

## A.4 Hydrogen atom orbitals

The electron in the hydrogen atom experiences a potential due to its attraction to the nucleus. This potential is negative (as there is an attraction) and it is inversely proportional to the distance,  $r$ , from the nucleus to the electron:

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

where  $e$  is the elementary charge (i.e. the charge on the electron and nucleus) and  $\epsilon_0$  is the permittivity of free space.

With this form of the potential, it is possible to solve the SE provided we move from the usual  $(x, y, z)$  coordinate system to the *spherical polar* coordinate system  $(r, \theta, \phi)$  introduced on p. 40 and illustrated again in Fig. A.6. As we described on p. 47, the wavefunctions can always be expressed as a product of a *radial* part,  $R_{n,l}(r)$ , which depends only on  $r$ , and an *angular* part,  $Y_{l,m_l}(\theta, \phi)$ , which only depends on  $\theta$  and  $\phi$ :

$$\Psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r) \times Y_{l,m_l}(\theta, \phi).$$

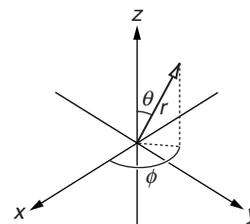
We saw in Section 4.6 on p. 44 that there are three quantum numbers needed to describe the wavefunction:  $n$ ,  $l$  and  $m_l$ . The radial part of the wavefunction turns out only to depend on the values of  $n$  and  $l$ , while the angular part turns out only to depend on  $l$  and  $m_l$ ; this dependence is indicated by the subscripts.

The precise forms of  $R_{n,l}(r)$  and  $Y_{l,m_l}(\theta, \phi)$  are a set of well known functions which arise in the study of certain types of differential equations. So, luckily for us, the problem is already solved and we can be content with looking at some of the solutions.

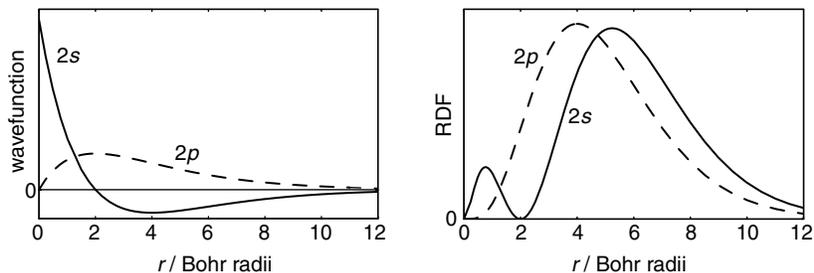
### The radial parts

Given below are some examples of the radial functions,  $R_{n,l}(r)$ ; for simplicity the normalization constants, which are different for each  $R_{n,l}(r)$ , have been left out:

$n$	$l$	$m_l$	$R_{n,l}(r)$
1s	0	0	$e^{-r/a_0}$
2s	0	0	$(2 - \frac{r}{a_0}) e^{-r/2a_0}$
2p	1	0	$\frac{r}{a_0} e^{-r/2a_0}$
3s	0	0	$\left(27 - 18\frac{r}{a_0} + 2\left(\frac{r}{a_0}\right)^2\right) e^{-r/3a_0}$
3p	1	0	$\left(\frac{r}{a_0}\right) \left(6 - \frac{r}{a_0}\right) e^{-r/3a_0}$
3d	2	0	$\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$



**Fig. A.6** The spherical polar coordinate system defines a point in terms of two angles,  $\theta$  and  $\phi$ , and a distance,  $r$ .



**Fig. A.7** On the left are plotted the radial parts of the  $2s$  and  $2p$  orbitals; the horizontal axis is marked in units of the Bohr radius. Note that whereas the  $2s$  orbital shows a radial node at  $r = 2$  Bohr radii, the  $2p$  orbital has no radial node. At  $r = 0$  the  $2s$  orbital is non-zero but the  $2p$  is zero. The RDFs are shown on the right; the minimum in the RDF of the  $2s$  orbital at 2 Bohr radii corresponds to the radial node in the wavefunction.

In the table  $a_0$  is the *Bohr radius* given by

$$a_0 = \frac{\varepsilon_0 h^2}{m_e e^2}$$

and where  $m_e$  is the mass of the electron.

One thing which is immediately apparent from these functions is that, by looking at the exponential terms, we can see that the  $1s$  radial function falls off more quickly than does the  $2s$ , and in turn this falls off more quickly than the  $3s$ . This is in line with the observation we made earlier that the orbitals increase in size as the principal quantum number increases.

We can see from the form of the functions  $R_{2,0}(r)$  (for the  $2s$ ) that:

- the wavefunction is non-zero at the nucleus ( $r = 0$ );
- there is a radial node when  $r = 2a_0$ , as at this value of  $r$  the term in the bracket zero;
- the wavefunction decays away to zero at large distances as a rate determined by the size of  $a_0$ .

All of these points can be seen in Fig. A.7 (which is the same as Fig. 4.20 on p. 48).

In contrast, from the form of  $R_{2,1}(r)$  (for the  $2p$ ) we can see that the wavefunction is zero at the nucleus ( $r = 0$ ), and that there are no radial nodes. Again, these points can be seen in Fig. A.7.

### The radial distribution function

In Section 4.5 on p. 42 we defined the radial distribution function, the RDF, as

$$\text{RDF} = (\text{wavefunction})^2 \times 4\pi r^2.$$

The RDF gives the probability of finding the electron in a thin shell at distance  $r$ .

For the 1s orbital the RDF is given by

$$\begin{aligned} \text{RDF} &= \left[ \exp\left(\frac{-r}{a_0}\right) \right]^2 \times 4\pi r^2 \\ &= 4\pi r^2 \exp\left(\frac{-2r}{a_0}\right) \end{aligned}$$

We saw in Fig. 4.15(b) on p. 43 that the RDF is a maximum when  $r = 1$  Bohr radius; we are now in a position to prove this.

To locate the minima and maxima in the RDF we simply differentiate with respect to  $r$  and set the derivative equal to zero. In computing the derivative we must remember that the RDF is a product of two functions of  $r$ :

$$\begin{aligned} \frac{d \text{RDF}}{dr} &= 4\pi \left[ 2r \exp\left(\frac{-2r}{a_0}\right) + r^2 \left(\frac{-2}{a_0}\right) \exp\left(\frac{-2r}{a_0}\right) \right] \\ &= 4\pi \exp\left(\frac{-2r}{a_0}\right) \left[ 2r - \frac{2r^2}{a_0} \right] \\ &= 4\pi \exp\left(\frac{-2r}{a_0}\right) 2r \left[ 1 - \frac{r}{a_0} \right]. \end{aligned}$$

Clearly the derivative is zero if  $r = 0$ ; this corresponds to the RDF itself going to zero at this point. The derivative also goes to zero as  $r$  becomes very large; this corresponds to the RDF tailing off to zero at large  $r$ .

Finally, the derivative is zero if  $(1 - r/a_0)$  is zero, which is when  $r = a_0$ ; this corresponds to the maximum in the RDF which was described earlier. All of these features are visible in Fig. 4.15 (b).

Using a similar approach we can find the positions of the maxima and minima in the RDFs of the 2s and 2p AOs; the mathematics is a little more complex, but the principle is the same.

### The angular parts

The angular part of the wavefunction, as the name implies, depends only on the angles  $\theta$  and  $\phi$ . For example, the angular part of the  $2p_x$  wavefunction is

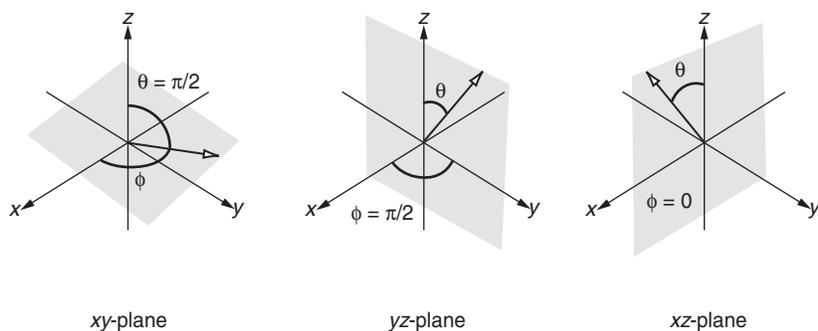
$$\sin \theta \times \cos \phi;$$

for simplicity, the normalization constant has been omitted. We can see from this that, for all values of  $\theta$ , the function is zero when  $\phi = \pi/2$  radians. Referring to Fig. A.8 we see that this range of angles corresponds to the  $yz$ -plane. This is therefore the angular node (or nodal plane) for the  $2p_x$  orbital shown in Fig. A.9 (which is identical to Fig. 4.19 on p. 47).

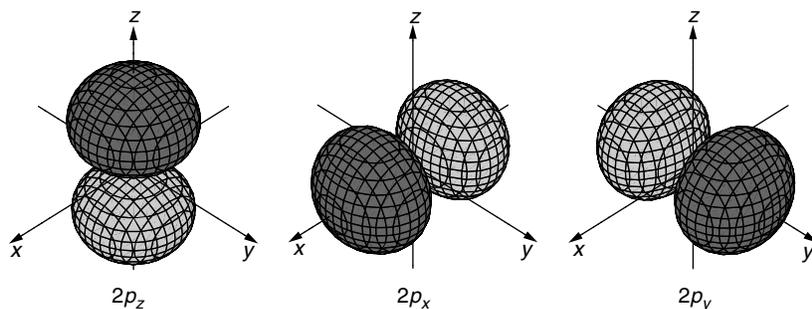
The angular part of the  $2p_y$  wavefunction is

$$\sin \theta \times \sin \phi$$

which is zero, for all values of  $\theta$ , when  $\phi = 0$ . Referring to Fig. A.8 we see that this specifies the  $xz$  plane which is therefore a nodal plane for this orbital. Again, this can be seen in Fig. A.9.



**Fig. A.8** In spherical polar coordinates planes can be described using a range of angles: the  $xy$ -plane corresponds to  $\theta = \pi/2$  and any value of  $\phi$ , the  $yz$ -plane corresponds to  $\phi = \pi/2$  and any value of  $\theta$ ; the  $xz$ -plane corresponds to  $\phi = 0$  and any value of  $\theta$ . The specified plane is shown tinted in each case.



**Fig. A.9** Surface plots of the three  $2p$  orbitals. The dark grey shading indicates a positive value for the wavefunction and light grey indicates a negative value.

The angular part of the  $3d_{xz}$  wavefunction is

$$\cos \theta \times \sin \theta \times \cos \phi$$

This is zero for  $\theta = \pi/2$  and all values of  $\phi$  i.e. the  $xy$ -plane (see Fig. A.8); it is also zero for  $\phi = \pi/2$  and for all values of  $\theta$  i.e. the  $yz$ -plane. These nodal planes are clearly visible in Fig. 4.25 on p. 51.

Finally, the angular part of the  $3d_{z^2}$  wavefunction is

$$3 \cos^2 \theta - 1$$

which is zero when

$$\cos \theta = \sqrt{\frac{1}{3}}$$

which is the case for  $\theta = 54.7^\circ$  and  $125.3^\circ$  (for all values of  $\phi$ ). So, the wavefunction is zero on the surface of two cones, as shown in Fig. 4.27 on p. 51. These two angular nodes are also visible in Fig. 4.26 on p. 51 and in Fig. 4.28 on p. 52.

**The Rydberg constant**

We saw in Section 4.6 on p. 44 that the energy of these orbitals only depends on the value of the principal quantum number,  $n$ . Before we gave the energy in terms of the Rydberg constant,  $R_H$ :

$$E_n = \frac{-R_H}{n^2}.$$

By solving the SE we can find that the Rydberg constant is:

$$R_H = \frac{m_e e^4}{8\epsilon_0^2 h^2}.$$

Very precise experimental work has confirmed that the value of the Rydberg constant determined from the spectrum of hydrogen atoms is in accord with this prediction from quantum mechanics.

**Multi-electron atoms and molecules**

As the number of electrons and nuclei increases, all we have to do is to add extra terms to the potential energy function in the SE to describe the interaction of these charged particles. Unfortunately, although it is easy enough to write down the SE, it is not possible to obtain an exact (i.e. analytic) solution for the resulting differential equation.

So, for systems with more than one electron we have to resort to a numerical solution of the SE. As we commented on earlier, computers are very good at solving this sort of problem and, with the presently available computing power, it is possible to find very precise wavefunctions and energies for small and medium-sized molecules.