is obeyed at each atom but which contains a separation of charge, and (b) a Lewis structure which does not have a separation of charge but does not obey the octet rule.
- (ii) Consider the bond between M and CO in an MCO species where M is a Lewis acid, i.e., contains a vacant site (M for example could be a transition metal). Using the resonance forms found above write down the different bonding schemes for the $\text{M}-\text{CO}$ bond in the two following cases; (a) M does not contain a lone pair, (b) M has a lone pair able to be delocalized in addition to a vacant site.

2 Properties of atoms

A number of experimental observations have shown that the movement of microscopic particles cannot be correctly described within the framework of classical or Newtonian mechanics. Since the development of quantum mechanics in the 1920s, this tool has become indispensable in understanding phenomena at the microscopic scale, from those associated with the atomic nucleus to those associated with molecules. The cornerstones of this approach require a substantial body of mathematical background but we will limit ourselves to just enough needed for an elementary description of atomic structure. We shall unashamedly sidestep many proofs and concepts which are too complex for this book and refer the interested reader to more specialist books in the bibliography.

2.1. Elements of quantum mechanics

Just as in classical mechanics, quantum mechanics possesses its fundamental equation, the Schrödinger equation from which, *in principle*, most properties may be derived. We will illustrate some of its general characteristics by using the hydrogen atom as an example. This, with its single electron moving around a nucleus comprising a single proton, is surely the simplest system which one can study.

2.1.1. Schrödinger's equation

Within the language of quantum mechanics the electron is not described as a point mass associated with a trajectory in space, but rather as a wave represented by the mathematical function Ψ whose value depends upon the x, y, z coordinates of the space which it occupies. Ψ is usually referred to as the *wavefunction*. This very non-classical idea makes contact with the notion that atoms consist of a collection of electrons surrounding a nucleus in the following way. The square of this function $\Psi^2(x, y, z)$ represents the probability density of finding the electron at this point. (Sometimes Ψ will turn out to be a complex function containing real and imaginary parts. In this case we need to use $\Psi\Psi^*$ where Ψ^* is the complex conjugate of Ψ). In other words the probability dP of finding the electron in an infinitesimal volume $d\tau$ centered around the point given by the coordinates x_0, y_0, z_0 is given by the expression

$$dP = \Psi^2(x_0, y_0, z_0) d\tau \quad (1)$$

The probability of finding the electron somewhere in space has to be unity and so the function Ψ has to satisfy the relationship (2), where the integration takes place over all space. We say that Ψ is *normalized*.

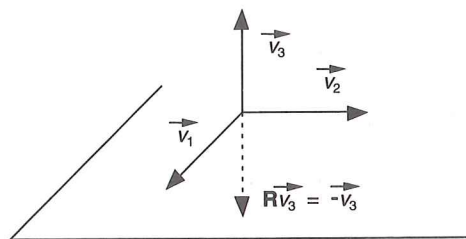
$$\int_{\text{space}} \Psi^2(x, y, z) d\tau = 1 \quad (2)$$

The function Ψ is determined by solution of the Schrödinger equation (3). Here \mathcal{H} is an operator, called the *Hamiltonian*

$$\mathcal{H}\Psi = E\Psi \quad (3)$$

which operates on the function Ψ and transforms it into another function. E is a scalar whose value is equal (in the cases we shall study) to the energy of the electron. Solution of equation (3) consists, therefore, of finding those functions, which after being transformed by the operator \mathcal{H} , may be written as a product of the original function multiplied by a scalar. Such solutions are called the *eigenfunctions* of the operator \mathcal{H} and the scalars with which they are associated, the corresponding *eigenvalues*. We finally note that from all the possible solutions we only retain those which make physical sense, namely those which are normalized as in equation (2). *Solution of the Schrödinger equation amounts to searching for the collection of pairs (Ψ_i, E_i) which satisfy the relationships (2) and (3).*

The principles behind the solution of the Schrödinger equation are difficult to illustrate in a simple fashion, but we can give a simple analog from the field of vector geometry. Let us consider an operator (\mathbf{R}) which behaves like a planar mirror (2.1) and search for the eigenfunctions (v) and eigenvalues (λ) obtained by solution



2-1

of the equation $\mathbf{R}v = \lambda v$. Obviously there are two types of functions. Those (for example v_1, v_2) which lie completely in this plane are transformed by the mirror plane operation into themselves and are therefore associated with an eigenvalue of $+1$ (i.e., $\mathbf{R}v_1 = (+1)v_1$). Those which lie perpendicular to the plane are transformed into vectors pointing in the opposite direction and therefore have an eigenvalue of -1 . (i.e., $\mathbf{R}v_3 = (-1)v_3$.) Three solutions of $\mathbf{R}v = \lambda v$ are therefore $(v_1, +1)$, $(v_2, +1)$ and $(v_3, -1)$.

Among the various solutions of the Schrödinger equation, that which corresponds to the lowest energy of the system (Ψ_1, E_1) has a special importance. This is the state

of the system, the *ground state*, which is the most stable. All the other solutions (Ψ_i, E_i) correspond to *excited states*.

2.1.2. Some important properties of the eigenfunctions

Some of the properties of the eigenfunctions of the Hamiltonian operator will be useful to us in what follows in subsequent chapters. To establish these we need first to state that the operator \mathcal{H} is linear, that is to say it satisfies the relationships

$$\mathcal{H}(\lambda\Psi) = \lambda\mathcal{H}(\Psi) \quad (4)$$

$$\mathcal{H}(\Psi_i + \Psi_j) = \mathcal{H}(\Psi_i) + \mathcal{H}(\Psi_j) \quad (5)$$

(a) The sign of ψ

Let us suppose that Ψ_i is a normalized solution of the Schrödinger equation associated with an eigenvalue E_i such that

$$\mathcal{H}\Psi_i = E_i\Psi_i \quad (6)$$

with

$$\int_{\text{space}} \Psi_i^2 d\tau = 1 \quad (7)$$

Let us consider for the moment the function $\lambda\Psi_i$, where λ is a scalar. Combining the relationships (4) and (6) we get

$$\mathcal{H}(\lambda\Psi_i) = \lambda\mathcal{H}(\Psi_i) = \lambda E_i\Psi_i = E_i(\lambda\Psi_i) \quad (8)$$

Thus the function $\lambda\Psi_i$ is also a solution of the Schrödinger equation and is associated with the same eigenvalue (E_i) as Ψ_i itself. This function has to be normalized such that

$$\int_{\text{space}} (\lambda\Psi_i)^2 d\tau = 1 \quad \text{i.e.} \quad \lambda^2 \int_{\text{space}} \Psi_i^2 d\tau = 1 \quad (9)$$

so that $\lambda^2 = 1$ or $\lambda = \pm 1$. There are therefore two solutions for λ , the first corresponding to the initial function Ψ_i ($\lambda = 1$) and the second to its negative, $-\Psi_i$ ($\lambda = -1$). Thus if Ψ_i is a normalized solution of the Schrödinger equation, so is its negative, $-\Psi_i$, and thus corresponds to the same electronic description as a result. *A physical sense may not then be attributed to the sign of the wavefunction. The function Ψ_i may be used as equally well as its negative $-\Psi_i$.*

(b) Overlap and the orthogonality of eigenfunctions

The overlap integral of two functions Ψ_i and Ψ_j is the integral over all space of their product. We use a useful notation, due to Dirac, to write this in a condensed

fashion

$$\langle \Psi_i | \Psi_j \rangle = \int_{\text{space}} \Psi_i \Psi_j \, d\tau \quad (10)$$

where $d\tau$ is the infinitesimal volume element. (Equation (10) describes the situation for real functions Ψ . For complex functions we need to use the expression $\int_{\text{space}} \Psi_i^* \Psi_j \, d\tau$ where Ψ_i^* is the complex conjugate of Ψ_i .) One of the properties of the set of eigenfunctions Ψ is that the overlap integral is zero (equation (11)) if they are different but of course equal to unity (equation (12)) if they are normalized according to equation (2).

$$\langle \Psi_i | \Psi_j \rangle = 0 \text{ if } i \neq j \quad (11)$$

$$\langle \Psi_i | \Psi_i \rangle = 1 \quad (12)$$

Thus the collection of eigenfunctions of the Hamiltonian operator form a set of orthonormal functions.

An analog might be the set of orthogonal vectors i, j, k normalized to be of unit length which are orthogonal and define the x, y and z directions of three-dimensional space.

(c) Degenerate solutions

Suppose for the present that we have two different solutions Ψ_i and Ψ_j which are associated with the same eigenvalue E , i.e.,

$$\mathcal{H} \Psi_i = E \Psi_i \quad (13)$$

$$\mathcal{H} \Psi_j = E \Psi_j \quad (14)$$

We say that these two solutions are degenerate. Applying the Hamiltonian operator to an arbitrary linear combination of them ($\lambda \Psi_i + \mu \Psi_j$) and using the relationships of equations (4), (5), (13) and (14), we get

$$\mathcal{H}(\lambda \Psi_i + \mu \Psi_j) = \lambda \mathcal{H}(\Psi_i) + \mu \mathcal{H}(\Psi_j) = \lambda E \Psi_i + \mu E \Psi_j = E(\lambda \Psi_i + \mu \Psi_j) \quad (15)$$

Thus all linear combinations of two degenerate eigenfunctions are themselves eigenfunctions of the Hamiltonian, associated with the same eigenvalue, E .

2.2. The hydrogen atom

2.2.1. Solutions of the Schrödinger equation

Solution of the Schrödinger equation for the case of the movement of a single electron under the influence of the nucleus leads to an infinite set of (Ψ_i, E_i) . The two particles,

nucleus and electron, interact via a Coulombic, electrostatic type of interaction and, if we were going to solve the equation algebraically, we would insert the kinetic and potential energy into the Hamiltonian to produce (as it turns out) a differential equation which is readily soluble.

(a) Allowed values of the energies (E_i) and atomic spectra

This book is not the place to detail the mathematical solution of the Schrödinger equation, but highlight the results. First, the eigenvalues of the Hamiltonian, E_i are all negative and second they are inversely proportional to n^2 , where n is a positive integer called the principal quantum number.

$$E_n = -Ry/n^2 \quad n = 1, 2, 3, \dots \quad (16)$$

Ry is a constant with units of energy and equal to 13.6 eV*. The allowed values of the energy are therefore

$$\begin{aligned} E_1 &= -Ry & (n=1) & \text{ground state} \\ E_2 &= -Ry/4 & (n=2) & \text{first excited state} \\ E_3 &= -Ry/9 & (n=3) & \text{second excited state} \\ & \text{etc.} \end{aligned}$$

We will always use the convention that the lowest energy state is the one with the most negative value of the energy. So the electron in the hydrogen atom may not have an arbitrary energy, but one of the possibilities given by equation (16). We say that the energy is quantized. It only depends upon the value of the principal quantum number, n .

Suppose that a hydrogen atom finds itself in an excited state ($n > 1$). The return of the electron to the electronic ground state with $n = 1$ is accompanied by the liberation of energy ΔE equal to the energy difference between the ground state and the excited state initially populated.

$$\Delta E = -Ry/n^2 - (-Ry/1^2) = Ry(1 - 1/n^2) \quad (17)$$

This change in energy is accomplished via the *emission* of a photon with an energy equal to ΔE . From the Planck-Einstein relationship the frequency (ν) of the emitted photon is given by

$$\Delta E = h\nu \quad (18)$$

* An electron volt (eV) is the energy acquired by an electron on moving through a potential difference of one volt. Although it is not an SI unit, it is frequently used to measure energies on the atomic scale. In numerical calculations its SI equivalent, $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ should be used (see exercise 2.1).

where h is Planck's constant ($h = 6.62 \times 10^{-34}$ J s). Thus the frequency of the photon emitted in the present case is given by

$$h\nu = Ry(1 - 1/n^2)$$

i.e.,

$$\nu = Ry/h(1 - 1/n^2) \quad (19)$$

When the excited state is sufficiently high in energy ($n > 2$) the electron doesn't necessarily have to return to the ground state ($n = 1$), but can instead move to another excited state (labelled by n') of lower energy than the initial one. This implies $n' < n$. In this case the frequency of the emitted photon is given by the relationship

$$\nu = Ry/n(1/n'^2 - 1/n^2) \quad (20)$$

As a general result of such processes one obtains for each value of n' a series of spectral lines which together constitute the emission spectrum of the atom. They may be grouped according to the value of n' and are traditionally named after the physicists who discovered them (Figure 2.1). The Lyman series is a special one in that it corresponds to the return of excited electrons to the ground state with $n' = 1$.

The inverse of emission is *absorption*. A hydrogen atom in its electronic ground state can absorb a photon, using its energy to move to an excited state. Such an absorption process can only occur if the photon energy corresponds exactly to the energy difference between the excited state and that of the ground state, namely

$$h\nu = Ry(1 - 1/n^2) \quad (21)$$

The larger the value of n and therefore the higher in energy the excited state, the higher the frequency of the photon needed for excitation. When $n \rightarrow \infty$ the energy of the excited state tends to zero, giving rise to a situation where the electron and nucleus are completely separated from each other. This corresponds to *ionization* of the hydrogen atom, $H \rightarrow H^+ + e^-$, and the energy involved, ΔE_∞ is simply given by

$$\Delta E_\infty = Ry = 13.6 \text{ eV} \quad (22)$$

Thus the quantity Ry is the energy needed to ionize the hydrogen atom in its electronic ground state (the ionization potential) and is found experimentally to be just this, 13.6 eV. It is the smallest amount of energy needed to detach an electron from the atom in its ground state. The energy needed to ionize the atom in an excited state can be obtained in the same way. In general the rules which define the allowed frequencies of light for photon absorption are just the same as the ones we have described above for photon emission.

(b) Nomenclature for the eigenfunctions, Ψ_i

The principal quantum number n is sufficient to characterize the allowed values of the energy, but the situation is more complex when it comes to a description of

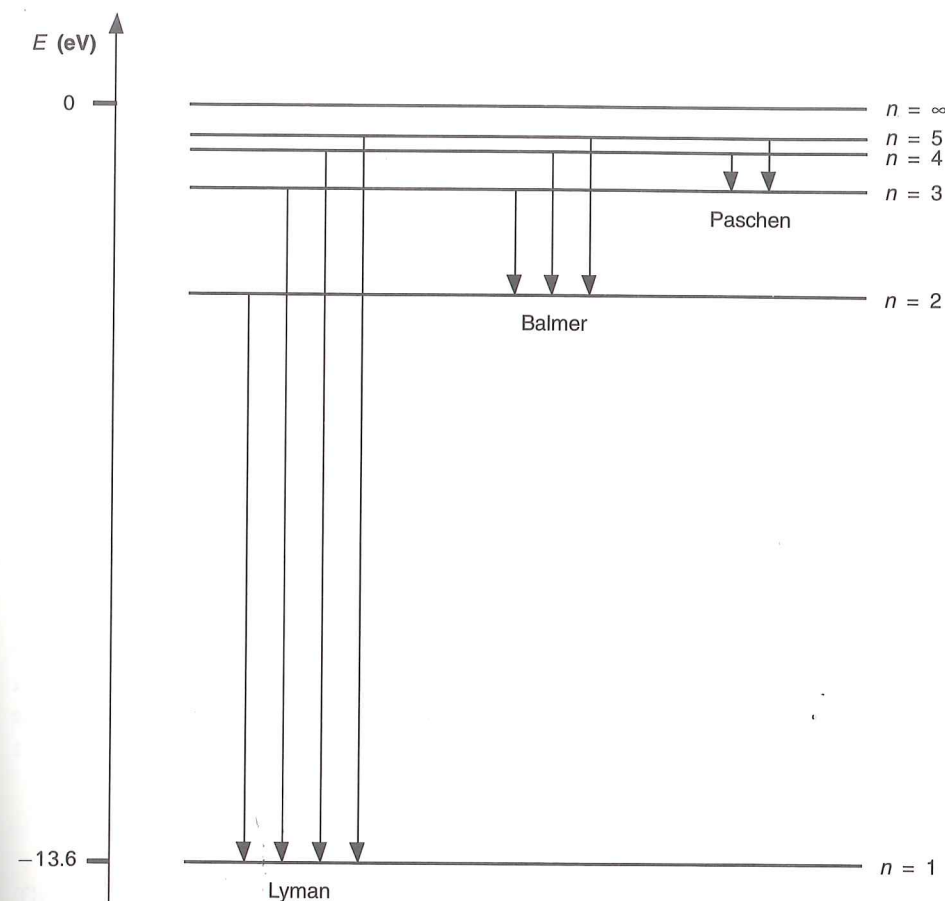


Figure 2.1. Transitions observed in the emission spectrum of atomic hydrogen.

the corresponding eigenfunctions. We need three quantum numbers to classify them.

- (i) The principal quantum number, n , which as we have seen is a positive integer ($n = 1, 2, 3, \dots$).
- (ii) A secondary quantum number, l often called the angular momentum, or azimuthal quantum number. It is an integer, positive or zero and is always less than n .

$$0 \leq l < n \quad (23)$$

- (iii) The magnetic quantum number, m . This is an integer, positive, negative or zero, lying between the values $\pm l$

$$-l \leq m \leq +l \quad (24)$$

Each wavefunction Ψ_i is characterized by a set of three quantum numbers n, l, m .

The simplest case is that for n equal to 1. Since the quantum number l has to be less than n , it must be equal to zero. As a consequence m is also equal to zero. There is then just a single collection of numbers ($n = 1, l = 0, m = 0$) which are possible and these describe a single wavefunction, or solution of the Schrödinger equation.

When n is equal to 2, l may take on the two values 0 and 1. As before if l is zero then m must be so too. If however l is equal to 1, there are three possibilities for m ; $-1, 0$ and $+1$. There are therefore four possible solutions (n, l, m) corresponding to the set of quantum numbers (2, 0, 0), (2, 1, -1), (2, 1, 0) and (2, 1, $+1$). These four functions are degenerate since they correspond to the same value of the principal quantum number, $n = 2$, with an energy of $E = -Ry/4$.

We can simply label these different functions by using a shorthand of the form nX_m where X is a letter used to represent a given value of l in the following way

l	0	1	2	3
X	s	p	d	f

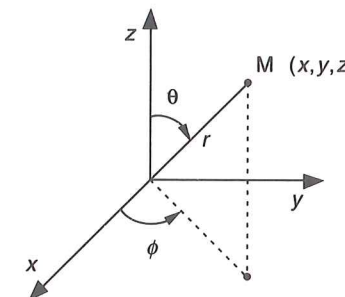
There is nothing magical about these labels. They are the first letters of some descriptive terms early spectroscopists used to characterize atomic spectra (namely sharp, principal, diffuse, and fundamental) and have been adopted for use in the present context. By convention when l is equal to zero (the ns functions) we don't need to specify the value of m , since it is always equal to zero. The names of the different solutions for the hydrogen atom for n up to 3 are given below.

$n = 1$	$l = 0$	$m = 0$	1s
$n = 2$	$l = 0$	$m = 0$	2s
	$l = 1$	$m = +1$	$2p_{+1}$
		$m = 0$	$2p_0$
$m = -1$	$2p_{-1}$		
$n = 3$	$l = 0$	$m = 0$	3s
	$l = 1$	$m = +1$	$3p_{+1}$
		$m = 0$	$3p_0$
		$m = -1$	$3p_{-1}$
	$l = 2$	$m = +2$	$3d_{+2}$
		$m = +1$	$3d_{+1}$
		$m = 0$	$3d_0$
$m = -1$		$3d_{-1}$	
$m = -2$	$3d_{-2}$		

There are a total of n^2 solutions with the same value of the principal quantum number n , and therefore with the same energy, $-Ry/n^2$.

2.2.2. Description of the eigenfunctions

The various eigenfunctions which describe these electronic situations depend upon the spatial coordinates i.e. $\Psi_{n,l,m}(x, y, z)$. Relying on the spherical symmetry of the hydrogen atom it is advantageous to express these functions in terms of the spherical coordinates, r, θ, ϕ shown in 2-2.



$$\begin{aligned} x &= r \sin \theta \cos \phi & r &\in [0, \infty[\\ y &= r \sin \theta \sin \phi & \theta &\in [0, \pi] \\ z &= r \cos \theta & \phi &\in [0, 2\pi] \end{aligned}$$

2-2

(a) Analytical form

Because of the form of the mathematics of the hydrogen atom problem it turns out that the wavefunctions may be written as a simple product of two functions, one radial in extent and the other containing all of the angular dependence.

$$\Psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi) \quad (25)$$

The first term, the radial one ($R_{n,l}(r)$) only dependent on r , contains the principal quantum number n and the angular momentum quantum number l . The second term $Y_{l,m}(\theta, \phi)$, the angular part, only depends on the variables θ, ϕ . Both terms are normalized so that the total wavefunction itself is normalized. The volume element $d\tau$ may be written in terms of spherical coordinates as $d\tau = r^2 \sin \theta dr d\theta d\phi$. Equations (26) and (27) show this process formally.

$$\int_0^\infty R_{n,l}^2(r) r^2 dr = 1 \quad (26)$$

$$\int_0^\pi \int_0^{2\pi} Y_{l,m}^2(\theta, \phi) \sin \theta d\theta d\phi = 1 \quad (27)$$

As we will see it will prove very useful to use a pictorial representation for the wavefunctions. However, since they in general depend upon the three variables r, θ , and ϕ , it is impossible to rigorously represent their shape in two dimensions. The most satisfactory way is to draw a contour map of the function by drawing lines of constant Ψ in a plane of interest.

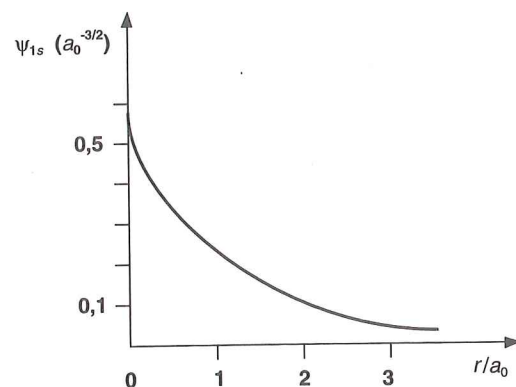
(b) The 1s function ($n = 1, l = 0, m = 0$)

The analytical expression for this function is

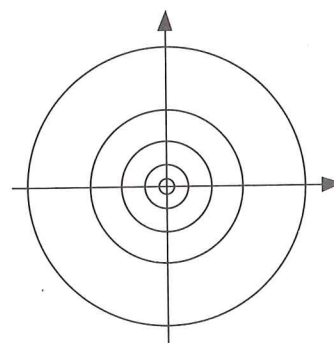
$$\Psi_{1s} = \left[\frac{2}{\sqrt{a_0^3}} \exp\left(-\frac{r}{a_0}\right) \right] \frac{1}{\sqrt{4\pi}} \quad (28)$$

The expression doesn't appear to contain the variables θ and ϕ . In fact the angular contribution is equal to $\sqrt{(1/4\pi)}$. The radial part varies via the term $\exp(-r/a_0)$ and the expression $2/a_0^{3/2}$ assures that this part of the wavefunction is normalized. a_0 is a universal constant of length, known as the *Bohr radius*, equal to 52.9 pm.

This wavefunction is said to be spherically symmetrical since its value at a point only depends on the distance of that point to the nucleus. It is thus easy to precisely describe the behavior of the 1s function using a plot of its dependence on r , the single variable on which it depends (2-3a). The amplitude of the wavefunction is largest at



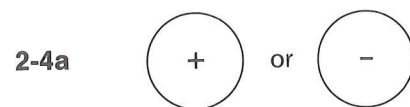
2-3a



2-3b

the nucleus and decreases exponentially via the term in $-r/a_0$. It is important to note that the wavefunction has the same sign (positive from equation (26)) for all values of r . The contour diagrams for Ψ_{1s} are easy to construct since the surfaces of constant Ψ are spheres (i.e. constant r) and their intersection with a plane containing the nucleus are circles (2-3b).

These two representations are not very convenient ones in a practical sense. A representation which captures the essence of the wavefunction in terms of spherical symmetry and a sign which doesn't change with r is shown in 2-4a. Ψ_{1s} is represented



by a circle centered at the nucleus and containing a positive sign to show that the wavefunction is positive everywhere. An equally valid possibility is one which contains a negative sign, indicative of a wavefunction which is negative everywhere.

Recall that from Section 2.1.2a this gives a completely equivalent description of the electron. The convention we will use in this book is shown in 2-4b. Hatching or shading is used to indicate where the wavefunction is positive, and the circle is left empty when it is negative.

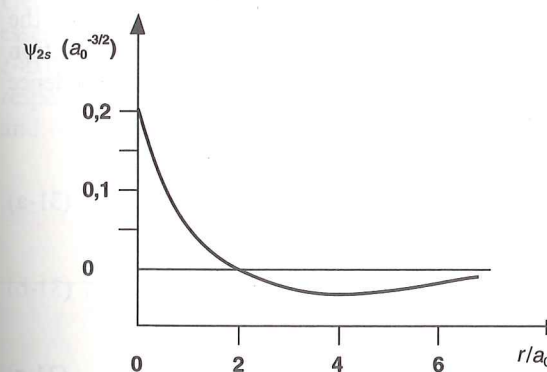
(c) The 2s function ($n = 2, l = 0, m = 0$)

The analytical expression for this function is

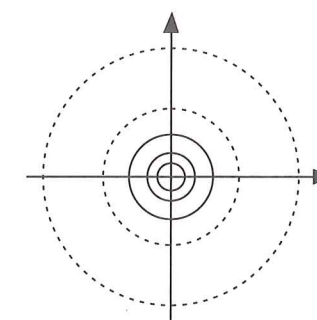
$$\Psi_{2s} = \left[\frac{1}{\sqrt{8a_0^3}} \left(2 - \frac{r}{a_0} \right) \exp\left(-\frac{r}{2a_0}\right) \right] \frac{1}{\sqrt{4\pi}} \quad (29)$$

Just as for the 1s orbital the angular part of the 2s function is also constant and equal to $\sqrt{(1/4\pi)}$. Thus the wavefunction depends only on r , and as a consequence is spherically symmetrical. Its amplitude tends to zero as r tends to infinity via the exponential term, just as for the 1s function. What is new here however is that the term $2 - r/a_0$ goes to zero when $r = 2a_0$, and the probability of finding the electron at this distance from the nucleus, described by the surface of a sphere of radius $2a_0$, is identically zero. We say that the 2s function possesses a *spherical node*. As defined in equation (29) it is positive when r is less than and negative when r is greater than $2a_0$. A surface where the wavefunction is zero everywhere on it is called a *nodal surface*. The wavefunction changes sign on moving from one side to the other.

It is again possible to describe the behavior of Ψ_{2s} as a function of r in a simple way since the wavefunction does not explicitly contain the variables θ, ϕ (2-5a). It

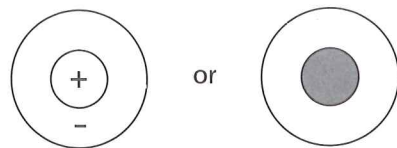


2-5a



2-5b

has a maximum at $r = 0$, changes sign at $r = 2a_0$, as indicated by the change from solid to dashed contour lines (2-5b) and then approaches zero as r becomes large. It is however more convenient to use the representation 2-6 which comprises a pair of concentric circles, containing plus and minus signs, or hatched and unhatched areas to describe the sign of the wavefunction as described earlier.



2-6

(d) The 2p functions ($n = 2, l = 1, m = +1, 0, -1$)

Although the function which describes $2p_0$ is real, it turns out that the functions describing $2p_{+1}$ and $2p_{-1}$ are complex conjugates of each other. In general the ϕ dependence of $Y_{l,m}(\theta, \phi)$ turns up in the form $e^{im\phi}$ leading to values of $e^{i\phi}$, 1 and $e^{-i\phi}$ for p_1 , p_0 and p_{-1} respectively. Since $2p_{+1}$ and $2p_{-1}$ are degenerate, judiciously chosen linear combinations of the two are also valid wavefunctions, as described in Section 2.1.2c. Thus we could write for one combination $(e^{i\phi} + e^{-i\phi})/2 = \cos \phi$ and $(e^{i\phi} - e^{-i\phi})/2i = \sin \phi$ for the other. This leads to two new, real, orthonormal functions. Along with the function for $2p_0$ we now have the three functions

$$\Psi_{2p_x} = \left[\frac{1}{2\sqrt{6}a_0^3} \frac{r}{a_0} \exp\left(-\frac{r}{2a_0}\right) \right] \sqrt{\frac{3}{4\pi}} \sin \theta \cos \phi \quad (30-a)$$

$$\Psi_{2p_y} = \left[\frac{1}{2\sqrt{6}a_0^3} \frac{r}{a_0} \exp\left(-\frac{r}{2a_0}\right) \right] \sqrt{\frac{3}{4\pi}} \sin \theta \sin \phi \quad (30-b)$$

$$\Psi_{2p_z} = \left[\frac{1}{2\sqrt{6}a_0^3} \frac{r}{a_0} \exp\left(-\frac{r}{2a_0}\right) \right] \sqrt{\frac{3}{4\pi}} \cos \theta \quad (30-c)$$

These functions take on a simple analytic form by transformation back to the cartesian coordinates of 2-2. The angular part of the three wavefunctions of equation (30) multiplied by r are just the cartesian functions x , y and z . Such a correspondence leads to the following description of the wavefunctions:

$$\Psi_{2p_x} = Nx \exp\left(-\frac{r}{2a_0}\right) \quad (31-a)$$

$$\Psi_{2p_y} = Ny \exp\left(-\frac{r}{2a_0}\right) \quad (31-b)$$

$$\Psi_{2p_z} = Nz \exp\left(-\frac{r}{2a_0}\right) \quad (31-c)$$

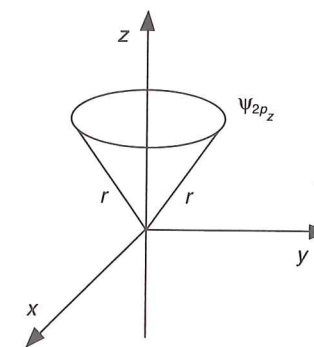
where

$$N = \frac{1}{2\sqrt{6}a_0^5} \sqrt{\frac{3}{4\pi}}$$

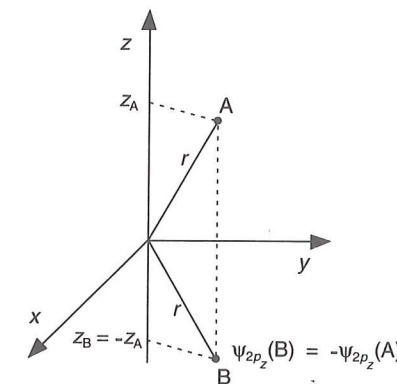
This new nomenclature emphasizes the similarities which exist between the three

functions. Each possesses the same local geometric properties, they just point along a different geometrical axis, x , y or z . It is sufficient to take a look at just one of them (p_z for example in equation (31-c)) to be able to understand them all.

For a given value of z the function $2p_z$ has the same value for all points located at the same distance, r , from the origin (2-7a). We say that this function is *cylindrically symmetrical* about the z -axis. On the other hand $2p_z$ is of opposite sign for two points related by the xy plane, namely $z_A = -z_B$ and $r_A = r_B$ (2-7b). This function is thus said to be *antisymmetric* with respect to the xy plane. Finally Ψ_{2p_z} is identically zero within the xy plane. This plane is consequently a nodal plane of p_z .

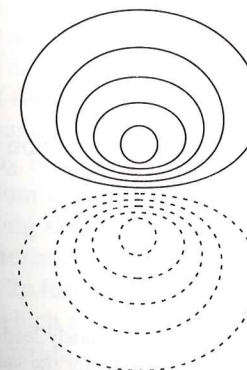


2-7a

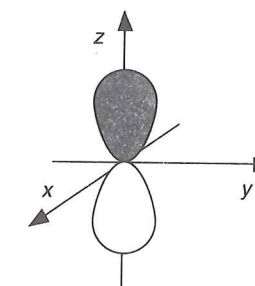


2-7b

A contour description of the $2p_z$ function is given in 2-8a. As before the change from solid to dashed contour lines indicates the change in sign of the wavefunction. Generally we prefer the representation shown in 2-8b, one which contains all of the essential information about the orbital, namely cylindrical symmetry around the z -axis, the presence of a nodal xy plane and a function which is antisymmetric with respect to it. We say that this function has two *lobes*, one positive (shaded in 2-8b) and one negative (unshaded).

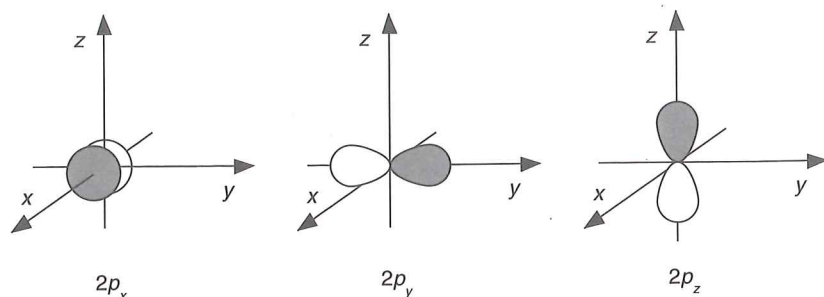


2-8a



2-8b

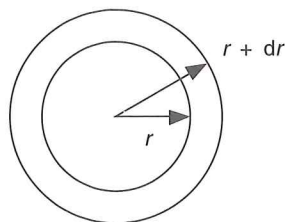
The representations we use for $2p_x$ and $2p_y$ can be obtained from 2-8b by changing the axis involved, and are shown in 2-9. Notice the special way we draw the $2p_x$ orbital to indicate that it is directed perpendicular to the page.



2-9

(e) Radial probability density

The probability of finding an electron somewhere is an important concept but one which is sometimes difficult to portray. Another way which is frequently used to characterize the wavefunction is the radial probability density which is the probability of finding the electron in the volume enclosed by the two spheres of radii r and $r + dr$ (2-10)*. We need to integrate the square of the function over the angular coordinates,



2-10

θ and ϕ :

$$\begin{aligned} dS &= \int_{\theta, \phi} R_{n,l}^2(r) Y_{l,m}^2(\theta, \phi) r^2 \sin \theta \, dr \, d\theta \, d\phi \\ &= R_{n,l}^2(r) r^2 \, dr \int_{\theta, \phi} Y_{l,m}^2(\theta, \phi) \sin \theta \, d\theta \, d\phi \end{aligned}$$

Taking into account the normalization of $Y_{l,m}(\theta, \phi)$ we obtain an expression of the form

$$dS = R_{n,l}^2(r) r^2 \, dr \quad (32)$$

* The form of the volume element as defined here is equal to $4\pi r^2 \, dr$, which immediately leads to the possibility of calculating dS via the relationship $dS = \Psi^2 4\pi r^2 \, dr$. However this is only the case for a spherically symmetrical function (i.e., s functions) whose probability density, Ψ^2 , is constant within the volume considered.

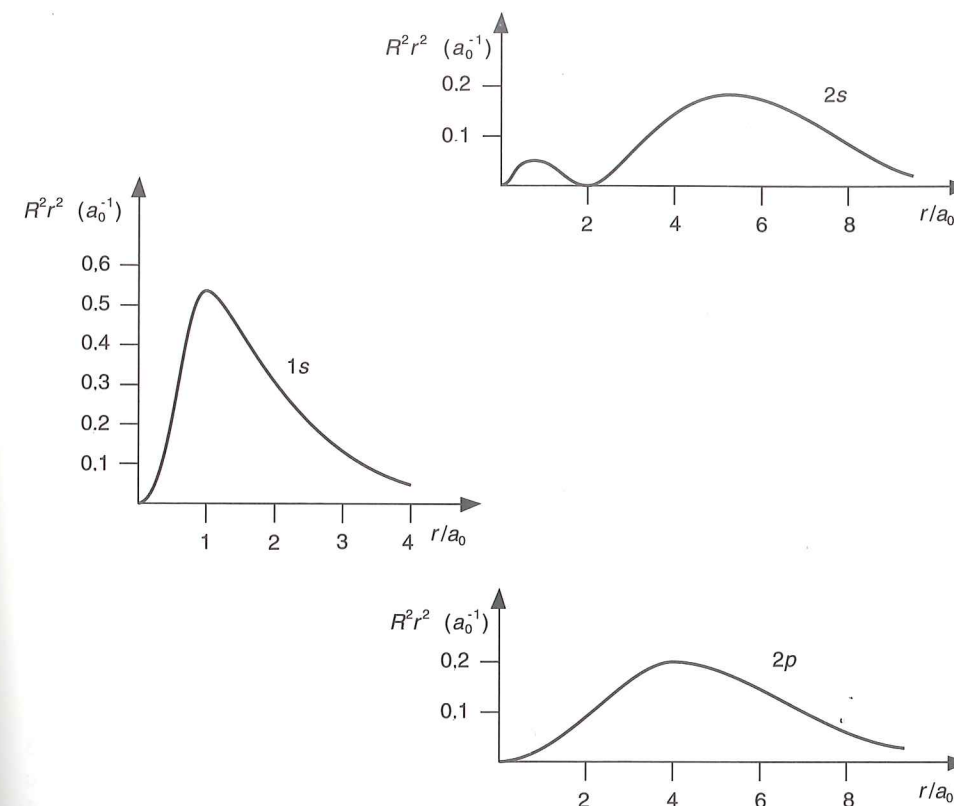


Figure 2.2. Radial probability densities for the functions ψ_{1s} , ψ_{2s} and ψ_{2p} .

The radial probability density is then written as

$$dS/dr = R_{n,l}^2(r) r^2 \quad (33)$$

This is shown for the $1s$, $2s$ and $2p$ functions in Figure 2.2. In each case the density is zero at the nucleus and tends to zero as r tends to infinity. It is also zero for the case of the $2s$ function at $r = 2a_0$ where there is a spherical node. Each curve has a maximum value, located at $r = a_0$ for the $1s$ function and clearly at larger r , at $5.24a_0$ and $4a_0$ for the $2s$ and $2p$ functions respectively. (The $2s$ function has a smaller maximum at $r = 0.76a_0$). These maxima correspond to the most probable distance of finding the electron from the nucleus. The value of r to which they correspond characterizes the spatial extent of the wavefunction, or its 'radius'. The radii of the $2s$ and $2p$ functions are clearly larger than that for the $1s$ function. This is a general result which may be extended to all the hydrogenic wavefunctions. The radius of the wavefunction (defined as that radius where there is a maximum in the radial probability density) increases with n (and is close to $n^2 a_0$) but depends only slightly on the value of l .

2.2.3. Electron spin

The characterization of the electron by a wavefunction of the type we have described uses just three quantum numbers, n , l and m . A complete description of the electron in the hydrogen atom however, requires consideration of a further concept. In addition to the classical ideas of mass and charge, the electron possesses a permanent magnetic moment, μ . It is difficult to visualize this purely quantum mechanical concept in classical terms, but it too is quantized. The magnetic moment may take one of two values and is generally expressed in units of Bohr magnetons (μ_B) viz:

$$\mu = -2m_s\mu_B$$

Here m_s is called the spin quantum number which may only adopt one of two values $\pm\frac{1}{2}$. By convention an electron with $m_s = \frac{1}{2}$ is called an electron with α spin and one with $m_s = -\frac{1}{2}$ is called an electron with β spin. *It is necessary to use these four quantum numbers, n , l , m and m_s to completely characterize the electron in the hydrogen atom.*

The experimental demonstration of the existence of a magnetic moment associated with the spin of the electron is due to two physicists, Stern and Gerlach. If one sends a beam of silver atoms (an element containing a single unpaired electron) through an inhomogeneous magnetic field it splits into two as indicated by the development of two separate regions of metallic silver deposited on a plate downstream of the magnet. The existence of just two areas of metallic silver show that the magnetic moment can take just two values. The atoms with $m_s = \frac{1}{2}$ are deflected one way and those with $m_s = -\frac{1}{2}$ the other.

2.2.4. Hydrogen-like atoms

An exactly analogous treatment to the one we have just given for hydrogen is applicable to all hydrogen-like atoms, namely those that possess a single electron moving around a nucleus of charge $+Ze$. These are the ions He^+ ($Z = 2$), Li^{2+} ($Z = 3$) and Be^{3+} ($Z = 4$) etc. The results pertaining to these situations are qualitatively identical to those found for hydrogen itself in terms of the form of the wavefunctions Ψ_{1s} , Ψ_{2s} , Ψ_{2p} etc. Again the energy only depends on the principal quantum number, n . There are however several quantitative differences which appear.

- (i) The eigenvalues are of the form $E_n = -RyZ^2/n^2$ leading to the important result that *the energy of the orbital is lowered as the nuclear charge increases.*

Thus whereas the energy of the $1s$ orbital is $-13.6 \text{ eV} (-Ry)$ in hydrogen, it is $-54.4 \text{ eV} (-4Ry)$ in the helium cation, He^+ . This lowering of the energy arises from the stronger electrostatic interaction between electron and nucleus as the nuclear charge increases.

- (ii) The analytical expression for the eigenfunctions may be generated from those obtained for hydrogen by replacing a_0 by a_0/Z in the relevant equations. For

example the expression for the $2s$ function is

$$\Psi_{2s} = \left[\sqrt{\frac{Z^3}{8a_0^3}} \left(2 - \frac{Zr}{a_0} \right) \exp\left(-\frac{Zr}{2a_0}\right) \right] \frac{1}{\sqrt{4\pi}} \quad (34)$$

This last point is important for it shows that the wavefunctions in the hydrogen-like atoms are more contracted, i.e., of smaller spatial extent than in hydrogen itself. So, whereas the radial maximum in the radial probability function for the $2s$ orbital is about $5a_0$ (265 pm) in hydrogen it is about $5(a_0/Z) = 2.5a_0$ (132 pm) in He^+ .

2.3. Many-electron atoms

In the case of hydrogen and hydrogen-like atoms an analytic solution of the Schrödinger wave equation is possible. The single interaction between electron and nucleus is simple to treat but the quantum mechanical problem for the situation where there are in addition interactions between electrons, the case in the many-electron atom, prevents such an analytical result. Since it is impossible to find the exact analytical wavefunctions for the Hamiltonian operator applicable to the many-electron atom, it is necessary to make some approximations in order to determine the wavefunctions which best approximate the state of affairs.

2.3.1. The orbital approximation

Let us call e_i the set of three spatial coordinates (x_i, y_i, z_i) appropriate to the electron i . The wavefunction which describes the collection of electrons depends on the coordinates of all the electrons and may be written as a many-electron function as

$$\Psi(e_1, e_2, \dots, e_i, \dots, e_z) \quad (35)$$

This function is a solution of the Schrödinger wave equation:

$$\mathcal{H}\Psi(e_1, e_2, \dots, e_i, \dots, e_z) = E\Psi(e_1, e_2, \dots, e_i, \dots, e_z) \quad (36)$$

In the orbital approximation one looks for solutions which approach that of the many-electron function by writing a product of single-electron functions, χ_i which only depend upon the coordinates of a single electron.

$$\Psi(e_1, e_2, \dots, e_i, \dots, e_z) = \chi_1(e_1)\chi_2(e_2) \dots \chi_i(e_i) \dots \chi_z(e_z) \quad (37)$$

The single-electron functions are called the *atomic orbitals* (AOs) of the atom. They are themselves solutions of an equation (38) which although having the same form as the Schrödinger equation, is considerably simpler since it only contains the

coordinates of a single electron.

$$\hbar\chi_i(e_i) = \varepsilon_i\chi_i(e_i) \quad (38)$$

There are an infinite set of solutions χ_i associated with the eigenvalues ε_i , the energies of the atomic orbitals, χ_i . The wavefunction Ψ , describing the many-electron atom is thus the product of a given set of the χ_i , the choice of which is determined by a set of rules which we will describe later (Section 2.3.4b).

2.3.2. Mathematical description and nomenclature of atomic orbitals

By analogy with the eigenfunctions for the hydrogen-like atoms, each orbital χ is written as a product of radial and angular functions

$$\chi_{n,l,m}(r, \theta, \varphi) = R_{n,l}(r)Y_{l,m}(\theta, \varphi) \quad (39)$$

The angular part of this expression, $Y_{l,m}(\theta, \varphi)$ is identical to that found for the hydrogen atom and is determined by the values of the two quantum numbers l and m . The radial part, set by the values of the two quantum numbers n and l , is determined by both the nuclear charge and the presence of the other electrons (see Section 2.5.2). Its functional form is thus expected to be rather different from the $R_{n,l}(r)$ of the hydrogen atom. As before, each orbital is characterized by the three quantum numbers n , l and m appropriate for the one-electron atom. The rules which determine the allowed values of these quantum numbers are also the same as those for the hydrogen-like atoms; $n = 1, 2, 3, \dots$, $0 \leq l < n$ and $-l \leq m \leq +l$. Orthogonal AOs, described as before, with the labels $1s$, $2s$, $2p$ etc., result.

The close similarities between the AOs for the many-electron atom and the wavefunctions for the hydrogen atom and the hydrogen-like atoms means that, although it is not strictly correct we use the same language to describe the orbitals in one- and many-electron atoms. Irrespective of whether the functions are determined via the orbital approximation or as exact solutions of the wave equation for one-electron atoms, we shall use the term atomic orbital (AO) for both.

2.3.3. Atomic orbital energies

For the hydrogen-like atoms we saw that the energy of the atomic orbital (ε_n), in this case the same as the eigenvalue E_n only depends upon the principal quantum number n ($\varepsilon_n = E_n = -RyZ^2/n^2$). Classification of the AOs in terms of increasing energy doesn't pose any particular problem. The energy of the orbital increases with increasing n and orbitals with the same n are degenerate, $2s$ and $2p$ for example. The situation is more complex in many-electron atoms. *In many-electron atoms, the energy of an atomic orbital depends on the two quantum numbers n and l .*

An immediate consequence of this result is that AOs with the same n and l remain degenerate. For example the three $2p$ orbitals are strictly degenerate, as are the five $3d$ orbitals. Such a group of orbitals with the same energy is called a *sub-shell*, the

term *shell* itself is reserved for all the orbitals with the same n . In this way the 2 shell ($n = 2$) is made up of the two sub-shells $2s$ and $2p$.

There are two general rules which allow, at least in part, the energetic ordering of the orbitals

- (i) For the same value of l the orbital energy increases with increasing n . Thus

$$\varepsilon_{1s} < \varepsilon_{2s} < \varepsilon_{3s} < \dots$$

$$\varepsilon_{2p} < \varepsilon_{3p} < \varepsilon_{4p} < \dots$$

- (ii) For the same value of n the orbital energy increases with increasing l . So

$$\varepsilon_{2s}(l=0) < \varepsilon_{2p}(l=1)$$

$$\varepsilon_{3s}(l=0) < \varepsilon_{3p}(l=1) < \varepsilon_{3d}(l=2)$$

These two rules are not, however, sufficient to completely fix the energetic ordering. For example they do not allow the placement of $2p$ relative to $3s$. However calculations show that it is the value of the principal quantum number which dominates here, i.e., $\varepsilon_{2p} < \varepsilon_{3s}$. In fact for all atoms the lowest five orbitals are found in the following order

$$\varepsilon_{1s} < \varepsilon_{2s} < \varepsilon_{2p} < \varepsilon_{3s} < \varepsilon_{3p}$$

Beyond this group the situation gets complicated. For example it is not possible to predict using these rules the energetic ordering of the $4s$ and $3d$ AOs since the actual state of affairs depends on the atom being considered, and sometimes its oxidation state.

2.3.4. The electronic configuration of atoms

The electronic configuration of an atom is the assignment of the available electrons to the different sub-shells open to them. The number of electrons in a sub-shell is generally indicated by an exponent. For example, $1s^2$ signifies the presence of two electrons in the $1s$ orbital. We speak then of two electrons 'occupying' the $1s$ orbital. Two rules limit the configurations which are possible.

(a) The Pauli exclusion principle

One way of stating this is that *in an atom no two electrons may have the same values for the four quantum numbers n , l , m , m_s* . This principle has two important consequences.

- (i) If two electrons have the same spin (that is to say the same value of the spin quantum number) they must occupy two different orbitals. (i.e., at least one of the n , l and m quantum numbers must be different for the two electrons.)