2 Electrons in atoms

2.1 The probability of finding an electron in a small volume δV located at a particular point is given by $\psi(x, y, z)^2\,\delta V$, where $\psi(x, y, z)$ is the wavefunction at that point.

For an electron in a $1s$ orbital, describe how this probability varies as the distance from the nucleus is increased. At what point is the probability (electron density) a maximum?

2.2 Explain what is meant by the *radial distribution function*. For an electron in a $1s$ orbital, how does the RDF vary with distance from the nucleus?

Explain why it is that although the $1s$ wavefunction is a maximum at the nucleus, the corresponding RDF goes to zero at the nucleus. Also, explain why the RDF shows a maximum, and why the RDF goes to zero for large values of the distance r.

2.3 **This question requires a knowledge of calculus.** The RDF for a $1s$ orbital is $4\pi r^2[\psi_{1s}(r)]^2$. Given that the $1s$ wavefunction is $\psi_{1s}(r) = N_{1s}\exp(-r/a_0)$, show that the RDF is given by

$$P_{1s}(r) = 4N_{1s}^2\pi r^2\exp(-2r/a_0).$$

We can find the maximum in this RDF by differentiating it with respect to r, and then setting the derivative to zero. Show that the required derivative is

$$\frac{\mathrm{d}P_{1s}(r)}{\mathrm{d}r} = 8N_{1s}^2\pi r\exp(-2r/a_0) - 8N_{1s}^2\pi\frac{r^2}{a_0}\exp(-2r/a_0).$$

Further show that this differential goes to zero at $r = a_0$, and use a graphical argument to explain why this must correspond to a maximum.

For a hydrogen-like atom with nuclear charge Z, the $1s$ wavefunction is $\psi_{1s}(r) = N_{1s}\exp(-Zr/a_0)$. Show that the corresponding RDF has a maximum at $r = a_0/Z$.

2.4 The N shell has the principal quantum number n equal to four. Determine the quantum numbers (l and m_l) of all the possible AOs in this shell. What new feature arises in this shell that is not present in the M shell? How do the energies of these orbitals in the N shell compare with one another?

How many electrons could be accommodated in the N shell?

Orbitals for which the orbital angular momentum quantum number, l, takes the value 4 are given the letter g. In which shell would you expect g orbitals first to appear?

2.5 For a hydrogen atom (with $Z = 1$), calculate the energies, in kJ mol^{-1}, of the four lowest energy levels. Do the same for the He^+ ion, which has $Z = 2$. Plot the levels of He^+ to scale in a similar way to Fig. 2.13 on page 45, labelling each with the value of the principal quantum number n. Discuss the choice of energy zero you have used.

2.6 What do you understand by the terms *radial node* and *nodal plane*, as applied to AO wavefunctions? Illustrate your answer using the $2s$ and $2p$ AOs.

Explain why radial nodes arise from the radial part of the wavefunction, whereas nodal planes arise from the angular part of the wavefunction.

2.7 The radial part of the 3*s* AO wavefunction is

$$R_{3,0}(r) = N_{3,0}\left[27 - 18\left(\frac{r}{a_0}\right) + 2\left(\frac{r}{a_0}\right)^2\right]\exp\left(-\frac{r}{3a_0}\right).$$

This function will go to zero, i.e. have a radial node, when the term in the large square bracket goes to zero

$$\left[27 - 18\left(\frac{r}{a_0}\right) + 2\left(\frac{r}{a_0}\right)^2\right] = 0.$$

Finding out the values of r at which this is the case is made easier if we substitute $x = r/a_0$. Show that the above equation then becomes

$$27 - 18x + 2x^2 = 0.$$

This is a simple quadratic whose roots can be found using the standard formula. Show that these roots are $x = 1.9$ and $x = 7.1$. Hence show that there are radial nodes at $r = 1.9\,a_0$ and $7.1\,a_0$. Compare these answers with the plot shown in Fig. 2.28 on page 55.

Using a similar approach, determine the position of the radial node in the 3*p* orbital; the radial part of the wavefunction is

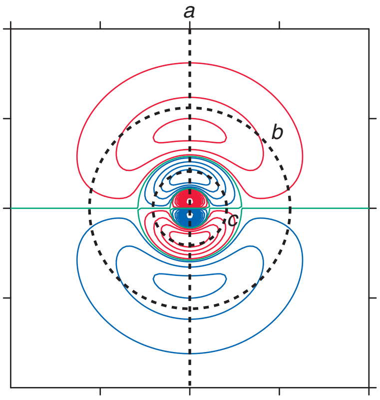
$$R_{3,1}(r) = N_{3,1}\left[6\left(\frac{r}{a_0}\right) - \left(\frac{r}{a_0}\right)^2\right]\exp\left(-\frac{r}{3a_0}\right).$$

2.8 Draw up a table showing the number of radial nodes, the number of angular nodes (nodal planes), and the total number of radial and angular nodes for 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* orbitals. Confirm that the numbers in your table are in accord with the general rules given on page 60.

Describe the nodal structures of 5*s*, 5*p*, 5*d*, 5*f* and 5*g* orbitals (5*g* has $l = 4$).

2.9 The contour plot shown below is of one of the 4*p* orbitals: positive intensity is indicated by red contours, negative by blue, and the zero contour is indicated in green.

Sketch how the wavefunction will vary along the dotted line *a*, and along the two circular paths *b* and *c* (for the latter two, this means making a plot of the wavefunction as a function of an *angle* which specifies how far we have moved around the circle).



2.10 Using the concepts of electron *screening* and *penetration*, and with reference to the relevant RDFs, explain the following observations concerning the orbital energies of 3*s* and 3*p* shown in Fig. 2.41 on page 66:

(a) The ground state configuration of Na is $\ldots 3s^1$ and not $\ldots 3p^1$.

(b) In Al, the 3*s* is lower in energy than the 3*p*.

(c) As we go along the series Na . . . Ar, the energy of both the 3*s* and the 3*p* orbitals falls steadily; however, the energy of the 3*s* falls more rapidly than does that of the 3*p*.

What would you expect to happen to the energies of the 3*s* and 3*p* orbitals for elements with $Z > 18$ i.e. along the fourth period?

2.11 Calculate the effective nuclear charges of the following orbitals for Al and Ar. Comment on the differences of Z_{eff} values seen between these two elements, and between the two different types of orbital.

element	Z	energy of 3*s* (eV)	energy of 3*p* (eV)
Al	13	−10.7	−5.71
Ar	18	−34.8	−16.1

2.12 The electron in hydrogen can be promoted from one orbital to another by the absorption of a photon whose energy matches the energy difference between the two orbitals. This process is described as a transition.

If the electron starts in an orbital with principal quantum number n_1 and moves to an orbital with principal quantum number n_2 ($n_2 > n_1$), show that the energy change $\Delta E(n_1 \rightarrow n_2)$ is given by

$$\begin{aligned}\Delta E(n_1 \rightarrow n_2) &= E_{n_2} - E_{n_1} \\ &= R_{\text{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).\end{aligned}$$

The energy of a photon with frequency υ is $h\upsilon$, where h is Planck's constant (6.626×10^{-34} J s). Show that it follows that the frequency of a photon which can cause a transition from n_1 to n_2, $\upsilon_{n_1 \rightarrow n_2}$, is

$$\upsilon_{n_1 \rightarrow n_2} = \frac{R_{\text{H}}}{h}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$

Using $R_{\text{H}} = 2.180 \times 10^{-18}$ J, work out the frequency (which will be in Hz), of the transitions 2 → 3, 2 → 4 and 2 → 5.

Convert these frequencies to wavelengths using $c = \upsilon\lambda$, where c is the speed of light (2.998×10^8 m s^{-1}) and λ is the wavelength in m. Give your answers in m and nm.

What region of the electromagnetic spectrum do these transitions appear in?

2.13 Using a similar approach to that in the previous question, show that for a hydrogen-like (one-electron) atom with nuclear charge Z, the frequency of the photon needed to cause a transition from an orbital with principal quantum number n_1 to one with quantum number n_2 is

$$\upsilon_{n_1 \rightarrow n_2} = \frac{Z^2 R_{\text{H}}}{h}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$

Super-nova remnant E0102-72 is located some 200,000 light years from the Earth, and is 20 light years across. The matter contained in the remnant is at extremely high temperatures, up to millions of degrees. At such extremes, very highly ionized atoms are found, such as O^{7+} (which is a hydrogen-like atom).

In the light from this remnant, astronomers have observed transitions attributed to this ion. The transitions are thought to be 1 → 2, 1 → 3 and 1 → 4. Work out the frequency (in Hz) and wavelength (in nm) of the light which would cause these transitions. What part of the electromagnetic spectrum does this appear in?

2.14 Explain why it is that in a hydrogen-like atom the ionization energy is exactly equal to minus the orbital energy, whereas this is only approximately true for multi-electron atoms.

2.15 There are five 3*d* orbitals, which can accommodate a maximum of ten electrons. The lowest energy arrangement of the electrons in these five orbitals is shown opposite for the configurations d^1, d^2 and d^3. Explain why these are the lowest energy arrangements, and go on to complete the figure showing the lowest energy arrangements for d^4 to d^{10}.

For each configuration, work out the number of pairs of electrons with parallel spins, and hence draw up a table similar to Table 2.2 on page 75 showing the exchange contribution to the energy of the atom, the corresponding ion, and the difference between the two.

Finally, plot the difference of these exchange energies in a similar way to Fig. 2.50 (b) on page 76. What do these data imply about the variation in ionization energies of atoms with the configurations $d^1 \dots d^{10}$?