3

Atomic structure and properties

3.1 The classical picture of the atom

- Dalton's atomic theory in the early 1800s explained the law of conservation of mass and explained why reagents always react together in the same mass ratio.
- The first evidence for the internal structure of the atom was obtained in the early twentieth century. Experiments led to a model of the atom consisting of a tiny dense positively charged nucleus surrounded by electrons.

3.2 Electromagnetic radiation and quantization

- Electromagnetic radiation is a form of energy, consisting of oscillating electric and magnetic fields that travel at the speed of light, c.
- Electromagnetic radiation is quantized into photons. The energy of a photon, E, is equal to $E = h\nu$.
- In some circumstances electromagnetic radiation behaves as a wave; in others it behaves as particles.

For practice questions on these topics, see questions 1 and 2 at the end of this chapter (p.165).

3.3 Atomic Spectra and the Bohr atom

- Spectroscopic measurements show that atoms can only absorb or emit certain frequencies of electromagnetic radiation.
- Atomic spectra demonstrate that the electronic energies of atoms are quantized, with only certain values allowed.
- The Bohr model was the first quantum model of the atom.

For practice questions on these topics, see questions 3 and 4 at the end of this chapter (p.165).

3.4 The nature of the electron

- All matter has a wavelength associated with it, and very small objects such as electrons can behave as either particles or waves.
- The Heisenberg uncertainty principle states that it is impossible to know *both* the precise position and momentum of an object. For everyday objects the uncertainty is small enough to be insignificant, but for atoms and subatomic particles the uncertainty cannot be ignored.

For a practice question on these topics, see question 5 at the end of this chapter (p.165).

3.5 Wavefunctions and atomic orbitals

- In wave mechanics, the electron in the hydrogen atom is represented by a wavefunction ψ that is obtained from the Schrödinger equation. The region of space defined by a wavefunction is called an atomic orbital.
- It is impossible to know simultaneously the precise location and momentum of an electron in an atom, though the probability of finding the electron within a volume $d\tau$ is related to ψ^2. This gives the electron density.
- The wavefunction ψ can be divided into a radial part, $R(r)$, and an angular part, $Y(\theta, \phi)$. $R(r)$ tells you how the atomic orbital changes with distance from the nucleus. $Y(\theta, \phi)$ tells you about the shape of the atomic orbital.
- Atomic orbitals are characterized by three quantum numbers, n, l, and m_l.
  - The principal quantum number n can be any positive integer.
  - The secondary quantum number l can be any whole number between 0 and $(n - 1)$.
  - The magnetic quantum number m_l can be any whole number from $-l$ to $+l$.
- The shape of an atomic orbital depends on the value of l.
  - *s* orbitals ($l = 0$) are spherical.
  - *p* orbitals ($l = 1$) have a dumb-bell shape with one angular node.
  - *d* orbitals ($l = 2$) have two angular nodes.

For practice questions on these topics, see questions 6–10 at the end of this chapter (p.165).

3.6 Many-electron atoms

- The energies of the atomic orbitals for hydrogen depend only on n, but for other atoms electron–electron repulsions mean that orbitals with different values of l have different orbital energies. The lower the value of l, the lower the orbital energy.
- Each atomic orbital can hold two electrons, one with the spin magnetic quantum number $m_s = +\frac{1}{2}$, the other with $m_s = -\frac{1}{2}$.
- In a many-electron atom, the orbitals are filled using the aufbau principle, with the lowest energy orbital filled first, in combination with the Pauli exclusion principle, which states that no two electrons in an atom can have the same four quantum numbers.
- Orbitals of the same energy are filled using Hund's rule, with the number of parallel electrons maximized.
- Slater's rules allow the effective nuclear charge for an electron in an atom to be calculated.

For practice questions on these topics, see questions 11–16 at the end of this chapter (p.165–166).

3.7 Atomic properties and periodicity

- Atomic radii tend to decrease from left to right across a period of the Periodic Table, whereas first ionization energies tend to increase across a period. This is due to the increase in the effective nuclear charge on crossing a period.
- Atomic radii tend to increase and first ionization energies tend to decrease down groups of the Periodic Table. This is because the outermost electrons are in atomic orbitals that are located farther away from the nuclei.
- The electron gain energy is the energy change when an electron is added to an atom in the gas phase. First electron gain energies are most negative for elements in the top right of the Periodic Table (excluding Group 18), though the trends are less clear cut than for ionization energies.

For practice questions on these topics, see questions 17 and 18 at the end of this chapter (p.166).

3.8 Nuclear chemistry

- There are three main types of ionizing radiation: α-, β-, and γ-radiation. α- and β-radiation consist of charged particles, whereas γ-radiation consists of high-energy photons.
- Elements with atomic number greater than 92 are not naturally occurring and are called transuranic elements. They can be made by colliding nuclei together with very high energies.

For practice questions on these topics, see questions 19 and 20 at the end of this chapter (p.166).

Concept review

By the end of this chapter, you should be able to do the following.

- Describe experiments that helped determine the structure of the atom and the charge on the electron.
- Interconvert frequency and wavelength for electromagnetic radiation, and calculate the energy associated with photons from the frequency.
- Describe experiments that helped show wave–particle duality of photons and electrons.
- Calculate the frequencies of the lines in the atomic spectrum of hydrogen.
- Understand the concept of quantization.
- Understand the origins of emission spectra and absorption spectra.
- Calculate the wavelength of an object based on its mass and velocity.
- Describe the Heisenberg uncertainty principle, and use it to calculate uncertainty in position or momentum.
- Understand the significance of the principal quantum number, n, the secondary quantum number, l, and the magnetic quantum number, m_l.
- Given a value of n, calculate the allowed values of l and m_l.
- Describe the significance of ψ, ψ^2, and the radial distribution function.
- Understand that the wavefunction can be divided into a radial part, $R(r)$, and an angular part, $Y(\theta, \phi)$.
- Sketch plots of the radial wavefunction and the radial distribution function for any atomic orbital.
- Sketch the boundary surface for any atomic orbital and understand what it means.
- Work out the electronic configuration for any element using the aufbau principle, the Pauli exclusion principle, and Hund’s rule.
- Describe how the structure of the Periodic Table is determined by the numbers of different atomic orbitals.
- Describe the concepts of shielding and penetration, and show how they affect the relative energies of atomic orbitals in many-electron atoms.
- Calculate effective nuclear charge using Slater’s rules.
- Predict how atomic properties such as atomic radii, ionization energies, and electron gain energies vary on going down a group and across a period.
- Describe the processes involved in α-, β-, and γ-radiation, and predict the identity of decay products.

Key equations

Relationship between electromagnetic radiation wavelength and frequency	$c = \lambda\nu$	(3.1)
Energy of a photon	$E = h\nu$	(3.2)
Rydberg equation	$\nu = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$	(3.6)
de Broglie equation	$\lambda = \frac{h}{mv}$	(3.9)
Radial and angular wavefunction	$\psi(x, y, z) = \psi(r, \theta, \phi) = R(r) \times Y(\theta, \phi)$	(3.13)
Radial distribution function	Radial distribution function $= 4\pi r^2 R(r)^2$	(3.17)
Effective nuclear charge	$Z_{eff} = Z - S$	(3.19)