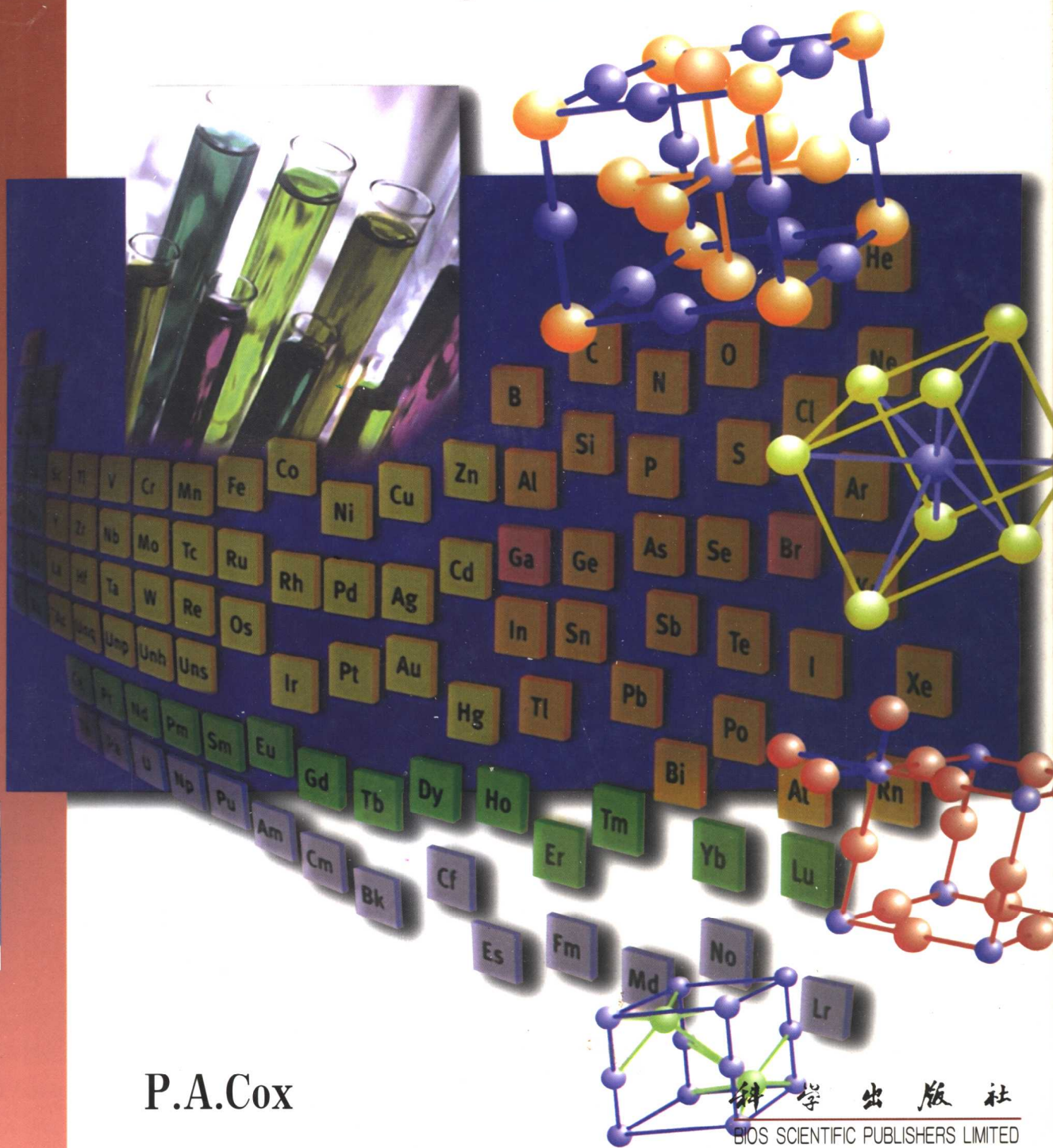精要速览系列 （影印版）

Instant Notes

INORGANIC CHEMISTRY

无机化学

P.A.Cox

科学出版社
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精要速览系列

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无 机 化 学

（影印版）

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内 容 简 介

本书是国外优秀教材畅销榜的上榜教材,面向大学本科生,由英国著名大学具有丰富教学经验的一流教授编写。它以一种风格独特的方式,全面、系统地概括了无机化学的核心内容和前沿动态,并以一种便于学习、利于复习的编写形式,使学生能快速、准确的掌握知识,很好地指导学习和考试。本书配有全新绘制和编写的插图与表格,非常有指导性,是其他教材无法比拟的。本书的简明和扼要也为大学教师备课提供了最好的参考。书中英文使用最为自然、易懂的语句,是提高专业外语的最佳用书。

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The Periodic Table of Elements. *A list of elements can be found inside the back cover.*

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac†															

*lanthanides

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

†actinides

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

ABBREVIATIONS

3c2e	three-center two-electron		IUPAC	International Union of Pure and Applied Chemistry
3c4e	three-center four-electron		L	unspecified ligand
3D	three dimensional		LCAO	linear combination of atomic orbitals
ADP	adenosine diphosphate			
An	actinide		LFSE	ligand field stabilization energy
AO	atomic orbital		LMCT	ligand-to-metal charge transfer
ATP	adenosine triphosphate		LUMO	lowest unoccupied molecular orbital
bcc	body-centered cubic		Ln	lanthanide
BO	bond order		M	unspecified (metallic) element
BP	boiling point		Me	methyl (CH_3)
CB	conduction band		MLCT	metal-to-ligand charge transfer
ccp	cubic close packing		MO	molecular orbital
CN	coordination number		MP	melting point
Cp	cyclopentadienyl (C_5H_5)		Ph	phenyl (C_6H_5)
E	unspecified (non-metallic) element		R	organic group (alkyl or aryl)
EA	electron affinity		RAM	relative atomic mass
EAN	effective atomic number		SN	steric number
EDTA	ethylenediamine tetraacetate		UV	ultraviolet
Et	ethyl (C_2H_5)		VB	valence band
fcc	face-centered cubic		VE	valence electron
hcp	hexagonal close packing		VSEPR	valence shell electron pair repulsion
HOMO	highest occupied molecular orbital		X	unspecified element (often a halogen)
HSAB	hard and soft acid-base		Z	atomic number
IE	(first) ionization energy			
I_n	nth ionization energy ($n = 1, 2, \ldots$)			

PREFACE

Inorganic chemistry is concerned with the chemical elements (of which there are about 100) and the extremely varied compounds they form. The essentially descriptive subject matter is unified by some general concepts of structure, bonding and reactivity, and most especially by the periodic table and its underlying basis in atomic structure. As with other books in the *Instant Notes* series, the present account is intended to provide a concise summary of the core material that might be covered in the first and second years of a degree-level course. The division into short independent topics should make it easy for students and teachers to select the material they require for their particular course.

Sections A–F discuss the general concepts of atomic structure, periodicity, structure and bonding, and solution chemistry. The following Sections F–I cover different areas of the periodic table in a more descriptive way, although in Section H some concepts that are peculiar to the study of transition metals are also discussed. The final section describes some aspects of inorganic chemistry in the world outside the laboratory.

I have assumed a basic understanding of chemical ideas and vocabulary, coming, for example, from an A-level chemistry course in the UK or a freshman chemistry course in the USA. Mathematics has been kept at a strict minimum in the discussion of atomic structure and bonding. A list of further reading is given for those interested in pursuing these or other aspects of the subject.

Many people have contributed directly or indirectly to the production of this book. I would particularly like to thank the following: Howard Stanbury for introducing me to the project; Lisa Mansell and other staff at BIOS for their friendliness and efficiency; the anonymous readers and my colleagues Bob Denning and Jenny Green for their helpful comments on the first draft; my students past and present for their enthusiasm, which has made teaching inorganic chemistry an enjoyable task; and Sue for her love and understanding.

CONTENTS

A1 THE NUCLEAR ATOM

Key Notes

Electrons and nuclei

An atom consists of a very small positively charged nucleus, surrounded by negative electrons held by electrostatic attraction. The motion of electrons changes when chemical bonds are formed, nuclei being unaltered.

Nuclear structure

Nuclei contain positive protons and uncharged neutrons. The number of protons is the atomic number (Z) of an element. The attractive strong interaction between protons and neutrons is opposed by electrostatic repulsion between protons. Repulsion dominates as Z increases and there is only a limited number of stable elements.

Isotopes

Isotopes are atoms with the same atomic number but different numbers of neutrons. Many elements consist naturally of mixtures of isotopes, with very similar chemical properties.

Radioactivity

Unstable nuclei decompose by emitting high-energy particles. All elements with Z > 83 are radioactive. The Earth contains some long-lived radioactive elements and smaller amount of short-lived ones.

Related topics

Actinium and the actinides (I2)

Origin and abundance of the elements (J1)

Electrons and nuclei

The familiar planetary model of the atom was proposed by Rutherford in 1912 following experiments by Geiger and Marsden showing that nearly all the mass of an atom was concentrated in a positively charged **nucleus**. Negatively charged **electrons** are attracted to the nucleus by the **electrostatic force** and were considered by Rutherford to 'orbit' it in a similar way to the planets round the Sun. It was soon realized that a proper description of atoms required the quantum theory; although the planetary model remains a useful analogy from the macroscopic world, many of the physical ideas that work for familiar objects must be abandoned or modified at the microscopic atomic level.

The lightest atomic nucleus (that of hydrogen) is 1830 times more massive than an electron. The size of a nucleus is around 10^{-15} m (1 fm), a factor of 10^5 smaller than the apparent size of an atom, as measured by the distances between atoms in molecules and solids. Atomic sizes are determined by the radii of the electronic orbits, the electron itself having apparently no size at all. Chemical bonding between atoms alters the motion of electrons, the nuclei remaining unchanged. Nuclei retain the 'chemical identity' of an element, and the occurrence of chemical elements depends on the existence of stable nuclei.

Nuclear structure

Nuclei contain positively charged **protons** and uncharged **neutrons**; these two particles with about the same mass are known as **nucleons**. The number of

protons is the **atomic number** of an element (Z), and is matched in a neutral atom by the same number of electrons. The total number of nucleons is the **mass number** and is sometimes specified by a superscript on the symbol of the element. Thus ^{1}H has a nucleus with one proton and no neutrons, ^{16}O has eight protons and eight neutrons, ^{208}Pb has 82 protons and 126 neutrons.

Protons and neutrons are held together by an attractive force of extremely short range, called the **strong interaction**. Opposing this is the longer-range electrostatic repulsion between protons. The balance of the two forces controls some important features of nuclear stability.

● Whereas lighter nuclei are generally stable with approximately equal numbers of protons and neutrons, heavier ones have a progressively higher proportion of neutrons (e.g. compare ^{16}O with ^{208}Pb).
● As Z increases the electrostatic repulsion comes to dominate, and there is a limit to the number of stable nuclei, all elements beyond Bi (Z = 83) being radioactive (see below).

As with electrons in atoms, it is necessary to use the quantum theory to account for the details of nuclear structure and stability. It is favorable to 'pair' nucleons so that nuclei with even numbers of either protons or neutrons (or both) are generally more stable than ones with odd numbers. The **shell model** of nuclei, analogous to the orbital picture of atoms (see Topics A2 and A3) also predicts certain **magic numbers** of protons or neutrons, which give extra stability. These are

2   8   20   28   50   82   126

^{16}O and ^{208}Pb are examples of nuclei with magic numbers of both protons and neutrons.

Trends in the stability of nuclei are important not only in determining the number of elements and their isotopes (see below) but also in controlling the proportions in which are they are made by nuclear reactions in stars. These determine the abundance of elements in the Universe as a whole (see Topic J1).

Isotopes

Atoms with the same atomic number and different numbers of neutrons are known as **isotopes**. The chemical properties of an element are determined largely by the charge on the nucleus, and different isotopes of an element have very similar chemical properties. They are not quite identical, however, and slight differences in chemistry and in physical properties allow isotopes to be separated if desired.

Some elements have only one stable isotope (e.g. ^{19}F, ^{27}Al, ^{31}P), others may have several (e.g. ^{1}H and ^{2}H, the latter also being called **deuterium**, ^{12}C and ^{13}C); the record is held by tin (Sn), which has no fewer than 10. Natural samples of many elements therefore consist of mixtures of isotopes in nearly fixed proportions reflecting the ways in which these were made by nuclear synthesis. The **molar mass** (also known as **relative atomic mass**, RAM) of elements is determined by these proportions. For many chemical purposes the existence of such isotopic mixtures can be ignored, although it is occasionally significant.

● Slight differences in chemical and physical properties can lead to small variations in the isotopic composition of natural samples. They can be exploited to give geological information (dating and origin of rocks, etc.) and lead to small variations in the molar mass of elements.

- Some spectroscopic techniques (especially **nuclear magnetic resonance, NMR**) exploit specific properties of particular nuclei. Two important NMR nuclei are ^{1}H and ^{13}C. The former makes up over 99.9% of natural hydrogen, but ^{13}C is present as only 1.1% of natural carbon. These different abundances are important both for the sensitivity of the technique and the appearance of the spectra.
- Isotopes can be separated and used for specific purposes. Thus the slight differences in chemical behavior between normal hydrogen (^{1}H) and deuterium (^{2}H) can be used to investigate the detailed mechanisms of chemical reactions involving hydrogen atoms.

In addition to stable isotopes, all elements have unstable **radioactive** ones (see below). Some of these occur naturally, others can be made artificially in particle accelerators or nuclear reactors. Many radioactive isotopes are used in chemical and biochemical research and for medical diagnostics.

Radioactivity

Radioactive decay is a process whereby unstable nuclei change into more stable ones by emitting particles of different kinds. **Alpha, beta** and **gamma** (α, β and γ) radiation was originally classified according to its different penetrating power. The processes involved are as follows.

- An α particle is a ^{4}He nucleus, and is emitted by some heavy nuclei, giving a nucleus with Z two units less and mass number four units less. For example, ^{238}U (Z = 92) undergoes α decay to give (radioactive) ^{234}Th (Z = 90).
- A β particle is an electron. Its emission by a nucleus increases Z by one unit, but does not change the mass number. Thus ^{14}C (Z = 6) decays to (stable) ^{14}N (Z = 7).
- γ radiation consists of high-energy electromagnetic radiation. It often accompanies α and β decay.

Some other decay processes are known. Very heavy elements can decay by **spontaneous fission**, when the nucleus splits into two fragments of similar mass. A transformation opposite to that in normal β decay takes place either by **electron capture** by the nucleus, or by emission of a positron (β^+) the positively charged antiparticle of an electron. Thus the natural radioactive isotope ^{40}K (Z = 19) can undergo normal β decay to ^{40}Ca (Z = 20), or electron capture to give ^{40}Ar (Z = 18).

Radioactive decay is a statistical process, there being nothing in any nucleus that allows us to predict when it will decay. The probability of decay in a given time interval is the only thing that can be determined, and this appears to be entirely constant in time and (except in the case of electron capture) unaffected by temperature, pressure or the chemical state of an atom. The probability is normally expressed as a **half-life**, the time taken for half of a sample to decay. Half-lives can vary from a fraction of a second to billions of years. Some naturally occurring radioactive elements on Earth have very long half-lives and are effectively left over from the synthesis of the elements before the formation of the Earth. The most important of these, with their half-lives in years, are ^{40}K (1.3×10^9), ^{232}Th (1.4×10^{10}) and ^{238}U (4.5×10^9).

The occurrence of these long-lived radioactive elements has important consequences. Radioactive decay gives a heat source within the Earth, which ultimately fuels many geological processes including volcanic activity and long-term generation and movement of the crust. Other elements result from radioactive decay, including helium and argon and several short-lived radioactive elements coming from the decay of thorium and uranium (see Topic I2).

All elements beyond bismuth ($Z = 83$) are radioactive, and none beyond uranium ($Z = 92$) occur naturally on Earth. With increasing numbers of protons heavier elements have progressively less stable nuclei with shorter half-lives. Elements with Z up to 110 have been made artificially but the half-lives beyond Lr ($Z = 103$) are too short for chemical investigations to be feasible. Two lighter elements, technetium (Tc, $Z = 43$) and promethium (Pm, $Z = 61$), also have no stable isotopes.

Radioactive elements are made artificially by bombarding other nuclei, either in particle accelerators or with neutrons in nuclear reactors (see Topic I2). Some short-lived radioactive isotopes (e.g. ^{14}C) are produced naturally in small amounts on Earth by cosmic-ray bombardment in the upper atmosphere.

A2 ATOMIC ORBITALS

Key Notes

Wavefunctions
The quantum theory is necessary to describe electrons. It predicts discrete allowed energy levels and wavefunctions, which give probability distributions for electrons. Wavefunctions for electrons in atoms are called atomic orbitals.

Quantum numbers and nomenclature
Atomic orbitals are labeled by three quantum numbers n, l and m. Orbitals are called s, p, d or f according to the value of l; there are respectively one, three, five and seven different possible m values for these orbitals.

Angular functions: 'shapes'
s orbitals are spherical. p orbitals have two directional lobes, which can point in three possible directions. d and f orbitals have correspondingly greater numbers of directional lobes.

Radial distributions
The radial distribution function shows how far from the nucleus an electron is likely to be found. The major features depend on n but there is some dependence on l.

Energies in hydrogen
The allowed energies in hydrogen depend on n only. They can be compared with experimental line spectra and the ionization energy.

Hydrogenic ions
Increasing nuclear charge in a one-electron ion leads to contraction of the orbital and an increase in binding energy of the electron.

Related topics
Many-electron atoms (A3)

Molecular orbitals: homonuclear diatomics (C3)

Wavefunctions

To understand the behavior of electrons in atoms and molecules requires the use of **quantum mechanics**. This theory predicts the allowed **quantized** energy levels of a system and has other features that are very different from 'classical' physics. Electrons are described by a **wavefunction**, which contains all the information we can know about their behavior. The classical notion of a definite trajectory (e.g. the motion of a planet around the Sun) is not valid at a microscopic level. The quantum theory predicts only **probability distributions**, which are given by the square of the wavefunction and which show where electrons are more or less likely to be found.

Solutions of **Schrödinger's wave equation** give the allowed energy levels and the corresponding wavefunctions. By analogy with the orbits of electrons in the 'classical planetary model (see Topic A1), wavefunctions for atoms are known as **atomic orbitals**. Exact solutions of Schrödinger's equation can be obtained only for one-electron atoms and ions, but the atomic orbitals that result from these solutions provide pictures of the behavior of electrons that can be extended to many-electron atoms and molecules (see Topics A3 and C3–C6).

Quantum numbers and nomenclature

The atomic orbitals of hydrogen are labeled by **quantum numbers**. Three integers are required for a complete specification.

- The **principal quantum number** n can take the values $1, 2, 3, \ldots$ It determines how far from the nucleus the electron is most likely to be found.
- The **angular momentum** (or **azimuthal**) **quantum number** l can take values from zero up to a maximum of $n - 1$. It determines the total angular momentum of the electron about the nucleus.
- The **magnetic quantum number** m can take positive and negative values from $-l$ to $+l$. It determines the direction of rotation of the electron. Sometimes m is written m_l to distinguish it from the spin quantum number m_s (see Topic A3).

Table 1 shows how these rules determine the allowed values of l and m for orbitals with $n = 1 - 4$. The values determine the structure of the periodic table of elements (see Section A4).

Atomic orbitals with $l = 0$ are called s **orbitals**, those with $l = 1, 2, 3$ are called p, d, f **orbitals**, respectively. It is normal to specify the value of n as well, so that, for example, $1s$ denotes the orbital with $n = 1, l = 0$, and $3d$ the orbitals with $n = 3, l = 2$. These labels are also shown in *Table 1*. For any type of orbital $2l + 1$ values of m are possible; thus there are always three p orbitals for any n, five d orbitals, and seven f orbitals.

Angular functions: 'shapes'

The mathematical functions for atomic orbitals may be written as a product of two factors: the **radial wavefunction** describes the behavior of the electron as a function of distance from the nucleus (see below); the **angular wavefunction** shows how it varies with the direction in space. Angular wavefunctions do not depend on n and are characteristic features of $s, p, d, \ldots$ orbitals.

Diagrammatic representations of angular functions for s, p and d orbitals are shown in *Fig. 1*. Mathematically, they are essentially **polar diagrams** showing how

Table 1. Atomic orbitals with $n = 1-4$

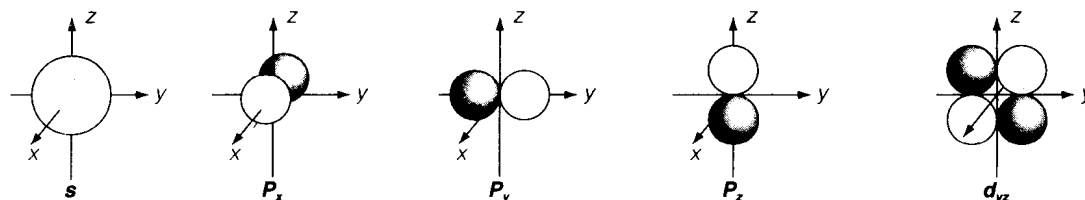| n	l	m	Name
1	0	0	1s
2	0	0	2s
2	1	$-1, 0, +1$	2p
3	0	0	3s
3	1	$-1, 0, +1$	3p
3	2	$-2, -1, 0 +1, +2$	3d
4	0	0	4s
4	1	$-1, 0, +1$	4p
4	2	$-2, -1, 0, +1, +2$	4d
4	3	$-3, -2, -1, 0, +1, +2, +3$	4f

Fig. 1. The shapes of s, p and d orbitals. Shading shows negative values of the wavefunction. More d orbitals are shown in Topic H2, Fig. 1.

the angular wavefunction depends on the polar angles θ and ϕ. More informally, they can be regarded as **boundary surfaces** enclosing the region(s) of space where the electron is most likely to be found. An s orbital is represented by a sphere, as the wavefunction does not depend on angle, so that the probability is the same for all directions in space. Each p orbital has two lobes, with positive and negative values of the wavefunction either side of the nucleus, separated by a **nodal plane** where the wavefunction is zero. The three separate p orbitals corresponding to the allowed values of m are directed along different axes, and sometimes denoted p_x, p_y and p_z. The five different d orbitals (one of which is shown in *Fig. 1*) each have two nodal planes, separating two positive and two negative regions of wavefunction. The f orbitals (not shown) each have three nodal planes.

The shapes of atomic orbitals shown in *Fig. 1* are important in understanding the bonding properties of atoms (see Topics C3–C5 and H2).

Radial distributions

Radial wavefunctions depend on n and l but not on m; thus each of the three $2p$ orbitals has the same radial form. The wavefunctions may have positive or negative regions, but it is more instructive to look at how the **radial probability distributions** for the electron depend on the distance from the nucleus. They are shown in *Fig. 2* and have the following features.

- Radial distributions may have several peaks, the number being equal to $n-l$.
- The outermost peak is by far the largest, showing where the electron is most likely to be found. The distance of this peak from the nucleus is a measure of the radius of the orbital, and is roughly proportional to n^2 (although it depends slightly on l also).
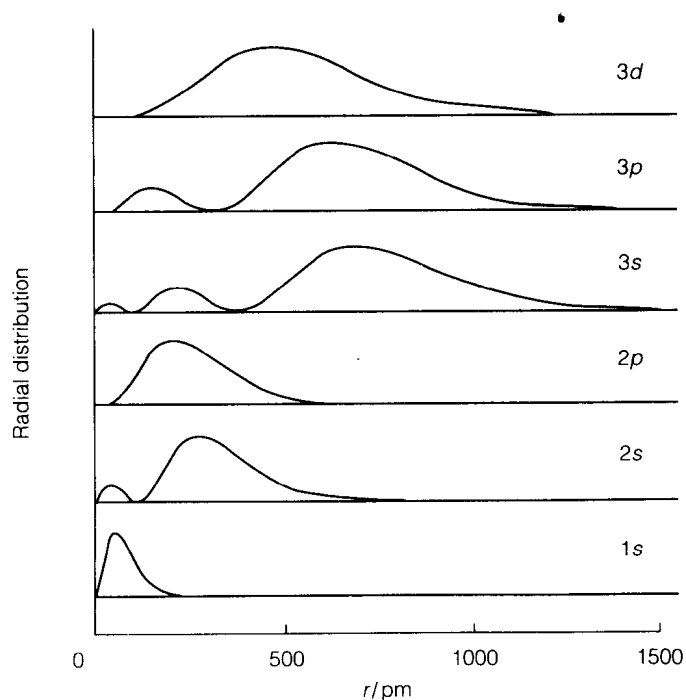

Fig. 2.   Radial probability distributions for atomic orbitals with n = 1 – 3.

Radial distributions determine the energy of an electron in an atom. As the average distance from the nucleus increases, an electron becomes less tightly bound. The subsidiary maxima at smaller distances are not significant in hydrogen, but are important in understanding the energies in many-electron atoms (see Topic A3).

Energies in hydrogen

The energies of atomic orbitals in a hydrogen atom are given by the formula

$$E_n = -R/n^2 \tag{1}$$

We write E_n to show that the energy depends only on the principal quantum number n. Orbitals with the same n but different values of l and m have the same energy and are said to be **degenerate**. The negative value of energy is a reflection of the definition of energy zero, corresponding to $n = \infty$ which is the **ionization limit** where an electron has enough energy to escape from the atom. All orbitals with finite n represent bound electrons with lower energy. The **Rydberg constant** R has the value 2.179×10^{-18} J, but is often given in other units. Energies of individual atoms or molecules are often quoted in **electron volts** (eV), equal to about 1.602×10^{-19} J. Alternatively, multiplying the value in joules by the Avogadro constant gives the energy per mole of atoms. In these units

$$R = 13.595 \text{ eV per atom}$$
$$= 1\,312 \text{ kJ mol}^{-1}$$

The predicted energies may be compared with measured **atomic line spectra** in which light quanta (photons) are absorbed or emitted as an electron changes its energy level, and with the **ionization energy** required to remove an electron. For a hydrogen atom initially in its lowest-energy **ground state**, the ionization energy is the difference between E_n with $n = 1$ and ∞, and is simply R.

Hydrogenic ions

The exact solutions of Schrödinger's equation can be applied to **hydrogenic ions** with one electron: examples are He^+ and Li^{2+}. Orbital sizes and energies now depend on the atomic number Z, equal to the number of protons in the nucleus. The average radius $<r>$ of an orbital is

$$<r> \approx n^2 a_0 / Z \tag{2}$$

where a_0 is the **Bohr radius** (59 pm), the average radius of a $1s$ orbital in hydrogen. Thus electron distributions are pulled in towards the nucleus by the increased electrostatic attraction with higher Z. The energy (see Equation 1) is

$$E_n = -Z^2 R/n^2 \tag{3}$$

The factor Z^2 arises because the electron-nuclear attraction at a given distance has increased by Z, and the average distance has also decreased by Z. Thus the ionization energy of He^+ ($Z = 2$) is four times that of H, and that of Li^{2+} ($Z = 3$) nine times.