

**Teoria quantistica**  
**Sistemi semplici risolvibili**  
**esattamente**

**ATOMO DI IDROGENO**

**Energia di ionizzazione**  
**Funzione di distribuzione radiale**  
**Orbitali atomici s,p,d**

**Chimica Fisica 2**

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# Atomic structure

## 9.2 Atomic orbitals and their energies

An atomic orbital is a one-electron wavefunction for an electron in an atom. Each hydrogenic atomic orbital is defined by three quantum numbers, designated  $n$ ,  $l$ , and  $m_l$ . When an electron is described by one of these wavefunctions, we say that it ‘occupies’ that orbital. We could go on to say that the electron is in the state  $|n, l, m_l\rangle$ . For instance, an electron described by the wavefunction  $\psi_{1,0,0}$  and in the state  $|1,0,0\rangle$  is said to ‘occupy’ the orbital with  $n = 1$ ,  $l = 0$ , and  $m_l = 0$ .

### (a) The specification of orbitals

The quantum number  $n$  is called the principal quantum number; it can take the value  $n = 1, 2, 3, \dots$  and determines the energy of the electron:

- An electron in an orbital with quantum number  $n$  has an energy given by eqn 9.9.

The two other quantum numbers,  $l$  and  $m_l$ , come from the angular solutions, and specify the angular momentum of the electron around the nucleus:

- An electron in an orbital with quantum number  $l$  has an angular momentum of magnitude  $\{l(l+1)\}^{1/2}\hbar$ , with  $l = 0, 1, 2, \dots, n-1$ .
- An electron in an orbital with quantum number  $m_l$  has a  $z$ -component of angular momentum  $m_l\hbar$ , with  $m_l = 0, \pm 1, \pm 2, \dots, \pm l$ .

Note how the value of the principal quantum number,  $n$ , controls the maximum value of  $l$  and  $l$  controls the range of values of  $m_l$ .

To define the state of an electron in a hydrogenic atom fully we need to specify not only the orbital it occupies but also its spin state. We saw in Section 8.8 that an electron

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possesses an intrinsic angular momentum that is described by the two quantum numbers  $s$  and  $m_s$  (the analogues of  $l$  and  $m_l$ ). The value of  $s$  is fixed at  $\frac{1}{2}$  for an electron, so we do not need to consider it further at this stage. However,  $m_s$  may be either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ , and to specify the state of an electron in a hydrogenic atom we need to specify which of these values describes it. It follows that, to specify the state of an electron in a hydrogenic atom, we need to give the values of four quantum numbers, namely  $n$ ,  $l$ ,  $m_l$  and  $m_s$ .

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## (b) The energy levels 9.2 Atomic orbitals and their energies

The energy levels predicted by eqn 9.9 are depicted in Fig. 9.5. The energies, and also the separation of neighbouring levels, are proportional to  $Z^2$ , so the levels are four times as wide apart (and the ground state four times deeper in energy) in  $\text{He}^+$  ( $Z = 2$ ) than in  $\text{H}$  ( $Z = 1$ ). All the energies given by eqn 9.9 are negative. They refer to the bound states of the atom, in which the energy of the atom is lower than that of the infinitely separated, stationary electron and nucleus (which corresponds to the zero of energy). There are also solutions of the Schrödinger equation with positive energies. These solutions correspond to unbound states of the electron, the states to which an electron is raised when it is ejected from the atom by a high-energy collision or photon. The energies of the unbound electron are not quantized and form the continuum states of the atom.

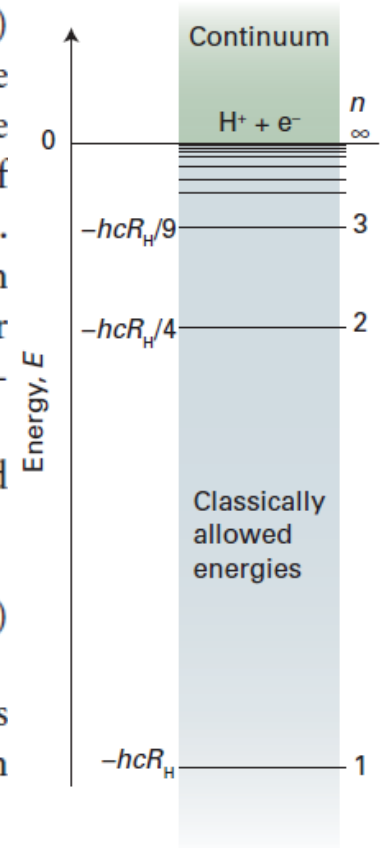
Equation 9.9 is consistent with the spectroscopic result summarized by eqn 9.1, and we can identify the Rydberg constant for hydrogen ( $Z = 1$ ) as

$$hcR_{\text{H}} = \frac{\mu_{\text{H}}e^4}{32\pi^2\varepsilon_0^2\hbar^2} \quad (9.14)$$

where  $\mu_{\text{H}}$  is the reduced mass for hydrogen. The Rydberg constant itself,  $R_{\infty}$ , is defined by the same expression except for the replacement of  $\mu_{\text{H}}$  by the mass of an electron,  $m_e$ , corresponding to a nucleus of infinite mass:

$$R_{\text{H}} = \frac{\mu_{\text{H}}}{m_e} R_{\infty} \quad R_{\infty} = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c} \quad \boxed{\text{Rydberg constant}} \quad [9.15]$$

Insertion of the values of the fundamental constants into the expression for  $R_{\text{H}}$  gives almost exact agreement with the experimental value. The only discrepancies arise from the neglect of relativistic corrections (in simple terms, the increase of mass with speed), which the non-relativistic Schrödinger equation ignores.



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### (c) Ionization energies

The ionization energy,  $I$ , of an element is the minimum energy required to remove an electron from the ground state, the state of lowest energy, of one of its atoms in the gas phase. Because the ground state of hydrogen is the state with  $n = 1$ , with energy  $E_1 = -hcR_H$  and the atom is ionized when the electron has been excited to the level corresponding to  $n = \infty$  (see Fig. 9.5), the energy that must be supplied is

$$I = hcR_H \quad (9.16)$$

The value of  $I$  is 2.179 aJ (a, for atto, is the prefix that denotes  $10^{-18}$ ), which corresponds to 13.60 eV.

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## 9.2 Atomic orbitals and their energies

### (c) Ionization energies

#### Example 9.1 Measuring an ionization energy spectroscopically

The emission spectrum of atomic hydrogen shows lines at 82 259, 97 492, 102 824, 105 292, 106 632, and 107 440  $\text{cm}^{-1}$ , which correspond to transitions to the same lower state. Determine (a) the ionization energy of the lower state, (b) the value of the Rydberg constant.

*Method* The spectroscopic determination of ionization energies depends on the determination of the series limit, the wavenumber at which the series terminates and becomes a continuum. If the upper state lies at an energy  $-hcR_{\text{H}}/n^2$ , then, when the atom makes a transition to  $E_{\text{lower}}$ , a photon of wavenumber

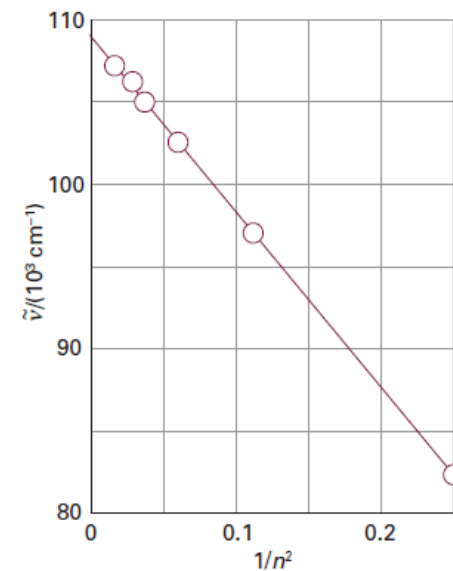
$$\tilde{\nu} = -\frac{R_{\text{H}}}{n^2} - \frac{E_{\text{lower}}}{hc}$$

is emitted. However, because  $I = -E_{\text{lower}}$ , it follows that

$$\tilde{\nu} = \frac{I}{hc} - \frac{R_{\text{H}}}{n^2}$$

A plot of the wavenumbers against  $1/n^2$  should give a straight line of slope  $-R_{\text{H}}$  and intercept  $I/hc$ . Use a computer to make a least-squares fit of the data in order to obtain a result that reflects the precision of the data.

*Answer* The wavenumbers are plotted against  $1/n^2$  in Fig. 9.6. The (least-squares) intercept lies at 109 679  $\text{cm}^{-1}$ , so the ionization energy is 2.1788 aJ (1312.1  $\text{kJ mol}^{-1}$ ).





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## 9.2 Atomic orbitals and their energies

### (d) Shells and subshells

All the orbitals of a given value of  $n$  are said to form a single shell of the atom. In a hydrogenic atom, all orbitals of given  $n$ , and therefore belonging to the same shell, have the same energy. It is common to refer to successive shells by letters:

$n =$	1	2	3	4 ...
	K	L	M	N ...

Specification  
of shells

Thus, all the orbitals of the shell with  $n = 2$  form the L shell of the atom, and so on.

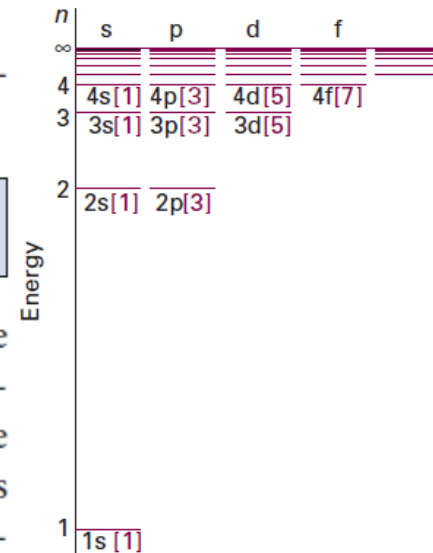
The orbitals with the same value of  $n$  but different values of  $l$  are said to form a subshell of a given shell. These subshells are generally referred to by letters:

$l =$	0	1	2	3	4	5	6 ...
	s	p	d	f	g	h	i ...

Specification  
of subshells

The letters then run alphabetically (j is not used because in some languages i and j are not distinguished). Figure 9.7 is a version of Fig. 9.5 that shows the subshells explicitly. Because  $l$  can range from 0 to  $n - 1$ , giving  $n$  values in all, it follows that there are  $n$  subshells of a shell with principal quantum number  $n$ . Thus, when  $n = 1$ , there is only one subshell, the one with  $l = 0$ . When  $n = 2$ , there are two subshells, the 2s subshell (with  $l = 0$ ) and the 2p subshell (with  $l = 1$ ).

When  $n = 1$  there is only one subshell, that with  $l = 0$ , and that subshell contains only one orbital, with  $m_l = 0$  (the only value of  $m_l$  permitted). When  $n = 2$ , there are four orbitals, one in the s subshell with  $l = 0$  and  $m_l = 0$ , and three in the  $l = 1$  subshell with  $m_l = +1, 0, -1$ . When  $n = 3$  there are nine orbitals (one with  $l = 0$ , three with  $l = 1$ ,



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## 9.2 Atomic orbitals and their energies

### (d) Shells and subshells

and five with  $l=2$ ). The organization of orbitals in the shells is summarized in Fig. 9.8. In general, the number of orbitals in a shell of principal quantum number  $n$  is  $n^2$ , so in a hydrogenic atom each energy level is  $n^2$ -fold degenerate.



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## 9.2 Atomic orbitals and their energies

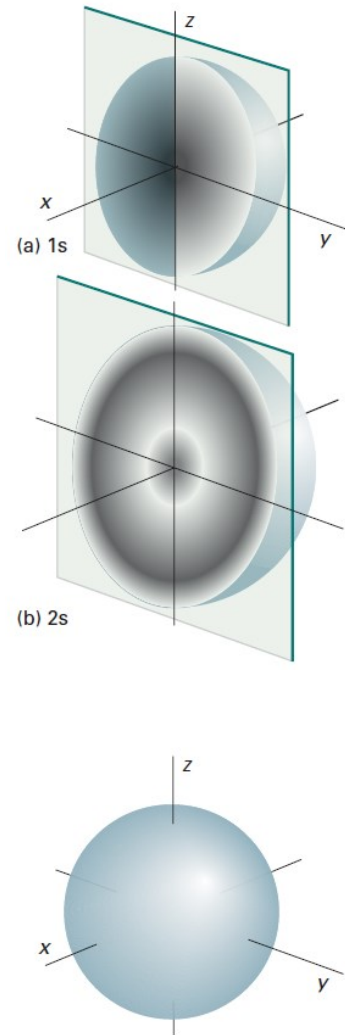
### (e) s Orbitals

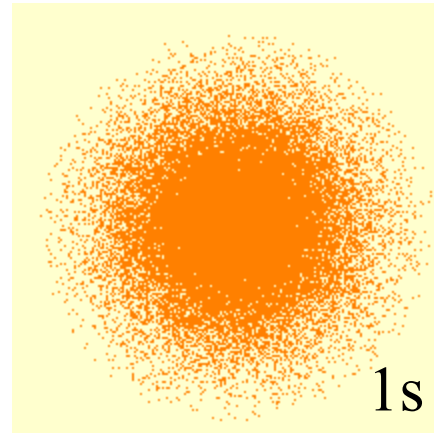
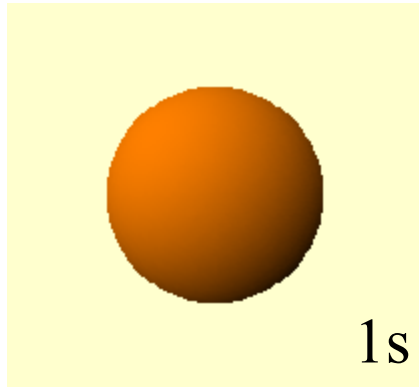
The orbital occupied in the ground state is the one with  $n = 1$  (and therefore with  $l = 0$  and  $m_l = 0$ , the only possible values of these quantum numbers when  $n = 1$ ). From Table 9.1 and  $Y_{0,0} = 1/2\pi^{1/2}$  we can write (for  $Z = 1$ ):

$$\psi = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0} \quad (9.17)$$

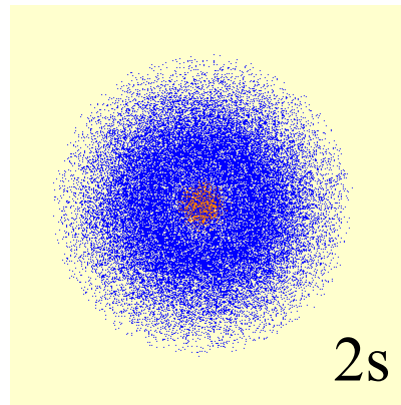
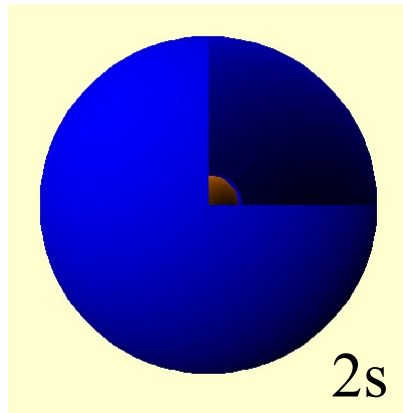
This wavefunction is independent of angle and has the same value at all points of constant radius, that is, the 1s orbital is *spherically symmetrical*. The wavefunction decays exponentially from a maximum value of  $1/(\pi a_0^3)^{1/2}$  at the nucleus (at  $r = 0$ ). It follows that the probability density of the electron is greatest at the nucleus itself.

We can understand the general form of the ground-state wavefunction by considering the contributions of the potential and kinetic energies to the total energy of the atom. The closer the electron is to the nucleus on average, the lower its average potential energy. This dependence suggests that the lowest potential energy should be obtained with a sharply peaked wavefunction that has a large amplitude at the nucleus and is zero everywhere else (Fig. 9.9). However, this shape implies a high kinetic energy, because such a wavefunction has a very high average curvature. The electron would have very low kinetic energy if its wavefunction had only a very low average curvature. However, such a wavefunction spreads to great distances from the nucleus and the average potential energy of the electron will be correspondingly high. The actual ground-state wavefunction is a compromise between these two extremes: the wavefunction spreads away from the nucleus (so the expectation value of the potential energy is not as low as in the first example, but nor is it very high) and has a

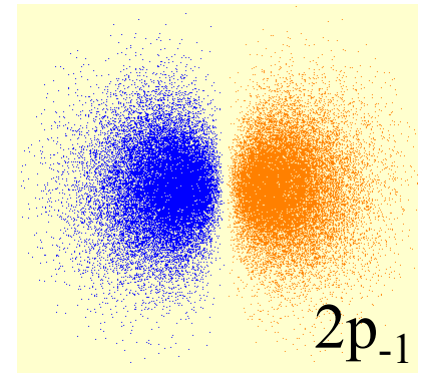
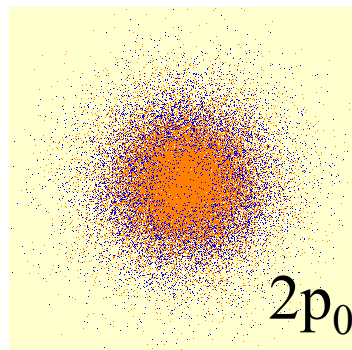
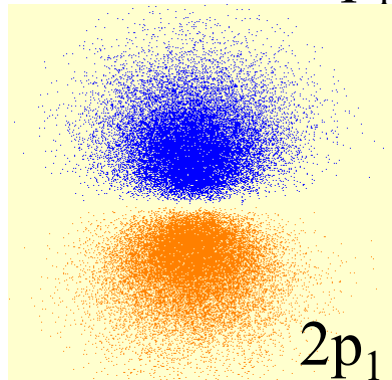
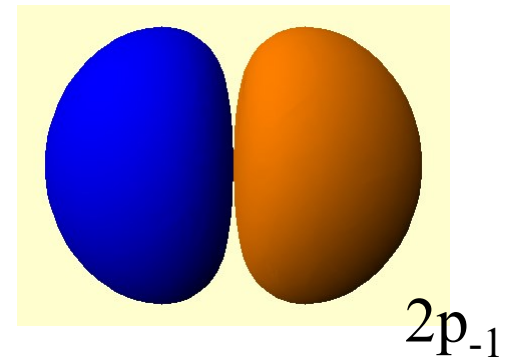
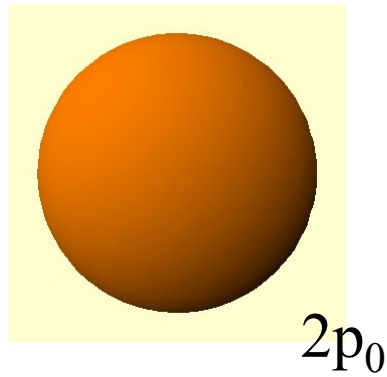
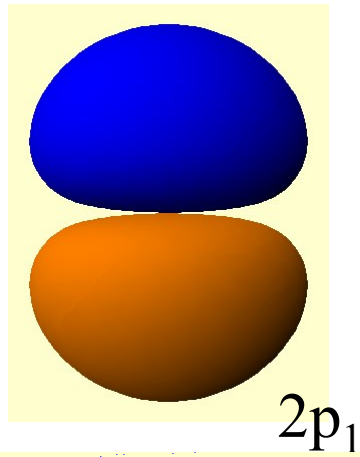




Esempi di orbitali  
atomici per l'atomo  
di **idrogeno**  
con **n=1**



Esempi di orbitali  
atomici per l'atomo  
di **idrogeno**  
con **n=2**



# Atomic structure

## 9.2 Atomic orbitals and their energies

### (e) s Orbitals

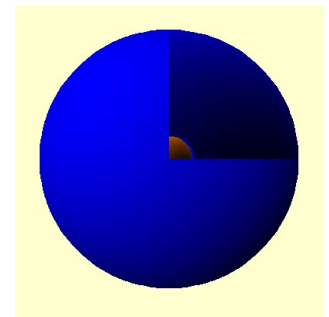
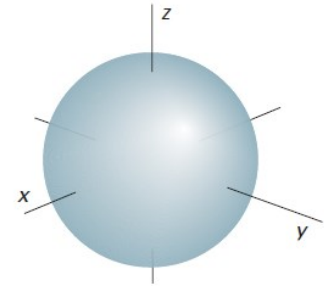
reasonably low average curvature (so the expectation of the kinetic energy is not very low, but nor is it as high as in the first example).

By the virial theorem with  $b = -1$  (eqn 8.35),  $\langle E_k \rangle = -\frac{1}{2}\langle V \rangle$  and therefore  $E = \langle E_k \rangle + \langle V \rangle = \frac{1}{2}\langle V \rangle$ , so the total energy of an s electron becomes less negative as  $n$  increases and it is found at greater distances from the nucleus with a less negative potential energy. Thus, as  $n$  approaches infinity,

1. The kinetic energy becomes less positive and has fallen to zero when  $n = \infty$ .
2. The potential energy becomes less negative and has risen to zero when  $n = \infty$ .
3. The total energy becomes less negative and has risen to zero when  $n = \infty$ .

One way of depicting the probability density of the electron is to represent  $|\psi|^2$  by the density of shading (Fig. 9.10). A simpler procedure is to show only the boundary surface, the surface that captures a high proportion (typically about 90 per cent) of the electron probability. For the 1s orbital, the boundary surface is a sphere centred on the nucleus (Fig. 9.11).

All s orbitals are spherically symmetric, but differ in the number of radial nodes. For example, the 1s, 2s, and 3s orbitals have 0, 1, and 2 radial nodes, respectively. In general, an  $ns$  orbital has  $n - 1$  radial nodes. As  $n$  increases, the radius of the spherical boundary surface that captures a given fraction of the probability also increases.





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## 9.2 Atomic orbitals and their energies

### (f) Radial distribution functions

The wavefunction tells us, through the value of  $|\psi|^2$ , the probability of finding an electron in any region. We can imagine a probe with a volume  $d\tau$  and sensitive to electrons, and which we can move around near the nucleus of a hydrogen atom. Because the probability density in the ground state of the atom is  $|\psi|^2 \propto e^{-2Zr/a_0}$ , the reading from the detector decreases exponentially as the probe is moved out along any radius but is constant if the probe is moved on a circle of constant radius (Fig. 9.12).

Now consider the total probability of finding the electron *anywhere* between the two walls of a spherical shell of thickness  $dr$  at a radius  $r$ . The sensitive volume of the probe is now the volume of the shell (Fig. 9.13), which is  $4\pi r^2 dr$  (the product of its surface area,  $4\pi r^2$ , and its thickness,  $dr$ ). The probability that the electron will be found between the inner and outer surfaces of this shell is the probability density at the radius  $r$  multiplied by the volume of the probe, or  $|\psi|^2 \times 4\pi r^2 dr$ . This expression has the form  $P(r)dr$ , where

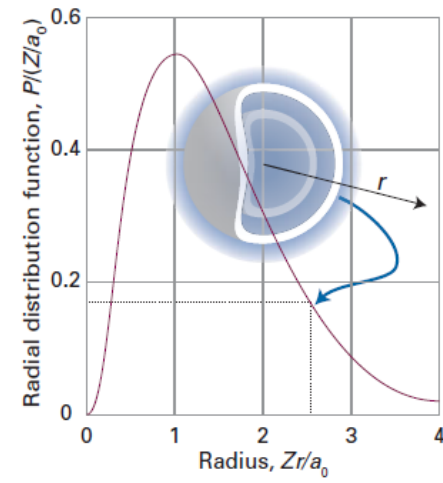
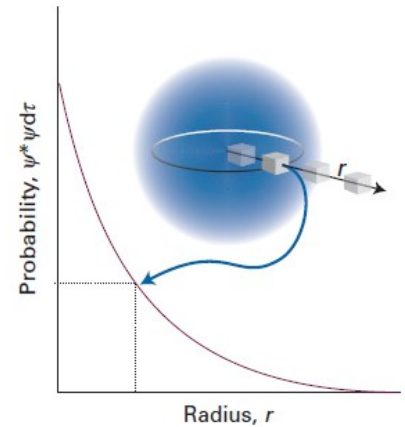
$$P(r) = 4\pi r^2 \psi^2 \quad (9.18a)$$

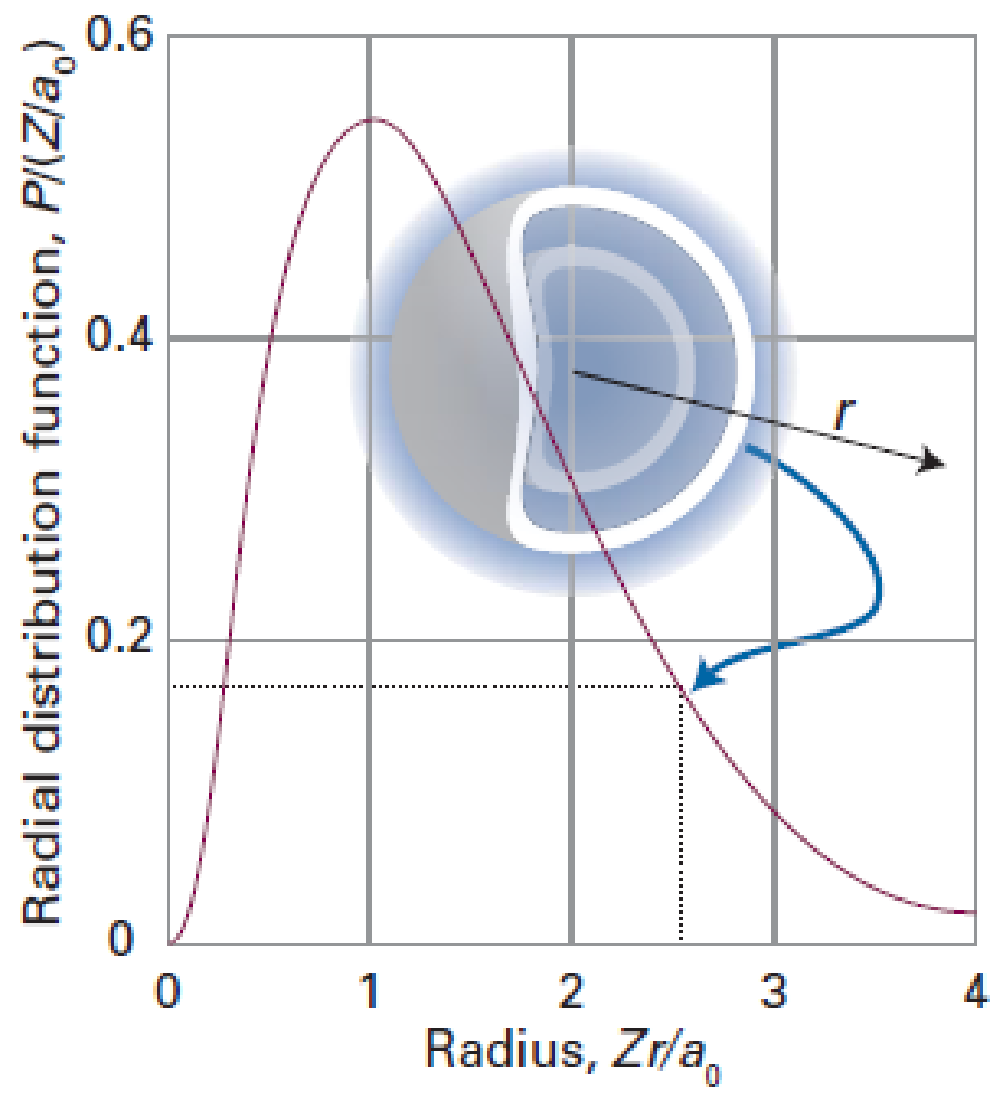
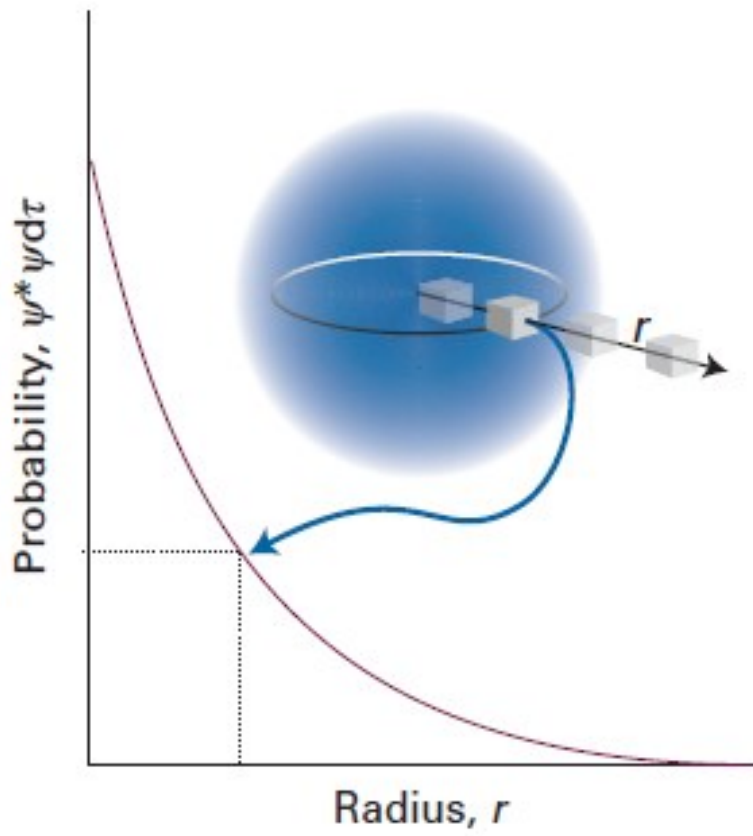
The more general expression, which also applies to orbitals that are not spherically symmetrical, is derived in the following *Justification*, and is

$$P(r) = r^2 R(r)^2 \quad (9.18b)$$

Radial distribution function

where  $R(r)$  is the radial wavefunction for the orbital in question.







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## 9.2 Atomic orbitals and their energies

### (f) Radial distribution functions

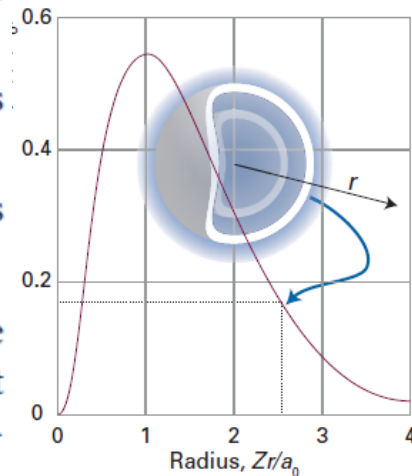
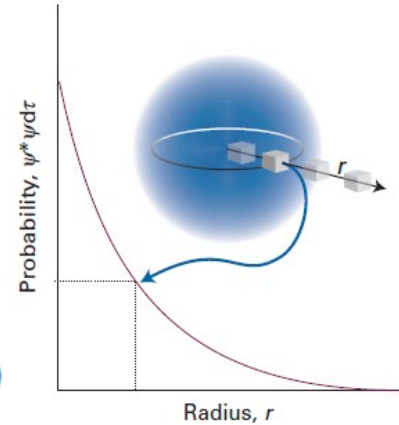
The radial distribution function,  $P(r)$ , is a probability density in the sense that, when it is multiplied by  $dr$ , it gives the probability of finding the electron anywhere between the two walls of a spherical shell of thickness  $dr$  at the radius  $r$ . For a 1s orbital,

$$P(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0} \quad (9.19)$$

Let's interpret this expression:

1. Because  $r^2 = 0$  at the nucleus,  $P(0) = 0$ . The volume of the shell of inspection is zero when  $r = 0$ .
2. As  $r \rightarrow \infty$ ,  $P(r) \rightarrow 0$  on account of the exponential term. The wavefunction has fallen to zero at great distances from the nucleus.
3. The increase in  $r^2$  and the decrease in the exponential factor means that  $P$  passes through a maximum at an intermediate radius (see Fig. 9.13).

The maximum of  $P(r)$ , which can be found by differentiation, marks the most probable radius at which the electron will be found, and for a 1s orbital in hydrogen occurs at  $r = a_0$ , the Bohr radius. When we carry through the same calculation for the radial distribution function of the 2s orbital in hydrogen, we find that the most probable radius is  $5.2a_0 = 275 \text{ pm}$ . This larger value reflects the expansion of the atom as its energy increases.



# Atomic structure

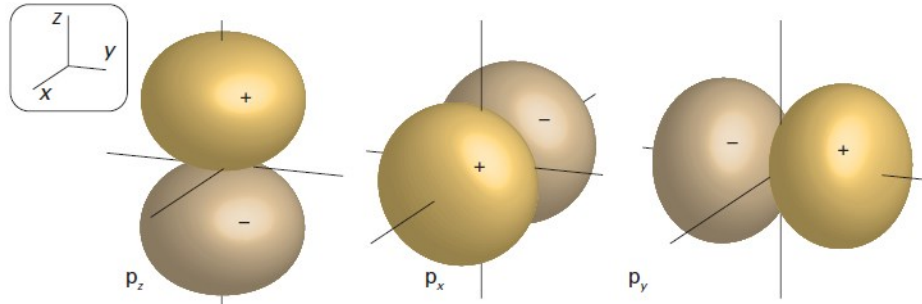
## 9.2 Atomic orbitals and their energies

### (g) p Orbitals

The three 2p orbitals are distinguished by the three different values that  $m_l$  can take when  $l = 1$ . Because the quantum number  $m_l$  tells us the orbital angular momentum around an axis, these different values of  $m_l$  denote orbitals in which the electron has different orbital angular momenta around an arbitrary  $z$ -axis but the same magnitude of that momentum (because  $l$  is the same for all three). The orbital with  $m_l = 0$ , for instance, has zero angular momentum around the  $z$ -axis. Its angular variation is proportional to  $\cos \theta$ , so the probability density, which is proportional to  $\cos^2 \theta$ , has its maximum value on either side of the nucleus along the  $z$ -axis (at  $\theta = 0$  and  $180^\circ$ ). The wavefunction of a 2p orbital with  $m_l = 0$  is

$$\begin{aligned}\psi_{p_0} &= R_{2,1}(r)Y_{1,0}(\theta,\phi) = \frac{1}{4(2\pi)^{1/2}} \left(\frac{Z}{a_0}\right)^{5/2} r \cos \theta e^{-Zr/2a_0} \\ &= r \cos \theta f(r)\end{aligned}\tag{9.20a}$$

where  $f(r)$  is a function only of  $r$ . Because in spherical polar coordinates  $z = r \cos \theta$ , this wavefunction may also be written

$$\psi_{p_0} = zf(r)\tag{9.20b}$$


# Atomic structure

## 9.2 Atomic orbitals and their energies

### (g) p Orbitals

All p orbitals with  $m_l = 0$  have wavefunctions of this form, but  $f(r)$  depends on the value of  $n$ . This way of writing the orbital is the origin of the name 'p<sub>z</sub> orbital': its boundary surface is shown in Fig. 9.15. The wavefunction is zero everywhere in the  $xy$ -plane, where  $z = 0$ , so the  $xy$ -plane is a nodal plane of the orbital: the wavefunction changes sign on going from one side of the plane to the other.

The wavefunctions of 2p orbitals with  $m_l = \pm 1$  have the following form:

$$\begin{aligned}\psi_{p_{\pm 1}} &= R_{2,1}(r)Y_{1,\pm 1}(\theta,\phi) = \mp \frac{1}{8\pi^{1/2}} \left(\frac{Z}{a_0}\right)^{5/2} r \sin \theta e^{\pm i\phi} e^{-Zr/2a_0} \\ &= \mp \frac{1}{2^{1/2}} r \sin \theta e^{\pm i\phi} f(r)\end{aligned}\tag{9.21}$$

We saw in Chapter 8 that a particle that has net motion is described by a complex wavefunction. In the present case, the functions correspond to nonzero angular momentum about the  $z$ -axis:  $e^{+i\phi}$  corresponds to clockwise rotation when viewed from below, and  $e^{-i\phi}$  corresponds to counterclockwise rotation (from the same viewpoint). They have zero amplitude where  $\theta = 0$  and  $180^\circ$  (along the  $z$ -axis) and maximum amplitude at  $90^\circ$ , which is in the  $xy$ -plane. To draw the functions it is usual to represent them as standing waves. To do so, we take the real linear combinations

$$\psi_{p_x} = -\frac{1}{2^{1/2}}(p_{+1} - p_{-1}) = r \sin \theta \cos \phi f(r) = xf(r)\tag{9.22}$$

$$\psi_{p_y} = \frac{i}{2^{1/2}}(p_{+1} + p_{-1}) = r \sin \theta \sin \phi f(r) = yf(r)$$

# Atomic structure

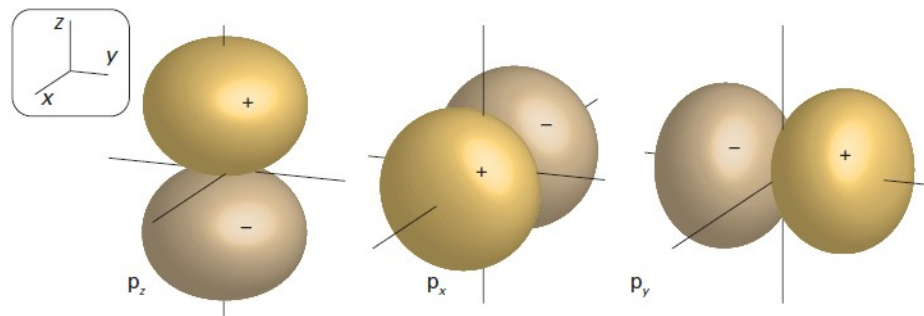
## 9.2 Atomic orbitals and their energies

### (g) p Orbitals

$$\psi_{p_x} = -\frac{1}{2^{1/2}}(p_{+1} - p_{-1}) = r \sin \theta \cos \phi f(r) = x f(r) \quad (9.22)$$

$$\psi_{p_y} = \frac{i}{2^{1/2}}(p_{+1} + p_{-1}) = r \sin \theta \sin \phi f(r) = y f(r)$$

(See the following *Justification*.) These linear combinations are indeed standing waves with no net orbital angular momentum around the  $z$ -axis, as they are superpositions of states with equal and opposite values of  $m_l$ . The  $p_x$  orbital has the same shape as a  $p_z$  orbital, but it is directed along the  $x$ -axis (see Fig. 9.15); the  $p_y$  orbital is similarly directed along the  $y$ -axis. The wavefunction of any p orbital of a given shell can be written as a product of  $x$ ,  $y$ , or  $z$  and the same radial function (which depends on the value of  $n$ ).



# Atomic structure

## 9.2 Atomic orbitals and their energies

### (g) p Orbitals

$$\psi_{p_x} = -\frac{1}{2^{1/2}}(p_{+1} - p_{-1}) = r \sin \theta \cos \phi f(r) = xf(r) \quad (9.22)$$

$$\psi_{p_y} = \frac{i}{2^{1/2}}(p_{+1} + p_{-1}) = r \sin \theta \sin \phi f(r) = yf(r)$$

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**Justification 9.3** *The linear combination of degenerate wavefunctions*

We justify here the step of taking linear combinations of degenerate orbitals when we want to indicate a particular point. The freedom to do so rests on the fact that, whenever two or more wavefunctions correspond to the same energy, any linear combination of them is an equally valid solution of the Schrödinger equation.

Suppose  $\psi_1$  and  $\psi_2$  are both solutions of the Schrödinger equation with energy  $E$ ; then we know that

$$\hat{H}\psi_1 = E\psi_1 \quad \hat{H}\psi_2 = E\psi_2$$

Now consider the linear combination  $\psi = c_1\psi_1 + c_2\psi_2$  where  $c_1$  and  $c_2$  are arbitrary coefficients. Then it follows that

$$\hat{H}\psi = \hat{H}(c_1\psi_1 + c_2\psi_2) = c_1\hat{H}\psi_1 + c_2\hat{H}\psi_2 = c_1E\psi_1 + c_2E\psi_2 = E\psi$$

Hence, the linear combination is also a solution corresponding to the same energy  $E$ .

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# Atomic structure

## 9.2 Atomic orbitals and their energies

### (h) d Orbitals

When  $n = 3$ ,  $l$  can be 0, 1, or 2. As a result, this shell consists of one 3s orbital, three 3p orbitals, and five 3d orbitals. Each value of the quantum number  $m_l = +2, +1, 0, -1, -2$  corresponds to a different value for the component of the angular momentum about the  $z$ -axis. As for the p orbitals, d orbitals with opposite values of  $m_l$  (and hence opposite senses of motion around the  $z$ -axis) may be combined in pairs to give real standing waves, and the boundary surfaces of the resulting shapes are shown in Fig. 9.16. The real linear combinations have the following forms:

