

CATHERINE E. HOUSECROFT & ALAN G. SHARPE

# INORGANIC CHEMISTRY

FIFTH EDITION



 Pearson

## Elements

Element	Symbol	Atomic number, Z	Relative atomic mass, $A_r^s/\text{g mol}^{-1}$	Element	Symbol	Atomic number, Z	Relative atomic mass, $A_r^s/\text{g mol}^{-1}$	Element	Symbol	Atomic number, Z	Relative atomic mass, $A_r^s/\text{g mol}^{-1}$
Actinium	Ac	89	[227]	Hafnium	Hf	72	178.49	Praseodymium	Pr	59	140.91
Aluminium	Al	13	26.98	Hassium	Hs	108	[270]	Promethium	Pm	61	[145]
Americium	Am	95	[243]	Helium	He	2	4.00	Protactinium	Pa	91	231.04
Antimony	Sb	51	121.76	Holmium	Ho	67	164.93	Radium	Ra	88	[226]
Argon	Ar	18	39.95	Hydrogen	H	1	1.008	Radon	Rn	86	[222]
Arsenic	As	33	74.92	Indium	In	49	114.82	Rhenium	Re	75	186.21
Astatine	At	85	[210]	Iodine	I	53	126.90	Rhodium	Rh	45	102.91
Barium	Ba	56	137.33	Iridium	Ir	77	192.22	Roentgenium	Rg	111	[281]
Berkelium	Bk	97	[247]	Iron	Fe	26	55.85	Rubidium	Rb	37	85.47
Beryllium	Be	4	9.01	Krypton	Kr	36	83.80	Ruthenium	Ru	44	101.07
Bismuth	Bi	83	208.98	Lanthanum	La	57	138.91	Rutherfordium	Rf	104	[267]
Bohrium	Bh	107	[270]	Lawrencium	Lr	103	[262]	Samarium	Sm	62	150.36
Boron	B	5	10.81	Lead	Pb	82	207.2	Scandium	Sc	21	44.96
Bromine	Br	35	79.91	Lithium	Li	3	6.94	Seaborgium	Sg	106	[269]
Cadmium	Cd	48	112.41	Livermorium	Lv	116	[293]	Selenium	Se	34	78.97
Caesium	Cs	55	132.91	Lutetium	Lu	71	174.97	Silicon	Si	14	28.09
Calcium	Ca	20	40.08	Magnesium	Mg	12	24.31	Silver	Ag	47	107.87
Californium	Cf	98	[251]	Manganese	Mn	25	54.94	Sodium	Na	11	22.99
Carbon	C	6	12.01	Meitnerium	Mt	109	[278]	Strontium	Sr	38	87.62
Cerium	Ce	58	140.12	Mendelevium	Md	101	[258]	Sulfur	S	16	32.06
Chlorine	Cl	17	35.45	Mercury	Hg	80	200.59	Tantalum	Ta	73	180.95
Chromium	Cr	24	52.00	Molybdenum	Mo	42	95.95	Technetium	Tc	43	[97]
Cobalt	Co	27	58.93	Moscovium	Mc	115	[289]	Tellurium	Te	52	127.60
Copernicium	Cn	112	[285]	Neodymium	Nd	60	144.24	Tennessee	Ts	117	[294]
Copper	Cu	29	63.54	Neon	Ne	10	20.18	Terbium	Tb	65	158.93
Curium	Cm	96	[247]	Neptunium	Np	93	[237]	Thallium	Tl	81	204.38
Darmstadtium	Ds	110	[281]	Nickel	Ni	28	58.69	Thorium	Th	90	232.04
Dubnium	Db	105	[270]	Nihonium	Nh	113	[285]	Thulium	Tm	69	168.93
Dysprosium	Dy	66	162.50	Niobium	Nb	41	92.91	Tin	Sn	50	118.71
Einsteinium	Es	99	[252]	Nitrogen	N	7	14.01	Titanium	Ti	22	47.87
Erbium	Er	68	167.26	Nobelium	No	102	[259]	Tungsten	W	74	183.84
Europium	Eu	63	151.96	Oganesson	Og	118	[294]	Uranium	U	92	283.03
Fermium	Fm	100	[257]	Osmium	Os	76	190.23	Vanadium	V	23	50.94
Flerovium	Fl	114	[289]	Oxygen	O	8	16.00	Xenon	Xe	54	131.29
Fluorine	F	9	19.00	Palladium	Pd	46	106.42	Ytterbium	Yb	70	173.04
Francium	Fr	87	[223]	Phosphorus	P	15	30.97	Yttrium	Y	39	88.91
Gadolinium	Gd	64	157.25	Platinum	Pt	78	195.08	Zinc	Zn	30	65.38
Gallium	Ga	31	69.72	Plutonium	Pu	94	[244]	Zirconium	Zr	40	91.22
Germanium	Ge	32	72.63	Polonium	Po	84	[209]				
Gold	Au	79	196.97	Potassium	K	19	39.10				

<sup>s</sup>Where an element does not possess a stable isotope, a mass number in [ ] is given; the mass number given is for the longest-lived isotope of the element. For each of Th, Pa and U, the value of  $A_r$  is based on the terrestrial isotopic composition.

# Periodic table

		1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18										
		Atomic number, Z		Element symbol		Relative atomic mass, A <sub>r</sub>																																								
1	1	H	1.008	2	He	4.00																																								
3	3	Li	6.94	4	Be	9.01																																								
11	11	Na	22.99	12	Mg	24.31																																								
19	19	K	39.10	20	Ca	40.08	21	Sc	44.96	22	Ti	47.87	23	V	50.94	24	Cr	52.00	25	Mn	54.94	26	Fe	55.85	27	Co	58.93	28	Ni	58.69	29	Cu	63.54	30	Zn	65.38										
37	37	Rb	85.47	38	Sr	87.62	39	Y	88.91	40	Zr	91.22	41	Nb	92.91	42	Mo	95.95	43	Tc	[97]	44	Ru	101.07	45	Rh	102.91	46	Pd	106.42	47	Ag	107.87	48	Cd	112.41										
55	55	Cs	132.91	56	Ba	137.33	57	La-Lu		72	Hf	178.49	73	Ta	180.95	74	W	183.84	75	Re	186.21	76	Os	190.23	77	Ir	192.22	78	Pt	195.08	79	Au	196.97	80	Hg	200.59										
87	87	Fr	[223]	88	Ra	[226]	89	Ac-Lr		104	Rf	[267]	105	Db	[270]	106	Sg	[269]	107	Bh	[270]	108	Hs	[270]	109	Mt	[278]	110	Ds	[281]	111	Rg	[281]	112	Cn	[285]										

<b>Lanthanoids</b>		57	La	138.91	58	Ce	140.12	59	Pr	140.91	60	Nd	144.24	61	Pm	[145]	62	Sm	150.36	63	Eu	151.96	64	Gd	157.25	65	Tb	158.93	66	Dy	162.50	67	Ho	164.93	68	Er	167.26	69	Tm	168.93	70	Yb	173.04	71	Lu	174.97
<b>Actinoids</b>		89	Ac	[227]	90	Th	232.04	91	Pa	231.04	92	U	238.03	93	Np	[237]	94	Pu	[244]	95	Am	[243]	96	Cm	[247]	97	Bk	[247]	98	Cf	[251]	99	Es	[252]	100	Fm	[257]	101	Md	[258]	102	No	[259]	103	Lr	[262]

Mass numbers in [ ] refer to elements which possess no stable nuclides; the mass number given is for the longest-lived isotope of the element. For each of Th, Pa and U, the value of A<sub>r</sub> is based on the terrestrial isotopic composition.

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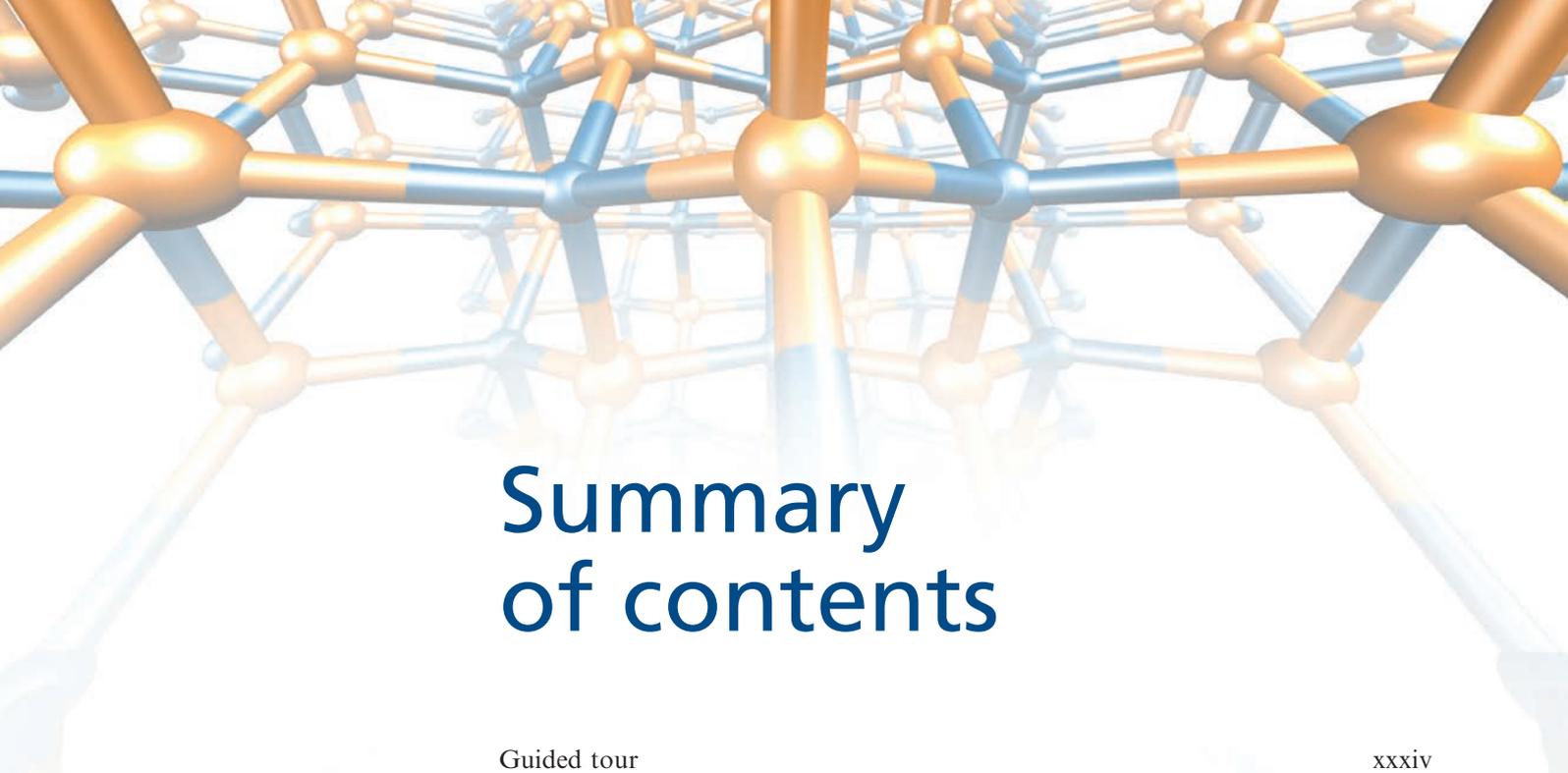
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- Interactive periodic table

### For instructors

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Also: The Companion Website provides the following features:

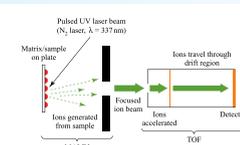
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# Guided tour

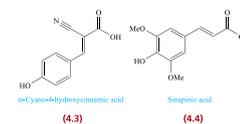
Key definitions are highlighted

100 CHAPTER 4 • Experimental techniques



**Fig. 4.9.** Schematic representation of the components in a MALDI-TOF mass spectrometer.

of the molecules of sample. Combination with  $H^+$  or  $Na^+$  produces  $[M+H]^+$  or  $[M+Na]^+$  ions and, since MALDI is a 'soft' method, there is usually little fragmentation of the parent ions. Multiply charged ions are rarely formed.



**(4.3)** **(4.4)**

ions leaving the sample plate are focused into a beam and accelerated in an electric field in such a way that all singly charged ions possess the same amount of kinetic energy. Since kinetic energy is  $\frac{1}{2}mv^2$ , ions with the highest masses have the lowest velocities and longer flight times along the drift region in the flight tube (Fig. 4.9), and vice versa. Ions with the same  $m/z$  ratio possess the same travel time and the data are converted into a conventional mass spectrum. However, the nature of the TOF method of analysis means that broader peaks are observed than in EI, FAB or ESI mass spectrometry with the result that isotope patterns are not usually well resolved.

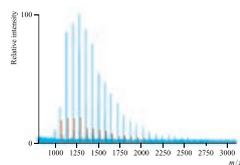
**Worked example 4.5 MALDI-TOF mass spectrum of a polydimethylsiloxane**

The MALDI-TOF mass spectrum (positive mode) of a sample of a polydimethylsiloxane elastomer is shown in the next column.

**Its repeat unit is:**



**Linear polymer chains may be terminated in Me or OH units; cyclic oligomers are also possible.**



The main spectrum (in blue) is accompanied by a sub-spectrum (in red), and in each spectrum, the spacings between consecutive lines is  $m/z$  74. Rationalize the appearance of the mass spectrum.

[Data: S.M. Hunt *et al.* (2000) *Polym. Int.*, vol. 49, p. 633.]

The value of  $m/z$  74 corresponds to an  $Me_2SiO$  monomer unit. Therefore the series of blue peaks arises from polymer chains of different lengths. Similarly for the set of red peaks. The observation of two series indicates that both cyclic and linear polymer chains are present. A cyclic oligomer has the formula  $(Me_2SiO)_n$ . For a particular chain length, a linear oligomer has a higher molecular mass than the corresponding cyclic oligomer because of the presence of the end groups (Me or OH).

The relative intensities of the two spectra reveal that cyclic oligomers dominate over linear chains.

**Self-study exercises**

These questions refer to the data in the worked example.

- Polydimethylsiloxanes are neutral species. How do the positive ions observed in the MALDI-TOF experiment arise?
- Give a formula for the positive ion observed at  $m/z$  985.
- Use Appendix 3 to explain why each of the peaks shown in the figure above consists of an envelope of peaks.

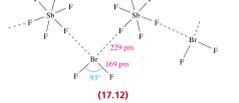
Worked examples are given throughout the text

Interhalogen compounds and polyhalogen ions 629

**Table 17.4** Structures of selected interhalogens and derived anions. Each is consistent with VSEPR theory.

Shape	Examples
Linear	$[ClF_2]^-$ , $[IF_2]^-$ , $[ICl_2]^-$ , $[IBr_2]^-$
Bent	$[ClF_3]^-$ , $[BrF_3]^-$ , $[ICl_3]^-$
T-shaped	$ClF_3$ , $BrF_3$ , $IF_3$ , $ICl_3$
Square planar	$[ClF_4]^-$ , $[BrF_4]^-$ , $[IF_4]^-$ , $[ICl_4]^-$
See saw, 17.11	$ClF_3$ , $BrF_3$ , $IF_3$
Square-based pyramidal	$ClF_5$ , $BrF_5$ , $IF_5$
Pentagonal planar	$[IF_6]^{2-}$
Octahedral	$[ClF_6]^{2-}$ , $[BrF_6]^{2-}$ , $[IF_6]^{2-}$
Pentagonal bipyramidal	$IF_7$
Square antiprismatic	$[IF_8]^{2-}$

Of particular interest in Table 17.4 is  $[IF_6]^{2-}$ . Only two examples of pentagonal planar  $XY_5$  species are known, the other being  $[XeF_5]^-$  (see Section 18.4). In salts such as  $[BrF_2][SbF_6]$ ,  $[ClF_2][SbF_6]$  and  $[BrF_2][Sb_2F_{11}]$ , there is significant cation-anion interaction. Diagram 17.12 focuses on the Br environment on the solid state structure of  $[BrF_2][SbF_6]$ , and Fig. 17.9b shows part of a chain of alternating cations and anions in crystalline  $[BrF_2][Sb_2F_{11}]$ .



**(17.12)**

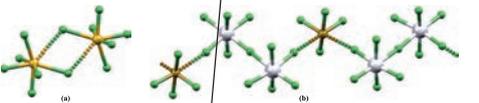
Low-temperature X-ray diffraction data show that solid  $ClF_3$  contains discrete T-shaped molecules, but in solid  $BrF_3$  and  $IF_3$  there are intermolecular X...F...X bridges resulting in coordination spheres not unlike those in  $[BrF_4]^-$  and  $[IF_4]^-$ .

On the whole, the observed structures of interhalogen anions and cations (Table 17.4) agree with the VSEPR model, but  $[BrF_6]^{2-}$  is regular octahedral, indicating the presence of a stereochemically inactive lone pair. Raman spectroscopic data suggest that  $[ClF_6]^{2-}$  is isostructural with  $[BrF_6]^{2-}$ . On the other hand, the vibrational spectrum of  $[IF_6]^{2-}$  shows it is not regular octahedral; however, on the  $^{19}F$  NMR timescale,  $[IF_6]^{2-}$  is stereochemically nonrigid. The difference between the structures of  $[BrF_6]^{2-}$  and  $[IF_6]^{2-}$  may be rationalized in terms of the difference in size of the central atom (see Section 16.7,  $[SbF_6]^{3-}$  versus  $[SbCl_6]^{3-}$ ). However, a word of caution: the solid state structure of  $[Me_4N][IF_6]$  reveals the presence of loosely bound  $[IF_5]^{2-}$  dimers (Fig. 17.9a).

**Self-study exercises**

$^{127}I$  (100%,  $J = \frac{5}{2}$ ) is a quadrupolar nucleus (see Section 4.8), but under certain circumstances (e.g. highly symmetrical environment), narrow line widths can be observed for signals in a  $^{127}I$  NMR spectrum. Rationalize why the  $^{127}I$  NMR spectrum of a liquid  $HF$  solution of  $[BrF_2][Sb_2F_{11}]$  exhibits a well-resolved binomial septet. (Ans. See J.F. Lehmann *et al.* (2004) *Inorg. Chem.*, vol. 43, p. 6905)

- Draw the structure of an  $[Sb_2F_{11}]^-$  anion which possesses  $D_{3h}$  symmetry. Indicate on the diagram where the  $C_2$  axis and  $\sigma_h$  plane lie. Compare this structure with the structures of the  $[Sb_2F_{11}]^-$  ions shown in Figs. 15.15b and 17.9. Comment on how the anion is able to change its conformation, and what factors might affect the structure.



**Fig. 17.9.** (a) The structure of the  $[BrF_2]^{2+}$  dimer present in  $[Me_4N][IF_6]$  (determined by X-ray diffraction): the I-F bond distances are 211 and 282 pm [A.R. Mahjoub *et al.* (1993) *Angew. Chem. Int. Ed.*, vol. 30, p. 321]. Colour code: I, gold; F, green. (b) The solid state structure of  $[BrF_2][Sb_2F_{11}]$  (determined by X-ray diffraction) consists of infinite chains of  $[BrF_2]^{2+}$  and  $[Sb_2F_{11}]^-$  ions supported by Br...F interactions (Br...F = 235 and 241 pm, Sb-F<sub>ax</sub> = 184 pm, Sb-F<sub>eq</sub> = 190 pm, Br-F<sub>ax</sub> = 173 pm, Br-F<sub>eq</sub> = 160 pm) [A. Vijay *et al.* (2002) *Inorg. Chem.*, vol. 41, p. 6397]. Colour code: Br, brown; Sb, silver; F, green.

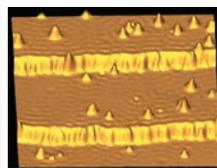
**Self-study exercises** allow students to test their understanding

**THEORY**

**Box 25.2 Some experimental techniques used in surface science**

In much of this book, we have been concerned with studying species that are soluble and subjected to solution techniques (see Chapter 4) such as NMR and electronic spectroscopy, or with structural data obtained from X-ray or neutron diffraction studies of single crystals or electron diffraction studies of gases. The investigation of solid surfaces requires specialist techniques, many of which have been developed relatively recently. Selected examples are listed in the table below.

For further details of solid state techniques, see:  
 S. Bordiga, E. Groppo, G. Agostini, J.A. van Bokhoven and C. Lamberti (2013) *Chem. Rev.*, vol. 113, p. 1736 – ‘Reactivity of surface species in heterogeneous catalysts probed by in situ X-ray absorption techniques’.  
 G. Brucco and B. Holst, eds. (2013) *Surface Science Techniques*, Springer-Verlag, Berlin.  
 J. Evans (1997) *Chem. Soc. Rev.*, vol. 26, p. 11 – ‘Shining light on metal catalysis’.  
 J. Evans (2006) *Phys. Chem. Chem. Phys.*, vol. 8, p. 3045 – ‘Brilliant opportunities across the spectrum’.  
 G.A. Somorjai and Y. Li (2010) *Introduction to Surface Chemistry and Catalysis*, 2nd edn, Wiley, New Jersey.  
 A.R. West (1999) *Basic Solid State Chemistry*, 2nd edn, Wiley, Chichester.



A false colour image obtained using scanning tunnelling microscopy (STM) of Co and Ag adatoms on a Cu surface. A one-atom high step edge runs across the image. Compare this to the schematic representation in Fig. 25.13.

Acronym	Technique	Application and description of technique
AES	Auger electron spectroscopy	Study of surface composition
AFM	Atomic force microscopy	Study of surface structure, composition and adsorbed species
EXAFS	Extended X-ray absorption fine structure	Estimation of internuclear distances around a central atom
FTIR	Fourier transform infrared spectroscopy	Study of adsorbed species
HREELS	High-resolution electron energy loss spectroscopy	Study of adsorbed species
LEED	Low-energy electron diffraction	Study of structural features of the surface and of adsorbed species
SIMS	Secondary ion mass spectrometry	Study of surface composition
STM	Scanning tunnelling microscopy	Obtaining images of a surface and adsorbed species at an atomic level
XANES	X-ray absorption near edge spectroscopy	Study of oxidation states of surface atoms
XRD	X-ray diffraction	Investigation of phases and particle sizes
XPS (ESCA)	X-ray photoelectron spectroscopy (electron spectroscopy for chemical analysis)	Study of surface composition and oxidation states of surface atoms

observed when the surface is half-occupied by a monolayer. At this point, significant reorganization of the adsorbed molecules is needed to accommodate still more. Changes in the mode of attachment of CO molecules to the surface alter the strength of the C–O bond and the extent to which the molecule is activated.

Diagrams of hep, fcc or bcc metal lattices such as we showed in Fig. 6.2 imply ‘flat’ metal surfaces. In practice, a surface contains imperfections such as those illustrated

in Fig. 25.13. The *kinks* on a metal surface are extremely important for catalytic activity, and their presence increases the rate of catalysis. In a close-packed lattice, sections of ‘flat’ surface contain  $M_1$  triangles (25.25), while a step possesses a line of  $M_1$  ‘butterflies’ (see Table 24.7), one of which is shown in blue in structure 25.26. Both can accommodate adsorbed species in sites which can be mimicked by discrete metal clusters. This has led to the *cluster-surface analogy* (see Section 25.9).

**Illustrated Topic boxes provide in-depth theoretical background for students**

**APPLICATIONS**

**Box 17.2 Iodine: from X-ray contrast agents to disinfectants and catalytic uses**

The annual output of iodine is significantly lower than that of chlorine or bromine, but, nonetheless, it has a wide range of important applications. Determining accurate data for end-uses of iodine is difficult because many iodine-containing intermediate compounds are marketed before the final application is reached. One major application of certain iodine-containing compounds is as X-ray contrast agents. Such agents are radio-opaque (i.e. they prevent X-rays from penetrating) and are used to assist the diagnosis of disorders of the heart, central nervous system, gall bladder, urinary tract and other organs. For example, following an injection of an iodine-based radio-opaque contrast agent, an X-ray examination of the kidneys, ureters and bladder results in an image called an intravenous pyelogram (IVP). The photograph below shows an IVP of a patient in whom a kidney stone has passed into the ureter but could not be passed into the bladder. The resulting obstruction causes dilation of the ureter and renal pelvis.



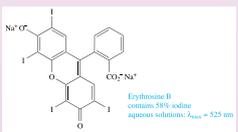
An intravenous pyelogram (IVP) imaged by using X-rays and an iodine-based contrast agent.

An important application of elemental iodine is as a bioicide and disinfectant. Since  $I_2$  is insoluble in water, solubilizing agents such as poly-N-vinyl-2-pyrrolidone (PVP) are required to prepare commercially useful aqueous iodine-containing solutions. PVP $_1$  antiseptic solutions are marketed under a number of trade names including Betadine. Although PVP $_1$

has been used as an antiseptic since the 1950s, the nature of the interaction between PVP and  $I_2$  is not fully elucidated. Electronic, Raman and IR spectroscopic data are consistent with the initial formation of a charge transfer complex (see Section 17.4) followed by release of  $I^-$  ion and formation of  $[I_2]^-$ . When  $I^-$  is released, the formation of  $[PVP \cdots I]^-$  has been proposed but not proven. An alternative proposal is the formation of  $[PVP \cdots I_2]^-$  with a proton hydrogen bonded between two PVP ketone oxygen atoms in the polymer backbone. Uses of  $I_2$  as a disinfectant range from wound antiseptics and disinfecting skin before surgery to maintaining germ-free swimming pools and water supplies.



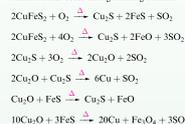
At an industrial level, the square planar iodo-complexes  $cis-[Ir(CO)_2I_2]^-$  and  $cis-[Ir(CO)_2I_2]^-$  are the catalysts for the Monsanto and Cativa acetic acid and Tennesse–Eastman acetic anhydride processes, discussed in detail in Section 25.4. Application of iodine as a stabilizer includes its incorporation into nylon used in carpet and tyre manufacture. Iodized animal feed supplements are responsible for reduced instances of goitre (enlarged thyroid gland) which are otherwise prevalent in regions where the iodine content of soil and drinking water is low; iodized hen feeds increase egg production. Iodine is usually added to feeds in the form of  $[H_2NCH_2CH_2NH_2]_2I_2$ , KI,  $Ca(IO_3)_2$  or  $Ca(CO_3)_2$ . Among diets that have a high iodine content is erythrosine B (food colour additive E127) which is added to carbonated soft drinks, gelatins and cake icings. The use of  $^{131}I$  as a medical radioisotope is described at the end of Section 17.3.



**ENVIRONMENT**

**Box 21.2 Copper: resources and recycling**

The resources of copper on the Earth’s surface have recently been re-estimated. About 550 million tonnes of copper are thought to be present in bedrock, minerals and deep-sea nodules. The main copper ore for traditional mining is chalcopyrite ( $CuFeS_2$ ). The conventional extraction process involves smelting and produces large quantities of  $SO_2$  (see 16.5). Reactions that occur during smelting include:



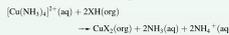
$FeO$  is converted to  $Fe_3O_4$  (called slag) by reaction with  $SiO_2$ . In the 1980s, a new copper extraction method was introduced that uses  $H_2SO_4$  from the smelting process to extract Cu from copper ores other than those used in traditional mining, e.g. azurite ( $Cu_3(OH)_2(CO_3)_2$ ) and malachite ( $Cu_2(OH)_2CO_3$ ). Copper is extracted in the form of aqueous  $CuSO_4$ . This is mixed with an organic solvent, chosen so that it can extract  $Cu^{2+}$  ions by exchanging  $H^+$  for  $Cu^{2+}$ , thus producing  $H_2SO_4$  which is recycled back into the leaching stage of the operation. The aqueous-to-organic phase change separates  $Cu^{2+}$  ions from impurities. Acid is again added, releasing  $Cu^{2+}$  ions from impurities. Acid is again added, releasing copper metal. The overall process is known as leach-solvent extraction-electrowinning (SX/EW) and operates at ambient temperatures. It is an environmentally friendly, hydrometallurgical process, but because it relies on  $H_2SO_4$ , it is currently coupled to conventional smelting of sulfide ores. In South America, ~40% of Cu is currently (in 2016) extracted by the SX/EW process. Worldwide, the SX/EW process is becoming increasingly important, and in 2017, accounted for ~21% of world copper production.

In regions where sulfide ores predominate, copper is leached using bacteria. Naturally occurring bacteria called *Acidithiobacillus thiooxidans* oxidize sulfide to sulfate ion, and this bioleaching process now works in parallel with SX/EW as a substitute for a significant fraction of conventional smelting operations. Among metals, consumption of Cu is exceeded only by steel and Al. The recovery of Cu from scrap metal is an essential part of copper-based industries, e.g. in 2013 in the US, recycled metal constituted 32% of the Cu supply. Worldwide mine production in 2015 was 18.7 Mt, with 30% originating from Chile, 9% from China, 9% from Peru and 7% from the US (the world’s leading producer). Recycling of the metal is

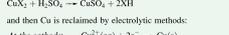


Bioleaching of copper from copper sulfide ores at the Skouriotissa copper mine in Cyprus.

important for environmental reasons: dumping of waste leads to pollution, e.g. of water supplies. In the electronics industry, solutions of  $NH_3-NH_4Cl$  in the presence of  $O_2$  are used to etch Cu in printed circuit boards. The resulting  $Cu(OH)_2$  waste is subjected to a process analogous to SX/EW described above. The waste is first treated with an organic solvent XH which is a compound of the type  $R_2C(OH)C(OH)R'$ , the conjugate base of which can function as a ligand.



where aq and org represent the aqueous and organic phases respectively. Treatment with  $H_2SO_4$  follows:



and then Cu is reclaimed by electrolytic methods. At the cathode:  $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

**Further reading**  
 C.L. Briley (2008) *Trans. Nonferrous Met. Soc. China*, vol. 18, p. 1302 – ‘How will bioleaching be applied in the future?’  
 F. Garrido et al. (2012) *J. Renew. Sustain. Energy*, vol. 4, article 053115 – ‘Solar pond technology for large-scale heat processing in a Chilean mine’.  
 M.E.E. Hoque and O.J. Philip (2011) *Mater. Sci. Eng. C*, vol. 31, p. 57 – ‘Biotechnological recovery of heavy metals from secondary sources – An overview’.  
 J. Lee, S. Acar, D.L. Doerr and J.A. Briley (2011) *Hydrometallurgy*, vol. 105, p. 213 – ‘Comparative bioleaching and mineralogy of composed sulfide ores containing enargite, covellite and chalcocite by mesophilic and thermophilic microorganisms’.  
[copperalliance.org/wordpress/wp-content/uploads/2012/01/ICSG-Factbook-2014.pdf](http://copperalliance.org/wordpress/wp-content/uploads/2012/01/ICSG-Factbook-2014.pdf)

Illustrated Topic boxes reveal how inorganic chemistry is applied to real-life situations

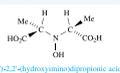
Illustrated Topic boxes relate inorganic chemistry to real-life in the areas of the Environment

## BIOLOGY AND MEDICINE

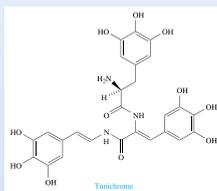
## Box 29.1 The specialists: organisms that store vanadium

Storage and transport of vanadium are specialized affairs. Just why certain organisms accumulate high levels of vanadium is unknown and the biological functions of this trace metal have yet to be established.

The fungus *Amantia muscaria* (the deadly poisonous fly agaric toadstool) contains  $\geq 400$  times more vanadium than is typical of plants, and the amount present does not reflect the vanadium content of the soil in which the fungus grows. *Amantia muscaria* takes up the metal by using the conjugate base of (S,S)-2,2'-dihydroxyiminodipropionic acid (HL<sup>-</sup>) to transport and store the trace metal as the V(IV) complex [VL<sub>2</sub>]<sup>2-</sup>, *amavadin*.



The formation of a complex of 'naked' V(IV) is in contrast to the more common occurrence of complexes containing [VO]<sup>2+</sup> (see Section 21.6). The structure of the amavadin derivative  $\Delta$ -[V(HL<sub>2</sub>)<sub>2</sub>]H<sub>2</sub>PO<sub>4</sub>H<sub>2</sub>O has been solved. The complex contains five chiral centres, one of which is the V(IV) centre. The latter is 8-coordinate and each HL<sup>-</sup> ligand acts as an *N,O,O'*-donor. The N-O unit coordinates in a side-on ( $\eta^2$ ) manner. *Amantia muscaria* contains a 1:1 mixture of the  $\Lambda$ - and  $\Delta$ -forms of amavadin. Amavadin undergoes a reversible 1-electron oxidation without a change in structure, and this observation may be significant in view of a possible role in electron transfer.



The levels of vanadium present in some ocean-dwelling ascidians, such as the sea squirt *Ascidia geminata*, are extraordinarily high, up to  $10^7$  times greater than in the surrounding water. The metal is taken up from seawater (where it is typically present  $\approx 1.1\text{--}1.8 \times 10^{-3}$  ppm) in the form of [VO<sub>2</sub>]<sup>+</sup> and is stored in vacuoles in specialized blood cells called *vanadocytes*. Here it is reduced to V<sup>3+</sup> or [VO]<sup>2+</sup> by the polyphenolic blood pigment *tunicchrome*. (Note the structural relationship between tunicchrome and L-DOPA, 25.13.) Storage of vanadium must involve the formation of V<sup>3+</sup> or [VO]<sup>2+</sup> complexes, but the nature of these species is not known.



The fly agaric fungus (*Amantia muscaria*).

## Further information

- R.E. Berry *et al.* (1999) *Angew. Chem. Int. Ed.*, vol. 38, p. 795 – 'The structural characterization of amavadin'.
- C.D. Garner *et al.* (2000) *J. Inorg. Biochem.*, vol. 80, p. 17 – 'Investigations of amavadin'.
- T. Hubregue *et al.* (2005) *J. Inorg. Biochem.*, vol. 99, p. 1264 – 'The first enantioselective synthesis of the amavadin ligand and its complexation to vanadium'.
- D. Rehder (2013) *Dalton Trans.*, vol. 42, p. 11749 – 'The future of vanadium'.
- D. Rehder (2015) *Metallomics*, vol. 7, p. 730 – 'The role of vanadium in biology'.
- J.A.L. de Silva, J.J.R. Frasco de Silva and A.J.L. Pombeiro (2013) *Coord. Chem. Rev.*, vol. 257, p. 2388 – 'Amavadin, a vanadium natural complex: Its role and applications'.
- T. Ueki, N. Yamaguchi, Romaidi, Y. Isono and H. Tanahashi (2015) *Coord. Chem. Rev.*, vol. 301–302, p. 300 – 'Vanadium accumulation in ascidians: a system overview'.

## Illustrated Topic boxes relate inorganic chemistry to real-life in the areas of Biology and Medicine

## KEY TERMS

The following terms were introduced in this chapter. Do you know what they mean?

- |   |  |  |
|---|--|--|
| <input type="checkbox"/> atom                 | <input type="checkbox"/> wavenumber                          | <input type="checkbox"/> ground state electronic configuration |
| <input type="checkbox"/> proton               | <input type="checkbox"/> Avogadro number                     | <input type="checkbox"/> effective nuclear charge              |
| <input type="checkbox"/> electron             | <input type="checkbox"/> wavefunction, $\psi$                | <input type="checkbox"/> screening effects of electrons        |
| <input type="checkbox"/> neutron              | <input type="checkbox"/> hydrogen-like species               | <input type="checkbox"/> penetration                           |
| <input type="checkbox"/> nucleus              | <input type="checkbox"/> principal quantum number, $n$       | <input type="checkbox"/> shielding                             |
| <input type="checkbox"/> protium              | <input type="checkbox"/> orbital quantum number, $l$         | <input type="checkbox"/> Slater's rules                        |
| <input type="checkbox"/> nuclide              | <input type="checkbox"/> magnetic quantum number, $m_l$      | <input type="checkbox"/> periodic table                        |
| <input type="checkbox"/> atomic number        | <input type="checkbox"/> magnetic spin quantum number, $m_s$ | <input type="checkbox"/> Aufbau principle                      |
| <input type="checkbox"/> mass number          | <input type="checkbox"/> degenerate                          | <input type="checkbox"/> Hund's rules                          |
| <input type="checkbox"/> relative atomic mass | <input type="checkbox"/> radial distribution function        | <input type="checkbox"/> Pauli exclusion principle             |
| <input type="checkbox"/> isotope              | <input type="checkbox"/> radial part of a wavefunction       | <input type="checkbox"/> valence electrons                     |
| <input type="checkbox"/> allotrope            | <input type="checkbox"/> angular part of a wavefunction      | <input type="checkbox"/> core electrons                        |
| <input type="checkbox"/> emission spectrum    | <input type="checkbox"/> atomic orbital                      | <input type="checkbox"/> ionization energy                     |
| <input type="checkbox"/> ground state         | <input type="checkbox"/> nodal plane                         | <input type="checkbox"/> electron affinity                     |
| <input type="checkbox"/> excited state        | <input type="checkbox"/> radial node                         |  |
| <input type="checkbox"/> quanta               |  |  |

## FURTHER READING

## First-year chemistry: basic principles

- C.E. Housecroft and E.C. Constable (2010) *Chemistry*, 4th edn, Prentice Hall, Harlow – A readable text covering fundamental aspects of inorganic, organic and physical chemistry which gives detailed background of all material that is taken as assumed knowledge in this book. An accompanying multiple-choice test bank and Solutions Manual can be found through [www.pearsoned.co.uk/housecroft](http://www.pearsoned.co.uk/housecroft).
- P. Atkins and J. de Paula (2012) *The Elements of Physical Chemistry*, 6th edn, OUP, Oxford – An excellent introductory text which covers important areas of physical chemistry.

## Basic quantum mechanics

- P. Atkins and J. de Paula (2014) *Atkins' Physical Chemistry*, 10th edn, OUP, Oxford – This text gives a solid and well-tested background in physical chemistry.

## PROBLEMS

- 1.1 Chromium has four isotopes,  $^{50}\text{Cr}$ ,  $^{52}\text{Cr}$ ,  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$ . How many electrons, protons and neutrons does each isotope possess?
- 1.2 'Arsenic is monatomic.' What does this statement mean? Using Appendix 5, write down three other elements that are monatomic.
- 1.3 Using the list of naturally occurring isotopes in Appendix 5, determine the number of electrons, protons and neutrons present in an atom of each

- D.O. Hayward (2002) *Quantum Mechanics for Chemists*, RSC Publishing, Cambridge – An undergraduate student text that covers the basic principles of quantum mechanics.

## Ionization energies and electron affinities

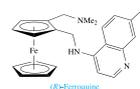
- P.F. Lang and B.C. Smith (2003) *J. Chem. Educ.*, vol. 80, p. 938 – 'Ionization energies of atoms and atomic ions'.
- D.M.P. Mingos (1998) *Essential Trends in Inorganic Chemistry*, OUP, Oxford – This text includes detailed discussions of trends in ionization energies and electron attachment enthalpies within the periodic table.
- J.C. Wheeler (1997) *J. Chem. Educ.*, vol. 74, p. 123 – 'Electron affinities of the alkaline earth metals and the sign convention for electron affinity'.

isotope of (a) Al, (b) Br and (c) Fe, and give appropriate notation to show these data for each isotope.

- 1.4 Hydrogen possesses three isotopes, but tritium ( $^3\text{H}$ ), which is radioactive, occurs as less than 1 in  $10^{17}$  atoms in a sample of natural hydrogen. If the value of  $A_r$  for hydrogen is 1.008, estimate the percentage abundance of protium,  $^1\text{H}$ , and deuterium,  $^2\text{H}$  (or D) present in a sample of natural hydrogen. Point out any

## INORGANIC CHEMISTRY MATTERS

24.40 Ferroquine has passed clinical phase II trials as an antimalarial drug. Both enantiomers of ferroquine are equally active *in vitro*. Explain why the molecule is chiral, and draw the structure of (S)-ferroquine.



24.41 Around 10 Mt per year of acetic acid are manufactured worldwide and  $\approx 25\%$  of this is produced using the Cativa<sup>TM</sup> process. The reaction:



is catalysed by  $\text{cis-}[\text{Ir}_2(\text{CO})_2]^-$ . Methanol is first converted to MeI by reaction with HI, and the catalyst undergoes oxidative addition of MeI to give a *fac*-A. In the presence of an  $\text{I}^-$  abstractor, substitution of  $\text{I}^-$  for CO leads to *fac*-B, which undergoes methyl migration. Reaction with  $\text{I}^-$  results in elimination of MeCOI and regeneration of the catalyst. (a) What is the stereochemistry of *cis*-[ $\text{Ir}_2(\text{CO})_2$ ]<sup>-</sup>? (b) Show what happens during the oxidative addition of MeI to *cis*-[ $\text{Ir}_2(\text{CO})_2$ ]<sup>-</sup>, and give the structure of *fac*-A. (c) Draw the structure of *fac*-B and describe the mechanism of the methyl migration step. (d) How does the valence electron count and the oxidation state of the Ir atom change during the catalytic cycle, starting and ending with the catalyst?

24.42 Ruthenium(II) complexes of the general type shown below are potential anticancer drugs:



The cytotoxicity of such complexes relies upon the replacement of the chlorido ligand by  $\text{H}_2\text{O}$ , and is pH dependent. (a) Write an equilibrium that defines the  $K_a$  value of the hydrolysis product of the above complex. (b) How does the introduction of electron-withdrawing substituents into the arene ring affect the  $\text{p}K_a$  value of the complex? (c) Suggest why the cytotoxicity is pH dependent.

24.43 The compound drawn below is an example of a ferrocenone:



It undergoes ring-opening polymerization (ROP) to yield a high molecular weight polymer in which the Cp rings in each ferrocene are parallel to one another. Potential applications of these polymers include those in materials and nano-sciences. (a) Starting from  $\text{Cp}_2\text{Fe}$ , suggest a synthesis of the compound shown above. (b) Give a reaction scheme for the ROP reaction, showing the repeat unit of the polymer. Comment on the driving force for the polymerization.

End-of-chapter problems, including a set of overview problems, which test the full range of material from each chapter

Inorganic Chemistry Matters problems, which are set in a contemporary real-world context



## Preface to the fifth edition

*Inorganic Chemistry* is a popular, internationally acknowledged textbook which gives a robust foundation for undergraduate and graduate students in physical inorganic principles, descriptive inorganic chemistry, bioinorganic chemistry and applications of the subject in catalysis, industrial processes and materials. Capturing the imagination and interest of students can be challenging, and *Inorganic Chemistry* addresses this challenge by the use of well-illustrated boxed material linking elements and inorganic compounds to the environment, biology, medicine and industry. The continuing success of *Inorganic Chemistry* is due in part to the extensive use of worked examples, self-study exercises and end-of-chapter problems which help students grasp basic principles as well as apply principles and methods to problems, many of which use literature data.

Twenty years ago, when I started working with Alan Sharpe on the first edition of *Inorganic Chemistry*, it was possible to manually trawl the high-impact journals to uncover major advances in the field, and to select material for inclusion in the textbook. In 2017, this is a daunting task, and it has become impossible to incorporate all significant developments without the textbook growing in size beyond practical limits. I have therefore had to apply rather stringent (and, probably, personal) criteria in selecting new compounds and topics to include in the 5th edition of *Inorganic Chemistry*.

A momentous development in the last few years has been the extension of the periodic table and the completion of the (currently) last row to the element with atomic number 118. In December 2016, the IUPAC published the accepted names for elements 113 (nihonium), 115 (moscovium), 117 (tennessine) and 118 (oganesson). The periodic table inside the cover of this book reflects the current state of our knowledge of these elements. The introductory sections to relevant chapters have been updated to include these new 'super-heavy' elements. However, the paucity of chemical data for them precludes in-depth discussion, and periodic trends (in particular in the *p*-block where the seventh row is now complete) are discussed in terms of the properties of the well-established elements.

In addition to updating data throughout the book, I have made significant changes to parts of two chapters. The Kapustinskii equation has been in use since 1956 for estimating lattice energies of ionic compounds. In this edition of *Inorganic Chemistry*, I have updated Chapter 6 to include the volume-based thermodynamic (VBT) approach to lattice energies. With appropriate ion volume data available in the literature, the VBT approach provides a straightforward method that students can apply in order to gain insight into the thermodynamic stability of a new material. In Chapter 24, the sections on electron-counting and bonding have been updated with the addition of the covalent bond classification (CBC) of ligands. This method complements the 'neutral metal atom and ligand' approach that has been used in previous editions of *Inorganic Chemistry*, and provides a valuable teaching tool already favoured by many inorganic chemists.

As in previous editions, IUPAC nomenclature has been foremost in my mind. However, old habits die hard and I have also retained trivial names where appropriate. In 2015, the IUPAC published a 'Brief guide to the nomenclature of inorganic chemistry'. This is an invaluable source of information to students and teachers alike and is available online ([www.iupac.org/cms/wp-content/uploads/2016/07/Inorganic-Brief-Guide-V1-1.pdf](http://www.iupac.org/cms/wp-content/uploads/2016/07/Inorganic-Brief-Guide-V1-1.pdf); <https://iupac.org/project/2010-055-1-800>) and is also included at the back of this book. The IUPAC Commission on Isotopic Abundances and Atomic weights ([www.ciaaw.org](http://www.ciaaw.org)) has published revised atomic weights for a number of elements and these data are now incorporated into *Inorganic Chemistry*; the most significant changes are to the atomic weights of Zn (changed from 65.409 to 65.38, reversing a change made in 2001) and Ti (updated from 47.90 to 47.87).

The full-colour, 3-dimensional molecular structures in *Inorganic Chemistry* which are so much part of the appeal of the textbook to students have been redrawn to give the book a more modern feel. Molecular structures have been constructed using Spartan '16, v. 1.1.1, Wavefunction Inc., or have been drawn using atomic coordinates accessed from the Cambridge Crystallographic Data Base (original citations are given throughout the book) or the Protein Data Bank ([www.rcsb.org/pdb](http://www.rcsb.org/pdb), original PDB codes are given in the figure captions in the book).

Accompanying this text is a *Solutions Manual* and there is an accompanying website ([www.pearsoned.co.uk/housecroft](http://www.pearsoned.co.uk/housecroft)) with multiple choice questions and rotatable structures based on the graphics in the hard-copy text.

The evolution of a text such as *Inorganic Chemistry* through a series of editions and many language translations is greatly assisted by the communications that I receive from those who use the book, and from my colleagues around the globe. On going from the fourth to fifth editions, I particularly acknowledge the input of Professor Anthony Addison (Drexel University), Professor Duncan Bruce (University of York), Professor Gareth Eaton (University of Denver), Professors Alan Hutton, Graham Jackson, Greg Smith and Tim Egan (University of Cape Town), Professor Dave McMillin (Purdue University), Dr Paul Seybold (Wright State University), Professor Steve Strauss (Colorado State University), Dr Jahansooz Toofan (California State University, Sacramento), Professor Davit Zargarian (University of Montreal), Dr Marcus Wolf and Daniela Goncalves. The panel of reviewers commissioned by the publisher is also thanked for providing thought-provoking feedback on the fourth edition of *Inorganic Chemistry*, and I am grateful to Professors Alan Hutton and Jan Reedijk for answering questions concerning IUPAC nomenclature.

I am indebted to Professor Don Jenkins for lively discussions about lattice energies which have helped me to reshape parts of Chapter 6, and I am also grateful to Professors Malcolm Green and Ged Parkin for feedback on new material in Chapter 24. I am also thankful for the time that several colleagues have spent reading and commenting upon specific sections of text, in particular Professors Gary Long and Fernande Grandjean (Mössbauer spectroscopy) and Professor Gareth Eaton (EPR spectroscopy). The publishing team at Pearson has been a great support for the fifth edition, and specific thanks go to Kevin Ancient, Anita Atkinson, Archana Makhija, Ros Woodward, Janey Webb and Richelle Zakrzewski.

My husband, Edwin Constable, is an endless source of enthusiastic chemical criticism – thank you from my heart, Ed, for your continued support. Rocco and Rya joined the writing team of *Inorganic Chemistry* for the fourth edition and have contributed to the fifth edition in their characteristic feline manner. Being at the top of the family hierarchy, they are not always the most patient of household members and are quick to let me know when attention, food and games are more important than chemistry. Writing would not be so much fun without my Siamese companions. Their nonchalant walks over the keyboard of my iMac occasionally lead to spurious characters in the manuscript. Nonetheless, any errors in the text remain the responsibility of the author.

Catherine E. Housecroft  
Basel  
March 2017

In the 3-dimensional structures, unless otherwise stated, the following colour coding is used: C, grey; H, white; O, red; N, blue; F and Cl, green; S, yellow; P, orange; B, blue.



# Acknowledgements

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## **Figures**

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### Text

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## Topics

Atomic structure  
Quantum theory  
Atomic orbitals  
Electronic configurations  
Periodic table  
Ionization energies  
Electron affinities

# 1

## Basic concepts: atoms



### 1.1 Introduction

#### Inorganic chemistry: it is not an isolated branch of chemistry

If organic chemistry is considered to be the ‘chemistry of carbon’, then inorganic chemistry is the chemistry of all elements except carbon. In its broadest sense, this is true, but of course there are overlaps between branches of chemistry. A topical example is the chemistry of graphene sheets which comprise carbon (see Sections 28.8 and 28.9). Does graphene fall into the remit of organic or inorganic chemistry, or does it even make sense to try to categorize graphene in this way? Indeed, an understanding of the properties of graphene and the related carbon nanotubes and fullerenes is a multidisciplinary affair and requires input from chemists (organic, inorganic and physical), physicists and materials scientists.

Inorganic chemistry is not simply the study of elements and compounds; it is also the study of physical principles. For example, in order to understand why some compounds are soluble in a given solvent and others are not, we apply laws of thermodynamics. If our aim is to propose details of a reaction mechanism, then a knowledge of reaction kinetics is needed. Overlap between physical and inorganic chemistry is also significant in the study of molecular structure. In the solid state, X-ray diffraction methods are routinely used to obtain pictures of the spatial arrangements of atoms in a molecule or molecular ion. To interpret the behaviour of molecules in solution, we use physical techniques such as nuclear magnetic resonance (NMR) spectroscopy; the equivalence or not of particular nuclei on a spectroscopic timescale may indicate whether a molecule

is static or undergoing a dynamic process. The application of a wide range of physical techniques in inorganic chemistry is the topic of Chapter 4.

#### The aims of Chapters 1 and 2

In Chapters 1 and 2, we outline some concepts fundamental to an understanding of inorganic chemistry. We have assumed that readers are to some extent familiar with most of these concepts and our aim is to give a point of reference for review purposes.

### 1.2 Fundamental particles of an atom

An *atom* is the smallest unit quantity of an element that is capable of existence, either alone or in chemical combination with other atoms of the same or another element. The fundamental particles of which atoms are composed are the *proton*, *electron* and *neutron*.

A neutron and a proton have approximately the same mass and, relative to these, an electron has negligible mass (Table 1.1). The charge on a proton is positive and of equal magnitude, but opposite sign, to that on a negatively charged electron. A neutron has no charge. In an atom of any element, there are equal numbers of protons and electrons and so an atom is neutral. The *nucleus* of an atom consists of protons and (with the exception of *protium*, see Section 10.3) neutrons, and is positively charged; the nucleus of *protium* consists of a single proton. The electrons occupy a region of space around the nucleus. Nearly all the mass of an atom is concentrated in the nucleus, but the volume of the nucleus is only a tiny fraction of that of the

**Table 1.1** Properties of the proton, electron and neutron.

	Proton	Electron	Neutron
Charge / C	$+1.602 \times 10^{-19}$	$-1.602 \times 10^{-19}$	0
Charge number (relative charge)	1	-1	0
Rest mass / kg	$1.673 \times 10^{-27}$	$9.109 \times 10^{-31}$	$1.675 \times 10^{-27}$
Relative mass	1837	1	1839

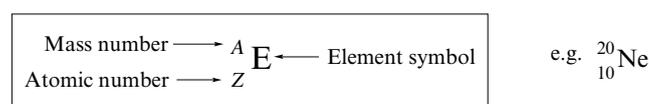
atom; the radius of the nucleus is about  $10^{-15}$  m while the atom itself is about  $10^5$  times larger than this. It follows that the density of the nucleus is enormous, more than  $10^{12}$  times that of the metal Pb.

Although chemists tend to consider the electron, proton and neutron as the fundamental (or elementary) particles of an atom, particle physicists deal with yet smaller particles.†

### 1.3 Atomic number, mass number and isotopes

#### Nuclides, atomic number and mass number

A *nuclide* is a particular type of atom and possesses a characteristic *atomic number*,  $Z$ , which is equal to the number of protons in the nucleus. Because the atom is electrically neutral,  $Z$  also equals the number of electrons. The *mass number*,  $A$ , of a nuclide is the number of protons and neutrons in the nucleus. A shorthand method of showing the atomic number and mass number of a nuclide along with its symbol, E, is:



Atomic number =  $Z$  = number of protons in the nucleus = number of electrons  
 Mass number =  $A$  = number of protons + number of neutrons  
 Number of neutrons =  $A - Z$

#### Self-study exercise

How many protons, electrons and neutrons does an atom of (a)  ${}_{6}^{12}\text{C}$ , (b)  ${}_{9}^{19}\text{F}$ , (c)  ${}_{17}^{35}\text{Cl}$  contain?

[Ans. (a) 6p, 6e, 6n; (b) 9p, 9e, 10n; (c) 17p, 17e, 18n]

#### Relative atomic mass

Since the electrons are of minute mass, the mass of an atom essentially depends upon the number of protons and neutrons in the nucleus. As Table 1.1 shows, the mass of a single atom is a very small, non-integral number, and for convenience a system of *relative atomic masses* is adopted. The atomic mass unit is defined as 1/12th of the mass of a  ${}_{6}^{12}\text{C}$  atom so that it has the value  $1.660 \times 10^{-27}$  kg. *Relative atomic masses* ( $A_r$ ) are therefore all stated relative to  ${}_{6}^{12}\text{C} = 12.0000$ . The masses of the proton and neutron can be considered to be  $\approx 1$  u where u is the *atomic mass unit* ( $1 \text{ u} \approx 1.660 \times 10^{-27}$  kg).

#### Isotopes

Nuclides of the same element possess the same number of protons and electrons but may have different mass numbers. The number of protons and electrons defines the element but the number of neutrons may vary. Nuclides of a particular element that differ in the number of neutrons and, therefore, their mass number, are called *isotopes* (see Appendix 5). Isotopes of some elements occur naturally while others may be produced artificially.

Elements that occur naturally with only one nuclide are *monotopic* and include phosphorus,  ${}_{15}^{31}\text{P}$ , and fluorine,  ${}_{9}^{19}\text{F}$ . Elements that exist as mixtures of isotopes include C ( ${}_{6}^{12}\text{C}$  and  ${}_{6}^{13}\text{C}$ ) and O ( ${}_{8}^{16}\text{O}$ ,  ${}_{8}^{17}\text{O}$  and  ${}_{8}^{18}\text{O}$ ). Since the atomic number is constant for a given element, isotopes are often distinguished only by stating the atomic masses, e.g.  ${}^{12}\text{C}$  and  ${}^{13}\text{C}$ .

#### Worked example 1.1 Relative atomic mass

Calculate the value of  $A_r$  for naturally occurring chlorine if the distribution of isotopes is 75.76%  ${}_{17}^{35}\text{Cl}$  and 24.24%  ${}_{17}^{37}\text{Cl}$ . Accurate masses for  ${}^{35}\text{Cl}$  and  ${}^{37}\text{Cl}$  are 34.97 and 36.97.

The relative atomic mass of chlorine is the weighted mean of the mass numbers of the two isotopes:

Relative atomic mass,

$$A_r = \left( \frac{75.76}{100} \times 34.97 \right) + \left( \frac{24.24}{100} \times 36.97 \right) = 35.45$$

† See: [www.symmetrymagazine.org/standard-model/](http://www.symmetrymagazine.org/standard-model/)



## THEORY

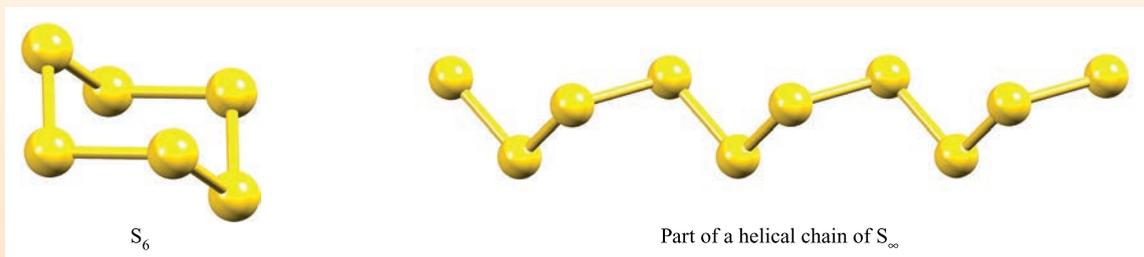
## Box 1.1 Isotopes and allotropes

**Do not confuse *isotope* and *allotrope*!** Sulfur has both isotopes and allotropes. Isotopes of sulfur (with percentage naturally occurring abundances) are  $^{32}\text{S}$  (94.99%),  $^{33}\text{S}$  (0.75%),  $^{34}\text{S}$  (4.25%),  $^{36}\text{S}$  (0.01%).

Allotropes of an element are different structural modifications of that element. Allotropes of sulfur include cyclic

structures, e.g.  $\text{S}_6$  (see below) and  $\text{S}_8$  (Fig. 1.1c), and chains of various lengths (*polycatenasulfur*).

Further examples of isotopes and allotropes appear throughout the book.



## Worked example 1.2

**If  $A_r$  for Cl is 35.45, what is the ratio of  $^{35}\text{Cl} : ^{37}\text{Cl}$  present in a sample of Cl atoms containing naturally occurring Cl? Accurate masses of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  are 34.97 and 36.97.**

The relative atomic mass is 35.45 and this is the weighted mean of the mass numbers of the isotopes. Let  $x$  be the percentage of  $^{35}\text{Cl}$  present in naturally occurring Cl:

$$35.45 = \left(\frac{x}{100} \times 34.97\right) + \left(\frac{100-x}{100} \times 36.97\right)$$

$$3545 = 34.97x + 3697 - 36.97x$$

$$2x = 152$$

$$x = 76$$

Therefore, naturally occurring Cl contains 76%  $^{35}\text{Cl}$  and 24%  $^{37}\text{Cl}$ .

$$\text{Ratio } ^{35}\text{Cl} : ^{37}\text{Cl} = 76 : 24 = 3.2 : 1$$

This worked example illustrates a problem of significant figures. If the percentage contributions given to four significant figures in worked example 1.1 are used, then:

$$\text{Ratio } ^{35}\text{Cl} : ^{37}\text{Cl} = 75.76 : 24.24 = 3.125 : 1$$

## Self-study exercises

- Calculate the value of  $A_r$  for naturally occurring Cu if the distribution of isotopes is 69.15%  $^{63}\text{Cu}$  and 30.85%  $^{65}\text{Cu}$ ; accurate masses are 62.93 and 64.93, respectively. [Ans. 63.45]

- Why in question 1 is it adequate to write  $^{63}\text{Cu}$  rather than  $^{63}_{29}\text{Cu}$ ?

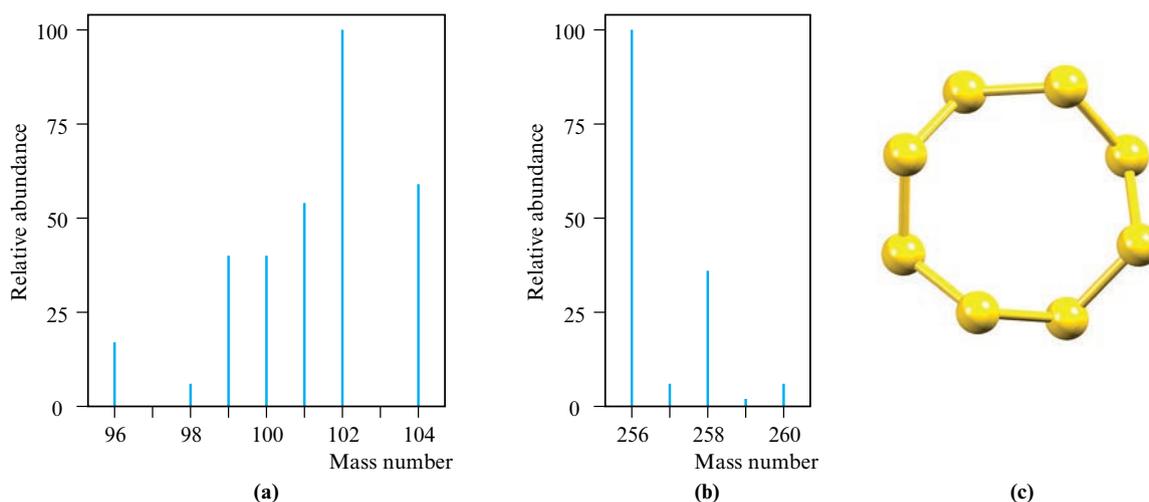
- Calculate  $A_r$  for naturally occurring Mg if the isotope distribution is 78.99%  $^{24}\text{Mg}$ , 10.00%  $^{25}\text{Mg}$  and 11.01%  $^{26}\text{Mg}$ ; accurate masses are 23.99, 24.99 and 25.98. [Ans. 24.31]

Isotopes can be separated by *mass spectrometry* and Fig. 1.1a shows the isotopic distribution in naturally occurring Ru. Compare this plot (in which the most abundant isotope is set to 100) with the values listed in Appendix 5. Figure 1.1b shows a mass spectrometric trace for molecular  $\text{S}_8$ , the structure of which is shown in Fig. 1.1c; five peaks are observed due to combinations of the isotopes of sulfur. (See end-of-chapter problem 1.5.)

**Isotopes** of an element have the same atomic number,  $Z$ , but different atomic masses.

The IUPAC Commission on Isotopic Abundances and Atomic Weights ([www.ciaaw.org](http://www.ciaaw.org)) is responsible for the critical evaluation of the isotope compositions of elements and of atomic weights. The atomic weights of a number of elements have been revised<sup>†</sup> since the last edition of this book and the values of  $A_r$  given in the periodic table (see inside the front cover of the book) and listed in the accompanying table, reflect updates. The most significant changes are to

<sup>†</sup>J. Meija *et al.* (2016) *Pure Appl. Chem.*, vol 88, p. 293 – ‘Isotopic compositions of the elements 2013’.



**Fig. 1.1.** Mass spectrometric traces for (a) atomic Ru and (b) molecular S<sub>8</sub>; the mass : charge ratio is  $m/z$  and in these traces  $z = 1$ . (c) The molecular structure of S<sub>8</sub>.

values of  $A_r$  for Zn (changed from 65.409 to 65.38, reversing a change made in 2001) and Ti (updated from 47.90 to 47.87).

## 1.4 Successes in early quantum theory

We saw in Section 1.2 that electrons in an atom occupy a region of space around the nucleus. The importance of electrons in determining the properties of atoms, ions and molecules, including the bonding between or within them, means that we must have an understanding of the electronic structures of each species. No adequate discussion of electronic structure is possible without reference to *quantum theory* and *wave mechanics*. In this and the next few sections, we review some crucial concepts. The treatment is mainly qualitative, and you should consult the further reading given at the end of Chapter 1 for greater detail and more rigorous derivations of mathematical relationships.

The development of quantum theory took place in two stages. In older theories (1900–1925), the electron was treated as a particle, and the achievements of greatest significance to inorganic chemistry were the interpretation of atomic spectra and assignment of electronic configurations. In more recent models, the electron is treated as a wave (hence the name *wave mechanics*) and the main successes in chemistry are the elucidation of the basis of stereochemistry and methods for calculating the properties of molecules (exact *only* for species involving light atoms).

Since all the results obtained by using the older quantum theory may also be obtained from wave mechanics, it may seem unnecessary to refer to the former; indeed, sophisticated treatments of theoretical chemistry seldom do. However, most chemists often find it easier and more convenient to consider the electron as a particle rather than a wave.

### Some important successes of classical quantum theory

Historical discussions of the developments of quantum theory are dealt with adequately elsewhere, and so we focus only on some key points of *classical* quantum theory (in which the electron is considered to be a particle).

At low temperatures, the radiation emitted by a hot body is mainly of low energy and occurs in the infrared, but as the temperature increases, the radiation becomes successively dull red, bright red and white. Attempts to account for this observation failed until, in 1901, Planck suggested that energy could be absorbed or emitted only in *quanta* of magnitude  $\Delta E$  related to the frequency of the radiation,  $\nu$ , by eq. 1.1. The proportionality constant is  $h$ , the Planck constant ( $h = 6.626 \times 10^{-34}$  J s).

$$\Delta E = h\nu \quad \text{Units: } E \text{ in J; } \nu \text{ in s}^{-1} \text{ or Hz} \quad (1.1)$$

$$c = \lambda\nu \quad \text{Units: } \lambda \text{ in m; } \nu \text{ in s}^{-1} \text{ or Hz} \quad (1.2)$$

The hertz, Hz, is the SI unit of frequency.

The frequency of radiation is related to the wavelength,  $\lambda$ , by eq. 1.2, in which  $c$  is the speed of light in a vacuum ( $c = 2.998 \times 10^8$  m s<sup>-1</sup>). Therefore, eq. 1.1 can be rewritten in the form of eq. 1.3. This relates the energy of radiation to its wavelength.

$$\Delta E = \frac{hc}{\lambda} \quad (1.3)$$

On the basis of this relationship, Planck derived a relative intensity/wavelength/temperature relationship which was in good agreement with experimental data. This derivation is not straightforward and we shall not reproduce it here.

When energy is provided (e.g. as heat or light) to an atom or other species, one or more electrons may be promoted from a ground state level to a higher energy state. This excited state is transient and the electron falls back to the ground state. This produces an *emission spectrum*.

One of the most important applications of early quantum theory was the interpretation of the atomic spectrum of hydrogen on the basis of the Rutherford–Bohr model of the atom. When an electric discharge is passed through a sample of dihydrogen, the  $\text{H}_2$  molecules dissociate into atoms, and the electron in a particular *excited* H atom may be *promoted* to one of many high energy levels. These states are transient and the electron falls back to a lower energy state, emitting energy as it does so. The consequence is the observation of *spectral lines* in the emission spectrum of hydrogen. The spectrum (a part of which is shown in Fig. 1.2) consists of groups of discrete lines corresponding to electronic transitions, each of *discrete energy*. In 1885, Balmer pointed out that the wavelengths of the spectral lines observed in the visible region of the atomic spectrum of hydrogen obeyed eq. 1.4, in which  $R$  is the Rydberg constant for hydrogen,  $\bar{\nu}$  is the wavenumber in  $\text{cm}^{-1}$ , and  $n$  is an integer 3, 4, 5... This series of spectral lines is known as the *Balmer series*.

**Wavenumber** is the reciprocal of wavelength; convenient (non-SI) units are ‘reciprocal centimetres’,  $\text{cm}^{-1}$ .

$$\bar{\nu} = \frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad (1.4)$$

$R$  = Rydberg constant for hydrogen

$$= 1.097 \times 10^7 \text{ m}^{-1} = 1.097 \times 10^5 \text{ cm}^{-1}$$

Other series of spectral lines occur in the ultraviolet (Lyman series) and infrared (Paschen, Brackett and Pfund series). All lines in all the series obey the general expression given in eq. 1.5 where  $n' > n$ . For the Lyman series,  $n = 1$ , for the

Balmer series,  $n = 2$ , and for the Paschen, Brackett and Pfund series,  $n = 3, 4$  and  $5$  respectively. Figure 1.3 shows some of the allowed transitions of the Lyman and Balmer series in the emission spectrum of atomic H. Note the use of the word *allowed*; the transitions must obey *selection rules*, to which we return in Section 20.7.

$$\bar{\nu} = \frac{1}{\lambda} = R \left( \frac{1}{n^2} - \frac{1}{n'^2} \right) \quad (1.5)$$

## Bohr’s theory of the atomic spectrum of hydrogen

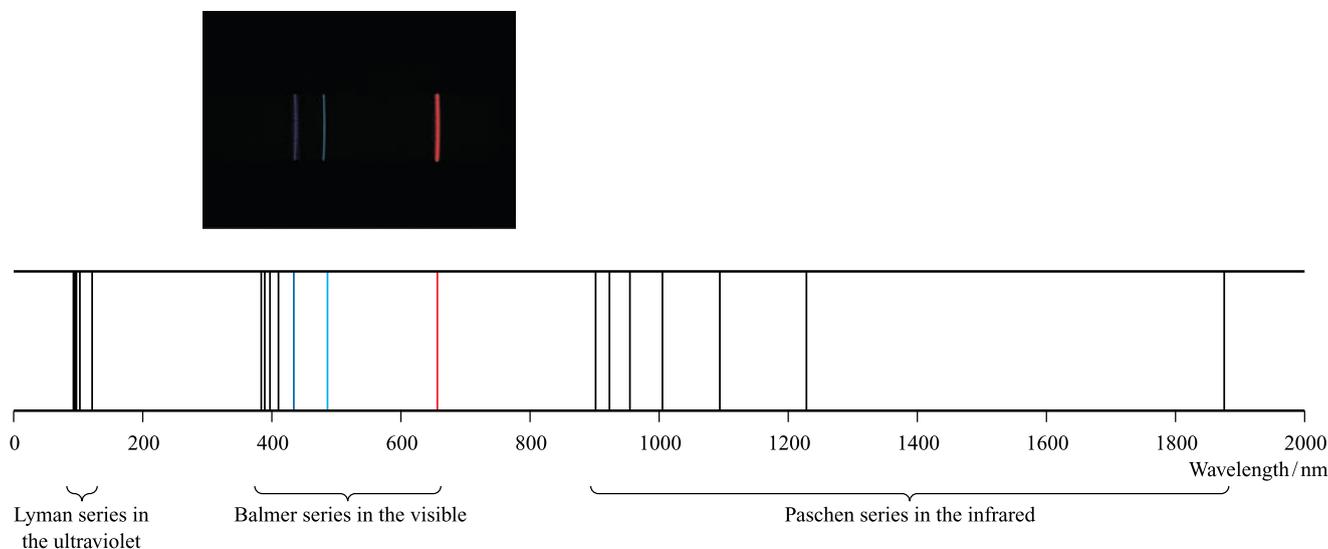
In 1913, Niels Bohr combined elements of quantum theory and classical physics in a treatment of the hydrogen atom. He stated two postulates for an electron in an atom:

- *Stationary states* exist in which the energy of the electron is constant; such states are characterized by *circular orbits* about the nucleus in which the electron has an angular momentum  $mvr$  given by eq. 1.6. The integer,  $n$ , is the *principal quantum number*.

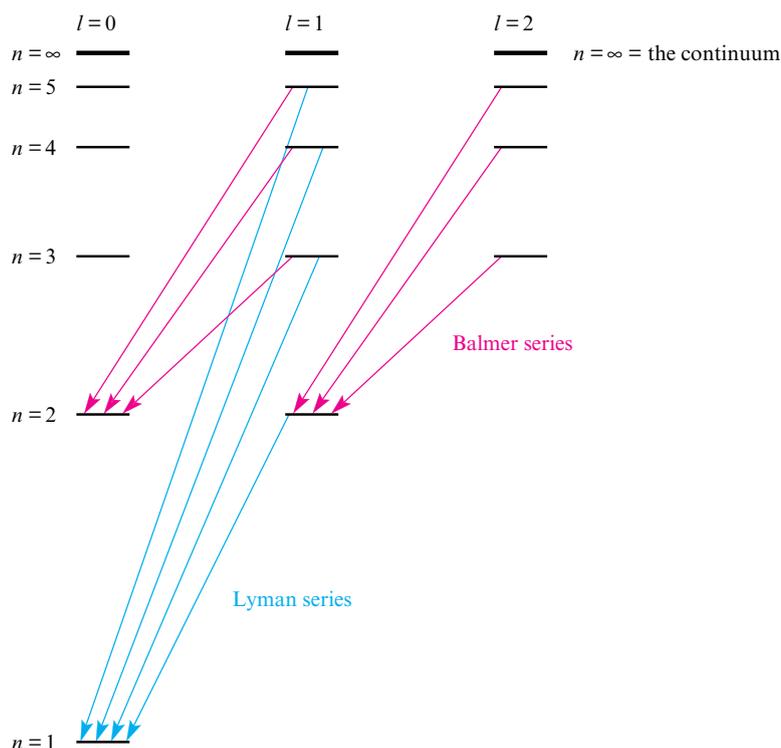
$$mvr = n \left( \frac{h}{2\pi} \right) \quad (1.6)$$

where  $m$  = mass of electron;  $v$  = velocity of electron;  $r$  = radius of the orbit;  $h$  = the Planck constant;  $h/2\pi$  may be written as  $\hbar$ .

- Energy is absorbed or emitted only when an electron moves from one stationary state to another and the energy change is given by eq. 1.7 where  $n_1$  and  $n_2$  are the principal quantum numbers referring to the energy levels  $E_{n_1}$  and  $E_{n_2}$  respectively.



**Fig. 1.2.** A schematic representation of part of the emission spectrum of hydrogen showing the Lyman, Balmer and Paschen series of emission lines. The photograph shows the predominant lines in the observed, visible part of the spectrum of hydrogen which appear at 656.3 (red), 486.1 (cyan) and 434.0 nm (blue). Other fainter lines are not visible in this photograph.



**Fig. 1.3.** Some of the transitions that make up the Lyman and Balmer series in the emission spectrum of atomic hydrogen.

$$\Delta E = E_{n_2} - E_{n_1} = h\nu \quad (1.7)$$

If we apply the Bohr model to the H atom, the radius of each allowed circular orbit can be determined from eq. 1.8. The origin of this expression lies in the centrifugal force acting on the electron as it moves in its circular orbit. For the orbit to be maintained, the centrifugal force must equal the force of attraction between the negatively charged electron and the positively charged nucleus.

$$r_n = \frac{\epsilon_0 h^2 n^2}{\pi m_e e^2} \quad (1.8)$$

where  $\epsilon_0$  = permittivity of a vacuum

$$= 8.854 \times 10^{-12} \text{ F m}^{-1}$$

$$h = \text{Planck constant} = 6.626 \times 10^{-34} \text{ J s}$$

$n = 1, 2, 3 \dots$  describing a given orbit

$$m_e = \text{electron rest mass} = 9.109 \times 10^{-31} \text{ kg}$$

$e$  = charge on an electron (elementary charge)

$$= 1.602 \times 10^{-19} \text{ C}$$

From eq. 1.8, substitution of  $n = 1$  gives a radius for the first orbit of the H atom of  $5.293 \times 10^{-11} \text{ m}$ , or 52.93 pm. This value is called the *Bohr radius* of the H atom and is given the symbol  $a_0$ .

An increase in the principal quantum number from  $n = 1$  to  $n = \infty$  has a special significance. It corresponds to the ionization of the atom (eq. 1.9) and the ionization energy,

$IE$ , can be determined by combining eqs. 1.5 and 1.7, as shown in eq. 1.10. Values of  $IE$ s are quoted *per mole of atoms*.

One mole of a substance contains the *Avogadro number*,  $L$ , of particles:

$$L = 6.022 \times 10^{23} \text{ mol}^{-1}$$



$$IE = E_\infty - E_1 = \frac{hc}{\lambda} = hcR \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) \quad (1.10)$$

$$= 2.179 \times 10^{-18} \text{ J}$$

Per mole:

$$IE = 2.179 \times 10^{-18} \times 6.022 \times 10^{23} \text{ J mol}^{-1}$$

$$= 1.312 \times 10^6 \text{ J mol}^{-1}$$

$$= 1312 \text{ kJ mol}^{-1}$$

Although the SI unit of energy is the joule, ionization energies are often expressed in electron volts (eV) ( $1 \text{ eV} = 96.4853 \approx 96.5 \text{ kJ mol}^{-1}$ ). Therefore, the ionization energy of hydrogen can also be given as 13.60 eV.

Impressive as the success of the Bohr model was when applied to the H atom, extensive modifications were required to cope with species containing more than one electron. We shall not pursue this topic further here.

## 1.5 An introduction to wave mechanics

### The wave-nature of electrons

The quantum theory of radiation introduced by Max Planck and Albert Einstein implies a particle theory of light, in addition to the wave theory of light required by the phenomena of interference and diffraction. In 1924, Louis de Broglie argued that if light were composed of particles and yet showed wave-like properties, the same should be true of electrons and other particles. This phenomenon is referred to as *wave-particle duality*. The de Broglie relationship (eq. 1.11) combines the concepts of classical mechanics with the idea of wave-like properties by showing that a particle with momentum  $mv$  ( $m$  = mass and  $v$  = velocity of the particle) possesses an associated wave of wavelength  $\lambda$ .

$$\lambda = \frac{h}{mv} \quad \text{where } h \text{ is the Planck constant} \quad (1.11)$$

An important physical observation which is a consequence of the de Broglie relationship is that electrons accelerated to a velocity of  $6 \times 10^6 \text{ m s}^{-1}$  (by a potential of 100 V) have an associated wavelength of  $\approx 120 \text{ pm}$  and such electrons are diffracted as they pass through a crystal. This phenomenon is the basis of electron diffraction techniques used to determine structures of chemical compounds (see Section 4.10).

### The uncertainty principle

If an electron has wave-like properties, there is an important and difficult consequence: it becomes impossible to know exactly both the momentum and position of the electron *at the same instant in time*. This is a statement of Heisenberg's *uncertainty principle*. In order to get around this problem, rather than trying to define its exact position and momentum, we use the *probability of finding the electron* in a given volume of space. The probability of finding an electron at a given point in space is determined from the function  $\psi^2$  where  $\psi$  is a mathematical function called the *wavefunction* which describes the behaviour of an electron-wave.

The probability of finding an electron at a given point in space is determined from the function  $\psi^2$  where  $\psi$  is the *wavefunction*.

### The Schrödinger wave equation

Information about the wavefunction is obtained from the Schrödinger wave equation, which can be set up and solved either exactly or approximately. The Schrödinger equation can be solved *exactly only* for a species

containing a nucleus and *only one* electron (e.g.  $^1\text{H}$ ,  $^4\text{He}^+$ ), i.e. a *hydrogen-like system*.

A *hydrogen-like atom* or *hydrogen-like ion* contains a nucleus and only one electron.

The Schrödinger wave equation may be represented in several forms and in Box 1.2 we examine its application to the motion of a particle in a 1-dimensional box. Equation 1.12 gives the form of the Schrödinger wave equation that is appropriate for motion in the  $x$  direction.

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - V)\psi = 0 \quad (1.12)$$

where  $m$  = mass

$E$  = total energy

$V$  = potential energy of the particle

Of course, in reality, electrons move in 3-dimensional space and an appropriate form of the Schrödinger wave equation is given in eq. 1.13.

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2m}{h^2}(E - V)\psi = 0 \quad (1.13)$$

Solving this equation will not concern us, although it is useful to note that it is advantageous to work in spherical polar coordinates (Fig. 1.4). When we look at the results obtained from the Schrödinger wave equation, we talk in terms of the *radial and angular parts of the wavefunction*, and this is represented in eq. 1.14 where  $R(r)$  and  $A(\theta, \phi)$  are radial and angular wavefunctions respectively.<sup>†</sup>

$$\psi_{\text{Cartesian}}(x, y, z) \equiv \psi_{\text{radial}}(r)\psi_{\text{angular}}(\theta, \phi) = R(r)A(\theta, \phi) \quad (1.14)$$

Having solved the wave equation, what are the results?

- The wavefunction  $\psi$  is a solution of the Schrödinger equation and describes the behaviour of an electron in a region of space called the *atomic orbital*.
- We can find energy values that are associated with particular wavefunctions.
- The quantization of energy levels arises naturally from the Schrödinger equation (see Box 1.2).

A *wavefunction*  $\psi$  is a mathematical function that contains detailed information about the behaviour of an electron. An atomic wavefunction  $\psi$  consists of a *radial component*,  $R(r)$ , and an *angular component*,  $A(\theta, \phi)$ . The region of space defined by a wavefunction is called an *atomic orbital*.

<sup>†</sup> The radial component in eq. 1.14 depends on the quantum numbers  $n$  and  $l$ , whereas the angular component depends on  $l$  and  $m_l$ , and the components should really be written as  $R_{n,l}(r)$  and  $A_{l,m_l}(\theta, \phi)$ .



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## Box 1.2 Particle in a box

The following discussion illustrates the so-called *particle in a 1-dimensional box* and illustrates quantization arising from the Schrödinger wave equation.

The *Schrödinger wave equation* for the motion of a particle in one dimension is given by:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - V)\psi = 0$$

where  $m$  is the mass,  $E$  is the total energy and  $V$  is the potential energy of the particle. The derivation of this equation is considered in the set of exercises on p. 9. For a given system for which  $V$  and  $m$  are known, Schrödinger's equation is used to obtain values of  $E$  (the *allowed energies of the particle*) and  $\psi$  (the *wavefunction*). The wavefunction itself has no physical meaning, but  $\psi^2$  is a probability (see main text) and for this to be the case,  $\psi$  must have certain properties:

- $\psi$  must be finite for all values of  $x$ ;
- $\psi$  can only have one value for any value of  $x$ ;
- $\psi$  and  $\frac{d\psi}{dx}$  must vary continuously as  $x$  varies.

Now, consider a particle that is undergoing simple-harmonic wave-like motion in one dimension, i.e. we can fix the direction of wave propagation to be along the  $x$  axis (the choice of  $x$  is arbitrary). Let the motion be further constrained such that the particle cannot go outside the fixed, vertical walls of a box of width  $a$ . There is no force acting on the particle *within* the box and so the potential energy,  $V$ , is zero. If we take  $V = 0$ , we are placing limits on  $x$  such that  $0 \leq x \leq a$ , i.e. the particle cannot move outside the box. The only restriction that we place on the total energy  $E$  is that it must be positive and cannot be infinite. There is one further restriction that we shall simply state: the *boundary condition* for the particle in the box is that  $\psi$  must be zero when  $x = 0$  and  $x = a$ .

Now rewrite the Schrödinger equation for the specific case of the particle in the 1-dimensional box where  $V = 0$ :

$$\frac{d^2\psi}{dx^2} = -\frac{8\pi^2mE}{h^2}\psi$$

which may be written in the simpler form:

$$\frac{d^2\psi}{dx^2} = -k^2\psi \quad \text{where} \quad k^2 = \frac{8\pi^2mE}{h^2}$$

The solution to this (a known general equation) is:

$$\psi = A \sin kx + B \cos kx$$

where  $A$  and  $B$  are integration constants. When  $x = 0$ ,  $\sin kx = 0$  and  $\cos kx = 1$ ; hence,  $\psi = B$  when  $x = 0$ . However, the boundary condition above stated that  $\psi = 0$  when  $x = 0$ , and this is only true if  $B = 0$ . Also from the boundary condition, we see that  $\psi = 0$  when  $x = a$ , and hence we can rewrite the above equation in the form:

$$\psi = A \sin ka = 0$$

Since the probability,  $\psi^2$ , that the particle will be at points between  $x = 0$  and  $x = a$  cannot be zero (i.e. the particle must be somewhere inside the box),  $A$  cannot be zero and the last equation is only valid if:

$$ka = n\pi$$

where  $n = 1, 2, 3 \dots$ ;  $n$  cannot be zero as this would make the probability,  $\psi^2$ , zero meaning that the particle would no longer be in the box.

Combining the last two equations gives:

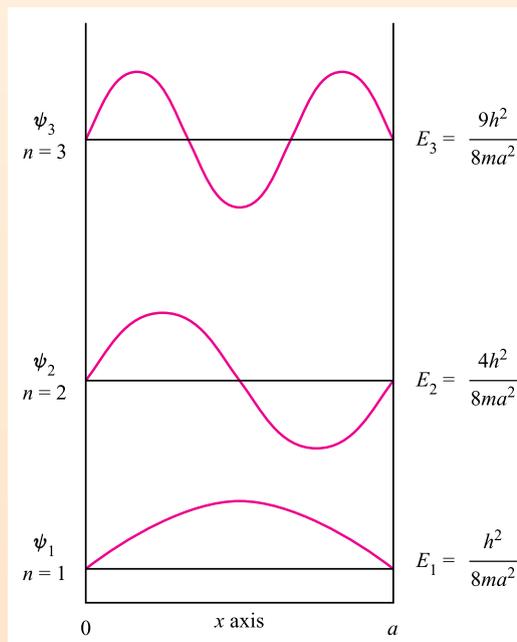
$$\psi = A \sin \frac{n\pi x}{a}$$

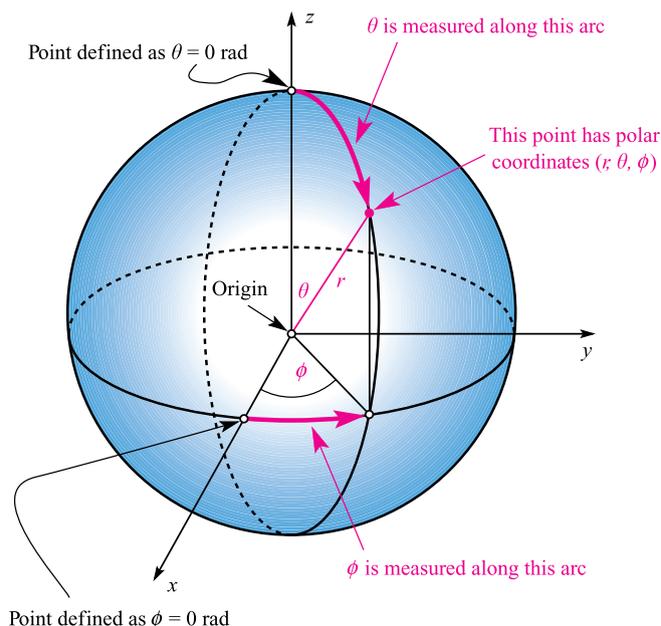
and, from earlier:

$$E = \frac{k^2 h^2}{8\pi^2 m} = \frac{n^2 h^2}{8ma^2}$$

where  $n = 1, 2, 3 \dots$ ;  $n$  is the *quantum number* determining the energy of a particle of mass  $m$  confined within a 1-dimensional box of width  $a$ . So, the limitations placed on the value of  $\psi$  have led to *quantized energy levels*, the spacing of which is determined by  $m$  and  $a$ .

The resultant motion of the particle is described by a series of standing sine waves, three of which are illustrated below. The wavefunction  $\psi_2$  has a wavelength of  $a$ , while wavefunctions  $\psi_1$  and  $\psi_3$  possess wavelengths of  $\frac{a}{2}$  and  $\frac{3a}{2}$  respectively. Each of the waves in the diagram has an amplitude of zero at the origin (i.e. at the point  $a = 0$ ); points at which  $\psi = 0$  are called *nodes*. For a given particle of mass  $m$ , the separations of the energy levels vary according to  $n^2$ , i.e. the spacings are not equal.





**Fig. 1.4.** Definition of the polar coordinates  $(r, \theta, \phi)$  for a point shown here in pink;  $r$  is the radial coordinate and  $\theta$  and  $\phi$  are angular coordinates.  $\theta$  and  $\phi$  are measured in radians (rad). Cartesian axes ( $x, y$  and  $z$ ) are also shown.

### Self-study exercises

Consider a particle that is undergoing simple-harmonic wave-like motion in one dimension, with the wave propagation along the  $x$  axis. The general equation for the wave is:

$$\psi = A \sin \frac{2\pi x}{\lambda}$$

where  $A$  is the amplitude of the wave.

1. If  $\psi = A \sin \frac{2\pi x}{\lambda}$ , find  $\frac{d\psi}{dx}$  and hence show that

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi$$

2. If the particle in the box is of mass  $m$  and moves with velocity  $v$ , what is its kinetic energy,  $KE$ ? Using the de Broglie equation (1.11), write an expression for  $KE$  in terms of  $m$ ,  $h$  and  $\lambda$ .
3. The equation you derived in part (2) applies only to a particle moving in a space in which the potential energy,  $V$ , is constant, and the particle can be regarded as possessing only kinetic energy,  $KE$ . If the potential energy of the particle does vary, the total energy,  $E = KE + V$ . Using this information and your answers to parts (1) and (2), derive the Schrödinger equation (stated on p. 8) for a particle in a 1-dimensional box.

## 1.6 Atomic orbitals

### The quantum numbers $n, l$ and $m_l$

An atomic orbital is usually described in terms of three integral *quantum numbers*. We have already encountered the *principal quantum number*,  $n$ , in the Bohr model of the hydrogen atom. The principal quantum number is a positive integer with values lying between the limits  $1 \leq n \leq \infty$ . Allowed values of  $n$  arise when the radial part of the wavefunction is solved.

Two more quantum numbers,  $l$  and  $m_l$ , appear when the angular part of the wavefunction is solved. The quantum number  $l$  is called the *orbital quantum number* and has allowed values of  $0, 1, 2, \dots, (n-1)$ . The value of  $l$  determines the shape of the atomic orbital, and the *orbital angular momentum* of the electron. The value of the *magnetic quantum number*,  $m_l$ , gives information about the directionality of an atomic orbital and has integral values between  $+l$  and  $-l$ .

Each atomic orbital may be uniquely labelled by a set of three **quantum numbers**:  $n, l$  and  $m_l$ .

The distinction among the *types* of atomic orbital arises from their *shapes* and *symmetries*. The four types of atomic orbital most commonly encountered are the  $s, p, d$  and  $f$  orbitals, and the corresponding values of  $l$  are 0, 1, 2 and 3 respectively. Each atomic orbital is labelled with

values of  $n$  and  $l$ , and hence we speak of  $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f$  etc. orbitals.

For an  $s$  orbital,  $l = 0$ . For a  $p$  orbital,  $l = 1$ .  
For a  $d$  orbital,  $l = 2$ . For an  $f$  orbital,  $l = 3$ .

### Worked example 1.3 Quantum numbers: atomic orbitals

Given that the principal quantum number,  $n$ , is 2, write down the allowed values of  $l$  and  $m_l$ , and determine the number of atomic orbitals possible for  $n = 2$ .

For a given value of  $n$ , the allowed values of  $l$  are  $0, 1, 2 \dots (n - 1)$ , and those of  $m_l$  are  $-l \dots 0 \dots +l$ .

For  $n = 2$ , allowed values of  $l = 0$  or  $1$ .

For  $l = 0$ , the allowed value of  $m_l = 0$ .

For  $l = 1$ , allowed values of  $m_l = -1, 0, +1$

Each set of three quantum numbers defines a particular atomic orbital, and, therefore, for  $n = 2$ , there are four atomic orbitals with the sets of quantum numbers:

$$n = 2, \quad l = 0, \quad m_l = 0$$

$$n = 2, \quad l = 1, \quad m_l = -1$$

$$n = 2, \quad l = 1, \quad m_l = 0$$

$$n = 2, \quad l = 1, \quad m_l = +1$$

### Self-study exercises

- If  $m_l$  has values of  $-1, 0, +1$ , write down the corresponding value of  $l$ . [Ans.  $l = 1$ ]
- If  $l$  has values  $0, 1, 2$  and  $3$ , deduce the corresponding value of  $n$ . [Ans.  $n = 4$ ]
- For  $n = 1$ , what are the allowed values of  $l$  and  $m_l$ ? [Ans.  $l = 0; m_l = 0$ ]
- Complete the following sets of quantum numbers: (a)  $n = 4, l = 0, m_l = \dots$ ; (b)  $n = 3, l = 1, m_l = \dots$ . [Ans. (a)  $0$ ; (b)  $-1, 0, +1$ ]

### Worked example 1.4 Quantum numbers: types of orbital

Using the rules that govern the values of the quantum numbers  $n$  and  $l$ , write down the possible types of atomic orbital for  $n = 1, 2$  and  $3$ .

The allowed values of  $l$  are integers between  $0$  and  $(n - 1)$ .

For  $n = 1, l = 0$ .

The only atomic orbital for  $n = 1$  is the  $1s$  orbital.

For  $n = 2, l = 0$  or  $1$ .

The allowed atomic orbitals for  $n = 2$  are the  $2s$  and  $2p$  orbitals.

For  $n = 3, l = 0, 1$  or  $2$ .

The allowed atomic orbitals for  $n = 3$  are the  $3s, 3p$  and  $3d$  orbitals.

### Self-study exercises

- Write down the possible types of atomic orbital for  $n = 4$ . [Ans.  $4s, 4p, 4d, 4f$ ]
- Which atomic orbital has values of  $n = 4$  and  $l = 2$ ? [Ans.  $4d$ ]
- Give the three quantum numbers that describe a  $2s$  atomic orbital. [Ans.  $n = 2, l = 0, m_l = 0$ ]
- Which quantum number distinguishes the  $3s$  and  $5s$  atomic orbitals? [Ans.  $n$ ]

**Degenerate orbitals possess the same energy.**

Now consider the consequence on these orbital types of the quantum number  $m_l$ . For an  $s$  orbital,  $l = 0$  and  $m_l$  can only equal  $0$ . This means that for any value of  $n$ , there is only one  $s$  orbital; it is said to be singly degenerate. For a  $p$  orbital,  $l = 1$ , and there are three possible  $m_l$  values:  $+1, 0, -1$ . This means that there are three  $p$  orbitals for a given value of  $n$  when  $n \geq 2$ ; the set of  $p$  orbitals is said to be triply or three-fold degenerate. For a  $d$  orbital,  $l = 2$ , and there are five possible values of  $m_l$ :  $+2, +1, 0, -1, -2$ , meaning that for a given value of  $n$  ( $n \geq 3$ ), there are five  $d$  orbitals; the set is said to be five-fold degenerate. As an exercise, you should show that there are seven  $f$  orbitals in a degenerate set for a given value of  $n$  ( $n \geq 4$ ).

For a given value of  $n$  ( $n \geq 1$ ) there is one  $s$  atomic orbital.  
For a given value of  $n$  ( $n \geq 2$ ) there are three  $p$  atomic orbitals.  
For a given value of  $n$  ( $n \geq 3$ ) there are five  $d$  atomic orbitals.  
For a given value of  $n$  ( $n \geq 4$ ) there are seven  $f$  atomic orbitals.

### The radial part of the wavefunction, $R(r)$

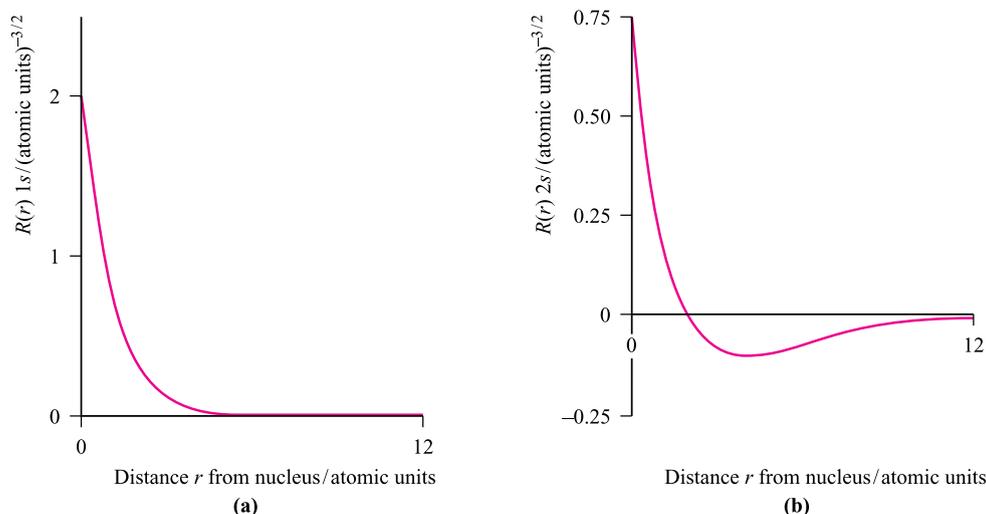
The mathematical forms of some of the wavefunctions for the H atom are listed in Table 1.2. Figure 1.5 shows plots of the radial parts of the wavefunction,  $R(r)$ , against distance,  $r$ , from the nucleus for the  $1s$  and  $2s$  atomic orbitals of the hydrogen atom, and Fig. 1.6 shows plots of  $R(r)$  against  $r$  for the  $2p, 3p, 4p$  and  $3d$  atomic orbitals; the nucleus is at  $r = 0$ .

From Table 1.2, we see that the radial parts of the wavefunctions decay exponentially as  $r$  increases, but the decay is slower for  $n = 2$  than for  $n = 1$ . This means that

**Table 1.2** Solutions of the Schrödinger equation for the hydrogen atom which define the  $1s$ ,  $2s$  and  $2p$  atomic orbitals. For these forms of the solutions, the distance  $r$  from the nucleus is measured in atomic units.

Atomic orbital	$n$	$l$	$m_l$	Radial part of the wavefunction, $R(r)^\dagger$	Angular part of wavefunction, $A(\theta, \phi)$
$1s$	1	0	0	$2e^{-r}$	$\frac{1}{2\sqrt{\pi}}$
$2s$	2	0	0	$\frac{1}{2\sqrt{2}}(2-r)e^{-r/2}$	$\frac{1}{2\sqrt{\pi}}$
$2p_x$	2	1	+1	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\sin\theta\cos\phi)}{2\sqrt{\pi}}$
$2p_z$	2	1	0	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\cos\theta)}{2\sqrt{\pi}}$
$2p_y$	2	1	-1	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\sin\theta\sin\phi)}{2\sqrt{\pi}}$

<sup>†</sup> For the  $1s$  atomic orbital, the formula for  $R(r)$  is actually  $2\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}$  but for the hydrogen atom,  $Z = 1$  and  $a_0 = 1$  atomic unit. Other functions are similarly simplified.



**Fig. 1.5.** Plots of the radial parts of the wavefunction,  $R(r)$ , against distance,  $r$ , from the nucleus for (a) the  $1s$  and (b) the  $2s$  atomic orbitals of the hydrogen atom; the nucleus is at  $r = 0$ . The vertical scales for the two plots are different but the horizontal scales are the same.

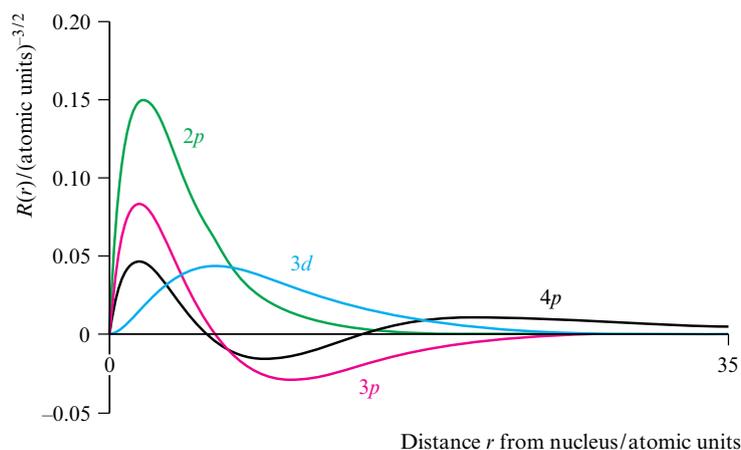
the likelihood of the electron being further from the nucleus increases as  $n$  increases. This pattern continues for higher values of  $n$ . The exponential decay can be seen clearly in Fig. 1.5a. Several points should be noted from the plots of the radial parts of wavefunctions in Figs. 1.5 and 1.6:

- $s$  atomic orbitals have a finite value of  $R(r)$  at the nucleus;
- for all orbitals other than  $s$ ,  $R(r) = 0$  at the nucleus;
- for the  $1s$  orbital,  $R(r)$  is always positive; for the first orbital of other types (i.e.  $2p$ ,  $3d$ ,  $4f$ ),  $R(r)$  is positive everywhere except at the origin;

- for the second orbital of a given type (i.e.  $2s$ ,  $3p$ ,  $4d$ ,  $5f$ ),  $R(r)$  may be positive or negative but the wavefunction has only one sign change; the point at which  $R(r) = 0$  (not including the origin) is called a radial node;
- for the third orbital of a given type (i.e.  $3s$ ,  $4p$ ,  $5d$ ,  $6f$ ),  $R(r)$  has two sign changes, i.e. it possesses two radial nodes.

#### Radial nodes:

$ns$  orbitals have  $(n - 1)$  radial nodes.  
 $np$  orbitals have  $(n - 2)$  radial nodes.  
 $nd$  orbitals have  $(n - 3)$  radial nodes.  
 $nf$  orbitals have  $(n - 4)$  radial nodes.



**Fig. 1.6.** Plots of radial parts of the wavefunction  $R(r)$  against  $r$  for the  $2p$ ,  $3p$ ,  $4p$  and  $3d$  atomic orbitals; the nucleus is at  $r = 0$ .

### The radial distribution function, $4\pi r^2 R(r)^2$

Let us now consider how we might represent atomic orbitals in 3-dimensional space. We said earlier that a useful description of an electron in an atom is the *probability of finding the electron* in a given volume of space. The function  $\psi^2$  (see Box 1.3) is proportional to the *probability density* of the electron at a point in space. By considering values of  $\psi^2$  at points around the nucleus, we can define a *surface boundary* which encloses the volume of space in which the electron will spend, say, 95% of its time. This effectively gives us a physical representation of the atomic orbital, since  $\psi^2$  may be described in terms of the radial and angular components  $R(r)^2$  and  $A(\theta, \phi)^2$ .

First consider the radial components. A useful way of depicting the probability density is to plot a *radial distribution function* (eq. 1.15) and this allows us to envisage the region in space in which the electron is found.

$$\text{Radial distribution function} = 4\pi r^2 R(r)^2 \quad (1.15)$$

The radial distribution functions for the  $1s$ ,  $2s$  and  $3s$  atomic orbitals of hydrogen are shown in Fig. 1.7, and

Fig. 1.8 shows those of the  $3s$ ,  $3p$  and  $3d$  orbitals. *Each* function is zero at the nucleus, following from the  $r^2$  term and the fact that at the nucleus  $r = 0$ . Since the function depends on  $R(r)^2$ , it is always positive in contrast to  $R(r)$ , plots for which are shown in Figs. 1.5 and 1.6. Each plot of  $4\pi r^2 R(r)^2$  shows at least one maximum value for the function, corresponding to a distance from the nucleus at which the electron has the highest probability of being found. Points at which  $4\pi r^2 R(r)^2 = 0$  (ignoring  $r = 0$ ) correspond to radial nodes where  $R(r) = 0$ .

### The angular part of the wavefunction, $A(\theta, \phi)$

Now let us consider the angular parts of the wavefunctions,  $A(\theta, \phi)$ , for different types of atomic orbitals. These are *independent* of the principal quantum number as Table 1.2 illustrates for  $n = 1$  and 2. Moreover, for  $s$  orbitals,  $A(\theta, \phi)$  is independent of the angles  $\theta$  and  $\phi$  and is of a constant value. Thus, an  $s$  orbital is spherically symmetric about the nucleus. We noted above that a set of



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### Box 1.3 Notation for $\psi^2$ and its normalization

Although we use  $\psi^2$  in the text, it should strictly be written as  $\psi\psi^*$  where  $\psi^*$  is the complex conjugate of  $\psi$ . In the  $x$ -direction, the probability of finding the electron between the limits  $x$  and  $(x + dx)$  is proportional to  $\psi(x)\psi^*(x)dx$ . In 3-dimensional space this is expressed as  $\psi\psi^*d\tau$  in which we are considering the probability of finding the electron in a volume element  $d\tau$ . For just the radial part of the wavefunction, the function is  $R(r)R^*(r)$ .

In all of our mathematical manipulations, we must ensure that the result shows that the electron is *somewhere* (i.e. it has not

vanished!) and this is done by *normalizing* the wavefunction to unity. This means that the probability of finding the electron somewhere in space is taken to be 1. Mathematically, the normalization is represented as follows:

$$\int \psi^2 d\tau = 1 \quad \text{or more correctly} \quad \int \psi\psi^* d\tau = 1$$

and this effectively states that the integral ( $\int$ ) is over all space ( $d\tau$ ) and that the total integral of  $\psi^2$  (or  $\psi\psi^*$ ) must be unity.

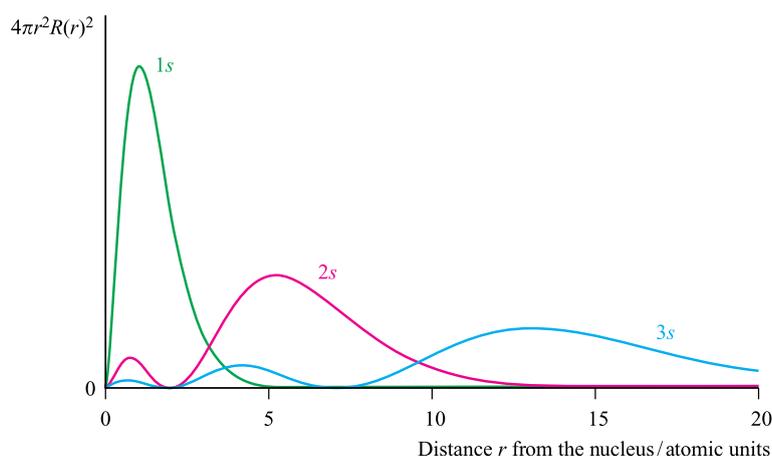


Fig. 1.7. Radial distribution functions,  $4\pi r^2 R(r)^2$ , for the 1s, 2s and 3s atomic orbitals of the hydrogen atom.

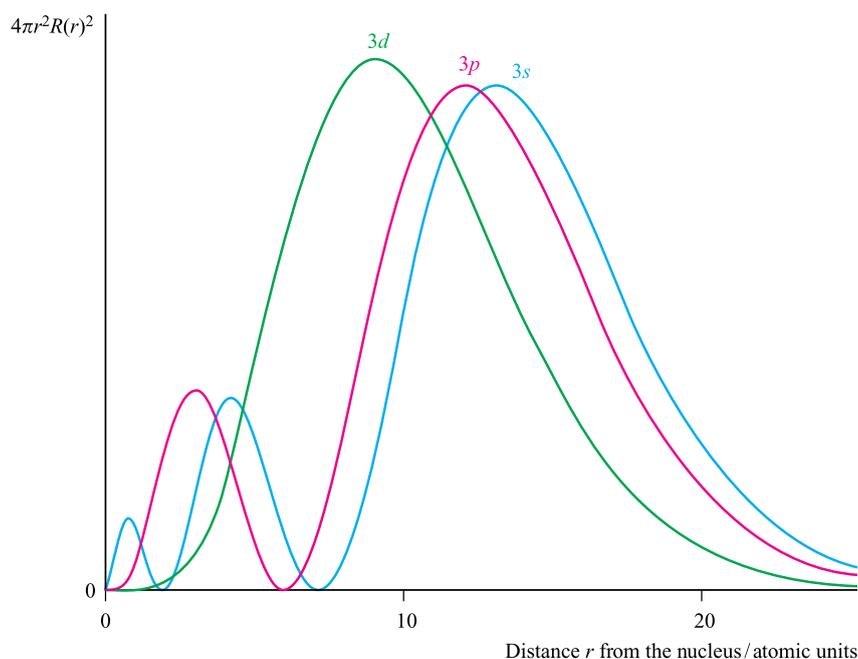
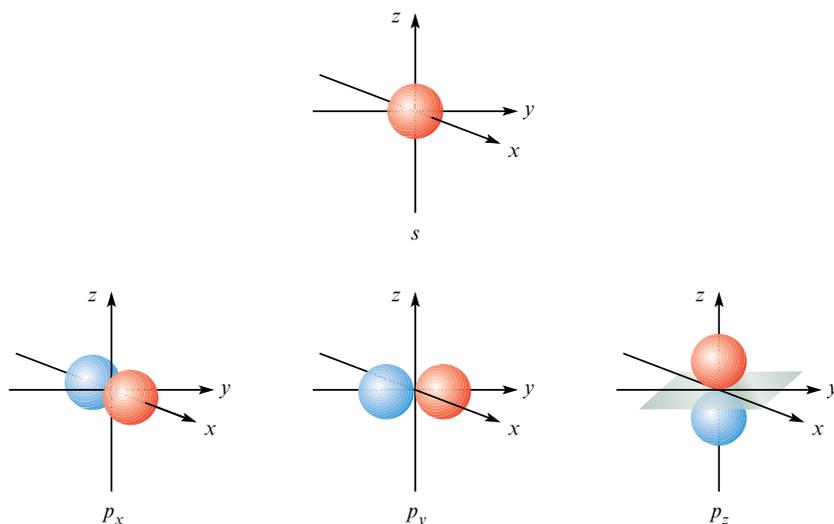


Fig. 1.8. Radial distribution functions,  $4\pi r^2 R(r)^2$ , for the 3s, 3p and 3d atomic orbitals of the hydrogen atom.

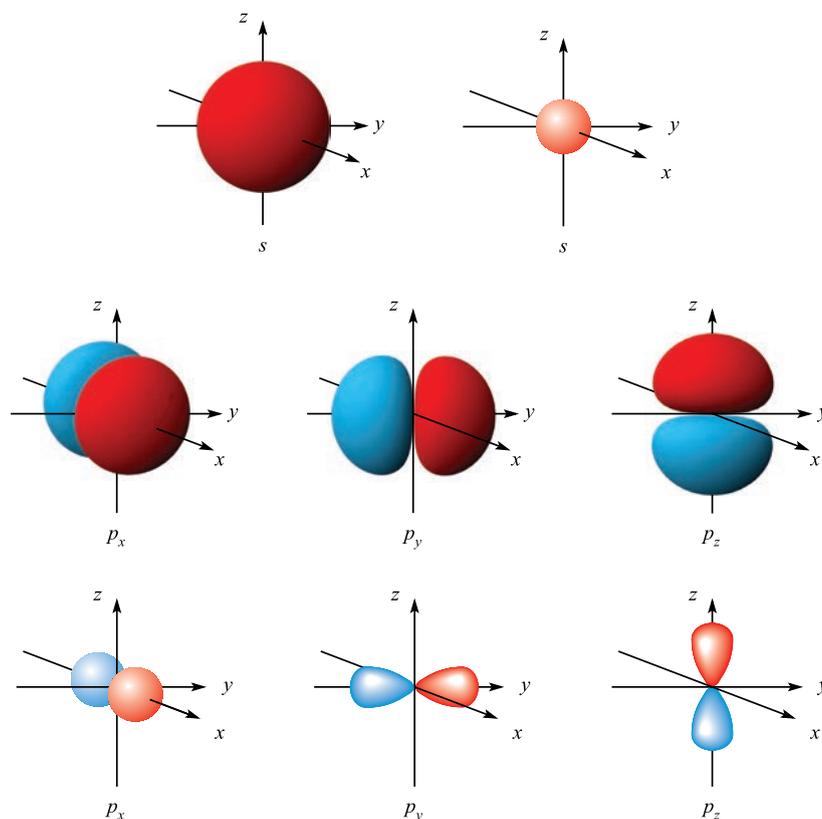
$p$  orbitals is triply degenerate; by convention the three orbitals that make up the degenerate set are given the labels  $p_x$ ,  $p_y$  and  $p_z$ . From Table 1.2, we see that the angular part of the  $p_z$  wavefunction is independent of  $\phi$ . The orbital can be represented as two spheres (touching at the origin)<sup>†</sup>, the centres of which lie on the  $z$  axis. For the  $p_x$  and  $p_y$  orbitals,  $A(\theta, \phi)$  depends on both the angles  $\theta$  and  $\phi$ ; these orbitals are similar to  $p_z$  but are oriented along the  $x$  and  $y$  axes.

<sup>†</sup> In order to emphasize that  $\phi$  is a continuous function we have extended boundary surfaces in representations of orbitals to the nucleus, but for  $p$  orbitals, this is strictly not true if we are considering  $\approx 95\%$  of the electronic charge.

Although we must not lose sight of the fact that wavefunctions are mathematical in origin, most chemists find such functions hard to visualize and prefer pictorial representations of orbitals. The boundary surfaces of the  $s$  and three  $p$  atomic orbitals are shown in Fig. 1.9. The different colours of the lobes are significant. The boundary surface of an  $s$  orbital has a constant phase, i.e. the amplitude of the wavefunction associated with the boundary surface of the  $s$  orbital has a constant sign. For a  $p$  orbital, there is one phase change with respect to the boundary surface and this occurs at a nodal plane as is shown for the  $p_z$  orbital in Fig. 1.9. The amplitude of a wavefunction may be positive or negative; this is shown using + and - signs, or by shading the lobes in different colours as in Fig. 1.9.



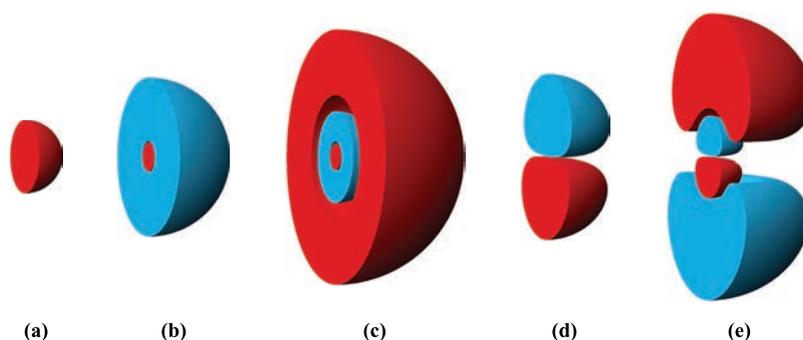
**Fig. 1.9.** Boundary surfaces for the angular parts of the  $1s$  and  $2p$  atomic orbitals of the hydrogen atom. The nodal plane shown in grey for the  $2p_z$  atomic orbital lies in the  $xy$  plane. This type of orbital picture is often called a ‘cartoon’ diagram because it is easily drawn, but is oversimplified; see Fig. 1.10.



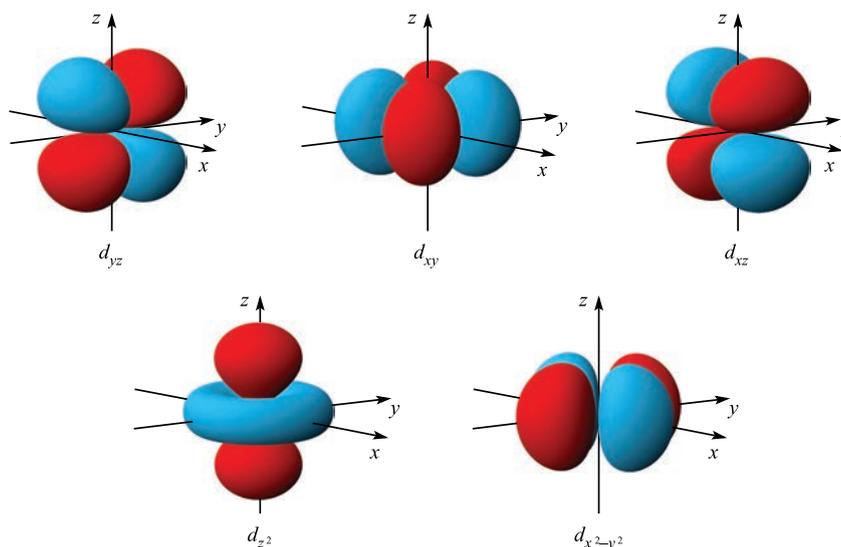
**Fig. 1.10.** Representations of an  $s$  and a set of three degenerate  $p$  atomic orbitals. The lobes of the  $p_x$  orbital are elongated like those of the  $p_y$  and  $p_z$  but are directed along the axis that passes through the plane of the paper. The figure shows ‘cartoon’ diagrams of the orbitals alongside more realistic representations generated using the program *Orbital Viewer* (David Manthey, [www.orbitals.com/orb/ov.htm](http://www.orbitals.com/orb/ov.htm)).

Just as the function  $4\pi r^2 R(r)^2$  represents the probability of finding an electron at a distance  $r$  from the nucleus, we use a function dependent upon  $A(\theta, \phi)^2$  to represent the probability in terms of  $\theta$  and  $\phi$ . For an  $s$  orbital, squaring

$A(\theta, \phi)$  causes no change in the spherical symmetry, and the surface boundary for the  $s$  atomic orbital shown in Fig. 1.10 looks similar to that in Fig. 1.9. For the  $p$  orbitals, however, going from  $A(\theta, \phi)$  to  $A(\theta, \phi)^2$  has the effect



**Fig. 1.11.** Cross-sections through the (a)  $1s$  (no radial nodes), (b)  $2s$  (one radial node), (c)  $3s$  (two radial nodes), (d)  $2p$  (no radial nodes) and (e)  $3p$  (one radial node) atomic orbitals of hydrogen. The orbitals have been generated using the program *Orbital Viewer* (David Manthey, [www.orbitals.com/orb/ov.htm](http://www.orbitals.com/orb/ov.htm)).



**Fig. 1.12.** Representations of a set of five degenerate  $d$  atomic orbitals. The orbitals have been generated using the program *Orbital Viewer* (David Manthey, [www.orbitals.com/orb/ov.htm](http://www.orbitals.com/orb/ov.htm)).

of altering the shapes of the lobes as illustrated in Fig. 1.10. Squaring  $A(\theta, \phi)$  necessarily means that the signs (+ or -) disappear, but in practice chemists often indicate the amplitude by a sign or the use of different colours (as in Fig. 1.10) because of the importance of the signs of the wavefunctions with respect to their overlap during bond formation (see Section 2.3). The consequence of the radial nodes that were introduced in Figs. 1.7 and 1.8 can be seen by looking at cross-sections through the atomic orbitals (Fig. 1.11).

Figure 1.12 shows the boundary surfaces for five hydrogen-like  $d$  orbitals. We shall not consider the mathematical forms of these wavefunctions, but merely represent the orbitals in the conventional manner. Each  $d$  orbital possesses *two* nodal planes and as an exercise you should recognize where these planes lie for each orbital. We consider  $d$  orbitals in more detail in Chapters 19 and 20, and  $f$  orbitals in Chapter 27.

### Orbital energies in a hydrogen-like species

Besides providing information about the wavefunctions, solutions of the Schrödinger equation give orbital energies,  $E$  (energy levels), and eq. 1.16 shows the dependence of  $E$  on the principal quantum number for *hydrogen-like species* where  $Z$  is the atomic number. For the hydrogen atom,  $Z = 1$ , but for the hydrogen-like  $\text{He}^+$  ion,  $Z = 2$ . The dependence of  $E$  on  $Z^2$  therefore leads to a significant lowering of the orbitals on going from H to  $\text{He}^+$ .

$$E = -\frac{kZ^2}{n^2} \quad k = \text{a constant} = 1.312 \times 10^3 \text{ kJ mol}^{-1} \quad (1.16)$$

By comparing eq. 1.16 with eq. 1.10, we can see that the constant  $k$  in eq. 1.16 is equal to the ionization energy of the H atom, i.e.  $k = hcR$  where  $h$ ,  $c$  and  $R$  are the Planck constant, the speed of light and the Rydberg constant, respectively.

For each value of  $n$  there is only one energy solution and for *hydrogen-like species*, all atomic orbitals with the same principal quantum number (e.g.  $3s$ ,  $3p$  and  $3d$ ) are degenerate. It follows from eq. 1.16 that the orbital energy levels get closer together as the value of  $n$  increases. This result is a general one for all other atoms.

### Self-study exercises

$$1 \text{ eV} = 96.485 \text{ kJ mol}^{-1}$$

1. Show that the energy of both the  $2s$  and  $2p$  orbitals for a hydrogen atom is  $-328 \text{ kJ mol}^{-1}$ .
2. For a hydrogen atom, confirm that the energy of the  $3s$  orbital is  $-1.51 \text{ eV}$ .
3. The energy of a hydrogen  $ns$  orbital is  $-13.6 \text{ eV}$ . Show that  $n = 1$ .
4. Determine the energy (in  $\text{kJ mol}^{-1}$ ) of the  $1s$  orbital of an  $\text{He}^+$  ion and compare it with that of the  $1s$  orbital of an H atom.  
[Ans.  $-5248 \text{ kJ mol}^{-1}$  for  $\text{He}^+$ ;  $-1312 \text{ kJ mol}^{-1}$  for H]

### Size of orbitals

For a given atom, a series of orbitals with different values of  $n$  but the same values of  $l$  and  $m_l$  (e.g.  $1s$ ,  $2s$ ,  $3s$ ,  $4s$ , ...) differ in their relative size (spatial extent). The larger the value of  $n$ , the larger the orbital, although this relationship is not linear. The relative spatial extents of the  $1s$ ,  $2s$  and  $3s$  orbitals, and of the  $2p$  and  $3p$  orbitals, are shown in Fig. 1.11. An increase in size also corresponds to an orbital being more *diffuse*.

### The spin quantum number and the magnetic spin quantum number

Before we place electrons into atomic orbitals, we must define two more quantum numbers. In a classical model, an electron is considered to spin about an axis passing through it and to have *spin angular momentum* in addition to orbital angular momentum (see Box 1.4). The *spin quantum number*,  $s$ , determines the magnitude of the spin angular momentum of an electron and has a value of  $\frac{1}{2}$ . Since angular momentum is a vector quantity, it must have direction, and this is determined by the *magnetic spin quantum number*,  $m_s$ , which has a value of  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .

Whereas an atomic orbital is defined by a unique set of *three* quantum numbers, an electron in an atomic orbital is defined by a unique set of *four* quantum numbers:  $n$ ,  $l$ ,  $m_l$  and  $m_s$ . As there are only two values of  $m_s$ , an orbital can accommodate only two electrons.

An **orbital is fully occupied** when it contains two **spin-paired electrons**; one electron has  $m_s = +\frac{1}{2}$  and the other has  $m_s = -\frac{1}{2}$ .

### Self-study exercises

For help with these exercises, refer to Box 1.4.

1. What do you understand by the term ‘the orbital angular momentum of an electron in an orbital’?
2. Explain why it is incorrect to write that ‘the quantum number  $s = \pm\frac{1}{2}$ ’.
3. For an  $s$  orbital,  $l = 0$ . Explain why this leads to a classical picture of an electron in an  $s$  orbital *not* moving around the nucleus.
4. By considering a  $2p$  orbital with values of  $m_l = +1, 0$  and  $-1$ , explain the physical significance of the quantum number  $m_l$ .
5. Show that for an electron in a  $2s$  orbital, the quantum number  $j$  can only take the value  $\frac{1}{2}$ .
6. Show that for an electron in a  $2p$  orbital, the quantum number  $j$  can take the value of  $\frac{3}{2}$  or  $\frac{1}{2}$ .
7. For a  $p$  electron circulating clockwise or counter-clockwise about an axis, the value of  $m_l$  is  $+1$  or  $-1$ . What can you say about a  $p$  electron for which  $m_l = 0$ ?

### Worked example 1.5 Quantum numbers: an electron in an atomic orbital

**Write down two possible sets of quantum numbers that describe an electron in a  $2s$  atomic orbital. What is the physical significance of these unique sets?**

The  $2s$  atomic orbital is defined by the set of quantum numbers  $n = 2$ ,  $l = 0$ ,  $m_l = 0$ .

An electron in a  $2s$  atomic orbital may have one of two sets of four quantum numbers:

$$n = 2, \quad l = 0, \quad m_l = 0, \quad m_s = +\frac{1}{2}$$

or

$$n = 2, \quad l = 0, \quad m_l = 0, \quad m_s = -\frac{1}{2}$$

If the orbital were fully occupied with two electrons, one electron would have  $m_s = +\frac{1}{2}$ , and the other electron would have  $m_s = -\frac{1}{2}$ , i.e. the two electrons would be spin-paired.

### Self-study exercises

1. Write down two possible sets of quantum numbers to describe an electron in a  $3s$  atomic orbital.  
[Ans.  $n = 3$ ,  $l = 0$ ,  $m_l = 0$ ,  $m_s = +\frac{1}{2}$ ;  $n = 3$ ,  $l = 0$ ,  $m_l = 0$ ,  $m_s = -\frac{1}{2}$ ]
2. If an electron has the quantum numbers  $n = 2$ ,  $l = 1$ ,  $m_l = -1$  and  $m_s = +\frac{1}{2}$  which type of atomic orbital is it occupying?  
[Ans.  $2p$ ]



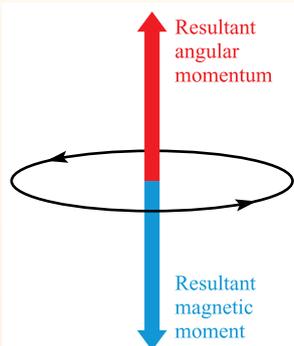
## THEORY

Box 1.4 Angular momentum, the inner quantum number,  $j$ , and spin-orbit coupling

The value of  $l$  determines not only the shape of an orbital but also the amount of orbital angular momentum associated with an electron in the orbital:

$$\text{Orbital angular momentum} = \left[ \sqrt{l(l+1)} \right] \frac{h}{2\pi}$$

The axis through the nucleus about which the electron (considered classically) can be thought to rotate defines the direction of the orbital angular momentum. The latter gives rise to a magnetic moment the direction of which is in the same sense as the angular vector and the magnitude of which is proportional to the magnitude of the vector.



In a classical model, an electron moving in a circular orbit has an angular momentum defined by the resultant vector shown in red.

Because the electron is a charged particle, there is an associated magnetic moment, the direction of which is represented in the diagram by the blue arrow.

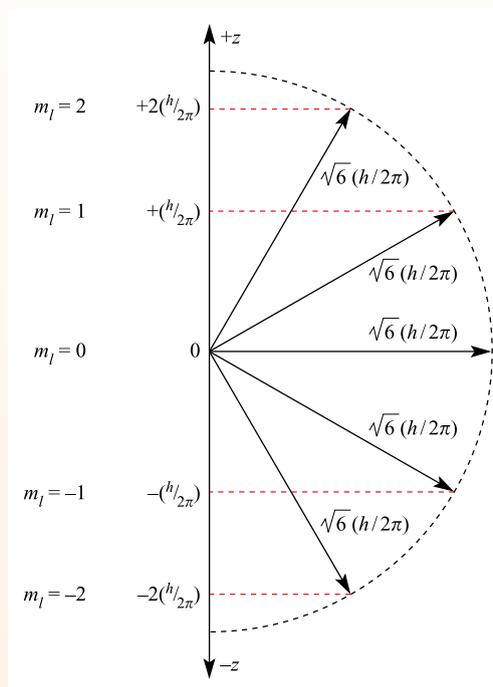
An electron in an  $s$  orbital ( $l = 0$ ) has no orbital angular momentum, an electron in a  $p$  orbital ( $l = 1$ ) has angular momentum  $\sqrt{2}(h/2\pi)$ , and so on. The orbital angular momentum vector has  $(2l + 1)$  possible directions in space corresponding to the  $(2l + 1)$  possible values of  $m_l$  for a given value of  $l$ . Consider the component of the angular momentum vector along the  $z$  axis; this has a different value for each of the possible orientations that this vector can take up. The actual magnitude of the  $z$  component is given by  $m_l(h/2\pi)$ . Thus, for an electron in a  $d$  orbital ( $l = 2$ ), the orbital angular momentum is  $\sqrt{6}(h/2\pi)$ , and the  $z$  component of this may have values of  $+2(h/2\pi)$ ,  $+(h/2\pi)$ ,  $0$ ,  $-(h/2\pi)$  or  $-2(h/2\pi)$  as shown in the figure opposite.

The orbitals in a sub-shell of given  $n$  and  $l$ , are degenerate. If, however, the atom is placed in a magnetic field, this degeneracy is removed. If we arbitrarily define the direction of the magnetic field as the  $z$  axis, electrons in the various  $d$  orbitals will interact to different extents with the magnetic field because of their different values of the  $z$  components of their angular momentum vectors (and, hence, orbital magnetic moment vectors).

An electron also has spin angular momentum which can be regarded as originating in the rotation of the electron about its own axis. The magnitude of this is given by:

$$\text{Spin angular momentum} = \left[ \sqrt{s(s+1)} \right] \frac{h}{2\pi}$$

where  $s$  = spin quantum number. The axis defines the direction of the spin angular momentum vector, but again it is the orientation of this vector with respect to the  $z$  direction in which we are interested. The  $z$  component is given by  $m_s(h/2\pi)$ ; since  $m_s$  can only equal  $+\frac{1}{2}$  or  $-\frac{1}{2}$ , there are only two possible orientations of the spin angular momentum vector, and these give rise to  $z$  components of magnitude  $+\frac{1}{2}(h/2\pi)$  and  $-\frac{1}{2}(h/2\pi)$ .



For an electron having both orbital and spin angular momentum, the total angular momentum vector is given by:

$$\text{Total angular momentum} = \left[ \sqrt{j(j+1)} \right] \frac{h}{2\pi}$$

where  $j$  is the *inner quantum number*;  $j$  may take values of  $|l + s|$  or  $|l - s|$ , i.e.  $|l + \frac{1}{2}|$  or  $|l - \frac{1}{2}|$ . The symbol ' $|$ ' is a modulus sign and signifies that the quantities  $(l + s)$  and  $(l - s)$  must have *positive* values. Thus, when  $l = 0$ ,  $j$  can only be  $\frac{1}{2}$  because  $|0 + \frac{1}{2}| = |0 - \frac{1}{2}| = \frac{1}{2}$ . (When  $l = 0$  and the electron has no orbital angular momentum, the total angular momentum is

$\left[ \sqrt{s(s+1)} \right] \frac{h}{2\pi}$  because  $j = s$ .) The  $z$  component of the total angular momentum vector is now  $j(h/2\pi)$  and there are  $(2j + 1)$  possible orientations in space.

For an electron in an  $ns$  orbital ( $l = 0$ ),  $j$  can only be  $\frac{1}{2}$ . When the electron is promoted to an  $np$  orbital,  $j$  may be  $\frac{3}{2}$  or  $\frac{1}{2}$ , and the energies corresponding to the different  $j$  values are not equal. In the emission spectrum of sodium, for example, transitions from the  $3p_{3/2}$  and  $3p_{1/2}$  levels to the  $3s_{1/2}$  level correspond to slightly different amounts of energy, and this *spin-orbit coupling* is the origin of the doublet structure of the strong yellow line in the spectrum of atomic sodium (see Fig. 1.18 p. 31). The fine structure of many other spectral lines arises in analogous ways, though the number of lines observed depends on the difference in energy between states differing only in  $j$  value and on the resolving power of the spectrometer. The difference in energy between levels for which  $\Delta j = 1$  (the spin-orbit coupling constant,  $\lambda$ ) increases with the atomic number of the element; e.g. that between the  $np_{3/2}$  and  $np_{1/2}$  levels for Li, Na and Cs is 0.23, 11.4 and  $370 \text{ cm}^{-1}$  respectively.

3. An electron has the quantum numbers  $n = 4$ ,  $l = 1$ ,  $m_l = 0$  and  $m_s = +\frac{1}{2}$ . Is the electron in a  $4s$ ,  $4p$  or  $4d$  atomic orbital? [Ans.  $4p$ ]
4. Write down a set of quantum numbers that describes an electron in a  $5s$  atomic orbital. How does this set of quantum numbers differ if you are describing the second electron in the same orbital? [Ans.  $n = 5$ ,  $l = 0$ ,  $m_l = 0$ ,  $m_s = +\frac{1}{2}$  or  $-\frac{1}{2}$ ]

## The ground state of the hydrogen atom

So far we have focused on the atomic orbitals of hydrogen and have talked about the probability of finding an electron in different atomic orbitals. The most energetically favourable (stable) state of the H atom is its *ground state* in which the single electron occupies the  $1s$  (lowest energy) atomic orbital. The electron can be promoted to higher energy orbitals (see Section 1.4) to give *excited states*.

The notation for the *ground state electronic configuration* of an H atom is  $1s^1$ , signifying that one electron occupies the  $1s$  atomic orbital.

## 1.7 Many-electron atoms

### The helium atom: two electrons

The preceding sections have been devoted mainly to hydrogen-like species containing one electron, the energy of which depends on  $n$  and  $Z$  (eq. 1.16). The atomic spectra of such species contain only a few lines associated with changes in the value of  $n$  (Fig. 1.3). It is *only* for such species that the Schrödinger equation has been solved exactly.

The next simplest atom is He ( $Z = 2$ ), and for its two electrons, three electrostatic interactions must be considered:

- attraction between electron (1) and the nucleus;
- attraction between electron (2) and the nucleus;
- repulsion between electrons (1) and (2).

The *net* interaction determines the energy of the system.

In the ground state of the He atom, two electrons with  $m_s = +\frac{1}{2}$  and  $-\frac{1}{2}$  occupy the  $1s$  atomic orbital, i.e. the electronic configuration is  $1s^2$ . For all atoms except hydrogen-like species, orbitals of the same principal quantum number but differing  $l$  are *not* degenerate. If one of the  $1s^2$  electrons is promoted to an orbital with  $n = 2$ , the energy of the system depends upon whether the electron goes into a  $2s$  or  $2p$  atomic orbital, because each situation gives rise to different electrostatic interactions involving the two electrons and the nucleus. However, there is no energy distinction among the three different  $2p$  atomic orbitals. If promotion is to an orbital with  $n = 3$ , different

amounts of energy are needed depending upon whether  $3s$ ,  $3p$  or  $3d$  orbitals are involved, although there is no energy difference among the three  $3p$  atomic orbitals, or among the five  $3d$  atomic orbitals. The emission spectrum of He arises as the electrons fall back to lower energy states or to the ground state and it follows that the spectrum contains more lines than that of atomic H.

In terms of obtaining wavefunctions and energies for the atomic orbitals of He, it has not been possible to solve the Schrödinger equation exactly and only approximate solutions are available. For atoms containing more than two electrons, it is even more difficult to obtain accurate solutions to the wave equation.

In a *multi-electron atom*, orbitals with the same value of  $n$  but different values of  $l$  are *not* degenerate.

### Ground state electronic configurations: experimental data

Now consider the ground state electronic configurations of isolated atoms of all the elements (Table 1.3). These are experimental data, and are nearly always obtained by analysing atomic spectra. Most atomic spectra are too complex for discussion here and we take their interpretation on trust.

We have already seen that the ground state electronic configurations of H and He are  $1s^1$  and  $1s^2$  respectively. The  $1s$  atomic orbital is fully occupied in He and its configuration is often written as [He]. In the next two elements, Li and Be, the electrons go into the  $2s$  orbital, and then from B to Ne, the  $2p$  orbitals are occupied to give the electronic configurations [He] $2s^2 2p^m$  ( $m = 1-6$ ). When  $m = 6$ , the energy level (or *shell*) with  $n = 2$  is fully occupied, and the configuration for Ne can be written as [Ne]. The filling of the  $3s$  and  $3p$  atomic orbitals takes place in an analogous sequence from Na to Ar, the last element in the series having the electronic configuration [Ne] $3s^2 3p^6$  or [Ar].

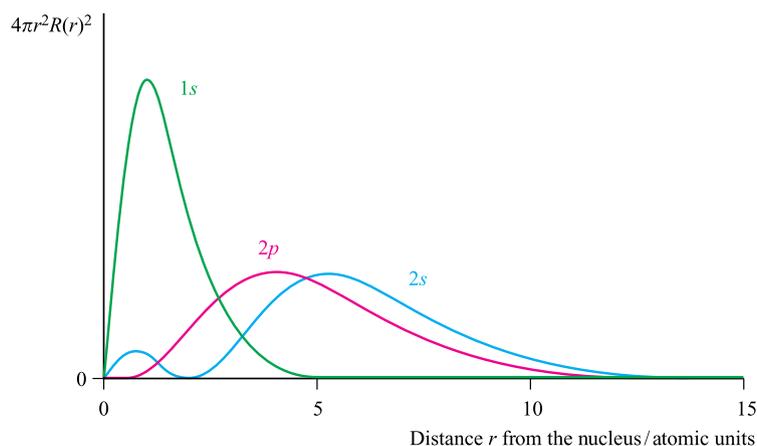
With K and Ca, successive electrons go into the  $4s$  orbital, and Ca has the electronic configuration [Ar] $4s^2$ . At this point, the pattern changes. To a first approximation, the 10 electrons for the next 10 elements (Sc to Zn) enter the  $3d$  orbitals, giving Zn the electronic configuration  $4s^2 3d^{10}$ . There are some irregularities (see Table 1.3) to which we return later. From Ga to Kr, the  $4p$  orbitals are filled, and the electronic configuration for Kr is [Ar] $4s^2 3d^{10} 4p^6$  or [Kr].

From Rb to Xe, the general sequence of filling orbitals is the same as that from K to Kr although there are once again irregularities in the distribution of electrons between  $s$  and  $d$  atomic orbitals (see Table 1.3).

From Cs to Rn, electrons enter  $f$  orbitals for the first time; Cs, Ba and La have configurations analogous to those of Rb, Sr and Y, but after that the configurations change as we

**Table 1.3** Ground state electronic configurations of the elements up to  $Z = 103$ .

Atomic number	Element	Ground state electronic configuration	Atomic number	Element	Ground state electronic configuration
1	H	$1s^1$	53	I	$[\text{Kr}]5s^2 4d^{10} 5p^5$
2	He	$1s^2 = [\text{He}]$	54	Xe	$[\text{Kr}]5s^2 4d^{10} 5p^6 = [\text{Xe}]$
3	Li	$[\text{He}]2s^1$	55	Cs	$[\text{Xe}]6s^1$
4	Be	$[\text{He}]2s^2$	56	Ba	$[\text{Xe}]6s^2$
5	B	$[\text{He}]2s^2 2p^1$	57	La	$[\text{Xe}]6s^2 5d^1$
6	C	$[\text{He}]2s^2 2p^2$	58	Ce	$[\text{Xe}]4f^1 6s^2 5d^1$
7	N	$[\text{He}]2s^2 2p^3$	59	Pr	$[\text{Xe}]4f^3 6s^2$
8	O	$[\text{He}]2s^2 2p^4$	60	Nd	$[\text{Xe}]4f^4 6s^2$
9	F	$[\text{He}]2s^2 2p^5$	61	Pm	$[\text{Xe}]4f^5 6s^2$
10	Ne	$[\text{He}]2s^2 2p^6 = [\text{Ne}]$	62	Sm	$[\text{Xe}]4f^6 6s^2$
11	Na	$[\text{Ne}]3s^1$	63	Eu	$[\text{Xe}]4f^7 6s^2$
12	Mg	$[\text{Ne}]3s^2$	64	Gd	$[\text{Xe}]4f^7 6s^2 5d^1$
13	Al	$[\text{Ne}]3s^2 3p^1$	65	Tb	$[\text{Xe}]4f^9 6s^2$
14	Si	$[\text{Ne}]3s^2 3p^2$	66	Dy	$[\text{Xe}]4f^{10} 6s^2$
15	P	$[\text{Ne}]3s^2 3p^3$	67	Ho	$[\text{Xe}]4f^{11} 6s^2$
16	S	$[\text{Ne}]3s^2 3p^4$	68	Er	$[\text{Xe}]4f^{12} 6s^2$
17	Cl	$[\text{Ne}]3s^2 3p^5$	69	Tm	$[\text{Xe}]4f^{13} 6s^2$
18	Ar	$[\text{Ne}]3s^2 3p^6 = [\text{Ar}]$	70	Yb	$[\text{Xe}]4f^{14} 6s^2$
19	K	$[\text{Ar}]4s^1$	71	Lu	$[\text{Xe}]4f^{14} 6s^2 5d^1$
20	Ca	$[\text{Ar}]4s^2$	72	Hf	$[\text{Xe}]4f^{14} 6s^2 5d^2$
21	Sc	$[\text{Ar}]4s^2 3d^1$	73	Ta	$[\text{Xe}]4f^{14} 6s^2 5d^3$
22	Ti	$[\text{Ar}]4s^2 3d^2$	74	W	$[\text{Xe}]4f^{14} 6s^2 5d^4$
23	V	$[\text{Ar}]4s^2 3d^3$	75	Re	$[\text{Xe}]4f^{14} 6s^2 5d^5$
24	Cr	$[\text{Ar}]4s^1 3d^5$	76	Os	$[\text{Xe}]4f^{14} 6s^2 5d^6$
25	Mn	$[\text{Ar}]4s^2 3d^5$	77	Ir	$[\text{Xe}]4f^{14} 6s^2 5d^7$
26	Fe	$[\text{Ar}]4s^2 3d^6$	78	Pt	$[\text{Xe}]4f^{14} 6s^1 5d^9$
27	Co	$[\text{Ar}]4s^2 3d^7$	79	Au	$[\text{Xe}]4f^{14} 6s^1 5d^{10}$
28	Ni	$[\text{Ar}]4s^2 3d^8$	80	Hg	$[\text{Xe}]4f^{14} 6s^2 5d^{10}$
29	Cu	$[\text{Ar}]4s^1 3d^{10}$	81	Tl	$[\text{Xe}]4f^{14} 6s^2 5d^{10} 6p^1$
30	Zn	$[\text{Ar}]4s^2 3d^{10}$	82	Pb	$[\text{Xe}]4f^{14} 6s^2 5d^{10} 6p^2$
31	Ga	$[\text{Ar}]4s^2 3d^{10} 4p^1$	83	Bi	$[\text{Xe}]4f^{14} 6s^2 5d^{10} 6p^3$
32	Ge	$[\text{Ar}]4s^2 3d^{10} 4p^2$	84	Po	$[\text{Xe}]4f^{14} 6s^2 5d^{10} 6p^4$
33	As	$[\text{Ar}]4s^2 3d^{10} 4p^3$	85	At	$[\text{Xe}]4f^{14} 6s^2 5d^{10} 6p^5$
34	Se	$[\text{Ar}]4s^2 3d^{10} 4p^4$	86	Rn	$[\text{Xe}]4f^{14} 6s^2 5d^{10} 6p^6 = [\text{Rn}]$
35	Br	$[\text{Ar}]4s^2 3d^{10} 4p^5$	87	Fr	$[\text{Rn}]7s^1$
36	Kr	$[\text{Ar}]4s^2 3d^{10} 4p^6 = [\text{Kr}]$	88	Ra	$[\text{Rn}]7s^2$
37	Rb	$[\text{Kr}]5s^1$	89	Ac	$[\text{Rn}]6d^1 7s^2$
38	Sr	$[\text{Kr}]5s^2$	90	Th	$[\text{Rn}]6d^2 7s^2$
39	Y	$[\text{Kr}]5s^2 4d^1$	91	Pa	$[\text{Rn}]5f^2 7s^2 6d^1$
40	Zr	$[\text{Kr}]5s^2 4d^2$	92	U	$[\text{Rn}]5f^3 7s^2 6d^1$
41	Nb	$[\text{Kr}]5s^1 4d^4$	93	Np	$[\text{Rn}]5f^4 7s^2 6d^1$
42	Mo	$[\text{Kr}]5s^1 4d^5$	94	Pu	$[\text{Rn}]5f^6 7s^2$
43	Tc	$[\text{Kr}]5s^2 4d^5$	95	Am	$[\text{Rn}]5f^7 7s^2$
44	Ru	$[\text{Kr}]5s^1 4d^7$	96	Cm	$[\text{Rn}]5f^7 7s^2 6d^1$
45	Rh	$[\text{Kr}]5s^1 4d^8$	97	Bk	$[\text{Rn}]5f^9 7s^2$
46	Pd	$[\text{Kr}]5s^0 4d^{10}$	98	Cf	$[\text{Rn}]5f^{10} 7s^2$
47	Ag	$[\text{Kr}]5s^1 4d^{10}$	99	Es	$[\text{Rn}]5f^{11} 7s^2$
48	Cd	$[\text{Kr}]5s^2 4d^{10}$	100	Fm	$[\text{Rn}]5f^{12} 7s^2$
49	In	$[\text{Kr}]5s^2 4d^{10} 5p^1$	101	Md	$[\text{Rn}]5f^{13} 7s^2$
50	Sn	$[\text{Kr}]5s^2 4d^{10} 5p^2$	102	No	$[\text{Rn}]5f^{14} 7s^2$
51	Sb	$[\text{Kr}]5s^2 4d^{10} 5p^3$	103	Lr	$[\text{Rn}]5f^{14} 7s^2 6d^1$
52	Te	$[\text{Kr}]5s^2 4d^{10} 5p^4$			



**Fig. 1.13.** Radial distribution functions,  $4\pi r^2 R(r)^2$ , for the  $1s$ ,  $2s$  and  $2p$  atomic orbitals of the hydrogen atom.

begin the sequence of the *lanthanoid* elements (see Chapter 27).<sup>†</sup> Cerium has the configuration  $[\text{Xe}]4f^1 6s^2 5d^1$  and the filling of the seven  $4f$  orbitals follows until an electronic configuration of  $[\text{Xe}]4f^{14} 6s^2 5d^1$  is reached for Lu. Table 1.3 shows that the  $5d$  orbital is not usually occupied for a lanthanoid element. After Lu, successive electrons occupy the remaining  $5d$  orbitals (Hf to Hg) and then the  $6p$  orbitals to Rn which has the configuration  $[\text{Xe}]4f^{14} 6s^2 5d^{10} 6p^6$  or [Rn]. Table 1.3 shows some irregularities along the series of *d*-block elements.

For the remaining elements in Table 1.3 beginning at francium (Fr), filling of the orbitals follows a similar sequence as that from Cs but the sequence is incomplete and some of the heaviest elements are too unstable for detailed investigations to be possible. The metals from Th to Lr are the *actinoid* elements, and in discussing their chemistry, Ac is generally considered with the actinoids (see Chapter 27).

A detailed inspection of Table 1.3 makes it obvious that there is no one sequence that represents accurately the occupation of different sets of orbitals with increasing atomic number. The following sequence is *approximately* true for the relative energies (lowest energy first) of orbitals in *neutral atoms*:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p \\ < 6s < 5d \approx 4f < 6p < 7s < 6d \approx 5f$$

The energies of different orbitals are close together for high values of  $n$  and their relative energies can change significantly on forming an ion (see Section 19.2).

### Penetration and shielding

Although it is not possible to calculate the dependence of the energies of orbitals on atomic number with the degree of accuracy that is required to obtain agreement with all the

electronic configurations listed in Table 1.3, some useful information can be gained by considering the different *screening effects* that electrons in different atomic orbitals have on one another. Figure 1.13 shows the radial distribution functions for the  $1s$ ,  $2s$  and  $2p$  atomic orbitals of the H atom. (It is a common approximation to assume hydrogen-like wavefunctions for multi-electron atoms.) Although values of  $4\pi r^2 R(r)^2$  for the  $1s$  orbital are much greater than those of the  $2s$  and  $2p$  orbitals at distances relatively close to the nucleus, the values for the  $2s$  and  $2p$  orbitals are still significant. We say that the  $2s$  and  $2p$  atomic orbitals *penetrate* the  $1s$  atomic orbital. Calculations show that the  $2s$  atomic orbital is more penetrating than the  $2p$  orbital.

Now let us consider the arrangement of the electrons in Li ( $Z = 3$ ). In the ground state, the  $1s$  atomic orbital is fully occupied and the third electron could occupy either a  $2s$  or  $2p$  orbital. Which arrangement will possess the lower energy? An electron in a  $2s$  or  $2p$  atomic orbital experiences the *effective nuclear charge*,  $Z_{\text{eff}}$ , of a nucleus partly *shielded* by the  $1s$  electrons. Since the  $2p$  orbital penetrates the  $1s$  orbital less than a  $2s$  orbital does (Fig. 1.13), a  $2p$  electron is shielded more than a  $2s$  electron. Thus, occupation of the  $2s$  rather than the  $2p$  atomic orbital gives a lower energy system. Although we should consider the energies of the *electrons* in atomic orbitals, it is common practice to think in terms of the orbital energies themselves:  $E(2s) < E(2p)$ . Similar arguments lead to the sequence  $E(3s) < E(3p) < E(3d)$  and  $E(4s) < E(4p) < E(4d) < E(4f)$ . As we move to atoms of elements of higher atomic number, the energy differences between orbitals with the same value of  $n$  become smaller, the validity of assuming hydrogen-like wavefunctions becomes more doubtful, and predictions of ground states become less reliable. The treatment above also ignores electron–electron interactions within the same principal quantum shell.

A set of empirical rules (Slater's rules) for estimating the effective nuclear charges experienced by electrons in different atomic orbitals is described in Box 1.5.

<sup>†</sup> The IUPAC recommends the names lanthanoid and actinoid in preference to lanthanide and actinide; the ending '-ide' usually implies a negatively charged ion. However, lanthanide and actinide are still widely used.



## THEORY

## Box 1.5 Effective nuclear charge and Slater's rules

## Slater's rules

Effective nuclear charges,  $Z_{\text{eff}}$ , experienced by electrons in different atomic orbitals may be estimated using *Slater's rules*. These rules are based on experimental data for electron promotion and ionization energies, and  $Z_{\text{eff}}$  is determined from the equation:

$$Z_{\text{eff}} = Z - S$$

where  $Z$  = nuclear charge,  $Z_{\text{eff}}$  = effective nuclear charge,  $S$  = screening (or shielding) constant.

Values of  $S$  may be estimated as follows:

- Write out the electronic configuration of the element in the following order and groupings: ( $1s$ ), ( $2s$ ,  $2p$ ), ( $3s$ ,  $3p$ ), ( $3d$ ), ( $4s$ ,  $4p$ ), ( $4d$ ), ( $4f$ ), ( $5s$ ,  $5p$ ) etc.
- Electrons in any group higher in this sequence than the electron under consideration contribute nothing to  $S$ .
- Consider a particular electron in an  $ns$  or  $np$  orbital:
  - Each of the other electrons in the ( $ns$ ,  $np$ ) group contributes  $S = 0.35$ .
  - Each of the electrons in the ( $n - 1$ ) shell contributes  $S = 0.85$ .
  - Each of the electrons in the ( $n - 2$ ) or lower shells contributes  $S = 1.00$ .
- Consider a particular electron in an  $nd$  or  $nf$  orbital:
  - Each of the other electrons in the ( $nd$ ,  $nf$ ) group contributes  $S = 0.35$ .
  - Each of the electrons in a lower group than the one being considered contributes  $S = 1.00$ .

## An example of how to apply Slater's rules

Question: Confirm that the experimentally observed electronic configuration of K,  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ , is energetically more stable than the configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ .

For K,  $Z = 19$ .

Applying Slater's rules, the effective nuclear charge experienced by the  $4s$  electron for the configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$  is:

$$Z_{\text{eff}} = Z - S$$

The nuclear charge,  $Z = 19$

The screening constant,  $S = (8 \times 0.85) + (10 \times 1.00)$   
 $= 16.8$

$$Z_{\text{eff}} = 19 - 16.8 = 2.2$$

The effective nuclear charge experienced by the  $3d$  electron for the configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$  is:

$$Z_{\text{eff}} = Z - S$$

The nuclear charge,  $Z = 19$

The screening constant,  $S = (18 \times 1.00)$   
 $= 18.0$

$$Z_{\text{eff}} = 19 - 18.0 = 1.0$$

Thus, an electron in the  $4s$  (rather than the  $3d$ ) atomic orbital is under the influence of a greater effective nuclear charge and in the ground state of potassium, it is the  $4s$  atomic orbital that is occupied.

Slater versus Clementi and Raimondi values of  $Z_{\text{eff}}$ 

Slater's rules have been used to estimate ionization energies, ionic radii and electronegativities. More accurate effective nuclear charges have been calculated by Clementi and Raimondi by using *self-consistent field* (SCF) methods, and indicate much higher  $Z_{\text{eff}}$  values for the  $d$  electrons. However, the simplicity of Slater's approach makes this an attractive method for 'back-of-the-envelope' estimations of  $Z_{\text{eff}}$ .

## Self-study exercises

- Show that Slater's rules give a value of  $Z_{\text{eff}} = 1.95$  for a  $2s$  electron in a Be atom.
- Show that Slater's rules give a value of  $Z_{\text{eff}} = 5.20$  for a  $2p$  electron of F.
- Use Slater's rules to estimate values of  $Z_{\text{eff}}$  for (a) a  $4s$  and (b) a  $3d$  electron in a V atom.  
 [Ans. (a) 3.30; (b) 4.30]
- Using your answer to question 3, explain why the valence configuration of the ground state of a  $V^+$  ion is likely to be  $3d^3 4s^1$  rather than  $3d^2 4s^2$ .

## Further reading

- J.L. Reed (1999) *J. Chem. Educ.*, vol. 76, p. 802 – 'The genius of Slater's rules'.
- D. Tudela (1993) *J. Chem. Educ.*, vol. 70, p. 956 – 'Slater's rules and electronic configurations'.
- G. Wulfsberg (2000) *Inorganic Chemistry*, University Science Books, Sausalito, CA – Contains a fuller treatment of Slater's rules and illustrates their application, particularly to the assessment of electronegativity.

## 1.8 The periodic table

In 1869 and 1870 respectively, Dmitri Mendeléeve and Lothar Meyer stated that the *properties of the elements can be represented as periodic functions of their atomic weights*, and set out their ideas in the form of a *periodic table*. As new elements have been discovered, the original form of the periodic table has been extensively modified, and it is now recognized that *periodicity* is a consequence of the variation in ground state electronic configurations. A modern periodic table (Fig. 1.14) emphasizes the blocks of 2, 6, 10 and 14 elements which result from the filling of the *s*, *p*, *d* and *f* atomic orbitals respectively. An exception is He, which, for reasons of its chemistry, is placed in a *group* with Ne, Ar, Kr, Xe and Rn. A more detailed periodic table is given inside the front cover of the book.

The IUPAC (International Union of Pure and Applied Chemistry) has produced guidelines<sup>†</sup> for naming blocks and groups of elements in the periodic table. In summary,

- blocks of elements may be designated by use of the letters *s*, *p*, *d* or *f* (Fig. 1.14);
- elements (except H) in groups 1, 2 and 13–18 are called *main group elements*;
- with the exception of group 18, the first two elements of each main group are called *typical elements*;
- elements in groups 3–12 (the *d*-block elements) are also commonly called the *transition elements*, although elements in group 12 are not always included;
- the *f*-block elements are sometimes called the *inner transition elements*.

Collective names for some of the groups of elements in the periodic table are given in Table 1.4.

At the end of 2016, the number of elements in the periodic table stood at 118. At the end of 2015, the IUPAC verified the discovery of elements with atomic numbers 113, 115, 117 and 118 (see Section 27.5).<sup>‡</sup>

<sup>†</sup> IUPAC: *Nomenclature of Inorganic Chemistry (Recommendations 2005)*, senior eds N.G. Connelly and T. Damhus, RSC Publishing, Cambridge.

<sup>‡</sup> P.J. Karol *et al.* (2003) *Pure Appl. Chem.*, vol. 75, p. 1601 – ‘On the claims for the discovery of elements 110, 111, 112, 114, 116 and 118’; K. Tatsumi and J. Corish (2010) *Pure Appl. Chem.*, vol. 82, p. 753 – ‘Name and symbol of the element with atomic number 112’; R.C. Barber *et al.* (2011) *Pure Appl. Chem.*, vol. 83, p. 1485; errata: vol. 83, p. 1801 – ‘Discovery of the elements with atomic numbers greater than or equal to 113’; R.D. Loss and J. Corish (2012) *Pure Appl. Chem.*, vol. 84, p. 1669 – ‘Names and symbols of the elements with atomic numbers 114 and 116’; P.J. Karol *et al.* (2016) *Pure Appl. Chem.*, vol. 88, p. 139 – ‘Discovery of the elements with atomic numbers  $Z = 113$ , 115 and 117’; P.J. Karol *et al.* (2016) *Pure Appl. Chem.*, vol. 88, p. 115 – ‘Discovery of the element with atomic number  $Z = 118$  completing the 7th row of the periodic table’; L. Öhrström and J.Reedijk (2016) *Pure Appl. Chem.*, vol. 88, p. 1225 – ‘Names and symbols of the elements with atomic numbers 113, 115, 117 and 118’.

**Table 1.4** IUPAC recommended names for groups of elements in the periodic table.

Group number	Recommended name
1	Alkali metals
2	Alkaline earth metals
15	Pnictogens
16	Chalcogens
17	Halogens
18	Noble gases

## 1.9 The aufbau principle

### Ground state electronic configurations

In the previous two sections, we have considered experimental electronic configurations and have seen that the organization of the elements in the periodic table depends on the number, and arrangement, of electrons that each element possesses. Establishing the ground state electronic configuration of an atom is the key to understanding its chemistry, and we now discuss the *aufbau* principle (*aufbau* means ‘building up’ in German) which is used in conjunction with Hund’s rules and the Pauli exclusion principle to determine electronic ground state configurations:

- Orbitals are filled in order of energy, the lowest energy orbitals being filled first.
- Hund’s first rule (often referred to simply as Hund’s rule): in a set of degenerate orbitals, electrons may not be spin-paired in an orbital until *each* orbital in the set contains one electron; electrons singly occupying orbitals in a degenerate set have parallel spins, i.e. they have the same values of  $m_s$ .
- Pauli exclusion principle: no two electrons in the same atom may have the same set of  $n$ ,  $l$ ,  $m_l$  and  $m_s$  quantum numbers; it follows that each orbital can accommodate a maximum of two electrons with different  $m_s$  values (different spins = spin-paired).

### Worked example 1.6 Using the aufbau principle

**Determine (with reasoning) the ground state electronic configurations of (a) Be ( $Z = 4$ ) and (b) P ( $Z = 15$ ).**

The value of  $Z$  gives the number of electrons to be accommodated in atomic orbitals in the ground state of the atom.

Assume an order of atomic orbitals (lowest energy first) as follows:  $1s < 2s < 2p < 3s < 3p$

continued

s-block elements		d-block elements										p-block elements					
Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57–71 La–Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89–103 Ac–Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

f-block elements														
Lanthanoids	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinoids	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

**Fig. 1.14.** The modern periodic table in which the elements are arranged in numerical order according to the number of protons (and electrons) they possess. The division into *groups* places elements with the same number of valence electrons into vertical columns within the table. Under IUPAC recommendations, the groups are labelled from 1 to 18 (Arabic numbers). Rows in the periodic table are called *periods*. The first period contains H and He, but the row from Li to Ne is usually referred to as the first period. Strictly, the lanthanoids include the 14 elements Ce–Lu, and the actinoids include Th–Lr; however, common usage places La with the lanthanoids, and Ac with the actinoids (see Chapter 27).

(a) Be  $Z = 4$

Two electrons (spin-paired) are accommodated in the lowest energy  $1s$  atomic orbital.

The next two electrons (spin-paired) are accommodated in the  $2s$  atomic orbital.

The ground state electronic configuration of Be is therefore  $1s^2 2s^2$ .

(b) P  $Z = 15$

Two electrons (spin-paired) are accommodated in the lowest energy  $1s$  atomic orbital.

The next two electrons (spin-paired) are accommodated in the  $2s$  atomic orbital.

The next six electrons are accommodated in the three degenerate  $2p$  atomic orbitals, two spin-paired electrons per orbital.

The next two electrons (spin-paired) are accommodated in the  $3s$  atomic orbital.

Three electrons remain and, applying Hund's rule, these singly occupy each of the three degenerate  $3p$  atomic orbitals.

The ground state electronic configuration of P is therefore  $1s^2 2s^2 2p^6 3s^2 3p^3$ .

### Self-study exercises

- Where, in the worked example above, is the Pauli exclusion principle applied?
- Will the three electrons in the P  $3p$  atomic orbitals possess the same or different values of the spin quantum number? [Ans. Same; parallel spins]
- Show, with reasoning, that the ground state electronic configuration of O ( $Z = 8$ ) is  $1s^2 2s^2 2p^4$ .
- Determine (with reasoning) how many unpaired electrons are present in a ground state Al atom ( $Z = 13$ ). [Ans. 1]

### Worked example 1.7 The ground state electronic configurations of the noble gases

The atomic numbers of He, Ne, Ar and Kr are 2, 10, 18 and 36 respectively. Write down the ground state electronic configurations of these elements and comment upon their similarities or differences.

Apply the *aufbau* principle using the atomic orbital energy sequence:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p$$

The ground state electronic configurations are:

He	$Z = 2$	$1s^2$
Ne	$Z = 10$	$1s^2 2s^2 2p^6$
Ar	$Z = 18$	$1s^2 2s^2 2p^6 3s^2 3p^6$
Kr	$Z = 36$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

Each element Ne, Ar and Kr has a ground state electronic configuration  $\dots ns^2 np^6$ . Helium is the odd one out, but still possesses a filled quantum level; this is a characteristic property of a noble gas.

### Self-study exercises

- Values of  $Z$  for Li, Na, K and Rb are 3, 11, 19 and 37 respectively. Write down their ground state configurations and comment on the result.

[Ans. All are of the form  $[X]ns^1$  where X is a noble gas]

- How are the ground state electronic configurations of O, S and Se ( $Z = 8, 16, 34$  respectively) alike? Give another element related in the same way.

[Ans. All are of the form  $[X]ns^2 np^4$  where X is a noble gas; Te or Po]

- State two elements that have ground state electronic configurations of the general type  $[X]ns^2 np^1$ .

[Ans. Any two elements from group 13]

### Valence and core electrons

**Core electrons** occupy lower energy quantum levels than **valence electrons**. The **valence electrons** of an element determine its chemical properties.

The configuration of the outer or *valence electrons* is of particular significance. These electrons determine the chemical properties of an element. Electrons that occupy lower energy quantum levels are called *core electrons*. The core electrons shield the valence electrons from the nuclear charge, resulting in the valence electrons experiencing only the effective nuclear charge,  $Z_{\text{eff}}$ . For an element of low atomic number, the core and valence electrons are readily recognized by looking at the ground state electronic configuration. That of oxygen is  $1s^2 2s^2 2p^4$ . The core electrons of oxygen are those in the  $1s$  atomic orbital; the six electrons with  $n = 2$  are the valence electrons.

### Diagrammatic representations of electronic configurations

The notation we have used to represent electronic configurations is convenient and is commonly adopted, but sometimes it is also useful to indicate the relative energies of the electrons. In this case, the electrons are represented by arrows  $\uparrow$  or  $\downarrow$  with the direction of the arrow corresponding to  $m_s = +\frac{1}{2}$  or  $-\frac{1}{2}$ . Figure 1.15 gives qualitative energy level diagrams which describe the ground state electronic configurations of O and Si.

#### Worked example 1.8 Quantum numbers for electrons

**Confirm that the ground state configuration shown for oxygen in Fig. 1.15 is consistent with each electron possessing a unique set of four quantum numbers.**

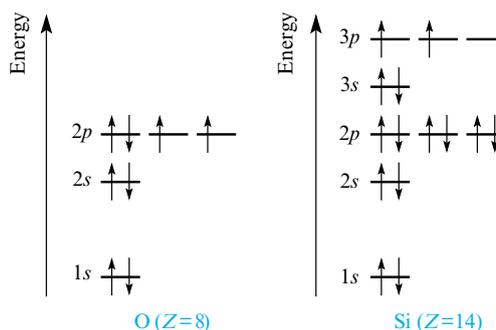
Each atomic orbital is designated by a unique set of three quantum numbers:

$1s$	$n = 1$	$l = 0$	$m_l = 0$
$2s$	$n = 2$	$l = 0$	$m_l = 0$
$2p$	$n = 2$	$l = 1$	$m_l = -1$
	$n = 2$	$l = 1$	$m_l = 0$
	$n = 2$	$l = 1$	$m_l = +1$

If an atomic orbital contains two electrons, they must have opposite spins so that the sets of quantum numbers for the two electrons are different: e.g. in the  $1s$  atomic orbital:

one electron has  $n = 1$   $l = 0$   $m_l = 0$   $m_s = +\frac{1}{2}$   
 the other electron has  $n = 1$   $l = 0$   $m_l = 0$   $m_s = -\frac{1}{2}$

[This discussion is extended in Section 20.6.]



**Fig. 1.15.** Diagrammatic representations of the ground state electronic configurations of O and Si. The complete configurations are shown here, but it is common to simply indicate the valence electrons. For O, this consists of the  $2s$  and  $2p$  levels, and for Si, the  $3s$  and  $3p$  levels.



## THEORY

Box 1.6 The relationship between  $\Delta U$  and  $\Delta H$ 

The relationship between the change in internal energy,  $\Delta U$ , and change in enthalpy,  $\Delta H$ , of the system for a reaction at a given temperature is given by the equation:

$$\Delta U = \Delta H - P\Delta V$$

where  $P$  is the pressure and  $\Delta V$  is the change in volume. The  $P\Delta V$  term corresponds to the work done, e.g. in expanding the system against the surroundings as a gas is liberated during a reaction. Often in a chemical reaction, the pressure  $P$  corresponds to atmospheric pressure (1 atm = 101 300 Pa, or 1 bar =  $10^5$  Pa).

In general, the work done by or on the system is much smaller than the enthalpy change, making the  $P\Delta V$  term negligible with respect to the values of  $\Delta U$  and  $\Delta H$ . Thus:

$$\Delta U(T \text{ K}) \approx \Delta H(T \text{ K})$$

However, in Section 1.10, we are considering two different temperatures and state that:

$$\Delta U(0 \text{ K}) \approx \Delta H(298 \text{ K})$$

In order to assess the variation in  $\Delta H$  with temperature, we apply Kirchhoff's equation where  $C_p$  = molar heat capacity at constant pressure:

$$\Delta C_p = \left( \frac{\partial \Delta H}{\partial T} \right)_p$$

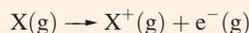
the integrated form of which (integrating between the limits of the temperatures 0 and 298 K) is:

$$\int_0^{298} d(\Delta H) = \int_0^{298} \Delta C_p dT$$

Integrating the left-hand side gives:

$$\Delta H(298 \text{ K}) - \Delta H(0 \text{ K}) = \int_0^{298} \Delta C_p dT$$

Consider the ionization of an atom X:



If X,  $\text{X}^+$  and  $\text{e}^-$  are all ideal monatomic gases, then the value of  $C_p$  for each is  $\frac{5}{2}R$  (where  $R$  is the molar gas constant =  $8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$ ), giving for the reaction a value of  $\Delta C_p$  of  $\frac{5}{2}R$ . Therefore:

$$\begin{aligned} \Delta H(298 \text{ K}) - \Delta H(0 \text{ K}) &= \int_0^{298} \frac{5}{2}R dT \\ &= \left( \frac{5 \times 8.314 \times 10^{-3}}{2} \right) [T]_0^{298} \\ &= 6.2 \text{ kJ mol}^{-1} \end{aligned}$$

Inspection of typical values of ionization energies in Appendix 8 shows that a correction of this magnitude is relatively insignificant because values of  $IE$  are so large.

## Self-study exercises

1. Show that the ground state electronic configuration  $1s^2 2s^2 2p^1$  for B corresponds to each electron having a unique set of four quantum numbers.
2. The ground state of N is  $1s^2 2s^2 2p^3$ . Show that each electron in the  $2p$  level possesses a unique set of four quantum numbers.
3. Explain why it is *not* possible for C to possess a ground state electronic configuration of  $1s^2 2s^2 2p^2$  with the  $2p$  electrons having paired spins.

## 1.10 Ionization energies and electron affinities

## Ionization energies

The ionization energy of hydrogen (eqs. 1.9 and 1.10) was discussed in Section 1.4. Since the H atom has only one electron, no additional ionization processes can occur. For multi-electron atoms, successive ionizations are possible.

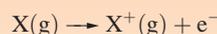
The first ionization energy,  $IE_1$ , of an atom is the internal energy change at 0 K,  $\Delta U(0 \text{ K})$ , associated with the removal

of the first valence electron (eq. 1.17). The energy change is defined for a *gas-phase* process. The units are  $\text{kJ mol}^{-1}$  or electron volts (eV).<sup>†</sup>



It is often necessary to incorporate ionization energies into thermochemical calculations (e.g. Born–Haber or Hess cycles) and it is convenient to define an associated *enthalpy change*,  $\Delta H(298 \text{ K})$ . Since the difference between  $\Delta H(298 \text{ K})$  and  $\Delta U(0 \text{ K})$  is very small (see Box 1.6), values of  $IE$  can be used in thermochemical cycles so long as extremely accurate answers are not required.

The **first ionization energy** ( $IE_1$ ) of a gaseous atom is the internal energy change,  $\Delta U$ , at 0 K associated with the removal of the first valence electron:



For thermochemical cycles, an associated change in enthalpy,  $\Delta H$ , at 298 K is used:

$$\Delta H(298 \text{ K}) \approx \Delta U(0 \text{ K})$$

<sup>†</sup> An electron volt is a non-SI unit with a value of  $\approx 1.60218 \times 10^{-19} \text{ J}$ ; to compare eV and  $\text{kJ mol}^{-1}$  units, it is necessary to multiply by the Avogadro number.  $1 \text{ eV} = 96.4853 \approx 96.5 \text{ kJ mol}^{-1}$ .

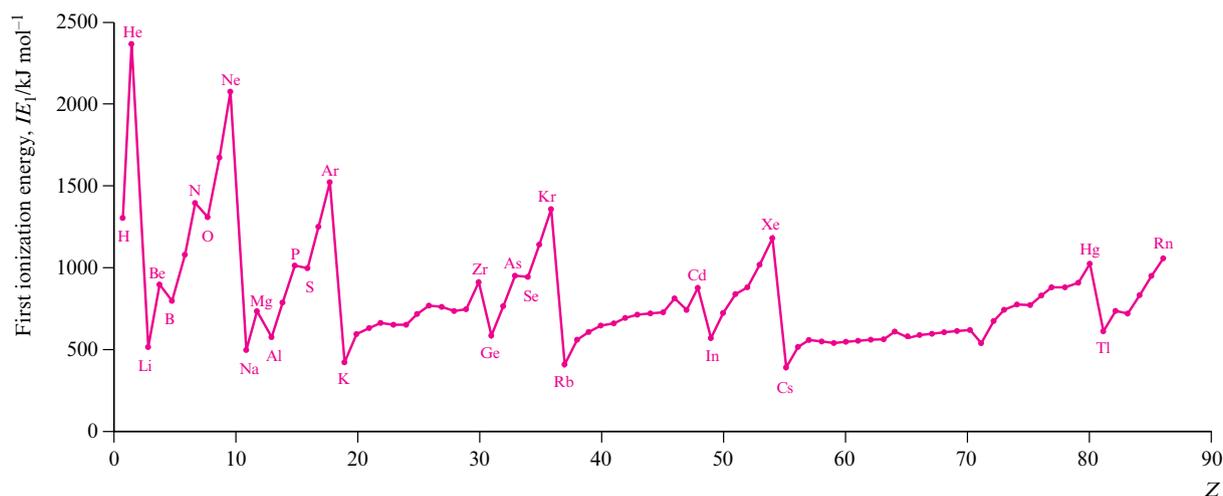


Fig. 1.16. The values of the first ionization energies of the elements up to Rn.

The second ionization energy,  $IE_2$ , of an atom refers to step 1.18; this is equivalent to the first ionization of the ion  $X^+$ . Equation 1.19 describes the step corresponding to the third ionization energy,  $IE_3$ , of  $X$ , and successive ionizations are similarly defined, all for gas phase processes.



Values of ionization energies for the elements are listed in Appendix 8. Figure 1.16 shows the variation in the values of  $IE_1$  as a function of  $Z$ . Several repeating patterns are apparent and some features to note are:

- the high values of  $IE_1$  associated with the noble gases;
- the very low values of  $IE_1$  associated with the group 1 elements;

- the *general* increase in values of  $IE_1$  across a given period;
- the discontinuity in values of  $IE_1$  on going from an element in group 15 to its neighbour in group 16;
- the decrease in values of  $IE_1$  on going from an element in group 2 or 12 to its neighbour in group 13;
- the rather similar values of  $IE_1$  for a given row of *d*-block elements.

Each of these trends can be rationalized in terms of ground state electronic configurations. The noble gases (except for He) possess  $ns^2np^6$  configurations which are particularly stable (see Box 1.7) and removal of an electron requires a great deal of energy. The ionization of a group 1 element involves loss of an electron from a singly occupied  $ns$  orbital with the resultant  $X^+$  ion possessing a noble gas



## THEORY

### Box 1.7 Exchange energies

Filled and half-filled shells are often referred to as possessing a 'special stability'. However, this is misleading, and we should really consider the *exchange energy* of a given configuration. This can only be justified by an advanced quantum mechanical treatment but we can summarize the idea as follows. Consider two electrons in *different* orbitals. The repulsion between the electrons if they have anti-parallel spins is greater than if they have parallel spins, e.g. for a  $p^2$  configuration:



The difference in energy between these two configurations is the *exchange energy*,  $K$ , i.e. this is the extra stability that the right-hand configuration has with respect to the left-hand one.

The total exchange energy is expressed in terms of  $K$  (the actual value of  $K$  depends on the atom or ion):

$$\text{Exchange energy} = \Sigma \frac{N(N-1)}{2} K$$

where  $N$  = number of electrons with parallel spins.

### Further reading

- A.B. Blake (1981) *J. Chem. Educ.*, vol. 58, p. 393.  
 B.J. Duke (1978) *Educ. Chem.*, vol. 15, p. 186.  
 D.M.P. Mingos (1998) *Essential Trends in Inorganic Chemistry*, OUP, Oxford, p. 14.

configuration. The *general* increase in  $IE_1$  across a given period is a consequence of an increase in  $Z_{\text{eff}}$ , e.g. Li to Ne, or Na to Ar. On going from Be ( $2s^2$ ) to B ( $2s^2 2p^1$ ), or from Mg ( $3s^2$ ) to Al ( $3s^2 3p^1$ ), there is a decrease in  $IE_1$ . This corresponds to the outer electron in the  $np$  orbital being shielded from the nuclear charge by the  $ns^2$  electrons. Similarly, the drop in  $IE_1$  from Zn ( $4s^2 3d^{10}$ ) to Ga ( $4s^2 3d^{10} 4p^1$ ) is because the electron being removed singly occupies the  $4p$  orbital. A drop in  $IE_1$  is also observed on going from N ( $2s^2 2p^3$ ) to O ( $2s^2 2p^4$ ). In N, the three  $p$  electrons occupy different atomic orbitals, whereas in O, one  $2p$  orbital is doubly occupied. These two electrons repel one another, making it is easier to remove the first electron from the valence shell of O (i.e. from the doubly occupied  $2p$  orbital) than from N. An additional factor to consider is the loss in *exchange energy* (see Box 1.7) when an N atom is ionized. Trends among  $IE$  values for  $d$ -block metals are discussed in Section 19.3.

### Self-study exercises

Refer to Fig. 1.16.

1. Why is there a decrease in  $IE_1$  on going from K to Rb?
2. Why does  $IE_1$  increase on going from Ga to Kr?
3. Suggest why there is a decrease in  $IE_1$  on going from As to Se < P to S < N to O.
4. Why does  $IE_1$  for the group 1 elements decrease in the order Li > Na > K > Rb > Cs?

### Electron affinities

The first electron affinity ( $EA_1$ ) is *minus* the internal energy change (eq. 1.20) for the gain of an electron by a *gaseous* atom (eq. 1.21). The second electron affinity of atom Y is defined for process 1.22. Each reaction occurs in the gas phase.

$$EA = -\Delta U(0\text{ K}) \quad (1.20)$$



As we saw for ionization energies, it is convenient to define an enthalpy change,  $\Delta_{\text{EA}}H$ , associated with each of the

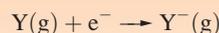
**Table 1.5** Approximate *enthalpy changes*  $\Delta_{\text{EA}}H(298\text{ K})$  associated with the attachment of an electron to an atom or anion.<sup>†</sup>

Process	$\approx \Delta_{\text{EA}}H/\text{kJ mol}^{-1}$
$\text{H}(\text{g}) + e^- \rightarrow \text{H}^-(\text{g})$	-73
$\text{Li}(\text{g}) + e^- \rightarrow \text{Li}^-(\text{g})$	-60
$\text{Na}(\text{g}) + e^- \rightarrow \text{Na}^-(\text{g})$	-53
$\text{K}(\text{g}) + e^- \rightarrow \text{K}^-(\text{g})$	-48
$\text{N}(\text{g}) + e^- \rightarrow \text{N}^-(\text{g})$	$\approx 0$
$\text{P}(\text{g}) + e^- \rightarrow \text{P}^-(\text{g})$	-72
$\text{O}(\text{g}) + e^- \rightarrow \text{O}^-(\text{g})$	-141
$\text{O}^-(\text{g}) + e^- \rightarrow \text{O}^{2-}(\text{g})$	+798
$\text{S}(\text{g}) + e^- \rightarrow \text{S}^-(\text{g})$	-201
$\text{S}^-(\text{g}) + e^- \rightarrow \text{S}^{2-}(\text{g})$	+640
$\text{F}(\text{g}) + e^- \rightarrow \text{F}^-(\text{g})$	-328
$\text{Cl}(\text{g}) + e^- \rightarrow \text{Cl}^-(\text{g})$	-349
$\text{Br}(\text{g}) + e^- \rightarrow \text{Br}^-(\text{g})$	-325
$\text{I}(\text{g}) + e^- \rightarrow \text{I}^-(\text{g})$	-295

<sup>†</sup> Tables of data differ in whether they list values of  $EA$  or  $\Delta_{\text{EA}}H$  and it is essential to note which is being used.

reactions 1.21 and 1.22. We approximate  $\Delta_{\text{EA}}H(298\text{ K})$  to  $\Delta_{\text{EA}}U(0\text{ K})$ . Selected values of these enthalpy changes are given in Table 1.5.

The *first electron affinity*,  $EA_1$ , of an atom is *minus* the internal energy change at 0 K associated with the gain of one electron by a gaseous atom:



For thermochemical cycles, an associated enthalpy change is used:

$$\Delta_{\text{EA}}H(298\text{ K}) \approx \Delta_{\text{EA}}U(0\text{ K}) = -EA$$

The attachment of an electron to an *atom* is usually exothermic. Two electrostatic forces oppose one another: the repulsion between the valence shell electrons and the additional electron, and the attraction between the nucleus and the incoming electron. In contrast, *repulsive* interactions are dominant when an electron is added to an *anion* and the process is endothermic (Table 1.5).

## KEY TERMS

The following terms were introduced in this chapter. Do you know what they mean?

- |   |  |  |
|---|--|--|
| <input type="checkbox"/> atom                 | <input type="checkbox"/> wavenumber                          | <input type="checkbox"/> ground state electronic configuration |
| <input type="checkbox"/> proton               | <input type="checkbox"/> Avogadro number                     | <input type="checkbox"/> effective nuclear charge              |
| <input type="checkbox"/> electron             | <input type="checkbox"/> wavefunction, $\psi$                | <input type="checkbox"/> screening effects of electrons        |
| <input type="checkbox"/> neutron              | <input type="checkbox"/> hydrogen-like species               | <input type="checkbox"/> penetration                           |
| <input type="checkbox"/> nucleus              | <input type="checkbox"/> principal quantum number, $n$       | <input type="checkbox"/> shielding                             |
| <input type="checkbox"/> protium              | <input type="checkbox"/> orbital quantum number, $l$         | <input type="checkbox"/> Slater's rules                        |
| <input type="checkbox"/> nuclide              | <input type="checkbox"/> magnetic quantum number, $m_l$      | <input type="checkbox"/> periodic table                        |
| <input type="checkbox"/> atomic number        | <input type="checkbox"/> magnetic spin quantum number, $m_s$ | <input type="checkbox"/> <i>aufbau</i> principle               |
| <input type="checkbox"/> mass number          | <input type="checkbox"/> degenerate                          | <input type="checkbox"/> Hund's rules                          |
| <input type="checkbox"/> relative atomic mass | <input type="checkbox"/> radial distribution function        | <input type="checkbox"/> Pauli exclusion principle             |
| <input type="checkbox"/> isotope              | <input type="checkbox"/> radial part of a wavefunction       | <input type="checkbox"/> valence electrons                     |
| <input type="checkbox"/> allotrope            | <input type="checkbox"/> angular part of a wavefunction      | <input type="checkbox"/> core electrons                        |
| <input type="checkbox"/> emission spectrum    | <input type="checkbox"/> atomic orbital                      | <input type="checkbox"/> ionization energy                     |
| <input type="checkbox"/> ground state         | <input type="checkbox"/> nodal plane                         | <input type="checkbox"/> electron affinity                     |
| <input type="checkbox"/> excited state        | <input type="checkbox"/> radial node                         |  |
| <input type="checkbox"/> quanta               |  |  |

## FURTHER READING

**First-year chemistry: basic principles**

C.E. Housecroft and E.C. Constable (2010) *Chemistry*, 4th edn, Prentice Hall, Harlow – A readable text covering fundamental aspects of inorganic, organic and physical chemistry which gives detailed background of all material that is taken as assumed knowledge in this book. An accompanying multiple-choice test bank and Solutions Manual can be found through [www.pearsoned.co.uk/housecroft](http://www.pearsoned.co.uk/housecroft).

P. Atkins and J. de Paula (2012) *The Elements of Physical Chemistry*, 6th edn, OUP, Oxford – An excellent introductory text which covers important areas of physical chemistry.

**Basic quantum mechanics**

P. Atkins and J. de Paula (2014) *Atkins' Physical Chemistry*, 10th edn, OUP, Oxford – This text gives a solid and well-tested background in physical chemistry.

D.O. Hayward (2002) *Quantum Mechanics for Chemists*, RSC Publishing, Cambridge – An undergraduate student text that covers the basic principles of quantum mechanics.

**Ionization energies and electron affinities**

P.F. Lang and B.C. Smith (2003) *J. Chem. Educ.*, vol. 80, p. 938 – 'Ionization energies of atoms and atomic ions'.

D.M.P. Mingos (1998) *Essential Trends in Inorganic Chemistry*, OUP, Oxford – This text includes detailed discussions of trends in ionization energies and electron attachment enthalpies within the periodic table.

J.C. Wheeler (1997) *J. Chem. Educ.*, vol. 74, p. 123 – 'Electron affinities of the alkaline earth metals and the sign convention for electron affinity'.

## PROBLEMS

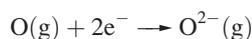
- Chromium has four isotopes,  $^{50}_{24}\text{Cr}$ ,  $^{52}_{24}\text{Cr}$ ,  $^{53}_{24}\text{Cr}$  and  $^{54}_{24}\text{Cr}$ . How many electrons, protons and neutrons does each isotope possess?
- 'Arsenic is monotopic.' What does this statement mean? Using Appendix 5, write down three other elements that are monotopic.
- Using the list of naturally occurring isotopes in Appendix 5, determine the number of electrons, protons and neutrons present in an atom of each isotope of (a) Al, (b) Br and (c) Fe, and give appropriate notation to show these data for each isotope.
- Hydrogen possesses three isotopes, but tritium ( $^3\text{H}$ ), which is radioactive, occurs as less than 1 in  $10^{17}$  atoms in a sample of natural hydrogen. If the value of  $A_r$  for hydrogen is 1.008, estimate the percentage abundance of protium,  $^1\text{H}$ , and deuterium,  $^2\text{H}$  (or D) present in a sample of natural hydrogen. Point out any

assumptions that you make. Explain why your answers are not the same as those quoted in Appendix 5.

- 1.5 (a) By using the data in Appendix 5, account for the isotopic distribution shown in Fig. 1.1b. (b) The mass spectrum of  $S_8$  shows other peaks at lower values of  $m/z$ . By considering the structure of  $S_8$  shown in Fig. 1.1c, suggest the origin of these lower-mass peaks.
- 1.6 Calculate the corresponding wavelengths of electromagnetic radiation with frequencies of (a)  $3.0 \times 10^{12}$  Hz, (b)  $1.0 \times 10^{18}$  Hz and (c)  $5.0 \times 10^{14}$  Hz. By referring to Appendix 4, assign each wavelength or frequency to a particular type of radiation (e.g. microwave).
- 1.7 State which of the following  $n' \rightarrow n$  transitions in the emission spectrum of atomic hydrogen belong to the Balmer, Lyman or Paschen series: (a)  $3 \rightarrow 1$ ; (b)  $3 \rightarrow 2$ ; (c)  $4 \rightarrow 3$ ; (d)  $4 \rightarrow 2$ ; (e)  $5 \rightarrow 1$ .
- 1.8 Calculate the energy (in kJ per mole of photons) of a spectroscopic transition, the corresponding wavelength of which is 450 nm.
- 1.9 Four of the lines in the Balmer series are at 656.28, 486.13, 434.05 and 410.17 nm. Show that these wavelengths are consistent with eq. 1.4.
- 1.10 Using the Bohr model, determine the values of the radii of the second and third orbits of the hydrogen atom.
- 1.11 How is the (a) energy and (b) size of an  $ns$  atomic orbital affected by an increase in  $n$ ?
- 1.12 Write down a set of quantum numbers that uniquely defines each of the following atomic orbitals: (a)  $6s$ , (b) each of the five  $4d$  orbitals.
- 1.13 Do the three  $4p$  atomic orbitals possess the same or different values of (a) principal quantum number, (b) the orbital quantum number and (c) the magnetic quantum number? Write down a set of quantum numbers for each  $4p$  atomic orbital to illustrate your answer.
- 1.14 How many radial nodes does each of the following orbitals possess: (a)  $2s$ ; (b)  $4s$ ; (c)  $3p$ ; (d)  $5d$ ; (e)  $1s$ ; (f)  $4p$ ?
- 1.15 Comment on differences between plots of  $R(r)$  against  $r$ , and  $4\pi r^2 R(r)^2$  against  $r$  for each of the following atomic orbitals of an H atom: (a)  $1s$ ; (b)  $4s$ ; (c)  $3p$ .
- 1.16 Write down the sets of quantum numbers that define the (a)  $1s$ , (b)  $4s$ , (c)  $5s$  atomic orbitals.
- 1.17 Write down the three sets of quantum numbers that define the three  $3p$  atomic orbitals.
- 1.18 How many atomic orbitals make up the set with  $n = 4$  and  $l = 3$ ? What label is given to this set of orbitals? Write down a set of quantum numbers that defines each orbital in the set.
- 1.19 Which of the following species are hydrogen-like: (a)  $H^+$ ; (b)  $He^+$ ; (c)  $He^-$ ; (d)  $Li^+$ ; (e)  $Li^{2+}$ ?
- 1.20 (a) Will a plot of  $R(r)$  for the  $1s$  atomic orbital of  $He^+$  be identical to that of the H atom (Fig. 1.5a)? [*Hint*: look at Table 1.2.] (b) On the *same axis set*, sketch approximate representations of the function  $4\pi r^2 R(r)^2$  for H and  $He^+$ .
- 1.21 Calculate the energy of the  $3s$  atomic orbital of an H atom. [*Hint*: see eq. 1.16.] Is the energy of the hydrogen  $3p$  atomic orbital the same as or different from that of the  $3s$  orbital?
- 1.22 Using eq. 1.16, determine the energies of atomic orbitals of hydrogen with  $n = 1, 2, 3, 4$  and  $5$ . What can you say about the relative spacings of the energy levels?
- 1.23 Write down the six sets of quantum numbers that describe the electrons in a degenerate set of  $5p$  atomic orbitals. Which pairs of sets of quantum numbers refer to spin-paired electrons?
- 1.24 For a neutral atom, X, arrange the following atomic orbitals in an approximate order of their relative energies (not all orbitals are listed):  $2s, 3s, 6s, 4p, 3p, 3d, 6p, 1s$ .
- 1.25 Using the concepts of shielding and penetration, explain why a ground state configuration of  $1s^2 2s^1$  for an Li atom is energetically preferred over  $1s^2 2p^1$ .
- 1.26 For each of the following atoms, write down a ground state electronic configuration and indicate which electrons are core and which are valence: (a) Na, (b) F, (c) N, (d) Sc.
- 1.27 Draw energy level diagrams (see Fig. 1.15) to represent the ground state electronic configurations of the atoms in problem 1.26.
- 1.28 Write down the ground state electronic configuration of boron, and give a set of quantum numbers that uniquely defines each electron.
- 1.29 Write down (with reasoning) the ground state electronic configurations of (a) Li, (b) O, (c) S, (d) Ca, (e) Ti, (f) Al.
- 1.30 Draw energy level diagrams to show the ground state electronic configurations of only the *valence* electrons in an atom of (a) F, (b) Al and (c) Mg.

- 1.31 The ground state electronic configuration of a group 16 element is of the type  $[X]ns^2np^4$  where X is a group 18 element. How are the outer four electrons arranged, and what rules are you using to work out this arrangement?
- 1.32 (a) Write down an equation that defines the process to which the value of  $IE_4$  of Sn refers. Is this process exothermic or endothermic? (b) To what overall process does a value of  $(IE_1 + IE_2 + IE_3)$  for Al refer?
- 1.33 The first four ionization energies of an atom X are 403, 2633, 3900 and  $5080 \text{ kJ mol}^{-1}$ . Suggest to what periodic group X belongs and give reasons for your choice.
- 1.34 In Fig. 1.16, identify the trends in the first ionization energies of the elements in (a) descending group 1, (b) descending group 13, (c) crossing the first row of the *d*-block, (d) crossing the row of elements from B to Ne, (e) going from Xe to Cs, and (f) going from P to S. Rationalize each of the trends you have described.
- 1.35 Figure 1.17 shows the values of  $IE_1$  for the first 10 elements. (a) Label each point with the symbol of the appropriate element. (b) Give detailed reasons for the observed trend in values.

- 1.36 (a) Using the data in Table 1.5, determine a value for  $\Delta H$  for the process:



- (b) Comment on the relevance of the sign and magnitude of your answer to part (a) in the light of the fact that many metal oxides with ionic lattices are thermodynamically stable.

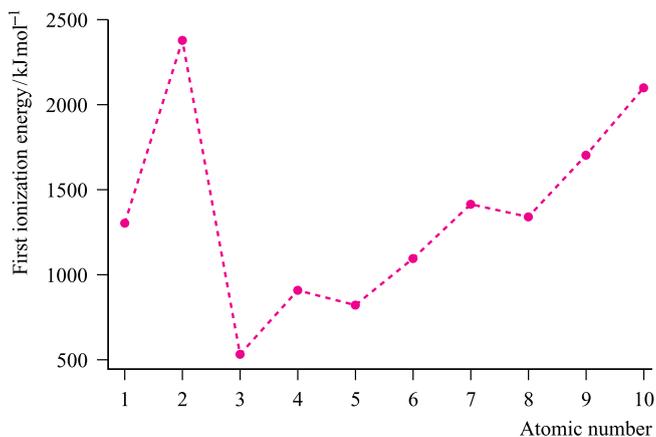


Fig. 1.17. Graph for problem 1.35.

## OVERVIEW PROBLEMS

- 1.37 How do you account for the fact that, although potassium is placed after argon in the periodic table, it has a lower relative atomic mass?

List 1	List 2
$S_6$ and $S_8$	electron
$^{19}\text{F}$ and $^{31}\text{P}$	proton
isotope of hydrogen	pnicogens
$^{12}\text{C}$ and $^{13}\text{C}$	<i>d</i> -block elements
hydrogen ion	protium
group 1 elements	fundamental particles
same energy	$m_s = \pm\frac{1}{2}$
negatively charged particle	allotropes
spin-paired electrons	degenerate
electron, proton and neutron	monotopic elements
group 15 elements	alkali metals
Cr, Mn, Fe	isotopes of an element

- 1.38 What is the evidence that the *aufbau* principle is only approximately true?
- 1.39 The first list in the table on the left contains symbols or phrases, each of which has a 'partner' in the second list. Match the 'partners'; there is only one match for each pair of symbols or phrases.
- 1.40 Suggest explanations for the following.
- (a) High values of ionization energies are associated with the noble gases.
- (b) The enthalpy changes associated with the attachment of the first and second electrons to an O atom are exothermic and endothermic, respectively.
- (c) In an Li atom in its ground state, the outer electron occupies a  $2s$  rather than a  $2p$  orbital.
- 1.41 Using data from Appendix 8, construct a graph to show the trend in the third ionization energies of the elements from Li to Kr. Compare the graph with that shown in Fig. 1.16, and rationalize what you observe.

- 1.42 The sign convention for electron affinity can often cause confusion for students. In this textbook, why have we referred to ‘an enthalpy change for the attachment of an electron’ rather than to an ‘electron affinity’?
- 1.43 (a) How would Fig. 1.9 have to be modified to show boundary surfaces for the  $2s$  and the  $3p$  wavefunctions of a one-electron species?
- (b) ‘The probability of finding the electron of a ground-state hydrogen atom at a distance  $r$  from the proton is at a maximum when  $r = 52.9$  pm.’ Why is this statement compatible with the maximum in the value of  $R(r)$  at  $r = 0$ ?

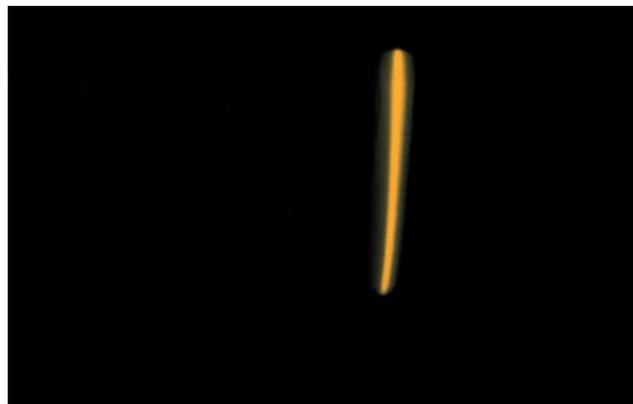
## INORGANIC CHEMISTRY MATTERS

- 1.44 Ruthenium, osmium, rhodium, iridium, palladium and platinum (Fig. 1.14) are called the platinum group metals. Most of the world’s reserves of these metals are in mineral deposits in Russia, Canada and South Africa. The platinum group metals are important as catalysts for air pollution control (e.g. in catalytic converters) and in the manufacture of organic and inorganic chemicals, and they have applications in the electronics industry. Thus, countries such as the US depend upon importing the metals and upon their recycling. The table below gives import data for the US for 2013:

Metal	Ru	Os	Rh	Ir	Pd	Pt
Imported amount/kg	15 300	77	11 100	1720	83 100	116 000

Plot bar charts to illustrate these data, first using mass on the vertical axis, and then using a logarithmic scale. Comment on the advantages or disadvantages of the two plots.

- 1.45 Figure 1.18 shows the emission spectrum of sodium. Low-pressure sodium street lamps depend upon this bright yellow emission from sodium atoms excited by an electrical discharge. Figure 1.18 shows a



**Fig. 1.18.** The emission spectrum of sodium. The apparent single line consists of two very close emissions at 589.0 and 589.6 nm.

simple spectrum (see figure caption), but the National Institute of Standards and Technology (NIST) atomic spectra database lists 5888 lines in the emission spectrum of sodium. (a) Suggest *three* reasons why no other lines are visible in Fig. 1.18. (b) The wavelengths of the yellow lines in Fig. 1.18 are close to 589 nm. To what frequency does this correspond? (c) Give a *general* explanation of how a series of spectral lines such as those in Fig. 1.18 arises.

## Topics

Lewis structures  
Valence bond theory  
Molecular orbital theory:  
  diatomics  
Octet rule  
Isoelectronic species  
Electronegativity  
Dipole moments  
VSEPR model  
Stereoisomerism

# 2

## Basic concepts: molecules

### 2.1 Bonding models: an introduction

In Sections 2.1–2.3 we summarize valence bond (VB) and molecular orbital (MO) theories of homonuclear bond formation, and include practice in generating *Lewis structures*.

#### A historical overview

The foundations of modern chemical bonding theory were laid in 1916–1920 by G.N. Lewis and I. Langmuir. They suggested that ionic species were formed by electron transfer while electron sharing was important in covalent molecules. In some cases, it was suggested that the shared electrons in a bond were provided by one of the atoms but that once the bond (sometimes called a *coordinate bond*) is formed, it is *indistinguishable from a 'normal' covalent bond*.

In a *covalent* species, electrons are shared between atoms. In an *ionic* species, one or more electrons are transferred between atoms to form ions.

Modern views of atomic structure are, as we have seen, based largely on the applications of wave mechanics to atomic systems. Modern views of *molecular structure* are based on applying wave mechanics to molecules; such studies provide answers as to how and why atoms combine. The Schrödinger equation can be written to describe the behaviour of electrons in molecules, but it can be solved only approximately. Two methods of doing this are the valence bond approach, developed by Heitler and Pauling, and the molecular orbital approach associated with Hund and Mulliken:

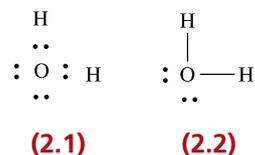
- *Valence bond (VB) theory* treats the formation of a molecule as arising from the bringing together of complete atoms which, when they interact, to a large extent retain their original character.
- *Molecular orbital (MO) theory* allocates electrons to molecular orbitals formed by the overlap (interaction) of atomic orbitals.

Although familiarity with both VB and MO concepts is necessary, it is often the case that a given situation is more conveniently approached by using one or other of these models. We begin with the conceptually simple approach of Lewis for representing the bonding in covalent molecules.

#### Lewis structures

Lewis presented a simple, but useful, method of describing the arrangement of valence electrons in molecules. The approach uses dots (or dots and crosses) to represent the number of *valence electrons*, and the nuclei are indicated by appropriate elemental symbols. A basic principle of the theory is that electrons in a molecule should be paired; the presence of a single (odd) electron indicates that the species is a *radical*.

Diagram 2.1 shows the Lewis structure for H<sub>2</sub>O with the O–H bonds designated by pairs of dots (electrons). An alternative representation is given in structure 2.2 where each line stands for *one pair* of electrons, i.e. a *single covalent bond*. Pairs of valence electrons which are not involved in bonding are *lone pairs*.



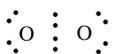
The Lewis structure for  $\text{N}_2$  shows that the N–N bond is composed of three pairs of electrons and is a *triple bond* (structures 2.3 and 2.4). Each N atom has one lone pair of electrons. The Lewis structures 2.5 and 2.6 for  $\text{O}_2$  indicate the presence of a *double bond*, with each O atom bearing two lone pairs of electrons.



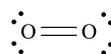
(2.3)



(2.4)



(2.5)



(2.6)

Lewis structures give the connectivity of an atom in a molecule, the bond order and the number of lone pairs, and these may be used to derive structures using the valence-shell electron-pair repulsion model (see Section 2.8).

## 2.2 Homonuclear diatomic molecules: valence bond (VB) theory

### Uses of the term *homonuclear*

The word *homonuclear* is used in two ways:

- A *homonuclear covalent bond* is one formed between two atoms of the same element, e.g. the H–H bond in  $\text{H}_2$ , the O=O bond in  $\text{O}_2$ , and the O–O bond in  $\text{H}_2\text{O}_2$  (Fig. 2.1).
- A *homonuclear molecule* contains one type of element. Homonuclear diatomic molecules include  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{F}_2$ , homonuclear triatomics include  $\text{O}_3$  (ozone) and examples of larger homonuclear molecules are  $\text{P}_4$ ,  $\text{S}_8$  (Fig. 2.2) and  $\text{C}_{60}$ .

### Covalent bond distance, covalent radius and van der Waals radius

Three important definitions are needed before we discuss covalent bonding.

The length of a covalent bond (*bond distance*),  $d$ , is the *internuclear separation* and may be determined experimentally by microwave spectroscopy or diffraction methods

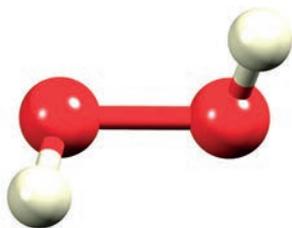


Fig. 2.1. The structure of hydrogen peroxide,  $\text{H}_2\text{O}_2$ ; O atoms are shown in red.

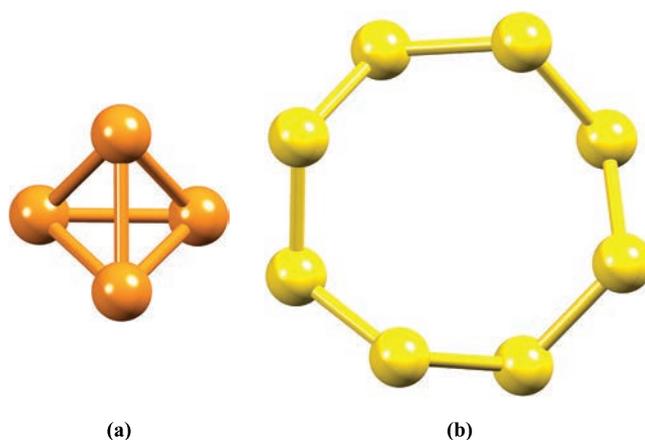


Fig. 2.2. The structures of the homonuclear molecules (a)  $\text{P}_4$  and (b)  $\text{S}_8$ .

(see Chapter 4). It is convenient to define the covalent radius,  $r_{\text{cov}}$ , of an atom: for an atom X,  $r_{\text{cov}}$  is half of the covalent bond length of a homonuclear X–X *single bond*. Thus,  $r_{\text{cov}}(\text{S})$  can be determined from the solid state structure of  $\text{S}_8$  (Fig. 2.2) determined by X-ray diffraction methods or, better still, by averaging the values of the bond distances of S–S single bonds found for all the allotropes of sulfur.

For an atom X, the value of the single bond *covalent radius*,  $r_{\text{cov}}$ , is half of the internuclear separation in a homonuclear X–X single bond.

The  $\alpha$ - and  $\beta$ -forms of sulfur (orthorhombic and monoclinic sulfur, respectively) both crystallize with  $\text{S}_8$  molecules stacked in a regular arrangement. The packing in the  $\alpha$ -form (Fig. 2.3, density =  $2.07 \text{ g cm}^{-3}$ ) is more efficient than that in the  $\beta$ -form (density =  $1.94 \text{ g cm}^{-3}$ ). Van der Waals forces operate between the molecules, and half of the distance of closest approach of two sulfur atoms belonging to *different*  $\text{S}_8$  rings is defined as the van der Waals radius,  $r_v$ , of sulfur. The *intermolecular* bonding is much weaker than the *intramolecular* S–S bonds, and this is evidenced by the fact that when  $\text{S}_8$  vaporizes, the ring structure is retained. The van der Waals radius of an

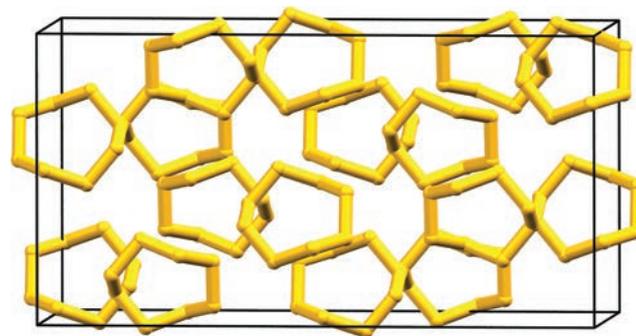


Fig. 2.3. The packing of  $\text{S}_8$  rings in the  $\alpha$ -allotrope of sulfur. The black box defines the unit cell (see Section 4.11). [Data: S. J. Rettig *et al.* (1987) *Acta Crystallogr., Sect. C*, vol. 43, p. 2260.]

element is necessarily larger than its covalent radius, e.g.  $r_v$  and  $r_{cov}$  for S are 185 and 103 pm, respectively. Van der Waals forces include dispersion and dipole–dipole interactions; dispersion forces are discussed in the latter part of Section 6.13 and dipole moments in Section 2.6. Because van der Waals forces operate *between* molecules, they are crucial in controlling the way in which molecules pack in the solid state. Values of  $r_v$  and  $r_{cov}$  for *s*-block, *p*-block and first row *d*-block elements are listed in Appendix 6.

The *van der Waals radius*,  $r_v$ , of an atom X is half of the distance of closest approach of two non-bonded atoms of X.

### The valence bond (VB) model of bonding in H<sub>2</sub>

Valence bond theory considers the interactions between separate atoms as they are brought together to form molecules. We begin by considering the formation of H<sub>2</sub> from two H atoms, the nuclei of which are labelled H<sub>A</sub> and H<sub>B</sub>, and the electrons of which are 1 and 2, respectively. When the atoms are so far apart that there is no interaction between them, electron 1 is exclusively associated with H<sub>A</sub>, while electron 2 resides with nucleus H<sub>B</sub>. Let this state be described by a wavefunction  $\psi_1$ .

When the H atoms are close together, we cannot tell which electron is associated with which nucleus since, although we gave them labels, the two nuclei are indistinguishable, as are the two electrons. Thus, electron 2 could be with H<sub>A</sub> and electron 1 with H<sub>B</sub>. Let this be described by the wavefunction  $\psi_2$ .

Equation 2.1 gives an overall description of the covalently bonded H<sub>2</sub> molecule;  $\psi_{\text{covalent}}$  is a *linear combination* of wavefunctions  $\psi_1$  and  $\psi_2$ .

$$\psi_{\text{covalent}} = \psi_+ = N(\psi_1 + \psi_2) \quad (2.1)$$

Equation 2.1 contains a *normalization factor*,  $N$  (see Box 1.3). In the general case where:

$$\psi_{\text{covalent}} = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \dots$$

$$N = \frac{1}{\sqrt{c_1^2 + c_2^2 + c_3^2 + \dots}}$$

Another linear combination of  $\psi_1$  and  $\psi_2$  can be written as shown in eq. 2.2.

$$\psi_- = N(\psi_1 - \psi_2) \quad (2.2)$$

In terms of the spins of electrons 1 and 2,  $\psi_+$  corresponds to spin-pairing, and  $\psi_-$  corresponds to parallel spins (non-spin-paired). Calculations of the energies associated with these states as a function of the internuclear separation of H<sub>A</sub> and H<sub>B</sub> show that, while  $\psi_-$  represents a repulsive state (high energy), the energy curve for  $\psi_+$  reaches a minimum value when the internuclear separation,  $d$ , is 87 pm and this corresponds to an H–H bond dissociation energy,  $\Delta U$ , of 303 kJ mol<sup>-1</sup>. While these are near enough

to the experimental values of  $d = 74$  pm and  $\Delta U = 458$  kJ mol<sup>-1</sup> to suggest that the model has some validity, they are far enough away from them to indicate that the expression for  $\psi_+$  needs refining.

The *bond dissociation energy* ( $\Delta U$ ) and *enthalpy* ( $\Delta H$ ) values for H<sub>2</sub> are defined for the process:



Improvements to eq. 2.1 can be made by:

- allowing for the fact that each electron screens the other from the nuclei to some extent;
- taking into account the possibility that *both* electrons 1 and 2 may be associated with either H<sub>A</sub> or H<sub>B</sub>, i.e. allowing for the transfer of one electron from one nuclear centre to the other to form a pair of ions H<sub>A</sub><sup>+</sup>H<sub>B</sub><sup>-</sup> or H<sub>A</sub><sup>-</sup>H<sub>B</sub><sup>+</sup>.

The latter modification is dealt with by writing two additional wavefunctions,  $\psi_3$  and  $\psi_4$  (one for each ionic form), and so eq. 2.1 can be rewritten in the form of eq. 2.3. The coefficient  $c$  indicates the relative contributions made by the two sets of wavefunctions. For a *homonuclear diatomic* such as H<sub>2</sub>, the situations described by  $\psi_1$  and  $\psi_2$  are equally probable, as are those described by  $\psi_3$  and  $\psi_4$ .

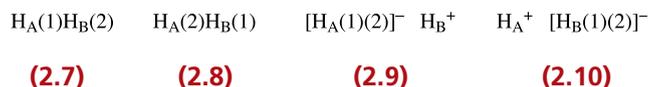
$$\psi_+ = N[(\psi_1 + \psi_2) + c(\psi_3 + \psi_4)] \quad (2.3)$$

Since the wavefunctions  $\psi_1$  and  $\psi_2$  arise from an internuclear interaction involving the *sharing* of electrons among nuclei, and  $\psi_3$  and  $\psi_4$  arise from electron *transfer*, we can simplify eq. 2.3 to 2.4, in which the overall wavefunction,  $\psi_{\text{molecule}}$ , is composed of covalent and ionic terms.

$$\psi_{\text{molecule}} = N[\psi_{\text{covalent}} + (c \times \psi_{\text{ionic}})] \quad (2.4)$$

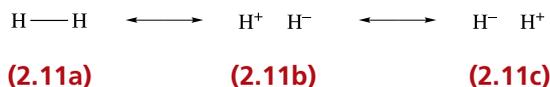
Based on this model of H<sub>2</sub>, calculations with  $c \approx 0.25$  give values of 75 pm for  $d(\text{H}–\text{H})$  and 398 kJ mol<sup>-1</sup> for the bond dissociation energy. Modifying eq. 2.4 still further leads to a value of  $\Delta U$  very close to the experimental value, but details of the procedure are beyond the scope of this book.<sup>†</sup>

Now consider the physical significance of eqs. 2.3 and 2.4. The wavefunctions  $\psi_1$  and  $\psi_2$  represent the structures shown in **2.7** and **2.8**, while  $\psi_3$  and  $\psi_4$  represent the ionic forms **2.9** and **2.10**. The notation H<sub>A</sub>(1) stands for ‘nucleus H<sub>A</sub> with electron (1)’, and so on.



<sup>†</sup> For detailed discussion, see: R. McWeeny (1979) *Coulson's Valence*, 3rd edn, OUP, Oxford. See also: A. Simões (2008) *Notes Rec. R. Soc.* vol. 62, p. 259 – ‘A quantum chemical dialogue mediated by textbooks: Pauling's *The Nature of the Chemical Bond* and Coulson's *Valence*'.

Dihydrogen is described as a *resonance hybrid* of these contributing *resonance* or *canonical structures*. In the case of  $H_2$ , an example of a homonuclear diatomic molecule which is necessarily symmetrical, we simplify the picture to **2.11**. Each of structures **2.11a**, **2.11b** and **2.11c** is a *resonance structure* and the double-headed arrows indicate the *resonance* between them. The contributions made by **2.11b** and **2.11c** are equal. The term ‘resonance hybrid’ is somewhat unfortunate but is too firmly established to be eradicated.



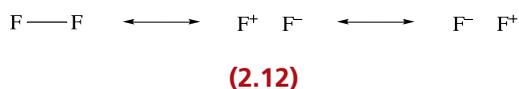
The bonding in a molecule is described in terms of contributing *resonance structures*. The *resonance* between these contributing structures results in a *resonance stabilization*. The relationship between resonance structures is indicated by using a double-headed arrow.

A crucial point about resonance structures is that they *do not exist as separate species*. Rather, they indicate extreme bonding pictures, the combination of which gives a description of the molecule overall. In the case of  $H_2$ , the contribution made by resonance structure **2.11a** is significantly greater than that of **2.11b** or **2.11c**.

Notice that **2.11a** describes the bonding in  $H_2$  in terms of a *localized 2-centre 2-electron, 2c-2e*, covalent bond. A particular resonance structure will always indicate a localized bonding picture, although the combination of several resonance structures may result in the description of the bonding in the species as a whole being delocalized (see Section 5.3).

### The valence bond (VB) model applied to $F_2$ , $O_2$ and $N_2$

Consider the formation of  $F_2$ . The ground state electronic configuration of F is  $[\text{He}]2s^22p^5$ , and the presence of the single unpaired electron indicates the formation of an F–F single bond. We can write down resonance structures **2.12** to describe the bonding in  $F_2$ , with the expectation that the covalent contribution will predominate.



The formation of  $O_2$  involves the combination of two O atoms with ground state electronic configurations of  $1s^22s^22p^4$ . Each O atom has two unpaired electrons and so VB theory predicts the formation of an O=O double bond. Since VB theory works on the premise that electrons are paired whenever possible, the model predicts that  $O_2$  is diamagnetic. One of the notable failures of VB theory is its inability to predict the observed *paramagnetism* of  $O_2$ . As we shall see,

molecular orbital theory is fully consistent with  $O_2$  being a diradical. When two N atoms ( $[\text{He}]2s^22p^3$ ) combine to give  $N_2$ , an  $N \equiv N$  triple bond results. Of the possible resonance structures, the predominant form is covalent and this gives a satisfactory picture of the bonding in  $N_2$ .

In a *diamagnetic* species, all electrons are spin-paired; a diamagnetic substance is repelled by a magnetic field. A *paramagnetic* species contains one or more unpaired electrons; a paramagnetic substance is attracted by a magnetic field.

### Self-study exercises

1. Within VB theory, the wavefunction that describes the bonding region between two H atoms in  $H_2$  can be written in the form:

$$\psi_{\text{molecule}} = N [\psi_{\text{covalent}} + (c \times \psi_{\text{ionic}})]$$

Explain the meaning of this equation, including the reason why the factor  $N$  is included.

2. It is *incorrect* to draw an equilibrium symbol between two resonance structures. The correct notation is a double-headed arrow. Explain why the distinction between these notations is so important.

3. Although  $O_2$  is paramagnetic, VB theory results in a prediction that it is diamagnetic. Explain why this is the case.

## 2.3 Homonuclear diatomic molecules: molecular orbital (MO) theory

### An overview of the MO model

In molecular orbital (MO) theory, we begin by placing the nuclei of a given molecule in their equilibrium positions and then calculate the *molecular orbitals* (i.e. regions of space spread over the entire molecule) that a single electron might occupy. Each MO arises from interactions between orbitals of atomic centres in the molecule, and such interactions are:

- allowed if the *symmetries* of the atomic orbitals are compatible with one another;
- efficient if the region of *overlap* between the two atomic orbitals is significant;
- efficient if the atomic orbitals are relatively close in energy.

An important ground-rule of MO theory is that *the number of MOs that can be formed must equal the number of atomic orbitals of the constituent atoms*.

Each MO has an associated energy and, to derive the electronic ground state of a molecule, the available electrons are placed, according to the *aufbau* principle, in MOs beginning with that of lowest energy. The sum of

the individual energies of the electrons in the orbitals (after correction for electron–electron interactions) gives the total energy of the molecule.

## Molecular orbital theory applied to the bonding in H<sub>2</sub>

An approximate description of the MOs in H<sub>2</sub> can be obtained by considering them as *linear combinations of atomic orbitals* (LCAOs). Each of the H atoms has one 1s atomic orbital; let the two associated wavefunctions be  $\psi_1$  and  $\psi_2$ . In Section 1.6, we mentioned the importance of the *signs of the wavefunctions* with respect to their overlap during bond formation. The sign of the wavefunction associated with the 1s atomic orbital may be either + or -. Just as transverse waves interfere in a constructive (in-phase) or destructive (out-of-phase) manner, so too do orbitals. Mathematically, we represent the possible combinations of the two 1s atomic orbitals by eqs. 2.5 and 2.6, where  $N$  and  $N^*$  are the normalization factors. Whereas  $\psi_{\text{MO}}$  is an in-phase (*bonding*) interaction,  $\psi_{\text{MO}}^*$  is an out-of-phase (*antibonding*) interaction.

$$\psi_{\text{MO(in-phase)}} = \psi_{\text{MO}} = N[\psi_1 + \psi_2] \quad (2.5)$$

$$\psi_{\text{MO(out-of-phase)}} = \psi_{\text{MO}}^* = N^*[\psi_1 - \psi_2] \quad (2.6)$$

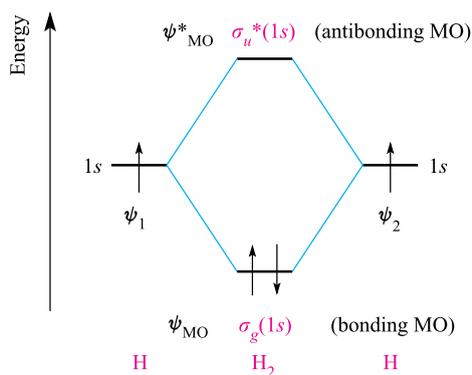
The values of  $N$  and  $N^*$  are determined using eqs. 2.7 and 2.8 where  $S$  is the *overlap integral*. This is a measure of the extent to which the regions of space described by the two wavefunctions  $\psi_1$  and  $\psi_2$  coincide. Although we mentioned earlier that orbital interaction is efficient if the region of overlap between the two atomic orbitals is significant, the numerical value of  $S$  is still much less than unity and is often neglected giving the approximate results shown in eqs. 2.7 and 2.8.

$$N = \frac{1}{\sqrt{2(1+S)}} \approx \frac{1}{\sqrt{2}} \quad (2.7)$$

$$N^* = \frac{1}{\sqrt{2(1-S)}} \approx \frac{1}{\sqrt{2}} \quad (2.8)$$

The interaction between the H 1s atomic orbitals on forming H<sub>2</sub> may be represented by the energy level diagram in Fig. 2.4. The bonding MO,  $\psi_{\text{MO}}$ , is stabilized with respect to the 1s atomic orbitals, while the antibonding MO,  $\psi_{\text{MO}}^*$ , is destabilized.<sup>†</sup> Each H atom contributes one electron and, by the *aufbau* principle, the two electrons occupy the lower of the two MOs in the H<sub>2</sub> molecule and are spin-paired (Fig. 2.4). It is important to remember that in MO theory we *construct the orbital interaction diagram first and then put in the electrons according to the aufbau principle*.

<sup>†</sup> The difference between the energies of the 1s atomic orbitals and  $\psi_{\text{MO}}^*$  is slightly greater than between those of the 1s atomic orbitals and  $\psi_{\text{MO}}$ , i.e. an antibonding MO is slightly more antibonding than the corresponding bonding MO is bonding; the origin of this effect is beyond the scope of this book.



**Fig. 2.4.** An orbital interaction diagram for the formation of H<sub>2</sub> from two hydrogen atoms. By the *aufbau* principle, the two electrons occupy the lowest energy (bonding) molecular orbital.

The bonding and antibonding MOs in H<sub>2</sub> are given the symmetry labels  $\sigma$  and  $\sigma^*$  (*‘sigma’* and *‘sigma-star’*) or, more fully,  $\sigma_g(1s)$  and  $\sigma_u^*(1s)$  to indicate their atomic orbital origins and the *parity* of the MOs (see Box 2.1). In order to define these labels, consider the pictorial representations of the two MOs. Figure 2.5a shows that when the 1s atomic orbitals interact in phase, the two wavefunctions reinforce each other, especially in the region of space between the nuclei. The two electrons occupying this MO will be found predominantly between the two nuclei, and the build-up of electron density reduces internuclear repulsion. Figure 2.5b illustrates that the out-of-phase interaction results in a *nodal plane between the two H nuclei*. If the antibonding orbital were to be occupied, there would be a zero probability of finding the electrons at any point on the nodal plane. This lack of electron density raises the internuclear repulsion and, as a result, destabilizes the MO.

Now let us return to the  $\sigma$  and  $\sigma^*$  labels. An MO has  $\sigma$ -symmetry if it is symmetrical with respect to a line joining the two nuclei; i.e. if you rotate the orbital about the internuclear axis (the axis joining the two nuclear centres marked in Figs. 2.5a and 2.5b), there is no phase change. A  $\sigma^*$ -orbital must exhibit two properties:

- the  $\sigma$  label means that rotation of the orbital about the internuclear axis generates no phase change, *and*
- the  $*$  label means that there is a nodal plane *between* the nuclei, and this plane is orthogonal to the internuclear axis.

The ground state electronic configuration of H<sub>2</sub> may be written using the notation  $\sigma_g(1s)^2$ , indicating that two electrons occupy the  $\sigma_g(1s)$  MO.

The orbital interaction diagram shown in Fig. 2.4 can be used to predict several properties of the H<sub>2</sub> molecule. Firstly, the electrons are paired and so we expect H<sub>2</sub> to be diamagnetic as is found experimentally. Secondly, the formal bond order can be found using eq. 2.9. For H<sub>2</sub> this gives a bond order of 1.

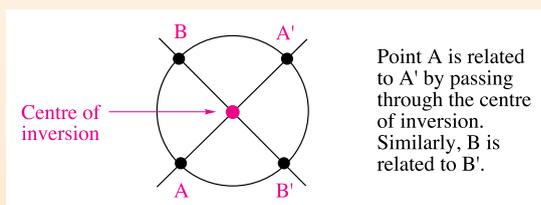


## THEORY

## Box 2.1 The parity of MOs for a molecule that possesses a centre of inversion

We consider symmetry in Chapter 3, but it is useful at this point to consider the labels that are commonly used to describe the *parity of a molecular orbital*. A *homonuclear* diatomic molecule (e.g.  $\text{H}_2$ ,  $\text{Cl}_2$ ) possesses a centre of inversion (centre of symmetry), and the parity of an MO describes the way in which the orbital behaves with respect to this centre of inversion.

First find the centre of inversion in the molecule; this is the point through which you can draw an infinite number of straight lines such that each line passes through a pair of similar points, one on each side of the centre of symmetry and at equal distances from it:



Now ask the question: 'Does the wavefunction have the same *sign* at the same distance but in opposite directions from the centre of symmetry?'

If the answer is 'yes', then the orbital is labelled *g* (from the word *gerade*, German for 'even'). If the answer is 'no',

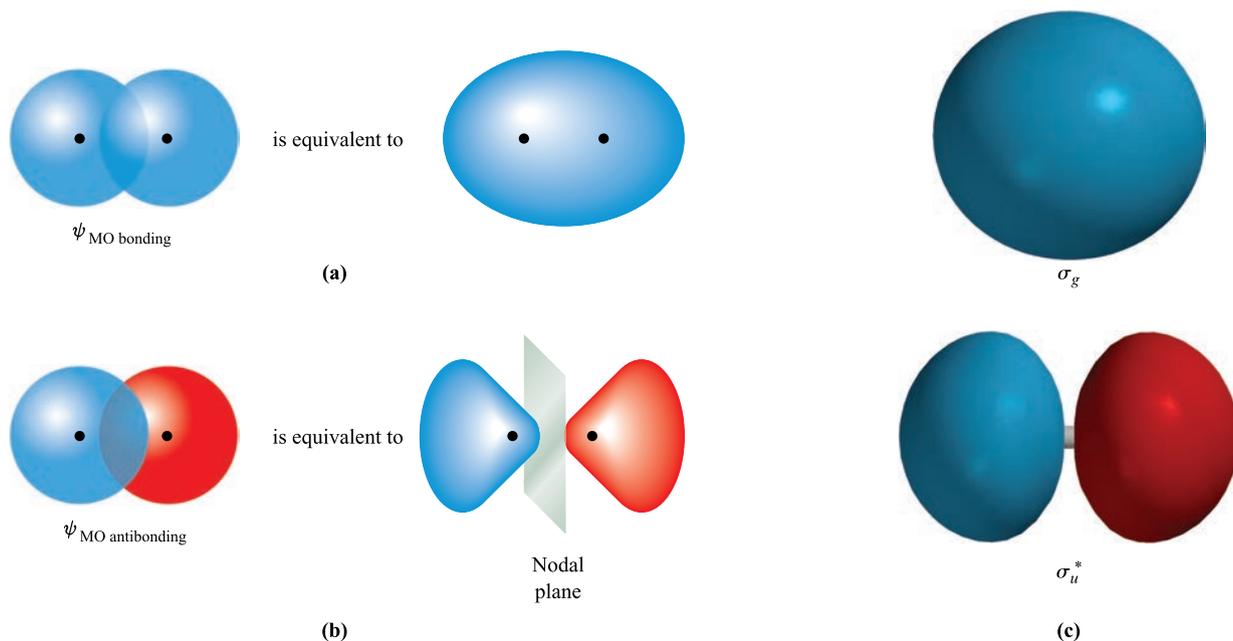
then the orbital is labelled *u* (from the word *ungerade*, German for 'odd'). For example, the  $\sigma$ -bonding MO in  $\text{H}_2$  (Fig. 2.5a) is labelled  $\sigma_g$ , while the antibonding MO (Fig. 2.5b) is  $\sigma_u^*$ .

Parity labels *only* apply to MOs in molecules that possess a centre of inversion (*centrosymmetric* molecules), e.g. homonuclear  $\text{X}_2$ , octahedral  $\text{EX}_6$  and square planar  $\text{EX}_4$  molecules. Heteronuclear  $\text{XY}$ , or tetrahedral  $\text{EX}_4$  molecules, for example, do not possess a centre of inversion and are called *non-centrosymmetric* species.

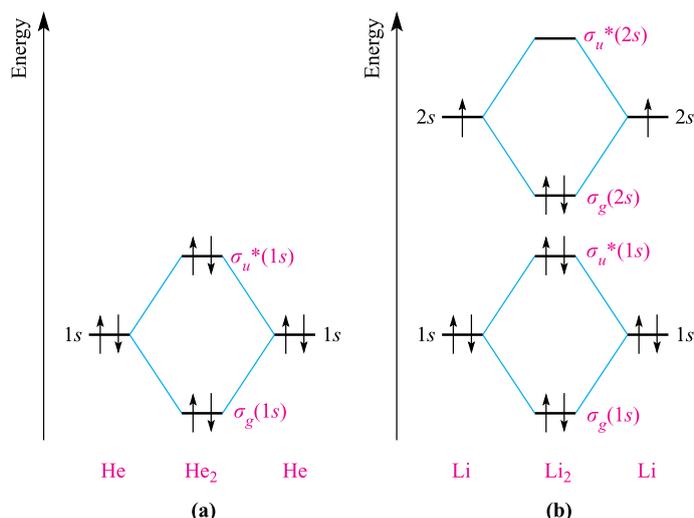
## Self-study exercises

Look at Fig. 2.7 which may be applied to the MOs in the homonuclear diatomic  $\text{O}_2$ .

1. Why does a  $\sigma$ -MO formed by the overlap of two  $2p_z$  orbitals (Fig. 2.7a) have the label  $\sigma_g$ ?
2. Why does a  $\pi$ -MO formed by the overlap of two  $2p_x$  orbitals (Fig. 2.7c) have the label  $\pi_u$ ?
3. The antibonding MOs shown at the right-hand sides of Figs. 2.7b and 2.7d carry the labels  $\sigma_u^*$  and  $\pi_g^*$ , respectively. Explain the difference in the parity labels.



**Fig. 2.5.** Schematic representations of (a) the bonding ( $\sigma_g$ ) and (b) the antibonding ( $\sigma_u^*$ ) molecular orbitals in the  $\text{H}_2$  molecule. The H nuclei are represented by black dots. The red orbital lobes could equally well be marked with a + sign, and the blue lobes with a - sign (or vice versa) to indicate the sign of the wavefunction. (c) More realistic representations of the molecular orbitals of  $\text{H}_2$ , generated computationally using Spartan '04, ©Wavefunction Inc. 2003.



**Fig. 2.6.** Orbital interaction diagrams for the formation of (a)  $\text{He}_2$  from two He atoms and (b)  $\text{Li}_2$  from two Li atoms.

$$\text{Bond order} = \frac{1}{2} [(\text{Number of bonding electrons}) - (\text{Number of antibonding electrons})] \quad (2.9)$$

We cannot measure the bond order experimentally but we can make some useful correlations between bond order and the experimentally measurable bond distances and bond dissociation energies or enthalpies. Along a series of species related by electron gain (reduction) or loss (oxidation), inspection of the corresponding MO diagram shows how the bond order may change (assuming that there are no major changes to the energy levels of the orbitals). For example, the oxidation of  $\text{H}_2$  to  $[\text{H}_2]^+$  (a change brought about by the action of an electric discharge on  $\text{H}_2$  at low pressures) can be considered in terms of the removal of one electron from the bonding MO shown in Fig. 2.4. The bond order of  $[\text{H}_2]^+$  is (eq. 2.9) 0.5, and we expect the H–H bond to be weaker than in  $\text{H}_2$ . Experimentally, the bond dissociation energy,  $\Delta U$ , for  $\text{H}_2$  is  $458 \text{ kJ mol}^{-1}$  and for  $[\text{H}_2]^+$  is  $269 \text{ kJ mol}^{-1}$ . Similar correlations can be made between bond order and bond length: the lower the bond order, the larger the internuclear separation; the experimentally determined bond lengths of  $\text{H}_2$  and  $[\text{H}_2]^+$  are 74 and 105 pm. While such correlations are useful, they must be treated with caution<sup>†</sup> and *only* used in series of closely related species.

### The bonding in $\text{He}_2$ , $\text{Li}_2$ and $\text{Be}_2$

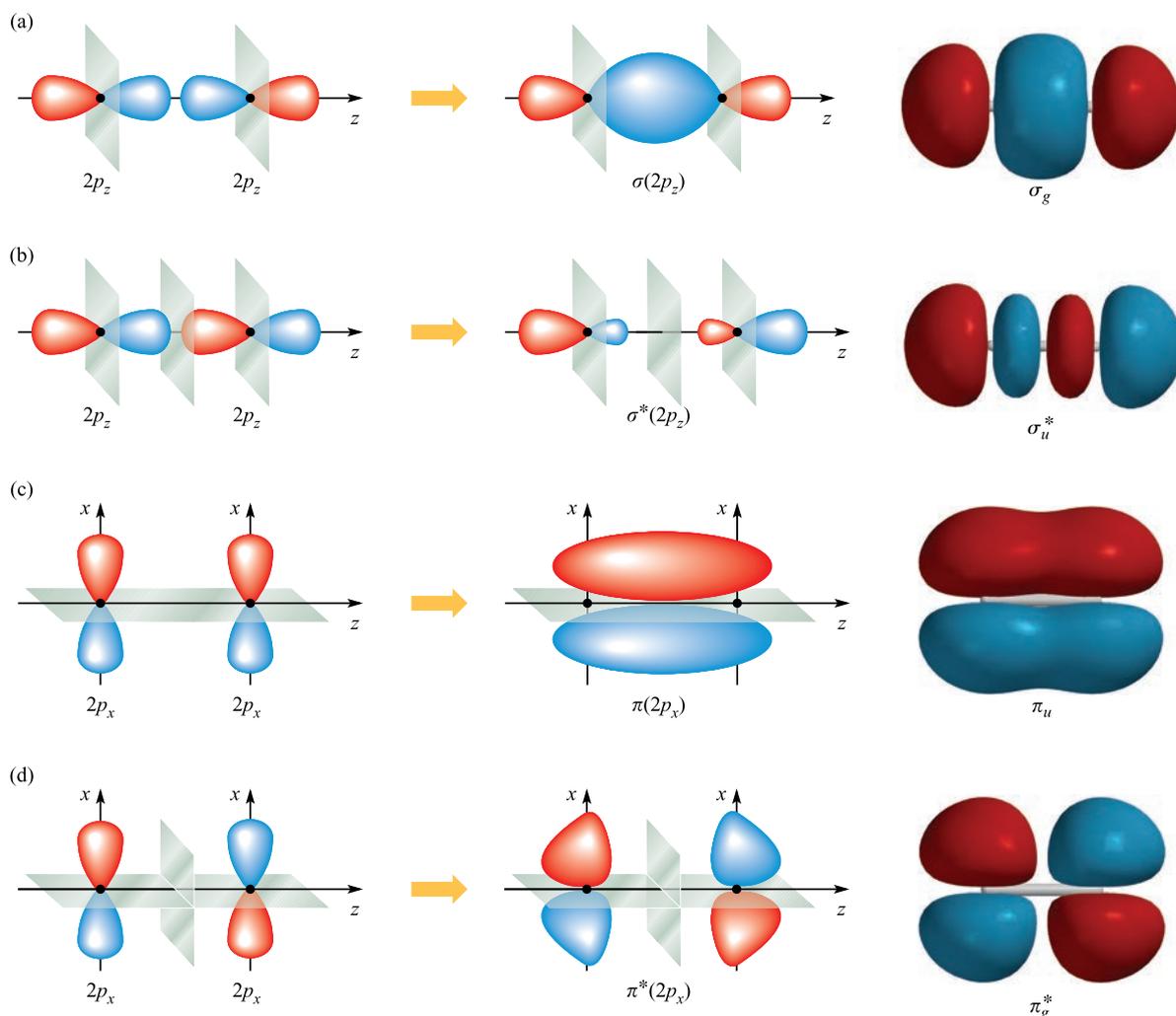
Molecular orbital theory can be applied to any homonuclear diatomic molecule, but as more valence atomic orbitals

become available, the MO diagram becomes more complex. Treatments of the bonding in  $\text{He}_2$ ,  $\text{Li}_2$  and  $\text{Be}_2$  are similar to that for  $\text{H}_2$ . In practice, He does not form  $\text{He}_2$ , and the construction of an MO diagram for  $\text{He}_2$  is a useful exercise because it rationalizes this observation. Figure 2.6a shows that when the two 1s atomic orbitals of two He atoms interact,  $\sigma$  and  $\sigma^*$  MOs are formed as in  $\text{H}_2$ . However, each He atom contributes two electrons, meaning that in  $\text{He}_2$ , both the bonding *and* antibonding MOs are fully occupied. The bond order (eq. 2.9) is zero and so the MO picture of  $\text{He}_2$  is consistent with its non-existence. Using the same notation as for  $\text{H}_2$ , the ground state electronic configuration of  $\text{He}_2$  is  $\sigma_g(1s)^2\sigma_u^*(1s)^2$ .

The ground state electronic configuration of Li ( $Z = 3$ ) is  $1s^2 2s^1$  and when two Li atoms combine, orbital overlap occurs efficiently between the 1s atomic orbitals and between the 2s atomic orbitals. To a first approximation we can ignore 1s–2s overlap since the 1s and 2s orbital energies are poorly matched. An approximate orbital interaction diagram for the formation of  $\text{Li}_2$  is given in Fig. 2.6b. Each Li atom provides three electrons, and the six electrons in  $\text{Li}_2$  occupy the lowest energy MOs to give a ground state electronic configuration of  $\sigma_g(1s)^2\sigma_u^*(1s)^2\sigma_g(2s)^2$ . Effectively, we could ignore the interaction between the core 1s atomic orbitals since the net bonding is determined by the interaction between the valence atomic orbitals, and a simpler, but informative, electronic ground state is  $\sigma_g(2s)^2$ . Figure 2.6b also shows that  $\text{Li}_2$  is predicted to be diamagnetic in keeping with experimental data. By applying eq. 2.9, we see that MO theory gives a bond order in  $\text{Li}_2$  of one. Note that the terminology ‘core and valence orbitals’ is equivalent to that for ‘core and valence electrons’ (see Section 1.9).

Like Li, Be has available 1s and 2s atomic orbitals for bonding; these atomic orbitals constitute the *basis set* of

<sup>†</sup> See for example: M. Kaupp and S. Riedel (2004) *Inorg. Chim. Acta*, vol. 357, p. 1865 – ‘On the lack of correlation between bond lengths, dissociation energies and force constants: the fluorine-substituted ethane homologues’; D. Setiswan, E. Kraka and D. Cremer (2015) *J. Phys. Chem. A*, vol. 119, p. 9541 – ‘Hidden bond anomalies: The peculiar case of the fluorinated amine chalcogenides’.



**Fig. 2.7.** The overlap of two  $2p$  atomic orbitals for which the atomic nuclei are defined to lie on the  $z$  axis: (a) direct overlap along the  $z$  axis gives a  $\sigma_g(2p_z)$  MO (bonding); (b) the formation of the  $\sigma_u^*(2p_z)$  MO (antibonding); (c) sideways overlap of two  $2p_x$  atomic orbitals gives a  $\pi_u(2p_x)$  MO (bonding); (d) the formation of  $\pi_g^*(2p_x)$  MO (antibonding). Atomic nuclei are marked in black and nodal planes in grey. The diagrams on the right-hand side are more realistic representations of the MOs and have been generated computationally using Spartan '04, ©Wavefunction Inc. 2003.

*orbitals.* An orbital interaction diagram similar to that for  $\text{Li}_2$  (Fig. 2.6b) is appropriate. The difference between  $\text{Li}_2$  and  $\text{Be}_2$  is that  $\text{Be}_2$  has two more electrons than  $\text{Li}_2$  and these occupy the  $\sigma^*(2s)$  MO. The predicted bond order in  $\text{Be}_2$  is thus zero. In practice, this prediction is essentially fulfilled, although there is evidence for an extremely unstable  $\text{Be}_2$  species with bond length 245 pm and bond energy  $10 \text{ kJ mol}^{-1}$ .

A **basis set of orbitals** is composed of those which are available for orbital interactions.

In each of  $\text{Li}_2$  and  $\text{Be}_2$ , it is unnecessary to include the core ( $1s$ ) atomic orbitals in order to obtain a useful bonding picture. This is true more generally, and throughout this book, MO treatments of bonding focus only on the interactions between the valence orbitals of the atoms concerned.

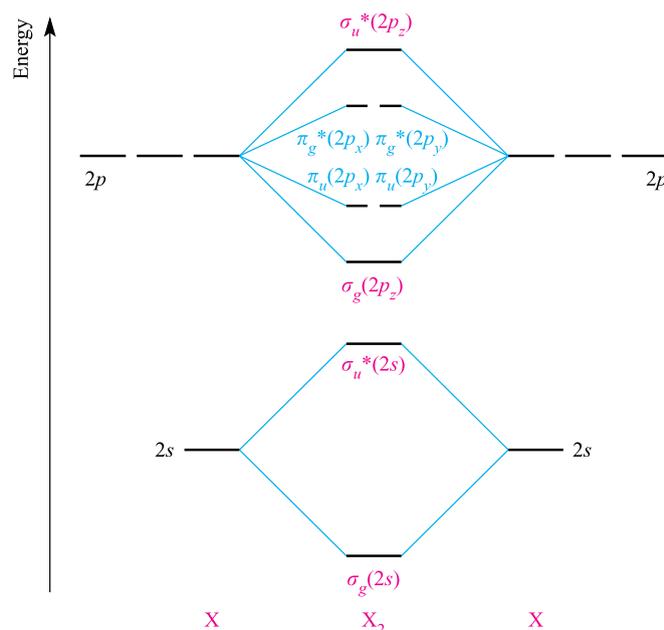
### The bonding in $\text{F}_2$ and $\text{O}_2$

The valence shell of an F atom contains  $2s$  and  $2p$  atomic orbitals, and the formation of an  $\text{F}_2$  molecule involves  $2s-2s$  and  $2p-2p$  orbital interactions. Before we can construct an MO diagram for the formation of  $\text{F}_2$ , we must consider what types of interactions are possible between  $p$  atomic orbitals.

By convention, each  $p$  atomic orbital is directed along one of the three Cartesian axes (Fig. 1.10), and, in considering the formation of a diatomic  $\text{X}_2$ , it is convenient to fix the positions of the X nuclei on one of the axes. In diagram 2.13, the nuclei are placed on the  $z$  axis, but this choice of axis is arbitrary. Defining these positions also defines the relative orientations of the two sets of  $p$  orbitals (Fig. 2.7).



(2.13)



**Fig. 2.8.** A general orbital interaction diagram for the formation of  $X_2$  in which the valence orbitals of atom X are the  $2s$  and  $2p$ . In constructing this diagram we assume that the  $s$ - $p$  separation is sufficiently large that no orbital mixing occurs. The X nuclei lie on the  $z$  axis.

Figures 2.7a and 2.7b show the in-phase and out-of-phase combinations of two  $2p_z$  atomic orbitals. In terms of the region between the nuclei, the  $p_z$ - $p_z$  interaction is similar to that of two  $s$  atomic orbitals (Fig. 2.5) and the symmetries of the resultant MOs are consistent with the  $\sigma_g$  and  $\sigma_u^*$  labels. Thus, the direct interaction of two  $p$  atomic orbitals (i.e. when the orbitals lie along a common axis) leads to  $\sigma_g(2p)$  and  $\sigma_u^*(2p)$  MOs. The  $p_x$  orbitals of the two atoms X can overlap only in a sideways manner, an interaction which has a smaller overlap integral than the direct overlap of the  $p_z$  atomic orbitals. The in-phase and out-of-phase combinations of two  $2p_x$  atomic orbitals are shown in Figs. 2.7c and 2.7d. The bonding MO is called a  $\pi$ -orbital ('*pi-orbital*'), and its antibonding counterpart is a  $\pi^*$ -orbital ('*pi-star-orbital*'). Note the positions of the nodal planes in each MO. A  $\pi$  molecular orbital is asymmetrical with respect to rotation about the internuclear axis, i.e. if you rotate the orbital about the internuclear axis (the  $z$  axis in Fig. 2.7), there is a phase change. A  $\pi^*$ -orbital must exhibit two properties:

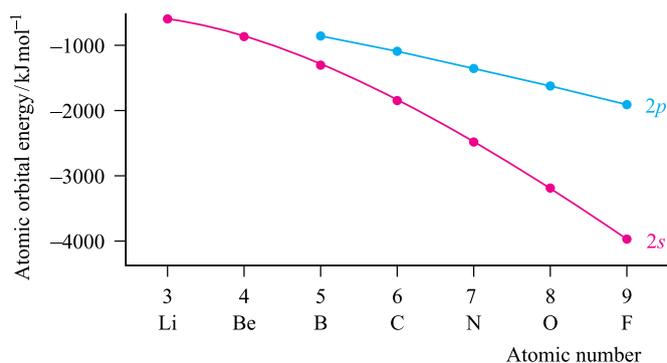
- the  $\pi$  label means that rotation of the orbital about the internuclear axis generates a phase change, *and*
- the  $*$  label means that there must be a nodal plane *between* the nuclei.

The parity (see Box 2.1) of a  $\pi$ -orbital is  $u$ , and that of a  $\pi^*$ -orbital is  $g$ . These labels are the reverse of those for  $\sigma$  and  $\sigma^*$ -orbitals, respectively (Fig. 2.7). The overlap between two  $p_y$  atomic orbitals generates an MO which has the same symmetry properties as that derived from the combination

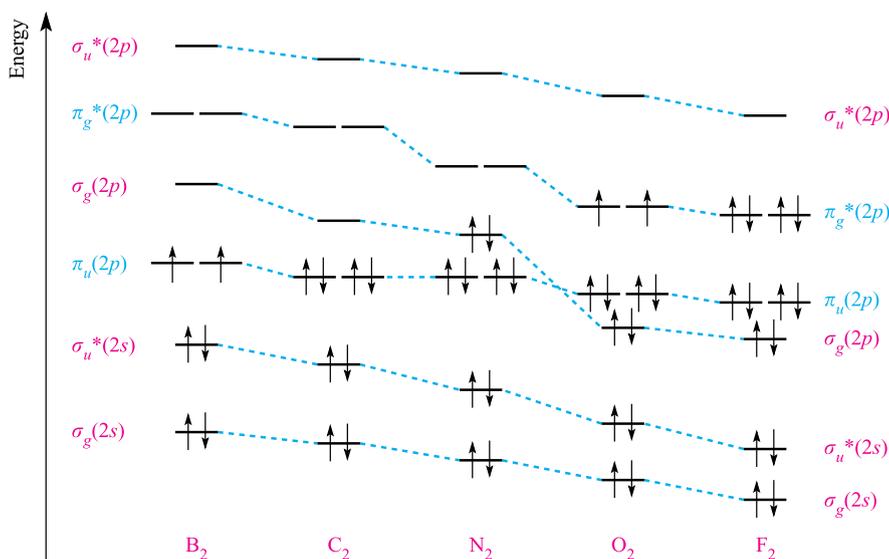
of the two  $p_x$  atomic orbitals, but the  $\pi_u(p_y)$  MO lies in a plane perpendicular to that of the  $\pi_u(p_x)$  MO. The  $\pi_u(p_x)$  and  $\pi_u(p_y)$  MOs lie at the same energy: they are *degenerate*. The  $\pi_g^*(p_y)$  and  $\pi_g^*(p_x)$  MOs are similarly related.

Now let us return to the formation of  $F_2$ . The valence orbitals of F are the  $2s$  and  $2p$ , and Fig. 2.8 shows a general orbital interaction diagram for the overlap of these orbitals. We may assume to a first approximation that the energy separation of the fluorine  $2s$  and  $2p$  atomic orbitals (the  $s$ - $p$  separation) is sufficiently great that only  $2s$ - $2s$  and  $2p$ - $2p$  orbital interactions occur. Notice that the stabilization of the  $\pi_u(2p_x)$  and  $\pi_u(2p_y)$  MOs relative to the  $2p$  atomic orbitals is less than that of the  $\sigma_g(2p_z)$  MO, consistent with the relative efficiencies of orbital overlap discussed above. In  $F_2$  there are 14 electrons to be accommodated and, according to the *aufbau* principle, this gives a ground state electronic configuration of  $\sigma_g(2s)^2\sigma_u^*(2s)^2\sigma_g(2p_z)^2\pi_u(2p_x)^2\pi_u(2p_y)^2\pi_g^*(2p_x)^2\pi_g^*(2p_y)^2$ . The MO picture for  $F_2$  is consistent with its observed diamagnetism. The predicted bond order is 1, in keeping with the result of the VB treatment (see Section 2.2).

Figure 2.8 can also be used to describe the bonding in  $O_2$ . Each O atom has six valence electrons ( $2s^2 2p^4$ ) and the total of 12 electrons in  $O_2$  gives an electronic ground state of  $\sigma_g(2s)^2\sigma_u^*(2s)^2\sigma_g(2p_z)^2\pi_u(2p_x)^2\pi_u(2p_y)^2\pi_g^*(2p_x)^1\pi_g^*(2p_y)^1$ . This result is one of the triumphs of early MO theory: the model correctly predicts that  $O_2$  possesses two unpaired electrons and is paramagnetic. From eq. 2.9, the bond order in  $O_2$  is 2.



**Fig. 2.9.** In crossing the period from Li to F, the energies of the 2s and 2p atomic orbitals decrease owing to the increased effective nuclear charge.



**Fig. 2.10.** Changes in the energy levels of the MOs and the ground state electronic configurations of homonuclear diatomic molecules involving first-row *p*-block elements.

### What happens if the *s*–*p* separation is small?

A comparison of theoretical with experimental data for  $F_2$  and  $O_2$  indicates that the approximations we have made above are appropriate. However, this is not the case if the *s*–*p* energy difference is relatively small. In going from Li to F, the effective nuclear charge experienced by an electron in a 2s or 2p atomic orbital increases and the orbital energy decreases. This is shown in Fig. 2.9: the trend is non-linear and the *s*–*p* separation increases significantly from B to F. The relatively small *s*–*p* separation observed for B and C means that the approximation made when constructing the orbital interaction diagram in Fig. 2.8 is no longer valid when we construct similar diagrams for the formation of  $B_2$  and  $C_2$ . Here, *orbital mixing* may occur<sup>†</sup> between orbitals of similar symmetry and energy, with the result that the ordering of the MOs in

$B_2$ ,  $C_2$  and  $N_2$  differs from that in  $F_2$  and  $O_2$ . Figure 2.10 compares the energy levels of the MOs and the ground state electronic configurations of the diatomics  $X_2$  for  $X = B, C, N, O$  and  $F$ . Notice the so-called *σ*–*π* crossover that occurs between  $N_2$  and  $O_2$ .

Since the MO approach is a theoretical model, what experimental evidence is there for this *σ*–*π* crossover? The actual electronic configurations of molecules are nearly always determined spectroscopically, particularly by *photoelectron spectroscopy*, a technique in which electrons in different orbitals are distinguished by their ionization energies (see Section 4.12). Experimental data support the orbital orderings shown in Fig. 2.10. Table 2.1 lists experimental bond distances and bond dissociation enthalpies for diatomics of the second period including  $Li_2$  and  $Be_2$ , and also gives their bond orders calculated from MO theory. Since the nuclear charges change along the series, we should not expect all bonds of order 1 to have the same bond dissociation enthalpy. However, the general relationship between the bond order, dissociation

<sup>†</sup> This effect is dealt with in detail but at a relatively simple level in Chapter 4 of C.E. Housecroft and E.C. Constable (2010) *Chemistry*, 4th edn, Prentice Hall, Harlow.

**Table 2.1** Experimental data and bond orders for homonuclear diatomic molecules X<sub>2</sub> in which X is an atom in the period Li to F.

Diatomic	Bond distance / pm	Bond dissociation enthalpy / kJ mol <sup>-1</sup>	Bond order	Magnetic properties
Li <sub>2</sub>	267	110	1	Diamagnetic
Be <sub>2</sub> <sup>†</sup>	–	–	0	–
B <sub>2</sub>	159	297	1	Paramagnetic
C <sub>2</sub>	124	607	2	Diamagnetic
N <sub>2</sub>	110	945	3	Diamagnetic
O <sub>2</sub>	121	498	2	Paramagnetic
F <sub>2</sub>	141	159	1	Diamagnetic

<sup>†</sup> See text on p. 39.

enthalpy and distance is unmistakable. Table 2.1 also states whether a given molecule is diamagnetic or paramagnetic. We have already seen that MO theory correctly predicts (as does VB theory) that Li<sub>2</sub> is diamagnetic. Similarly, both the MO and VB models are consistent with the diamagnetism of C<sub>2</sub>, N<sub>2</sub> and F<sub>2</sub>. The paramagnetism of O<sub>2</sub> is predicted by MO theory as we have already seen, and this result is independent of whether the crossover of the  $\sigma_g(2p)$  and  $\pi_u(2p)$  occurs or not (Fig. 2.10). However, the MO model is only consistent with B<sub>2</sub> being paramagnetic if the  $\pi_u(2p)$  level is at a lower energy than the  $\sigma_g(2p)$ . Consider in Fig. 2.10 what would happen if the relative orbital energies of the  $\sigma_g(2p)$  and  $\pi_u(2p)$  were reversed.

### Worked example 2.1 Molecular orbital theory: properties of diatomics

**The bond dissociation enthalpies for the nitrogen–nitrogen bond in N<sub>2</sub> and [N<sub>2</sub>]<sup>-</sup> are 945 and 765 kJ mol<sup>-1</sup> respectively. Account for this difference in terms of MO theory, and state whether [N<sub>2</sub>]<sup>-</sup> is expected to be diamagnetic or paramagnetic.**

Each N atom has the ground state configuration of [He]2s<sup>2</sup>2p<sup>3</sup>.

An MO diagram for N<sub>2</sub>, assuming only 2s–2s and 2p–2p orbital interactions, can be constructed, the result being as shown in Fig. 2.10. From this diagram, the bond order in N<sub>2</sub> is 3.0.

The change from N<sub>2</sub> to [N<sub>2</sub>]<sup>-</sup> is a one-electron reduction and, assuming that Fig. 2.10 is still applicable, an electron is added to a  $\pi_g^*(2p)$  orbital. The calculated bond order in [N<sub>2</sub>]<sup>-</sup> is therefore 2.5.

The lower bond order of [N<sub>2</sub>]<sup>-</sup> compared with N<sub>2</sub> is consistent with a lower bond dissociation enthalpy.

The electron in the  $\pi_g^*(2p)$  orbital is unpaired and [N<sub>2</sub>]<sup>-</sup> is expected to be paramagnetic.

### Self-study exercises

- Using Fig. 2.10 as a basis, account for the fact that [N<sub>2</sub>]<sup>+</sup> is paramagnetic.
- Using MO theory, rationalize why the N–N bond distance in [N<sub>2</sub>]<sup>+</sup> is greater (112 pm) than in N<sub>2</sub> (110 pm).  
[Ans. Loss of electron from  $\sigma_g(2p)$  MO]
- Use Fig. 2.10 to rationalize why the bond orders in [N<sub>2</sub>]<sup>+</sup> and [N<sub>2</sub>]<sup>-</sup> are both 2.5.
- Classify the changes from (a) N<sub>2</sub> to [N<sub>2</sub>]<sup>+</sup>, (b) from [N<sub>2</sub>]<sup>-</sup> to N<sub>2</sub> and (c) from [N<sub>2</sub>]<sup>+</sup> to [N<sub>2</sub>]<sup>-</sup> as 1- or 2-electron, oxidation or reduction steps.  
[Ans. (a) 1e oxidation; (b) 1e oxidation; (c) 2e reduction]
- Use MO theory to show that B<sub>2</sub> has a bond order of one, and that B<sub>2</sub> is paramagnetic.  
[Ans. Check answer against Fig. 2.10]
- Starting from Fig. 2.10: explain why (a) [O<sub>2</sub>]<sup>-</sup> is paramagnetic, but [O<sub>2</sub>]<sup>2-</sup> is diamagnetic, and (b) the trend in bond orders is [O<sub>2</sub>]<sup>2-</sup> < [O<sub>2</sub>]<sup>-</sup> < O<sub>2</sub>.

## 2.4 The octet rule and isoelectronic species

### The octet rule: first row p-block elements

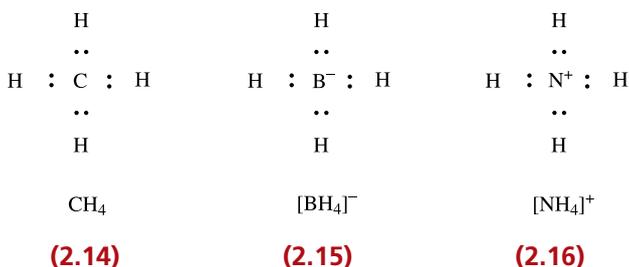
The ground state electronic configurations in Table 1.3 reveal a pattern illustrating that filled quantum levels provide ‘building blocks’ within the electronic configurations of the heavier elements. Worked example 1.7 emphasized that each noble gas is characterized by having a filled quantum level. With the exception of He, this configuration is of

the form  $ns^2np^6$ , and this gives rise to the concept of the *octet rule*.

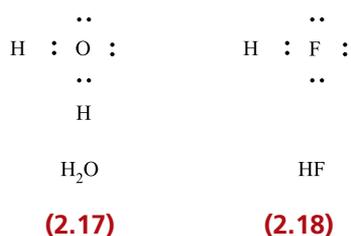
An atom obeys the *octet rule* when it gains, loses or shares electrons to give an *outer* shell containing eight electrons (an octet) with a configuration  $ns^2np^6$ .

Ions such as  $\text{Na}^+$  ( $2s^22p^6$ ),  $\text{Mg}^{2+}$  ( $2s^22p^6$ ),  $\text{F}^-$  ( $2s^22p^6$ ),  $\text{Cl}^-$  ( $3s^23p^6$ ) and  $\text{O}^{2-}$  ( $2s^22p^6$ ) obey the octet rule. In the gas phase, formation of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions from Na, Mg and O atoms is endothermic (Fig. 1.6 and Table 1.5), and the ions typically exist in environments in which electrostatic interaction energies compensate for the energies needed to form the ions (see Chapter 6). In general, the octet rule is most usefully applied in covalently bonded compounds involving *p*-block elements.

In structures 2.14–2.16, Lewis structures are used to illustrate how the octet rule is obeyed by elements from the first row of the *p*-block. A carbon atom has four valence electrons ( $2s^22p^2$ ) and if it forms four covalent single bonds, it achieves an octet of electrons in its valence shell (structure 2.14). A boron atom has three valence electrons ( $2s^22p^1$ ) and the formation of three single bonds generates a sextet (six electrons). The  $\text{BH}_3$  molecule deals with this problem by dimerizing as we discuss in Section 5.8. In  $[\text{BH}_4]^-$ , the negative charge can formally be assigned to the B centre. By forming four single bonds, the B atom achieves an octet of electrons as shown in structure 2.15. Nitrogen is in group 15 and an N atom has five valence electrons ( $2s^22p^3$ ). In  $[\text{NH}_4]^+$ , if we formally assign the positive charge to the N atom, this centre then has four valence electrons and the formation of four single bonds provides the N atom with an octet of electrons (structure 2.16).



In these examples, only bonding electrons contribute to the octet of electrons. Lone pairs of electrons may also contribute as illustrated in  $\text{H}_2\text{O}$  (2.17) and  $\text{HF}$  (2.18).



### Self-study exercises

1. Show that *each* atom in each of the following molecules obeys the octet rule:  $\text{NF}_3$ ,  $\text{CF}_4$ ,  $\text{OF}_2$ ,  $\text{F}_2$ . Draw Lewis structures for the molecules and confirm that the bond order of each bond is one.
2. Show that *each* atom in the  $[\text{BF}_4]^-$  ion obeys the octet rule.
3. Show that *each* atom in each of the following molecules obeys the octet rule:  $\text{CO}_2$ ,  $\text{OCF}_2$ ,  $\text{ONF}$ . Draw Lewis structures for the molecules and state the bond order of each bond.

### Isoelectronic species

The series of molecular species shown in structures 2.14–2.16 illustrates the important concept of *isoelectronic species*.

Two species are *isoelectronic* if they possess the same *total* number of electrons.

Boron, carbon and nitrogen are adjacent and in the same row in the periodic table, and atoms of B, C and N contain three, four and five valence electrons, respectively. It follows that each of  $\text{B}^-$ , C and  $\text{N}^+$  possesses four valence electrons, and  $[\text{BH}_4]^-$ ,  $\text{CH}_4$  and  $[\text{NH}_4]^+$  are therefore *isoelectronic*. The word *isoelectronic* is often used in the context of meaning ‘*same number of valence electrons*’, but strictly such usage should always be qualified. For example,  $\text{HF}$ ,  $\text{HCl}$  and  $\text{HBr}$  are *isoelectronic with respect to their valence electrons*.

The isoelectronic principle is simple but important. Often, species that are isoelectronic possess the same structure, i.e. they are *isostructural*, e.g.  $[\text{BH}_4]^-$ ,  $\text{CH}_4$  and  $[\text{NH}_4]^+$ .

If two species are *isostructural*, they possess the same structure.

### Worked example 2.2 Isoelectronic molecules and ions

Show that  $\text{N}_2$  and  $[\text{NO}]^+$  are isoelectronic.

N is in group 15 and has five valence electrons.

O is in group 16 and has six valence electrons.

$\text{O}^+$  has five valence electrons.

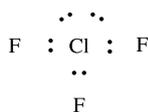
Therefore, each of  $\text{N}_2$  and  $[\text{NO}]^+$  possesses 10 valence electrons and the species are isoelectronic.

## Self-study exercises

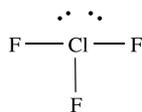
1. Show that  $[\text{SiF}_6]^{2-}$  and  $[\text{PF}_6]^-$  are isoelectronic.
2. Confirm that  $[\text{CN}]^-$  and  $[\text{NO}]^+$  are isoelectronic.
3. Are  $\text{I}_2$  and  $\text{F}_2$  isoelectronic?
4. In terms only of valence electrons, which of the following species is not isoelectronic with the remaining three:  $\text{NH}_3$ ,  $[\text{H}_3\text{O}]^+$ ,  $\text{BH}_3$  and  $\text{AsH}_3$ ? [Ans.  $\text{BH}_3$ ]
5. Are  $\text{GaCl}_3$  and  $\text{BF}_3$  isoelectronic?
6. Show that  $[\text{AlCl}_4]^-$ ,  $\text{SiCl}_4$  and  $[\text{PCl}_4]^+$  are isoelectronic.

The octet rule: heavier *p*-block elements

As one descends a given group in the *p*-block, there is a tendency towards increased coordination numbers. Thus for example, a coordination number of 6 is found in  $\text{SF}_6$ ,  $[\text{PF}_6]^-$  and  $[\text{SiF}_6]^{2-}$ , but is not found in simple molecular species for the analogous first row elements O, N and C. Similarly, the heavier group 17 elements form compounds such as  $\text{ClF}_3$ ,  $\text{BrF}_5$  and  $\text{IF}_7$  in which F is always a terminal atom and forms only one single bond. The Lewis structures 2.19 and 2.20 for  $\text{ClF}_3$  imply that the Cl atom is surrounded by 10 valence electrons, i.e. it has ‘expanded its octet’. Such species are referred to as being *hypervalent*.

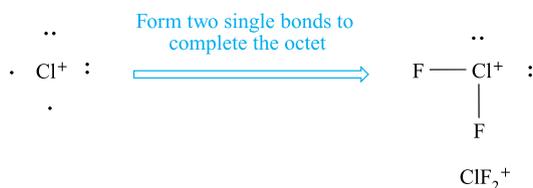


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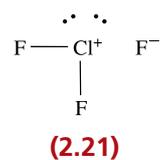


(2.20)

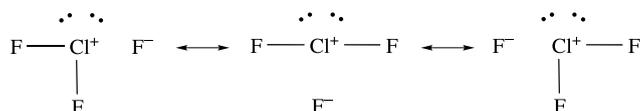
It is, however, not necessary to exceed a valence octet if we make use of *charge-separated* species as contributing resonance structures. In order to maintain the octet of electrons around the Cl centre in  $\text{ClF}_3$ , we have to follow a similar strategy to that adopted in  $[\text{NH}_4]^+$  described above (2.16). Whereas a Cl atom ( $3s^23p^5$ ) can form only one bond while obeying the octet rule, a  $\text{Cl}^+$  centre can form two bonds:



Thus, we can write a Lewis structure for  $\text{ClF}_3$  in terms of the charge-separated species 2.21.



There is, however, a problem: structure 2.21 implies that one Cl–F interaction is ionic, while the other two are covalent. This problem is readily overcome by drawing a set of three resonance structures:



We look again at the bonding in hypervalent species in Sections 5.2, 5.8 and 15.3.

## Self-study exercises

1. Show that As in  $\text{AsF}_3$  obeys the octet rule.
2. Show that Se in  $\text{H}_2\text{Se}$  obeys the octet rule.
3. In which of the following molecules is it necessary to invoke charge-separated resonance structures in order that the central atom obeys the octet rule: (a)  $\text{H}_2\text{S}$ ; (b)  $\text{HCN}$ ; (c)  $\text{SO}_2$ ; (d)  $\text{AsF}_5$ ; (e)  $[\text{BF}_4]^-$ ; (f)  $\text{CO}_2$ ; (g)  $\text{BrF}_3$ . [Ans. (c); (d); (g)]
4. Draw Lewis structures for the following ions, ensuring that all atoms obey the octet rule: (a)  $[\text{NO}]^+$ ; (b)  $[\text{CN}]^-$ ; (c)  $[\text{AlH}_4]^-$ ; (d)  $[\text{NO}_2]^-$ .

## 2.5 Electronegativity values

In a homonuclear diatomic molecule  $\text{X}_2$ , the electron density in the region between the nuclei is symmetrical; each X nucleus has the same effective nuclear charge. On the other hand, the disposition of electron density in the region between the two nuclei of a *heteronuclear* diatomic molecule  $\text{X}-\text{Y}$  may be asymmetrical. If the effective nuclear charge of Y is greater than that of X, the pair of electrons in the  $\text{X}-\text{Y}$  covalent bond will be drawn towards Y and away from X.

Pauling electronegativity values,  $\chi^{\text{P}}$ 

**Electronegativity,  $\chi^{\text{P}}$** , was defined by Pauling as ‘the power of an atom in a molecule to attract electrons to itself’.

In the early 1930s, Linus Pauling established the concept of *electronegativity*. The symbol for electronegativity is  $\chi$  but we distinguish between different electronegativity scales by

use of a superscript, e.g.  $\chi^P$  for Pauling. Pauling first developed the idea in response to the observation that experimentally determined bond dissociation enthalpy values for heteronuclear bonds often did not agree with those obtained by simple additivity rules. Equation 2.10 shows the relationship between the bond dissociation enthalpy,  $D$ , of the gas phase homonuclear diatomic  $X_2$  and the enthalpy change of atomization,  $\Delta_a H^\circ$ , of  $X(g)$ . Effectively, this partitions bond enthalpy into a contribution made by each atom and, in the case of  $X_2$ , the contribution made by each atom is the same.

$$\Delta_a H^\circ(X, g) = \frac{1}{2} \times D(X-X) \quad (2.10)$$

In eq. 2.11, the same type of additivity is applied to the bond in the heteronuclear diatomic  $XY$ . Estimates obtained for  $D(X-Y)$  using this method sometimes agree quite well with experimental data (e.g.  $ClBr$  and  $ClI$ ), but may differ significantly (e.g.  $HF$  and  $HCl$ ) as worked example 2.3 shows.

$$D(X-Y) = \frac{1}{2} \times [D(X-X) + D(Y-Y)] \quad (2.11)$$

### Worked example 2.3 Bond enthalpy additivity

**Given that  $D(H-H)$  and  $D(F-F)$  in  $H_2$  and  $F_2$  are 436 and 158  $\text{kJ mol}^{-1}$ , estimate the bond dissociation enthalpy of  $HF$  using a simple additivity rule. Compare the answer with the experimental value of 570  $\text{kJ mol}^{-1}$ .**

Assume that you can transfer the contribution made to  $D(H-H)$  by an H atom to  $D(H-F)$ , and similarly for F.

$$\begin{aligned} D(H-F) &= \frac{1}{2} \times [D(H-H) + D(F-F)] \\ &= \frac{1}{2} \times [436 + 158] \\ &= 297 \text{ kJ mol}^{-1} \end{aligned}$$

Clearly, this model is unsatisfactory since it grossly underestimates the value of  $D(H-F)$  which, experimentally, is found to be 570  $\text{kJ mol}^{-1}$ .

### Self-study exercises

1. Given that  $D(H-H)$ ,  $D(Cl-Cl)$ ,  $D(Br-Br)$  and  $D(I-I)$  in  $H_2$ ,  $Cl_2$ ,  $Br_2$  and  $I_2$  are 436, 242, 193 and 151  $\text{kJ mol}^{-1}$  respectively, estimate (by the above method) values of  $D(H-X)$  in  $HCl$ ,  $HBr$  and  $HI$ .

[Ans. 339; 315; 294  $\text{kJ mol}^{-1}$ ]

2. Compare your answers to question 1 with experimental values of 432, 366 and 298  $\text{kJ mol}^{-1}$  for  $D(H-X)$  in  $HCl$ ,  $HBr$  and  $HI$ .

Within the framework of the VB approach, Pauling suggested that the difference,  $\Delta D$ , between an experimental value of  $D(X-Y)$  and that obtained using eq. 2.11 could be attributed to the ionic contribution to the bond (eq. 2.4). The greater the *difference* in electron attracting powers (the *electronegativities*) of atoms X and Y, the greater the contribution made by  $X^+Y^-$  (or  $X^-Y^+$ ), and the greater the value of  $\Delta D$ . Pauling determined an approximately self-consistent scale of electronegativities,  $\chi^P$ , as follows. He first converted  $\Delta D$  values (obtained from  $D_{\text{experimental}} - D_{\text{calculated}}$ , the calculated value coming from eq. 2.11) from units of  $\text{kJ mol}^{-1}$  to eV in order to obtain a numerically small value of  $\Delta D$ . He then arbitrarily related  $\sqrt{\Delta D}$  to the difference in electronegativity values between atoms X and Y (eq. 2.12).

$$\Delta\chi = \chi^P(Y) - \chi^P(X) = \sqrt{\Delta D} \quad \text{units of } \Delta D = \text{eV} \quad (2.12)$$

Over the years, the availability of more accurate thermochemical data has allowed Pauling's initial values of  $\chi^P$  to be more finely tuned. Values listed in Table 2.2 are those in current use. Some intuition is required in deciding whether X or Y has the higher electronegativity value and in order to avoid giving an element a negative value of  $\chi^P$ ,  $\chi^P(H)$  has been taken as 2.2. Although eq. 2.12 implies that the units of  $\chi^P$  are  $\text{eV}^{\frac{1}{2}}$ , it is not usual to give units to electronegativity values. By virtue of their different definitions, values of  $\chi$  on different electronegativity scales (see below) possess different units.

In Table 2.2, more than one value of  $\chi^P$  is listed for some elements. This follows from the fact that the electron withdrawing power of an element varies with its oxidation state (see Section 8.1); remember that the Pauling definition of  $\chi^P$  refers to an atom *in a compound*. Electronegativity values also vary with bond order. Thus for C,  $\chi^P$  has the values of 2.5 for a C–C bond, 2.75 for a C=C bond and 3.3 for a C≡C bond. For most purposes, the value of  $\chi^P(C) = 2.6$  suffices, although the variation underlines the fact that such values must be used with caution.

Following from the original concept of electronegativity, various scales have been devised. We focus on those of Mulliken and of Allred and Rochow;  $\chi$  values from these scales are *not directly comparable* with Pauling values, although *trends* in the values should be similar (Fig. 2.11). Scales may be adjusted so as to be comparable with the Pauling scale.

### Mulliken electronegativity values, $\chi^M$

In one of the simplest approaches to electronegativity, Mulliken took the value of  $\chi^M$  for an atom to be the mean of the values of the first ionization energy,  $IE_1$ , and the first electron affinity,  $EA_1$  (eq. 2.13).

$$\chi^M = \frac{IE_1 + EA_1}{2} \quad \text{where } IE_1 \text{ and } EA_1 \text{ are in eV} \quad (2.13)$$

**Table 2.2** Pauling electronegativity ( $\chi^P$ ) values for the *s*- and *p*-block elements.

Group 1	Group 2		Group 13	Group 14	Group 15	Group 16	Group 17
H 2.2							
Li 1.0	Be 1.6		B 2.0	C 2.6	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3		Al(III) 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8	Ca 1.0	( <i>d</i> -block elements)	Ga(III) 1.8	Ge(IV) 2.0	As(III) 2.2	Se 2.6	Br 3.0
Rb 0.8	Sr 0.9		In(III) 1.8	Sn(II) 1.8	Sb 2.1	Te 2.1	I 2.7
Cs 0.8	Ba 0.9		Tl(I) 1.6	Pb(II) 1.9	Bi 2.0	Po 2.0	At 2.2
			Tl(III) 2.0	Pb(IV) 2.3			

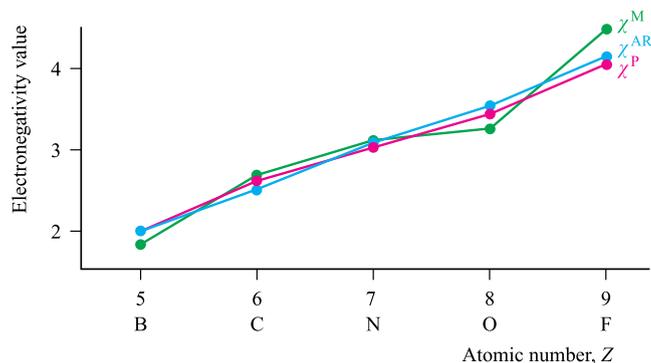
### Allred-Rochow electronegativity values, $\chi^{AR}$

Allred and Rochow chose as a measure of electronegativity of an atom the electrostatic force exerted by the effective nuclear charge  $Z_{\text{eff}}$  (estimated from Slater's rules, see Box 1.5) on the valence electrons. The latter are assumed

to reside at a distance from the nucleus equal to the covalent radius,  $r_{\text{cov}}$ , of the atom. Equation 2.14 gives the method of calculating values of the Allred–Rochow electronegativity,  $\chi^{AR}$ .

$$\chi^{AR} = \left( 3590 \times \frac{Z_{\text{eff}}}{r_{\text{cov}}^2} \right) + 0.744 \quad \text{where } r_{\text{cov}} \text{ is in pm} \quad (2.14)$$

Since, however, Slater's rules are partly empirical and covalent radii are unavailable for some elements, the Allred–Rochow scale is no more rigid or complete than the Pauling one.



**Fig. 2.11.** Although electronegativity values for a given element from different scales cannot be expected to be the same, trends in values along a series of elements are comparable. This is illustrated with scaled values of  $\chi^P$  (Pauling; red),  $\chi^M$  (Mulliken; green) and  $\chi^{AR}$  (Allred–Rochow; blue) for first row elements from the *p*-block.

### Electronegativity: final remarks

Despite the very different (and empirical) approaches to  $\chi^P$ ,  $\chi^M$  and  $\chi^{AR}$ , the trends in electronegativities are roughly in agreement, as Fig. 2.11 exemplifies. The most useful of the scales for application in inorganic chemistry is probably the Pauling scale, which, being based empirically on thermochemical data, can reasonably be used to predict similar data. For example, if the electronegativities of two elements X and Y have been derived from the single covalent bond enthalpies of HX, HY, X<sub>2</sub>, Y<sub>2</sub> and H<sub>2</sub>, we can estimate the bond dissociation enthalpy of the bond in XY with a fair degree of reliability.

### Worked example 2.4 Estimation of a bond dissociation enthalpy from $\chi^P$ values

Using the following data, estimate a value for  $D(\text{Br-F})$ :

$$D(\text{F-F}) = 158 \text{ kJ mol}^{-1} \quad D(\text{Br-Br}) = 224 \text{ kJ mol}^{-1}$$

$$\chi^P(\text{F}) = 4.0 \quad \chi^P(\text{Br}) = 3.0$$

First, use the values of  $\chi^P$  to find  $\Delta D$ :

$$\sqrt{\Delta D} = \chi^P(\text{F}) - \chi^P(\text{Br}) = 4.0 - 3.0 = 1.0$$

$$\Delta D = 1.0^2 = 1.0$$

This gives the value in eV; convert to  $\text{kJ mol}^{-1}$ :

$$1.0 \text{ eV} \approx 96.5 \text{ kJ mol}^{-1}$$

$\Delta D$  is defined as follows:

$$\Delta D = [D(\text{Br-F})_{\text{experimental}}] - \left\{ \frac{1}{2} \times [D(\text{Br-Br}) + D(\text{F-F})] \right\}$$

So an estimate of  $D(\text{Br-F})$  is given by:

$$D(\text{Br-F}) = \Delta D + \left\{ \frac{1}{2} \times [D(\text{Br-Br}) + D(\text{F-F})] \right\}$$

$$= 96.5 + \left\{ \frac{1}{2} \times [224 + 158] \right\}$$

$$= 287.5 \text{ kJ mol}^{-1}$$

[This compares with an experimental value of  $250.2 \text{ kJ mol}^{-1}$ .]

### Self-study exercises

- Use the following data to estimate the bond dissociation enthalpy of  $\text{BrCl}$ :  $D(\text{Br-Br}) = 224 \text{ kJ mol}^{-1}$ ;  $D(\text{Cl-Cl}) = 242 \text{ kJ mol}^{-1}$ ;  $\chi^P(\text{Br}) = 3.0$ ;  $\chi^P(\text{Cl}) = 3.2$ .  
[Ans.  $\approx 237 \text{ kJ mol}^{-1}$ ; actual experimental value =  $218 \text{ kJ mol}^{-1}$ ]
- Use the following data to estimate the bond dissociation enthalpy of  $\text{HF}$ :  $D(\text{H-H}) = 436 \text{ kJ mol}^{-1}$ ;  $D(\text{F-F}) = 158 \text{ kJ mol}^{-1}$ ;  $\chi^P(\text{H}) = 2.2$ ;  $\chi^P(\text{F}) = 4.0$ .  
[Ans.  $\approx 610 \text{ kJ mol}^{-1}$ ; actual experimental value =  $570 \text{ kJ mol}^{-1}$ ]
- Estimate the bond dissociation enthalpy of  $\text{ICl}$  given that  $\chi^P(\text{I}) = 2.7$ ,  $\chi^P(\text{Cl}) = 3.2$ , and  $D(\text{I-I})$  and  $D(\text{Cl-Cl}) = 151$  and  $242 \text{ kJ mol}^{-1}$  respectively.  
[Ans.  $221 \text{ kJ mol}^{-1}$ ]

In this book, we tend to base the systemization of descriptive inorganic chemistry on rigidly defined and independently measured thermochemical quantities such as ionization energies, electron affinities, bond dissociation

enthalpies, lattice energies and hydration enthalpies. Nonetheless, electronegativity values give valuable information about bond and molecular polarities (see below) and allow you to qualitatively assess trends in, for example, acid dissociation constants for families of related oxoacids.

## 2.6 Dipole moments

### Polar diatomic molecules

The symmetrical electron distribution in the bond of a homonuclear diatomic renders the bond *non-polar*. In a heteronuclear diatomic, the electron withdrawing powers of the two atoms may be different, and the bonding electrons are drawn closer towards the more electronegative atom. The bond is *polar* and possesses an *electric dipole moment* ( $\mu$ ). Be careful to distinguish between *electric* and *magnetic* dipole moments (see Section 20.10).

The dipole moment of a diatomic  $\text{XY}$  molecule is given by eq. 2.15 where  $d$  is the distance between the point electronic charges (i.e. the internuclear separation),  $e$  is the charge on the electron ( $1.602 \times 10^{-19} \text{ C}$ ) and  $q$  is point charge. The SI unit of  $\mu$  is the coulomb metre (Cm) but for convenience,  $\mu$  tends to be given in units of debyes (D) where  $1 \text{ D} = 3.336 \times 10^{-30} \text{ Cm}$ .

$$\mu = q \times e \times d \quad (2.15)$$

### Worked example 2.5 Dipole moments

The dipole moment of a gas phase  $\text{HBr}$  molecule is **0.827 D**. Determine the charge distribution in this diatomic if the bond distance is **141.5 pm**. ( $1 \text{ D} = 3.336 \times 10^{-30} \text{ Cm}$ )

To find the charge distribution, you need to find  $q$  using the expression:

$$\mu = qed$$

Units must be consistent:

$$d = 141.5 \times 10^{-12} \text{ m}$$

$$\mu = 0.827 \times 3.336 \times 10^{-30} = 2.76 \times 10^{-30} \text{ Cm (to 3 sig. fig.)}$$

$$q = \frac{\mu}{ed}$$

$$= \frac{2.76 \times 10^{-30}}{1.602 \times 10^{-19} \times 141.5 \times 10^{-12}}$$

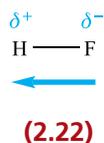
$$= 0.12 \text{ (no units)}$$

The charge distribution can be written as  $\overset{+0.12}{\text{H}} \text{---} \overset{-0.12}{\text{Br}}$  since Br is more electronegative than H.

## Self-study exercises

- The bond length in HF is 92 pm, and the dipole moment is 1.83 D. Determine the charge distribution in the molecule.  
[Ans.  $\overset{+0.41}{\text{H}}-\overset{-0.41}{\text{F}}$  ]
- The bond length in ClF is 163 pm. If the charge distribution is  $\overset{+0.11}{\text{Cl}}-\overset{-0.11}{\text{F}}$ , show that the molecular dipole moment is 0.86 D.

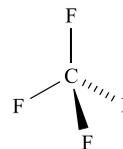
In worked example 2.5, the result indicates that the electron distribution in HBr is such that effectively 0.12 electrons have been transferred from H to Br. The partial charge separation in a polar diatomic molecule can be represented by use of the symbols  $\delta^+$  and  $\delta^-$  assigned to the appropriate nuclear centres, and an arrow represents the direction in which the dipole moment acts. By SI convention, the arrow points from the  $\delta^-$  end of the bond to the  $\delta^+$  end, which is contrary to long-established chemical practice. This is shown for HF in structure 2.22. Keep in mind that a dipole moment is a vector quantity.



*A word of caution:* attempts to calculate the degree of ionic character of the bonds in heteronuclear diatomics from their observed dipole moments and the moments calculated on the basis of charge separation neglect the effects of any lone pairs of electrons and are therefore of doubtful validity. The significant effects of lone pairs are illustrated below in Example 3.

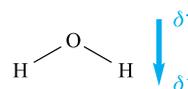
## Molecular dipole moments

Polarity is a *molecular property*. For polyatomic species, the net molecular dipole moment depends upon the magnitudes and relative directions of all the bond dipole moments in the molecule. In addition, lone pairs of electrons may contribute significantly to the overall value of  $\mu$ . We consider three examples below, using the Pauling electronegativity values of the atoms involved to give an indication of individual bond polarities. This practice is useful but must be treated with caution as it can lead to spurious results, e.g. when the bond multiplicity is not taken into account when assigning a value of  $\chi^{\text{P}}$ . Experimental values of molecular electric dipole moments are determined by microwave spectroscopy or other spectroscopic methods.

Example 1: CF<sub>4</sub>

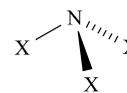
(2.23)

The values of  $\chi^{\text{P}}(\text{C})$  and  $\chi^{\text{P}}(\text{F})$  are 2.6 and 4.0, respectively, indicating that each C–F bond is polar in the sense  $\text{C}^{\delta^+}-\text{F}^{\delta^-}$ . The CF<sub>4</sub> molecule (2.23) is tetrahedral and the four bond moments (each a vector of equivalent magnitude) oppose and cancel one another. The effects of the F lone pairs also cancel out, and the net result is that CF<sub>4</sub> is non-polar.

Example 2: H<sub>2</sub>O

(2.24)

For O and H,  $\chi^{\text{P}} = 3.4$  and 2.2, respectively, showing that each O–H bond is polar in the sense  $\text{O}^{\delta^-}-\text{H}^{\delta^+}$ . Since the H<sub>2</sub>O molecule is non-linear, resolution of the two bond vectors gives a resultant dipole moment which acts in the direction shown in structure 2.24. In addition, the O atom has two lone pairs of electrons which will reinforce the overall moment. The experimental value of  $\mu$  for H<sub>2</sub>O in the gas phase is 1.85 D.

Example 3: NH<sub>3</sub> and NF<sub>3</sub>

X = H or F

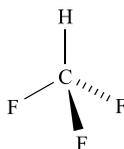
(2.25)

The molecules NH<sub>3</sub> and NF<sub>3</sub> have trigonal pyramidal structures (2.25), and have dipole moments of 1.47 and 0.24 D respectively. This significant difference may be rationalized by considering the bond dipole moments and the effects of the N lone pair. The values of  $\chi^{\text{P}}(\text{N})$  and  $\chi^{\text{P}}(\text{H})$  are 3.0 and 2.2, so each bond is polar in the sense  $\text{N}^{\delta^-}-\text{H}^{\delta^+}$ . The resultant dipole moment acts in a direction that is reinforced by the lone pair. Ammonia is a polar molecule with N carrying a partial negative charge. In NF<sub>3</sub>, each N–F bond is polar in the sense  $\text{N}^{\delta^+}-\text{F}^{\delta^-}$  since F is more electronegative ( $\chi^{\text{P}}(\text{F}) = 4.0$ ) than N. The resultant dipole moment *opposes* the effects of the lone pair, rendering the NF<sub>3</sub> molecule far less polar than NH<sub>3</sub>.

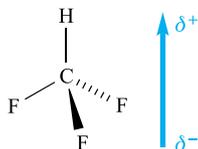
Clearly, molecular shape is an important factor in determining whether a molecule is polar or not. The examples below and in end-of-chapter problem 2.19 consider this further.

### Worked example 2.6 Molecular dipole moments

Use electronegativity values in Table 2.2 to work out whether or not the following molecule is polar and, if so, in what direction the dipole acts.

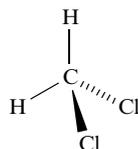
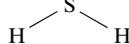


First, look up values of  $\chi^P$  from Table 2.2:  $\chi^P(\text{H}) = 2.2$ ,  $\chi^P(\text{C}) = 2.6$ ,  $\chi^P(\text{F}) = 4.0$ . The molecule is therefore polar with F atoms  $\delta^-$ , and the molecular dipole moment acts as shown below:

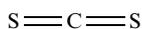
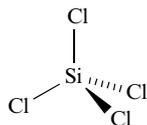
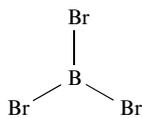


### Self-study exercises

- Use electronegativity values in Table 2.2 to confirm that each of the following molecules is polar. Draw diagrams to show the directions of the molecular dipole moments.



- Explain why each of the following molecules is non-polar.



## 2.7 MO theory: heteronuclear diatomic molecules

In this section, we return to MO theory and apply it to heteronuclear diatomic molecules. In each of the orbital interaction diagrams constructed in Section 2.3 for *homonuclear* diatomics, the resultant MOs contained *equal* contributions from each atomic orbital involved. This is represented in

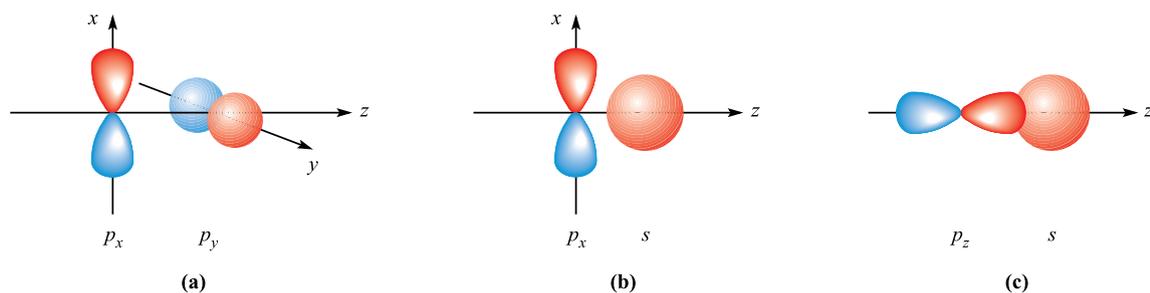
eq. 2.5 for the bonding MO in  $\text{H}_2$  by the fact that each of the wavefunctions  $\psi_1$  and  $\psi_2$  contributes equally to  $\psi_{\text{MO}}$ , and the representations of the MOs in  $\text{H}_2$  (Fig. 2.5) depict *symmetrical* orbitals. Now we look at representative examples of diatomics in which the MOs may contain *different* atomic orbital contributions, a scenario that is typical for heteronuclear diatomics.

First, we must consider likely restrictions when we are faced with the possibility of combining different types of atomic orbitals.

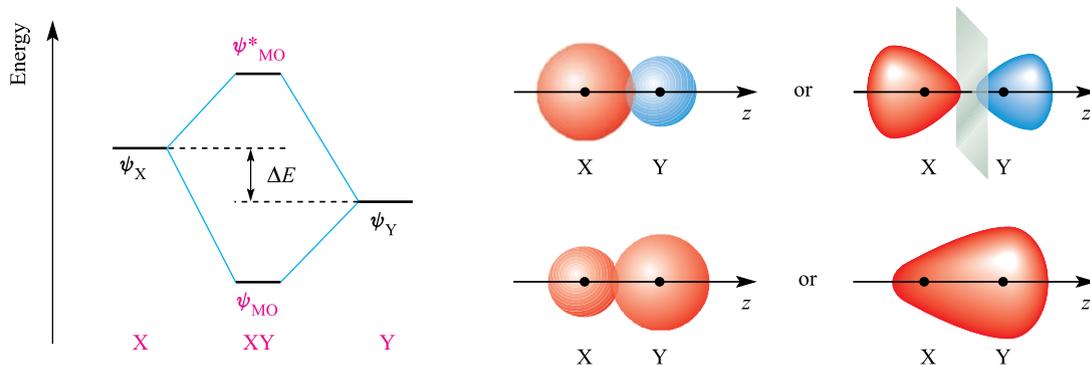
### Which orbital interactions should be considered?

At the beginning of Section 2.3 we stated some general requirements that should be met for orbital interactions to take place efficiently. We stated that orbital interactions are allowed if the *symmetries* of the atomic orbitals are compatible with one another. In our approach to the bonding in a diatomic, we made the assumption that only the interactions between *like* atomic orbitals, e.g.  $2s-2s$ ,  $2p_z-2p_z$ , need be considered. Such interactions are *symmetry-allowed*, and in addition, in a *homonuclear* diatomic the energies of like atomic orbitals on the two atoms are exactly matched.

In a heteronuclear diatomic, we often encounter two atoms that have different basis sets of atomic orbitals, or have sets of similar atomic orbitals lying at different energies. For example, in CO, although both C and O possess valence  $2s$  and  $2p$  atomic orbitals, the greater effective nuclear charge of O means that its atomic orbitals lie at a lower energy than those of C (Fig. 2.9). Before we look more closely at some examples of heteronuclear diatomics, let us briefly consider some symmetry-allowed and -disallowed orbital interactions. It is important to remember that we are looking at these symmetry properties *with respect to the internuclear axis*. In our earlier discussion of homonuclear diatomics (e.g. Fig. 2.8), we ignored the possibility of overlap between the  $p_x$  and  $p_y$  orbitals. Such an interaction between orthogonal  $p$  atomic orbitals (Fig. 2.12a) would give a zero overlap integral. Similarly, for nuclei lying on the  $z$  axis, interaction between  $p_x$  and  $p_z$ , or  $p_y$  and  $p_z$ , orbitals gives zero overlap. An interaction between an  $s$  and a  $p$  atomic orbital *may* occur depending upon the orientation of the  $p$  orbital. In Fig. 2.12b, overlap would be partly bonding and partly antibonding and the net effect is a *non-bonding* interaction. On the other hand, Fig. 2.12c shows an  $s-p$  interaction that *is* allowed by symmetry. Whether or not this leads to effective overlap depends upon the relative energies of the two atomic orbitals. This is illustrated in Fig. 2.13 for a diatomic XY. Let the interaction between  $\psi_X$  and  $\psi_Y$  be symmetry-allowed; the orbital energies are not the same but are close enough that overlap between the orbitals is efficient. The orbital interaction diagram shows that the energy of the bonding MO is closer to  $E(\psi_Y)$  than to  $E(\psi_X)$  and the consequence of this is that the bonding orbital possesses *greater Y than X*



**Fig. 2.12.** Overlap between atomic orbitals is not always allowed by symmetry. Combinations (a) and (b) lead to non-bonding situations but (c) is symmetry-allowed and gives rise to a bonding interaction.



**Fig. 2.13.** The relative energies of atomic orbitals of X and Y will dictate whether an interaction (formally allowed by symmetry) will lead to efficient overlap or not. Here, an interaction occurs but the contribution made by  $\psi_Y$  to  $\psi_{MO}$  is greater than that made by  $\psi_X$ , while  $\psi_X$  contributes more than  $\psi_Y$  to the antibonding MO. The diagrams on the right give pictorial representations of the bonding and antibonding MOs.

*character*. This is expressed in eq. 2.16 in which  $c_2 > c_1$ . For the antibonding MO, the situation is reversed, and  $\psi_X$  contributes more than  $\psi_Y$ ; in eq. 2.17,  $c_3 > c_4$ .

$$\psi_{MO} = N[(c_1 \times \psi_X) + (c_2 \times \psi_Y)] \quad (2.16)$$

$$\psi^*_{MO} = N^*[(c_3 \times \psi_X) + (c_4 \times \psi_Y)] \quad (2.17)$$

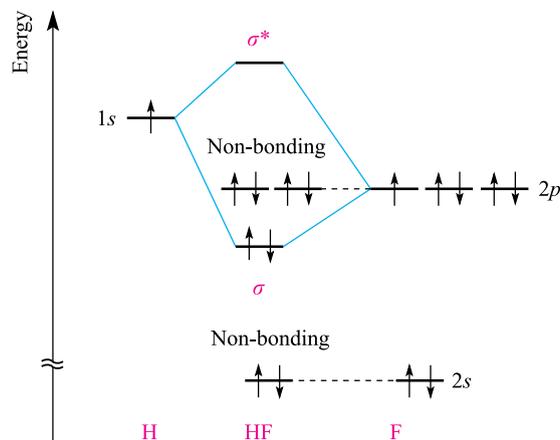
The energy separation  $\Delta E$  in Fig. 2.13 is critical. If it is large, interaction between  $\psi_X$  and  $\psi_Y$  will be poor (the overlap integral is very small). In the extreme case, there is no interaction at all and both  $\psi_X$  and  $\psi_Y$  appear in the XY molecule as unperturbed *non-bonding* atomic orbitals. This is exemplified below.

### Hydrogen fluoride

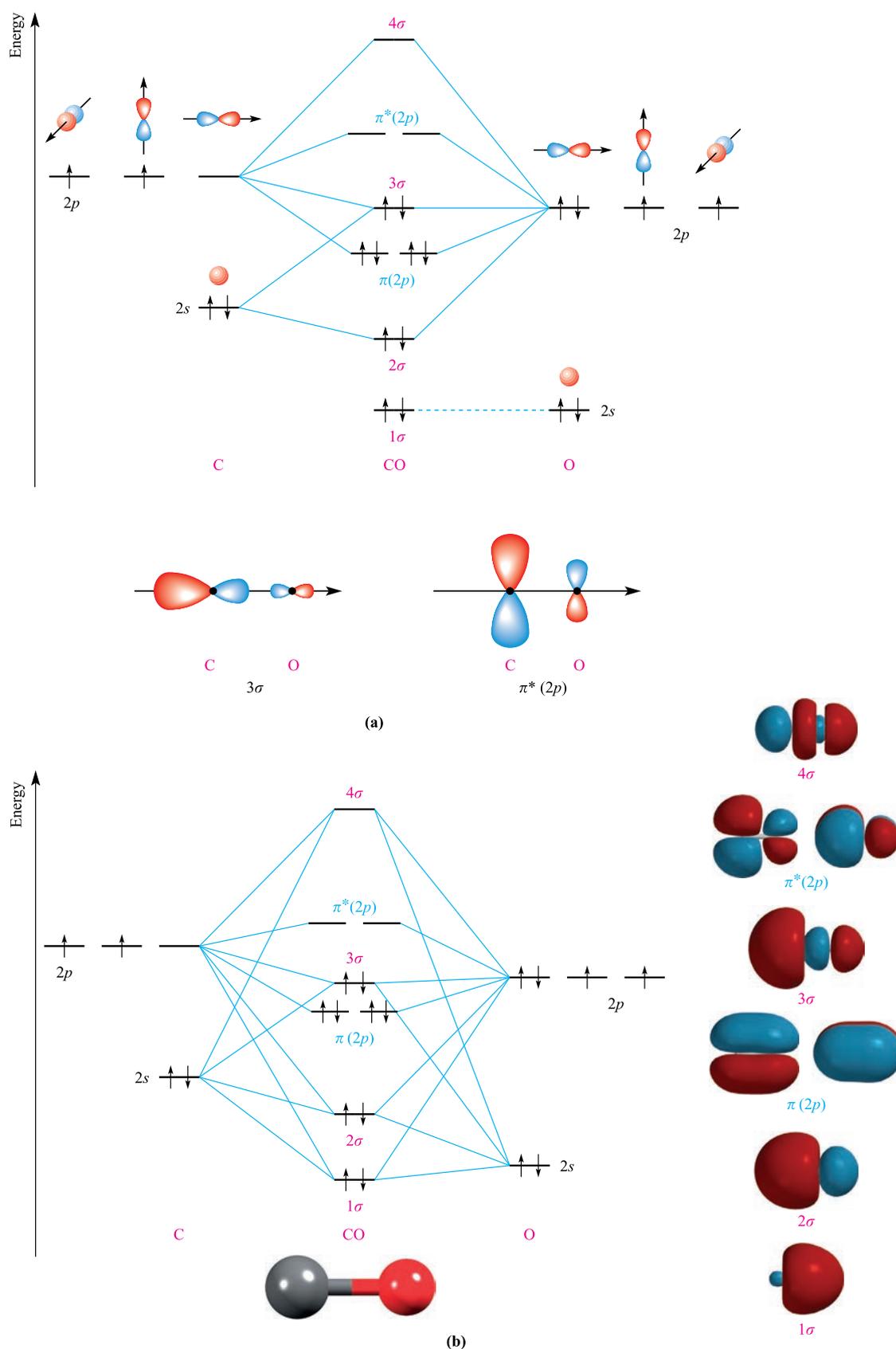
The ground state configurations of H and F are  $1s^1$  and  $[\text{He}]2s^2 2p^5$  respectively. Since  $Z_{\text{eff}}(\text{F}) > Z_{\text{eff}}(\text{H})$ , the F  $2s$  and  $2p$  atomic orbital energies are significantly lowered with respect to the H  $1s$  atomic orbital (Fig. 2.14).

We now have to consider which atomic orbital interactions are symmetry-allowed and then ask whether the atomic orbitals are sufficiently well energy-matched. First, define the axis set for the orbitals; let the nuclei lie on the  $z$  axis. Overlap between the H  $1s$  and F  $2s$  orbitals is allowed by symmetry, but the energy separation is very large (note the break on the energy axis in Fig. 2.14). Overlap between the H  $1s$  and F  $2p_z$  atomic orbitals is also symmetry-allowed

and there is a reasonable orbital energy match. As Fig. 2.14 shows, an interaction occurs leading to  $\sigma$  and  $\sigma^*$  MOs; the  $\sigma$ -orbital has greater F than H character. Notice that, because HF is *non-centrosymmetric* (see Box 2.1), the symmetry labels of the orbitals for HF do *not* involve  $g$  and  $u$  labels. The two F  $2p_x$  and  $2p_y$  atomic orbitals become non-bonding orbitals in HF since no net bonding interaction with the H  $1s$  atomic orbital is possible. Once the orbital interaction



**Fig. 2.14.** An orbital interaction diagram for the formation of HF. Only the valence atomic orbitals and electrons are shown. The break in the vertical (energy) axis indicates that the energy of the F  $2s$  atomic orbital is much lower than is actually shown.



**Fig. 2.15.** (a) A simplified orbital interaction diagram for CO which allows for the effects of some orbital mixing. The labels  $1\sigma$ ,  $2\sigma$  ... rather than  $\sigma(2s)$  ... are used because some orbitals contain both  $s$  and  $p$  character. (b) A more rigorous (but still qualitative) orbital interaction diagram for CO. The diagrams on the right-hand side show representations of the MOs and have been generated computationally using Spartan '04, ©Wavefunction Inc. 2003. These diagrams illustrate that the  $1\sigma$  MO has mainly oxygen character, while the  $2\sigma$ ,  $3\sigma$  and  $\pi^*(2p)$  MOs have more carbon than oxygen character.

diagram has been constructed, the eight valence electrons are accommodated as shown in Fig. 2.14, giving a bond order of 1 in HF. The MO picture of HF indicates that the electron density is greater around the F than H nucleus; the model is consistent with a polar H–F bond in the sense  $H^{\delta+}-F^{\delta-}$ .

### Self-study exercises

1. Sketch pictorial representations of the  $\sigma$  and  $\sigma^*$  MOs in HF.
2. Why is the lowest MO in Fig. 2.14 non-bonding?
3. If the HF molecule lies along the  $z$  axis, the degenerate level shown in Fig. 2.14 comprises F  $2p_x$  and  $2p_y$ . Why are these MOs non-bonding?
4. Explain why the MO treatment of HF shown in Fig. 2.14 is consistent with a bond order of one.

### Carbon monoxide

In Chapter 24 we discuss the chemistry of compounds containing metal–carbon bonds (*organometallic compounds*) of which *metal carbonyls* of the type  $M_x(CO)_y$  are one group. In order to investigate the way in which CO bonds to metals, we must appreciate the electronic structure of the carbon monoxide molecule.

Before constructing an orbital interaction diagram for CO, we note the following:

- $Z_{\text{eff}}(\text{O}) > Z_{\text{eff}}(\text{C})$ ;
- the energy of the O  $2s$  atomic orbital is lower than that of the C  $2s$  atomic orbital (Fig. 2.9);
- the  $2p$  level in O is at lower energy than that in C (Fig. 2.9);
- the  $2s-2p$  energy separation in O is greater than that in C (Fig. 2.9).

We could generate an approximate orbital interaction diagram by assuming that only  $2s-2s$  and  $2p-2p$  overlap occurs, but, as a consequence of the relative atomic orbital energies, such a picture is too simplistic. Figure 2.15a gives a more accurate MO picture of the electronic structure of CO obtained computationally, although even this is over-simplified. Figure 2.15b illustrates more fully the extent of orbital mixing, but for our discussion, the simplified picture presented in Fig. 2.15a suffices. Two of the more important features to notice are:

- The highest occupied MO (HOMO) is  $\sigma$ -bonding and possesses predominantly *carbon* character; occupation of this MO effectively creates an outward-pointing lone pair centred on C.
- A degenerate pair of  $\pi^*(2p)$  MOs make up the lowest unoccupied MOs (LUMOs); each MO possesses more C than O character.

Pictorial representations of the HOMO and one of the LUMOs are given in Fig. 2.15; refer to end-of-chapter problem 2.21.

**HOMO** = highest occupied molecular orbital.  
**LUMO** = lowest unoccupied molecular orbital.

## 2.8 Molecular shape and the VSEPR model

### Valence-shell electron-pair repulsion model

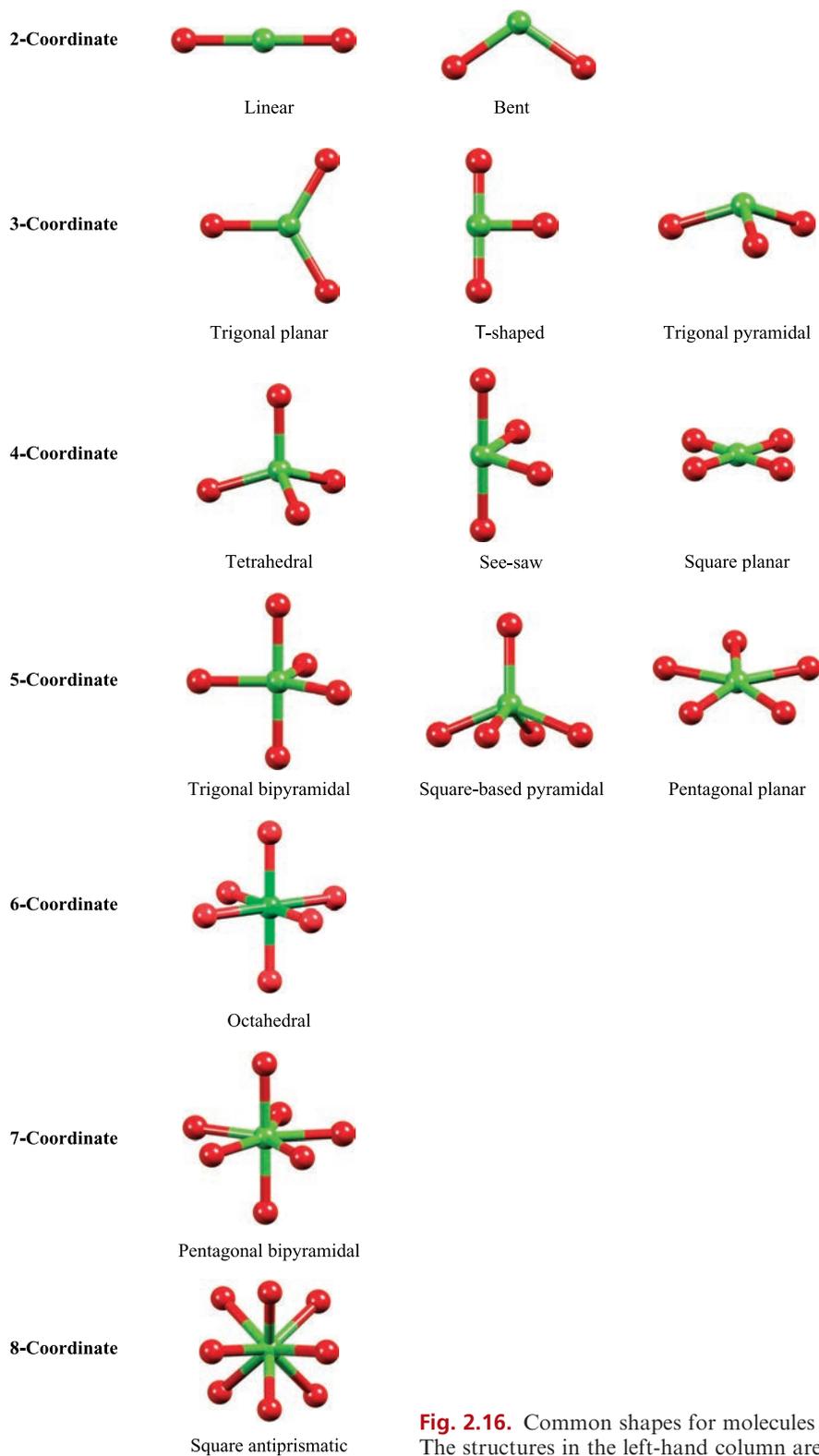
The *valence-shell electron-pair repulsion (VSEPR)* model is used to rationalize or predict the shapes of molecular species. It is based on the assumption that electron pairs adopt arrangements that minimize repulsions between them.

The shapes of molecules containing a central  $p$ -block atom tend to be controlled by the number of electrons in the valence shell of the central atom. The *valence-shell electron-pair repulsion (VSEPR)* model provides a simple model for predicting the shapes of such species. The model combines original ideas of Sidgwick and Powell with extensions developed by Nyholm and Gillespie, and may be summarized as follows:

- Each valence shell electron pair of the central atom E in a molecule  $EX_n$  containing E–X single bonds is stereochemically significant, and repulsions between them determine the molecular shape.
- Electron–electron repulsions decrease in the sequence:  
lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair.
- Where the central atom E is involved in multiple bond formation to atoms X, electron–electron repulsions decrease in the order:  
triple bond–single bond > double bond–single bond > single bond–single bond.
- Repulsions between the bonding pairs in  $EX_n$  depend on the difference between the electronegativities of E and X; electron–electron repulsions are less the more the E–X bonding electron density is drawn away from the central atom E.

The VSEPR model works best for simple halides of the  $p$ -block elements, but may also be applied to species with other substituents. However, the model does *not* take *steric factors* (i.e. the relative sizes of substituents) into account.

In a molecule  $EX_n$ , there is a minimum energy arrangement for a given number of electron pairs. In  $\text{BeCl}_2$  (Be, group 2), repulsions between the two pairs of electrons in the valence shell of Be are minimized if the Cl–Be–Cl unit is linear. In  $\text{BCl}_3$  (B, group 13), electron–electron repulsions are minimized if a trigonal planar arrangement of electron pairs (and thus Cl atoms) is adopted. The structures in the left-hand column of Fig. 2.16 represent the minimum energy structures for  $EX_n$  molecules for  $n = 2-8$  and in which there are no lone pairs of electrons associated with E. Table 2.3

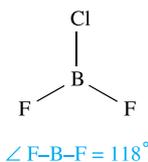


**Fig. 2.16.** Common shapes for molecules of type  $EX_n$  or ions of type  $[EX_n]^{m+/-}$ . The structures in the left-hand column are 'parent' shapes used in the VSEPR model.

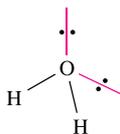
**Table 2.3** ‘Parent’ shapes for  $EX_n$  molecules ( $n = 2-8$ ).

Formula $EX_n$	Coordination number of atom E	Shape	Spatial representation	Ideal bond angles ( $\angle X-E-X$ ) / degrees
$EX_2$	2	Linear	$X-E-X$	180
$EX_3$	3	Trigonal planar		120
$EX_4$	4	Tetrahedral		109.5
$EX_5$	5	Trigonal bipyramidal		$\angle X_{ax}-E-X_{eq} = 90$ $\angle X_{eq}-E-X_{eq} = 120$
$EX_6$	6	Octahedral		$\angle X_1-E-X_2 = 90$
$EX_7$	7	Pentagonal bipyramidal		$\angle X_{ax}-E-X_{eq} = 90$ $\angle X_{eq}-E-X_{eq} = 72$
$EX_8$	8	Square antiprismatic		$\angle X_1-E-X_2 = 78$ $\angle X_1-E-X_3 = 73$

gives further representations of these structures, along with their *ideal* bond angles. Ideal bond angles may be expected when all the X substituents are identical, but in, for example,  $BF_2Cl$  (2.26) some distortion occurs because Cl is larger than F, and the shape is only *approximately* trigonal planar.



(2.26)



(2.27)

The presence of lone pairs is taken into account using the guidelines above and the ‘parent structures’ in Fig. 2.16. In

$H_2O$  (2.27), repulsions between the two bonding pairs and two lone pairs of electrons lead to a tetrahedral arrangement, but owing to the inequalities between the lone pair–lone pair, lone pair–bonding pair and bonding pair–bonding pair interactions, distortion from an ideal arrangement arises and this is consistent with the observed  $H-O-H$  bond angle of  $104.5^\circ$ .

### Worked example 2.7 The VSEPR model

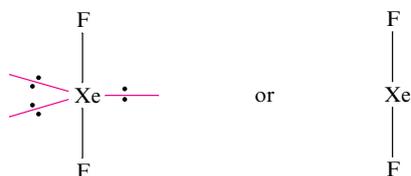
Predict the structures of (a)  $XeF_2$  and (b)  $[XeF_5]^-$ .

Xe is in group 18 and possesses eight electrons in its valence shell. F is in group 17, has seven valence electrons and forms

one covalent single bond. Before applying the VSEPR model, decide which is the central atom in the molecule. In each of  $\text{XeF}_2$  and  $[\text{XeF}_5]^-$ , Xe is the central atom.

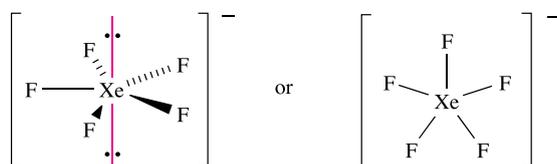
(a)  $\text{XeF}_2$ . Two of the eight valence electrons of the Xe atom are used for bonding (two Xe–F single bonds), and so around the Xe centre there are two bonding pairs of electrons and three lone pairs.

The parent shape is a trigonal bipyramid (Fig. 2.16) with the three lone pairs in the equatorial plane to minimize lone pair–lone pair repulsions. The  $\text{XeF}_2$  molecule is therefore linear:



(b)  $[\text{XeF}_5]^-$ . The electron from the negative charge is conveniently included within the valence shell of the central atom. Five of the nine valence electrons are used for bonding and around the Xe centre there are five bonding pairs and two lone pairs of electrons.

The parent shape is a pentagonal bipyramid (Fig. 2.16) with the two lone pairs opposite to each other to minimize lone pair–lone pair repulsions. The  $[\text{XeF}_5]^-$  anion is therefore pentagonal planar:



When structures are determined by diffraction methods, *atom* positions are effectively located. Thus, in terms of a molecular structure,  $\text{XeF}_2$  is linear and  $[\text{XeF}_5]^-$  is pentagonal planar. In the diagrams above, two representations of each species are shown, one with the lone pairs to emphasize the origin of the prediction from the VSEPR model.

### Self-study exercise

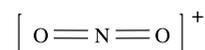
Show that the VSEPR model is in agreement with the following molecular shapes:

$\text{BF}_3$	trigonal planar
$[\text{IF}_5]^{2-}$	pentagonal planar
$[\text{NH}_4]^+$	tetrahedral
$\text{SF}_6$	octahedral
$\text{XeF}_4$	square planar
$\text{AsF}_5$	trigonal bipyramidal
$[\text{AlCl}_4]^-$	tetrahedral
$[\text{I}_3]^-$	linear
$[\text{I}_3]^+$	non-linear (bent)
$[\text{PF}_4]^+$	tetrahedral

### Worked example 2.8 VSEPR: molecules with double bonds

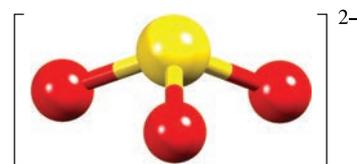
Is the VSEPR model consistent with a linear or bent structure for  $[\text{NO}_2]^+$ ?

N is in group 15 and has five valence electrons. Allow the positive charge to be localized on the nitrogen centre; an  $\text{N}^+$  centre has four valence electrons. O is in group 16 and has six valence electrons; an atom of O requires two electrons to complete its octet. All four electrons in the valence shell of the  $\text{N}^+$  centre are involved in bonding, forming two double bonds in  $[\text{NO}]^+$ . Since there are no lone pairs on the N atom, the VSEPR model is consistent with a linear structure:



### Self-study exercises

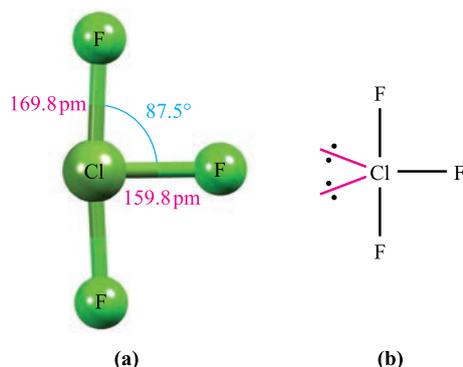
1. Show that the VSEPR model is consistent with a trigonal planar structure for  $\text{SO}_3$ .
2. Using the VSEPR model, rationalize why a  $\text{CO}_2$  molecule is linear whereas an  $[\text{NO}_2]^-$  ion is bent.
3. The sulfite ion,  $[\text{SO}_3]^{2-}$ , has the following structure:



Show that the VSEPR model is consistent with this structure.

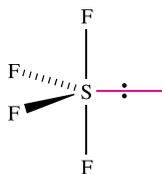
### Structures derived from a trigonal bipyramid

In this section, we consider the structures of species such as  $\text{ClF}_3$  and  $\text{SF}_4$  which have five electron pairs in the valence shell of the central atom. The experimentally determined structure of  $\text{ClF}_3$  is shown in Fig. 2.17, and the VSEPR model can be used to rationalize this T-shaped arrangement. The valence shell of the Cl atom contains three bonding pairs and two lone pairs of electrons. If both lone pairs occupy equatorial sites (see Table 2.3), then a T-shaped  $\text{ClF}_3$  molecule results. The choice of locations for the bonding and lone pairs arises from a consideration of the difference between the  $X_{\text{ax}}\text{--E--}X_{\text{eq}}$  and  $X_{\text{eq}}\text{--E--}X_{\text{eq}}$  bond angles (Table 2.3), coupled with the relative magnitudes of lone pair–lone pair, bonding pair–lone pair and bonding pair–bonding pair repulsions. It follows that the chlorine lone pairs in  $\text{ClF}_3$  preferentially occupy the equatorial sites where there is greatest space. The small departure of the F–Cl–F bond angle from the ideal value of  $90^\circ$  (Table 2.3) may be attributed to lone pair–bonding pair repulsion. Figure 2.17 also shows that there is a significant difference

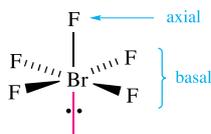


**Fig. 2.17.** (a) The experimentally determined structure of  $\text{ClF}_3$  and (b) the rationalization of this structure using the VSEPR model.

between the axial and equatorial Cl–F bond lengths, and this is a trend that is seen in a range of structures of molecules derived from a trigonal bipyramidal arrangement. In  $\text{PF}_5$ , the axial (ax) and equatorial (eq) bond distances are 158 and 153 pm respectively, in  $\text{SF}_4$  (2.28), they are 165 and 155 pm, and in  $\text{BrF}_3$ , they are 181 and 172 pm.<sup>†</sup> Bond distance variation is, however, not restricted to species derived from a trigonal bipyramid. For example, in  $\text{BrF}_5$  (2.29), the Br atom lies a little below the plane containing the basal F atoms ( $\angle \text{F}_{\text{ax}}\text{--Br--F}_{\text{bas}} = 84.5^\circ$ ) and the  $\text{Br--F}_{\text{ax}}$  and  $\text{Br--F}_{\text{bas}}$  bond distances are 168 and 178 pm respectively.



(2.28)



(2.29)

### Limitations of the VSEPR model

The generalizations of the VSEPR model are useful, but there are limitations to its use. In this section, we give examples that illustrate some problems.

The isoelectronic species  $\text{IF}_7$  and  $[\text{TeF}_7]^-$  are predicted by the VSEPR model to be pentagonal bipyramidal and this is observed. However, electron diffraction data for  $\text{IF}_7$  and X-ray diffraction data for  $[\text{Me}_4\text{N}][\text{TeF}_7]$  reveal that the equatorial F atoms are not coplanar, a result that cannot be predicted by the VSEPR model. Moreover, in  $\text{IF}_7$ , the  $\text{I--F}_{\text{ax}}$  and  $\text{I--F}_{\text{eq}}$  distances are 179 and 186 pm respectively, and in  $[\text{TeF}_7]^-$ , the  $\text{Te--F}_{\text{ax}}$  bond distance is 179 pm and the  $\text{Te--F}_{\text{eq}}$  distances lie in the range 183 to 190 pm.

Among species in which the VSEPR model appears to fail are  $[\text{SeCl}_6]^{2-}$ ,  $[\text{TeCl}_6]^{2-}$  and  $[\text{BrF}_6]^-$  (see also Section 16.7). When characterized as alkali metal salts, these anions are found to possess *regular octahedral* structures in the *solid state*, whereas the VSEPR model suggests shapes based on there being seven electron pairs around the central atom.

<sup>†</sup> For further discussion of this topic, see: R.J. Gillespie and P.L.A. Popelier (2001) *Chemical Bonding and Molecular Geometry*, OUP, Oxford, Chapter 4.

Although these structures cannot readily be predicted, we can rationalize them in terms of having a *stereochemically inactive* pair of electrons. Stereochemically inactive lone pairs are usually observed for the heaviest members of a periodic group, and the tendency for valence shell *s* electrons to adopt a non-bonding role in a molecule is called the *stereochemical inert pair effect*. Similarly,  $[\text{SbCl}_6]^-$  and  $[\text{SbCl}_6]^{3-}$  both possess regular octahedral structures. Finally, consider  $[\text{XeF}_8]^{2-}$ ,  $[\text{IF}_8]^-$  and  $[\text{TeF}_8]^{2-}$ . As expected from the VSEPR model,  $[\text{IF}_8]^-$  and  $[\text{TeF}_8]^{2-}$  are square antiprismatic (Fig. 2.16); this structure is related to the cube but with one face of the cube rotated through  $45^\circ$ . However,  $[\text{XeF}_8]^{2-}$  also adopts this structure, indicating that the lone pair of electrons is stereochemically inactive.

It is important to note that whereas the VSEPR model may be applicable to *p*-block species, it is *not* appropriate to apply it to *d*-electron configurations of transition metal compounds.

If the presence of a lone pair of electrons influences the shape of a molecule or ion, the lone pair is *stereochemically active*. If it has no effect, the lone pair is *stereochemically inactive*. The tendency for the pair of *valence s* electrons to adopt a non-bonding role in a molecule or ion is termed the *stereochemical inert pair effect*.

## 2.9 Molecular shape: stereoisomerism

An *isomer* is one of several species that have the same atomic composition (molecular formula), but have different constitutional formulae (atom connectivities) or different stereochemical formulae. Isomers exhibit different physical and/or chemical properties.

In this section we discuss *stereoisomerism*. Examples are taken from both *p*- and *d*-block chemistry. Other types of isomerism are described in Section 19.8.

If two species have the same molecular formula and the same atom connectivity, but differ in the spatial arrangement of different atoms or groups about a central atom or a double bond, then the compounds are *stereoisomers*.

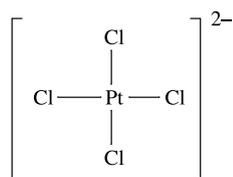
Stereoisomers fall into two categories, *diastereoisomers* and *enantiomers*.

*Diastereoisomers* are stereoisomers that *are not* mirror-images of one another. *Enantiomers* are stereoisomers that *are* mirror-images of one another.

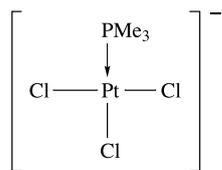
In this section, we shall only be concerned with diastereoisomers. We return to enantiomers in Sections 3.8 and 19.8.

### Square planar species

In a square planar species such as  $[\text{ICl}_4]^-$  or  $[\text{PtCl}_4]^{2-}$  (2.30), the four Cl atoms are equivalent. Similarly, in  $[\text{PtCl}_3(\text{PMe}_3)]^-$  (2.31), there is only one possible arrangement of the groups around the square planar Pt(II) centre. (The use of arrows or lines to depict bonds in coordination compounds is discussed in Section 7.11.)

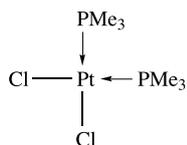


(2.30)

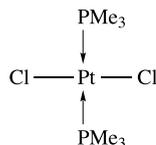


(2.31)

The introduction of two  $\text{PMe}_3$  groups to give  $[\text{PtCl}_2(\text{PMe}_3)_2]$  leads to the possibility of two *stereoisomers*, i.e. two possible spatial arrangements of the groups around the square planar Pt(II) centre. These are shown in structures 2.32 and 2.33 and the names *cis* and *trans* refer to the positioning of the Cl (or  $\text{PMe}_3$ ) groups, adjacent to or opposite one another.

*cis-isomer*

(2.32)

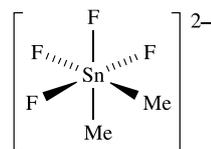
*trans-isomer*

(2.33)

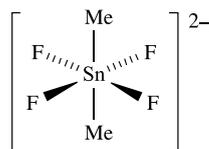
**Square planar** species of the general form  $\text{EX}_2\text{Y}_2$  or  $\text{EX}_2\text{YZ}$  may possess *cis*- and *trans*-isomers.

### Octahedral species

There are two types of stereoisomerism associated with octahedral species. In  $\text{EX}_2\text{Y}_4$ , the X groups may be mutually *cis* or *trans* as shown for  $[\text{SnF}_4\text{Me}_2]^{2-}$  (2.34 and 2.35). In the solid state structure of  $[\text{NH}_4]_2[\text{SnF}_4\text{Me}_2]$ , the anion is present as the *trans*-isomer.

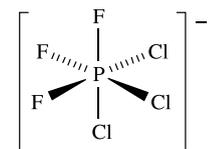
*cis-isomer*

(2.34)

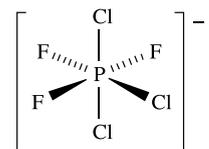
*trans-isomer*

(2.35)

If an octahedral species has the general formula  $\text{EX}_3\text{Y}_3$ , then the X groups (and also the Y groups) may be arranged so as to define one face of the octahedron or may lie in a plane that also contains the central atom E (Fig. 2.18). These stereoisomers are labelled *fac* (facial) and *mer* (meridional) respectively. In  $[\text{PCl}_4][\text{PCl}_3\text{F}_3]$ , the  $[\text{PCl}_3\text{F}_3]^-$  anion exists as both *fac*- and *mer*-isomers (2.36 and 2.37).

*fac-isomer*

(2.36)

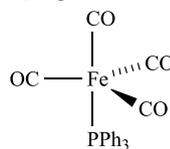
*mer-isomer*

(2.37)

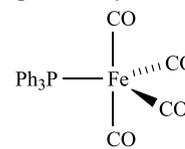
An *octahedral* species containing two identical groups (e.g. of type  $\text{EX}_2\text{Y}_4$ ) may possess *cis*- and *trans*-arrangements of these groups. An octahedral species containing three identical groups (e.g. of type  $\text{EX}_3\text{Y}_3$ ) may possess *fac*- and *mer*-isomers.

### Trigonal bipyramidal species

In trigonal bipyramidal  $\text{EX}_5$ , there are two types of X atom: axial and equatorial. This leads to the possibility of stereoisomerism when more than one type of substituent is attached to the central atom. Iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , is trigonal bipyramidal and when one CO is exchanged for  $\text{PPh}_3$ , two stereoisomers are possible depending on whether the  $\text{PPh}_3$  ligand is axially (2.38) or equatorially (2.39) sited.

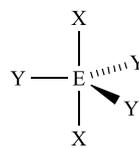


(2.38)

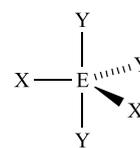


(2.39)

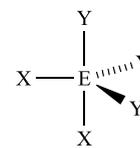
For trigonal bipyramidal  $\text{EX}_2\text{Y}_3$ , three stereoisomers (2.40 to 2.42) are possible depending on the relative positions of the X atoms. Steric factors may dictate which isomer is preferred for a given species; e.g. in the static structure of  $\text{PCl}_3\text{F}_2$ , the F atoms occupy the two axial sites, and the larger Cl atoms reside in the equatorial plane.



(2.40)



(2.41)

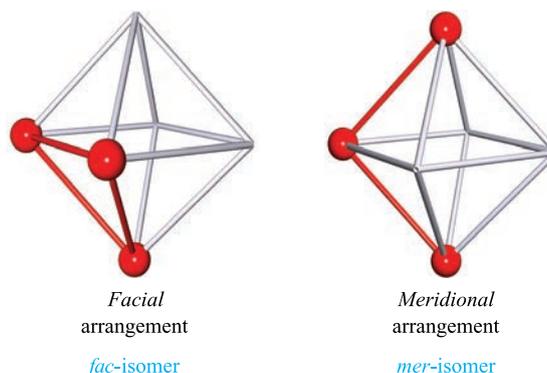


(2.42)

In a *trigonal bipyramidal* species, stereoisomerism arises because of the presence of *axial* and *equatorial* sites.

### High coordination numbers

The presence of axial and equatorial sites in a pentagonal bipyramidal molecule leads to stereoisomerism in a similar manner to that in a trigonal bipyramidal species. In a square

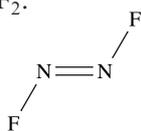


**Fig. 2.18.** The origin of the names *fac*- and *mer*-isomers. For clarity, the central atom is not shown.

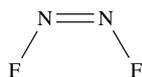
antiprismatic molecule  $EX_8$ , each X atom is identical (Fig. 2.16). Once two or more different atoms or groups are present, e.g.  $EX_6Y_2$ , stereoisomers are possible. As an exercise, draw out the four possibilities for square antiprismatic  $EX_6Y_2$ .

### Double bonds

In contrast to a single ( $\sigma$ ) bond where free rotation is generally assumed, rotation about a double bond is not a low energy process. The presence of a double bond may therefore lead to stereoisomerism as is observed for  $N_2F_2$ . Each N atom carries a lone pair as well as forming one N–F single bond and an N=N double bond. Structures 2.43 and 2.44 show the *trans*- and *cis*-isomers<sup>†</sup> respectively of  $N_2F_2$ .



(2.43)



(2.44)

<sup>†</sup> In organic chemistry, IUPAC nomenclature uses the prefix (*E*)- for a *trans*-arrangement of groups and (*Z*)- for a *cis*-arrangement, but for inorganic compounds, the terms *trans*- and *cis*- remain in use.

### Self-study exercises

1. Draw the structures of the two isomers of octahedral  $[Cr(OH_2)_4Cl_2]^+$  and give labels that distinguish the isomers.
2.  $[PtCl_2(PEt_3)_2]$  possesses two stereoisomers. Is the complex square planar or tetrahedral? Rationalize your answer.
3. Draw the structures of *mer*- and *fac*- $[RhCl_3(OH_2)_3]$ . What is the coordination geometry at the metal centre?
4. Tetrahydrofuran (THF) has the following structure and coordinates to metal ions through the oxygen atom. Draw the structures of the three possible isomers of trigonal bipyramidal  $[MnI_2(THF)_3]$ .



THF

### FURTHER READING

- P. Atkins and J. de Paula (2014) *Atkins' Physical Chemistry*, 10th edn, OUP, Oxford – This text gives a solid and well-tested background in physical chemistry.
- J. Barrett (2002) *Structure and Bonding*, RSC Publishing, Cambridge – An introductory text that includes valence bond, molecular orbital and VSEPR theories.
- R.J. Gillespie (2008) *Coord. Chem. Rev.*, vol. 252, p. 1315 – ‘Fifty years of the VSEPR model’.
- R.J. Gillespie and E.A. Robinson (2005) *Chem. Soc. Rev.*, vol. 34, p. 396 – A ‘tutorial review’ ‘Models of molecular geometry’ that considers the VSEPR model and the more recently developed ligand close-packing (LCP) model.
- D.O. Hayward (2002) *Quantum Mechanics for Chemists*, RSC Publishing, Cambridge – An undergraduate student text that covers the basic principles of quantum mechanics.
- C.E. Housecroft and E.C. Constable (2010) *Chemistry*, 4th edn, Prentice Hall, Harlow – This text provides clear discussion of the fundamental principles of bonding in molecules at an introductory level.
- R. McWeeny (1979) *Coulson's Valence*, 3rd edn, OUP, Oxford – A classic book containing a general treatment of chemical bonding with a detailed mathematical approach.
- D.W. Smith (2004) *J. Chem. Educ.*, vol. 81, p. 886 – A useful article entitled ‘Effects of exchange energy and spin-orbit coupling on bond energies’.
- M.J. Winter (1994) *Chemical Bonding*, OUP, Oxford – This ‘primer’ for first year undergraduates approaches chemical bonding non-mathematically.

### PROBLEMS

- 2.1 Draw Lewis structures to describe the bonding in the following molecules: (a)  $F_2$ ; (b)  $BF_3$ ; (c)  $NH_3$ ; (d)  $H_2Se$ ; (e)  $H_2O_2$ ; (f)  $BeCl_2$ ; (g)  $SiH_4$ ; (h)  $PF_5$ .
- 2.2 Use the Lewis structure model to deduce the type of nitrogen–nitrogen bond present in (a)  $N_2H_4$ , (b)  $N_2F_4$ , (c)  $N_2F_2$  and (d)  $[N_2H_5]^+$ .
- 2.3 Draw the resonance structures for the  $O_3$  molecule. What can you conclude about the net bonding picture?
- 2.4 Draw Lewis structures for (a)  $CO_2$ , (b)  $SO_2$ , (c)  $OF_2$  and (d)  $H_2CO$ .
- 2.5 Each of the following is a radical. For which does a Lewis structure correctly confirm this property: (a)  $NO$ , (b)  $O_2$ , (c)  $NF_2$ ?
- 2.6 (a) Use VB theory to describe the bonding in the diatomic molecules  $Li_2$ ,  $B_2$  and  $C_2$ . (b) Experimental data show that  $Li_2$  and  $C_2$  are

- diamagnetic whereas  $B_2$  is paramagnetic. Is the VB model consistent with these facts?
- 2.7 Using VB theory and the Lewis structure model, determine the bond order in (a)  $H_2$ , (b)  $Na_2$ , (c)  $S_2$ , (d)  $N_2$  and (e)  $Cl_2$ . Is there any ambiguity with finding the bond orders by this method?
- 2.8 Does VB theory indicate that the diatomic molecule  $He_2$  is a viable species? Rationalize your answer.
- 2.9 (a) Use MO theory to determine the bond order in each of  $[He_2]^+$  and  $[He_2]^{2+}$ . (b) Does the MO picture of the bonding in these ions suggest that they are viable species?
- 2.10 (a) Construct an MO diagram for the formation of  $O_2$ ; use only the valence orbitals of the oxygen atoms. (b) Use the diagram to rationalize the following trend in O–O bond distances:  $O_2$ , 121 pm;  $[O_2]^+$ , 112 pm;  $[O_2]^-$ , 134 pm;  $[O_2]^{2-}$ , 149 pm. (c) Which of these species are paramagnetic?
- 2.11 Confirm that the octet rule is obeyed by *each* of the atoms in the following molecules: (a)  $CF_4$ , (b)  $O_2$ , (c)  $AsBr_3$ , (d)  $SF_2$ .
- 2.12 Draw charge-separated resonance structures to give a representation of the bonding in  $PF_5$  such that the octet rule is strictly obeyed.
- 2.13 One member of each of the following sets of compounds is not isoelectronic with the others. Which one in each set is the odd one out?
- (a)  $[NO_2]^+$ ,  $CO_2$ ,  $[NO_2]^-$  and  $[N_3]^-$   
 (b)  $[CN]^-$ ,  $N_2$ ,  $CO$ ,  $[NO]^+$  and  $[O_2]^{2-}$   
 (c)  $[SiF_6]^{2-}$ ,  $[PF_6]^-$ ,  $[AlF_6]^{3-}$  and  $[BrF_6]^-$
- 2.14 In the following table, match a species in list 1 with an isoelectronic partner in list 2. Some species may have more than one partner. Qualify how you have interpreted the term *isoelectronic*.

List 1	List 2
$F_2$	$[H_3O]^+$
$NH_3$	$[GaCl_4]^-$
$[GaBr_4]^-$	$Cl_2$
$[SH]^-$	$[NH_4]^+$
$[BH_4]^-$	$[OH]^-$
$[AsF_6]^-$	$[O_2]^{2-}$
$[PBr_4]^+$	$SeF_6$
$HF$	$SiBr_4$

- 2.15 Using the data in Table 2.2, determine which of the following covalent single bonds is polar and (if appropriate) in which direction the dipole moment acts. (a) N–H; (b) F–Br; (c) C–H; (d) P–Cl; (e) N–Br.
- 2.16 Pick out *pairs* of isoelectronic species from the following list; not all species have a ‘partner’:  $HF$ ;  $CO_2$ ;  $SO_2$ ;  $NH_3$ ;  $PF_3$ ;  $SF_4$ ;  $SiF_4$ ;  $SiCl_4$ ;  $[H_3O]^+$ ;  $[NO_2]^+$ ;  $[OH]^-$ ;  $[AlCl_4]^-$ .
- 2.17 Use the VSEPR model to predict the structures of (a)  $H_2Se$ , (b)  $[BH_4]^-$ , (c)  $NF_3$ , (d)  $SbF_5$ , (e)  $[H_3O]^+$ , (f)  $IF_7$ , (g)  $[I_3]^-$ , (h)  $[I_3]^+$ , (i)  $SO_3$ .
- 2.18 Use the VSEPR model to rationalize the structure of  $SOF_4$  shown in Fig. 2.19. What are the bond orders of (a) each S–F bond and (b) the S–O bond?
- 2.19 Determine the shapes of each of the following molecules and then, using the data in Table 2.2, state whether each is expected to be polar or not: (a)  $H_2S$ ; (b)  $CO_2$ ; (c)  $SO_2$ ; (d)  $BF_3$ ; (e)  $PF_5$ ; (f) *cis*- $N_2F_2$ ; (g) *trans*- $N_2F_2$ ; (h)  $HCN$ .
- 2.20 State whether you expect the following species to possess stereoisomers and, if so, draw their structures and give them distinguishing labels: (a)  $BF_2Cl$ ; (b)  $POCl_3$ ; (c)  $MePF_4$ ; (d)  $[PF_2Cl_4]^-$ .

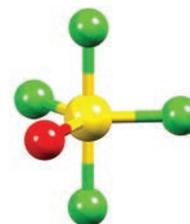


Fig. 2.19. The structure of  $SOF_4$ .

## OVERVIEW PROBLEMS

- 2.21 (a) Draw resonance structures for  $CO$ , choosing only those that you think contribute significantly to the bonding.
- (b) Figure 2.15a shows an MO diagram for  $CO$ . Two MOs are illustrated by schematic representations. Draw similar diagrams for the remaining six MOs.

- 2.22 (a) On steric grounds, should *cis*- or *trans*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] be favoured?  
 (b) Use the VSEPR model to rationalize why SNF<sub>3</sub> is tetrahedral but SF<sub>4</sub> has a see-saw geometry.  
 (c) Suggest why KrF<sub>2</sub> is a linear rather than bent molecule.
- 2.23 Account for each of the following observations.  
 (a) IF<sub>5</sub> is a polar molecule.  
 (b) The first ionization energy of K is lower than that of Li.  
 (c) BI<sub>3</sub> is trigonal planar while PI<sub>3</sub> is trigonal pyramidal in shape.
- 2.24 Suggest reasons for the following observations.  
 (a) The second ionization energy of He is higher than the first despite the fact that both electrons are removed from the 1s atomic orbital.  
 (b) Heating N<sub>2</sub>F<sub>2</sub> at 373 K results in a change from a non-polar to polar molecule.  
 (c) S<sub>2</sub> is paramagnetic.
- 2.25 Account for each of the following observations.  
 (a) The mass spectrum of molecular bromine shows three lines for the parent ion [Br<sub>2</sub>]<sup>+</sup>.  
 (b) In the structure of solid bromine, each Br atom has one nearest neighbour at a distance of 227 pm, and several other next nearest neighbours at 331 pm.  
 (c) In the salt formed from the reaction of Br<sub>2</sub> and SbF<sub>5</sub>, the Br–Br distance in the [Br<sub>2</sub>]<sup>+</sup> ion (215 pm) is shorter than in Br<sub>2</sub>.
- 2.26 (a) Draw possible stereoisomers for the trigonal bipyramidal [SiF<sub>3</sub>Me<sub>2</sub>]<sup>−</sup> anion (Me = CH<sub>3</sub>). An X-ray diffraction study of a salt of [SiF<sub>3</sub>Me<sub>2</sub>]<sup>−</sup> shows that two F atoms occupy axial sites. Suggest why this stereoisomer is preferred over the other possible structures that you have drawn.  
 (b) Account for the fact that members of the series of complexes [PtCl<sub>4</sub>]<sup>2−</sup>, [PtCl<sub>3</sub>(PMe<sub>3</sub>)]<sup>−</sup>, [PtCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] and [PtCl(PMe<sub>3</sub>)<sub>3</sub>]<sup>+</sup> do not possess the same number of stereoisomers.
- 2.27 (a) Write down the ions that are present in the compound [PCl<sub>4</sub>][PCl<sub>3</sub>F<sub>3</sub>]. What shape do you expect each ion to adopt? In theory, does either ion possess stereoisomers?  
 (b) Use the VSEPR model to rationalize why BCl<sub>3</sub> and NCl<sub>3</sub> do not adopt similar structures. Is either molecule expected to be polar? Rationalize your answer.
- 2.28 Assuming that the VSEPR model can be applied successfully to each of the following species, determine how many different fluorine environments are present in each molecule or ion: (a) [SiF<sub>6</sub>]<sup>2−</sup>, (b) XeF<sub>4</sub>, (c) [NF<sub>4</sub>]<sup>+</sup>, (d) [PHF<sub>5</sub>]<sup>−</sup>, (e) [SbF<sub>5</sub>]<sup>2−</sup>.
- 2.29 Critically compare the VB and MO treatments of the bonding in O<sub>2</sub>, paying particular attention to the properties of O<sub>2</sub> that the resulting bonding models imply.

## INORGANIC CHEMISTRY MATTERS

- 2.30 The table below gives the average composition of the Earth's atmosphere (ppm = parts per million). Water vapour is also present in small and variable amounts.

Gas	Average amount/ppm	Gas	Average amount/ppm
He	5.2	CH <sub>4</sub>	1.72
Ne	18	CO	0.12
Ar	9340	CO <sub>2</sub>	355
Kr	1.1	N <sub>2</sub> O	0.31
Xe	0.09	NO	<0.01
H <sub>2</sub>	0.58	O <sub>3</sub>	0.1–0.01
N <sub>2</sub>	780840	SO <sub>2</sub>	<10 <sup>−4</sup>
O <sub>2</sub>	209460	NH <sub>3</sub>	<10 <sup>−3</sup>

- (a) Draw a Lewis structure for N<sub>2</sub>O, ensuring that each atom obeys the octet rule. (b) Use the VSEPR model to predict the molecular shapes of SO<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub>. (c) Which of the gases in the table are radicals? For each of the gases you have chosen,

explain how the radical nature arises. (d) O<sub>3</sub> (ozone) is only present in <0.1 ppm. Nonetheless, it is a vital component of the Earth's atmosphere. Why? (e) Draw an MO diagram for the formation of N<sub>2</sub> from two N atoms, using only the valence orbitals. Use the diagram to rationalize why N<sub>2</sub> is chemically very inert. (f) What is the relationship between the monoatomic gases in the Earth's atmosphere?

- 2.31 Carbon monoxide is a toxic pollutant which arises from the partial combustion of carbon-based fuels. Complete combustion produces CO<sub>2</sub>. The toxicity of CO is a result of its competition for the O<sub>2</sub>-binding sites in blood, i.e. the iron present in haemoglobin (see Chapter 29). When CO binds to the iron, it prevents O<sub>2</sub> from being carried in the bloodstream. The following are resonance structures for CO:



- (a) Comment on these structures in terms of the octet rule. (b) How is the right-hand resonance structure related to a Lewis structure for  $\text{N}_2$ ? (c) A primary interaction between CO and iron in haemoglobin involves a lone pair of electrons on the carbon atom. Using MO theory, explain how this lone pair arises. (d) Without treatment, severe CO poisoning is fatal. Explain why a hyperbaric chamber containing pure  $\text{O}_2$  at a pressure of 1.4 bar is used to treat a patient with severe CO poisoning. Normal air contains 21%  $\text{O}_2$ .
- 2.32 Volcanoes and deep sea hydrothermal vents are both associated with sulfur-rich environments. Mount Etna is classed as a continuously degassing volcano and emissions of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  are around  $1.5 \text{ Tg y}^{-1}$  and  $100 \text{ Gg y}^{-1}$ , respectively ( $\text{Tg} = 10^{12} \text{ g}$ ;  $\text{Gg} = 10^9 \text{ g}$ ). (a) Draw Lewis structures for  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , ensuring that the octet rule is obeyed by the S and O atoms. Your answer must be consistent with the fact that in  $\text{SO}_2$ , the two sulfur–oxygen bonds are the same length. (b) Are  $\text{H}_2\text{S}$  and  $\text{SO}_2$  polar or non-polar molecules? If polar, draw a diagram to show the direction of the molecular dipole moment. (c) In the troposphere,  $\text{SO}_2$  reacts with  $\text{HO}^\bullet$  radicals. Construct an MO diagram for  $\text{HO}^\bullet$  from H and O atoms, and deduce what you can about the bonding in  $\text{HO}^\bullet$ .

## Topics

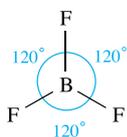
Symmetry operators  
Symmetry elements  
Point groups  
Character tables  
Vibrational modes in molecules  
Chiral molecules

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$

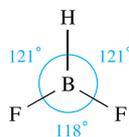
# Introduction to molecular symmetry

## 3.1 Introduction

In chemistry, symmetry is important both at a molecular level and within crystalline systems. An understanding of symmetry is essential in discussions of molecular spectroscopy and calculations of molecular properties. A discussion of *crystal symmetry* is not included in this book, and we introduce only *molecular symmetry*. For qualitative purposes, it is sufficient to refer to the shape of a molecule using terms such as tetrahedral, octahedral or square planar. However, the common use of these descriptors is not always precise, e.g. consider the structures of  $\text{BF}_3$ , **3.1**, and  $\text{BF}_2\text{H}$ , **3.2**, both of which are planar. A molecule of  $\text{BF}_3$  is correctly described as being trigonal planar, since its symmetry properties are fully consistent with this description; all the F–B–F bond angles are  $120^\circ$  and the B–F bond distances are all identical (131 pm). It is correct to say that the boron centre in  $\text{BF}_2\text{H}$ , **3.2**, is in a *pseudo-trigonal planar* environment but the molecular symmetry properties are not the same as those of  $\text{BF}_3$ . The F–B–F bond angle in  $\text{BF}_2\text{H}$  is smaller than the two H–B–F angles, and the B–H bond is shorter (119 pm) than the B–F bonds (131 pm).



(3.1)



(3.2)

The descriptor *symmetrical* implies that a species possesses a number of indistinguishable configurations. When structure **3.1** is rotated in the plane of the paper

through  $120^\circ$ , the resulting structure is indistinguishable from the first; another  $120^\circ$  rotation results in a third indistinguishable molecular orientation (Fig. 3.1). This is *not* true if we carry out the same rotational operations on  $\text{BF}_2\text{H}$ .

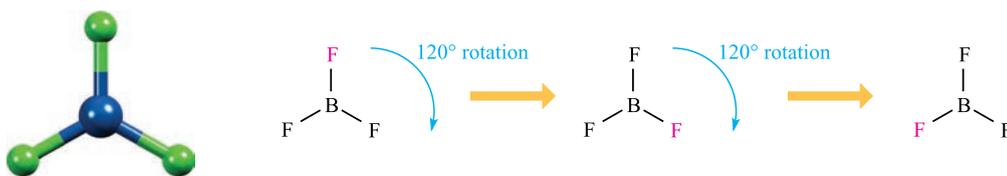
*Group theory* is the mathematical treatment of symmetry. In this chapter, we introduce the fundamental language of group theory (*symmetry operator*, *symmetry element*, *point group* and *character table*). The chapter does not set out to give a comprehensive survey of molecular symmetry, but rather to introduce some common terminology and its meaning. We include an introduction to the vibrational spectra of simple inorganic molecules and show how to use this technique to distinguish between possible structures for  $\text{XY}_2$ ,  $\text{XY}_3$  and  $\text{XY}_4$  molecules. Complete normal coordinate analysis of such species is beyond the remit of this book.

## 3.2 Symmetry operations and symmetry elements

In Fig. 3.1, we applied  $120^\circ$  rotations to  $\text{BF}_3$  and saw that each rotation generated a representation of the molecule that was indistinguishable from the first. Each rotation is an example of a *symmetry operation*.

A *symmetry operation* is an operation performed on an object which leaves it in a configuration that is indistinguishable from, and superimposable on, the original configuration.

The rotations described in Fig. 3.1 are performed about an axis perpendicular to the plane of the paper and passing through the boron atom; the axis is an example of a *symmetry element*.



**Fig. 3.1.** Rotation of the trigonal planar  $\text{BF}_3$  molecule through  $120^\circ$  generates a representation of the structure that is indistinguishable from the first; one F atom is marked in red simply as a label. A second  $120^\circ$  rotation gives another indistinguishable structural representation.

A symmetry operation is carried out with respect to points, lines or planes, the latter being the *symmetry elements*.

### Rotation about an $n$ -fold axis of symmetry

The symmetry operation of rotation about an  $n$ -fold axis (the symmetry element) is denoted by the symbol  $C_n$ , in which the angle of rotation is  $\frac{360^\circ}{n}$ ;  $n$  is an integer, e.g. 2, 3 or 4. Applying this notation to the  $\text{BF}_3$  molecule in Fig. 3.1 gives a value of  $n = 3$  (eq. 3.1), and therefore we say that the  $\text{BF}_3$  molecule contains a  $C_3$  rotation axis. In this case, the axis lies perpendicular to the plane containing the molecule.

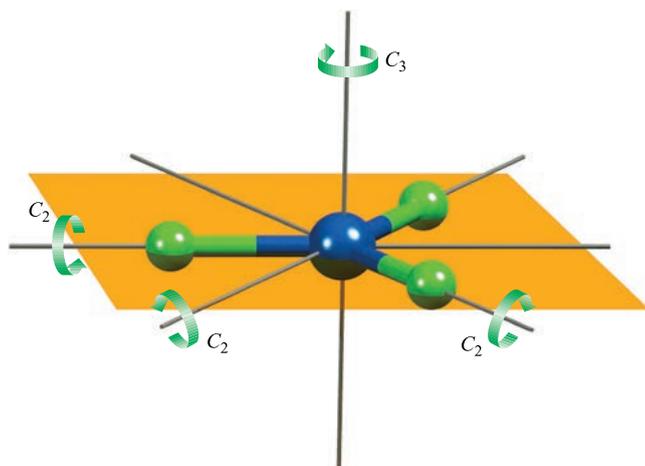
$$\text{Angle of rotation} = 120^\circ = \frac{360^\circ}{n} \quad (3.1)$$

In addition,  $\text{BF}_3$  also contains three 2-fold ( $C_2$ ) rotation axes, each coincident with a B–F bond as shown in Fig. 3.2.

If a molecule possesses more than one type of  $n$ -axis, the axis of highest value of  $n$  is called the *principal axis*; it is the axis of *highest molecular symmetry*. For example, in  $\text{BF}_3$ , the  $C_3$  axis is the principal axis.

In some molecules, rotation axes of lower orders than the principal axis may be coincident with the principal axis. For example, in square planar  $\text{XeF}_4$ , the principal axis is a  $C_4$  axis but this also coincides with a  $C_2$  axis (see Fig. 3.4).

Where a molecule contains more than one type of  $C_n$  axis with the same value of  $n$ , they are distinguished by using



**Fig. 3.2.** The 3-fold ( $C_3$ ) and three 2-fold ( $C_2$ ) axes of symmetry possessed by the trigonal planar  $\text{BF}_3$  molecule.

prime marks, e.g.  $C_2$ ,  $C_2'$  and  $C_2''$ . We return to this in the discussion of  $\text{XeF}_4$  (see Fig. 3.4).

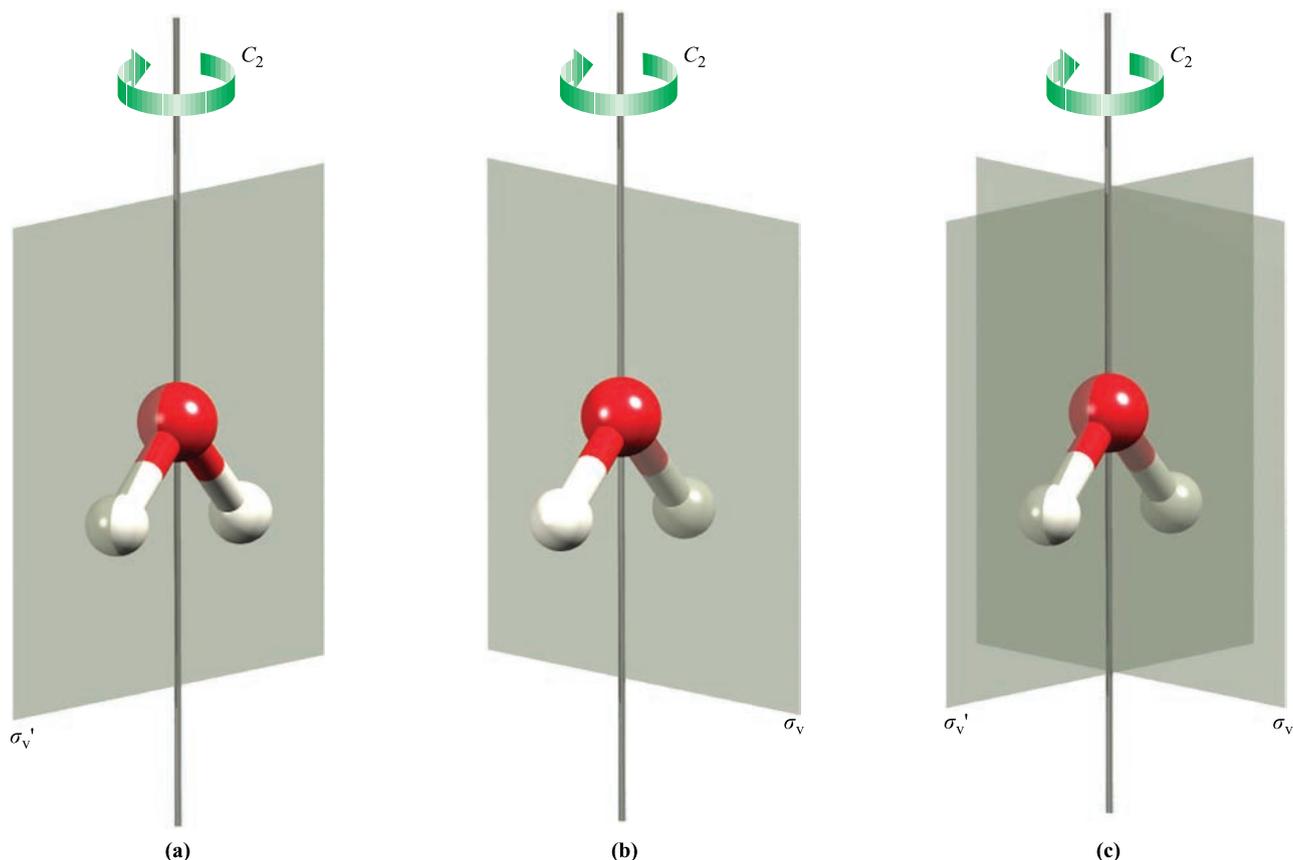
### Self-study exercises

- Each of the following contains a 6-membered ring: benzene, borazine (see Fig. 13.24), pyridine and  $\text{S}_6$  (see Box 1.1). Explain why only benzene contains a 6-fold principal rotation axis.
- Among the following, why does only  $\text{XeF}_4$  contain a 4-fold principal rotation axis:  $\text{CF}_4$ ,  $\text{SF}_4$ ,  $[\text{BF}_4]^-$  and  $\text{XeF}_4$ ?
- Draw the structure of  $[\text{XeF}_5]^-$ . On the diagram, mark the  $C_5$  axis. The ion contains five  $C_2$  axes. Where are these axes? [Ans. For structure, see worked example 2.7]
- Look at the structure of  $\text{B}_5\text{H}_9$  in Fig. 13.30. Where is the  $C_4$  axis in this molecule?
- $\text{ClF}_3$  contains a  $C_2$  axis, but does not contain a  $C_3$  axis. Use this information to suggest a structure for  $\text{ClF}_3$ . Confirm that your answer is consistent with the VSEPR model.
- Propose structures for the following molecules given that only  $\text{BCl}_3$  has  $C_2$  axes:  $\text{BCl}_3$ ,  $\text{NH}_3$ ,  $\text{CHCl}_3$ ,  $\text{PCl}_3$ . Confirm that your answers are consistent with the VSEPR model.

### Reflection through a plane of symmetry (mirror plane)

If reflection of all parts of a molecule through a plane produces an indistinguishable configuration, the plane is a *plane of symmetry*; the symmetry operation is one of reflection and the symmetry element is the mirror plane (denoted by  $\sigma$ ). For  $\text{BF}_3$ , the plane containing the molecular framework (the brown plane shown in Fig. 3.2) is a *mirror plane*. In this case, the plane lies perpendicular to the vertical principal axis and is denoted by the symbol  $\sigma_h$ .

The framework of atoms in a linear, bent or planar molecule can always be drawn in a plane, but this plane can be labelled  $\sigma_h$  *only* if the molecule possesses a  $C_n$  axis *perpendicular* to the plane. If the plane *contains* the



**Fig. 3.3.** The  $\text{H}_2\text{O}$  molecule possesses one  $C_2$  axis and two mirror planes. (a) The  $C_2$  axis and the plane of symmetry that contains the  $\text{H}_2\text{O}$  molecule. (b) The  $C_2$  axis and the plane of symmetry that is perpendicular to the plane of the  $\text{H}_2\text{O}$  molecule. (c) Planes of symmetry in a molecule are often shown together on one diagram; this representation for  $\text{H}_2\text{O}$  combines diagrams (a) and (b).

principal axis, it is labelled  $\sigma_v$ . Consider the  $\text{H}_2\text{O}$  molecule. This possesses a  $C_2$  axis (Fig. 3.3) but it also contains *two* mirror planes, one containing the  $\text{H}_2\text{O}$  framework, and one perpendicular to it. Each plane contains the principal axis of rotation and so may be denoted as  $\sigma_v$ , but in order to distinguish between them, we use the notations  $\sigma_v$  and  $\sigma_v'$ . The  $\sigma_v$  label refers to the plane that bisects the H–O–H bond angle and the  $\sigma_v'$  label refers to the plane in which the molecule lies.

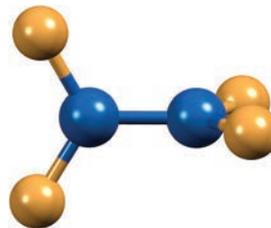
A special type of  $\sigma$  plane which contains the principal rotation axis, but which bisects the angle between two adjacent 2-fold axes, is labelled  $\sigma_d$ . A square planar molecule such as  $\text{XeF}_4$  provides an example. Figure 3.4a shows that  $\text{XeF}_4$  contains a  $C_4$  axis (the principal axis) and perpendicular to this is the  $\sigma_h$  plane in which the molecule lies. Coincident with the  $C_4$  axis is a  $C_2$  axis. Within the plane of the molecule, there are two sets of  $C_2$  axes. One type (the  $C_2'$  axis) coincides with F–Xe–F bonds, while the second type (the  $C_2''$  axis) bisects the F–Xe–F  $90^\circ$  angle (Fig. 3.4). We can now define two sets of mirror planes: one type ( $\sigma_v$ ) contains the principal axis and a  $C_2'$  axis (Fig. 3.4b), while the second type ( $\sigma_d$ ) contains the principal axis and a  $C_2''$

axis (Fig. 3.4c). Each  $\sigma_d$  plane bisects the angle between two  $C_2'$  axes.

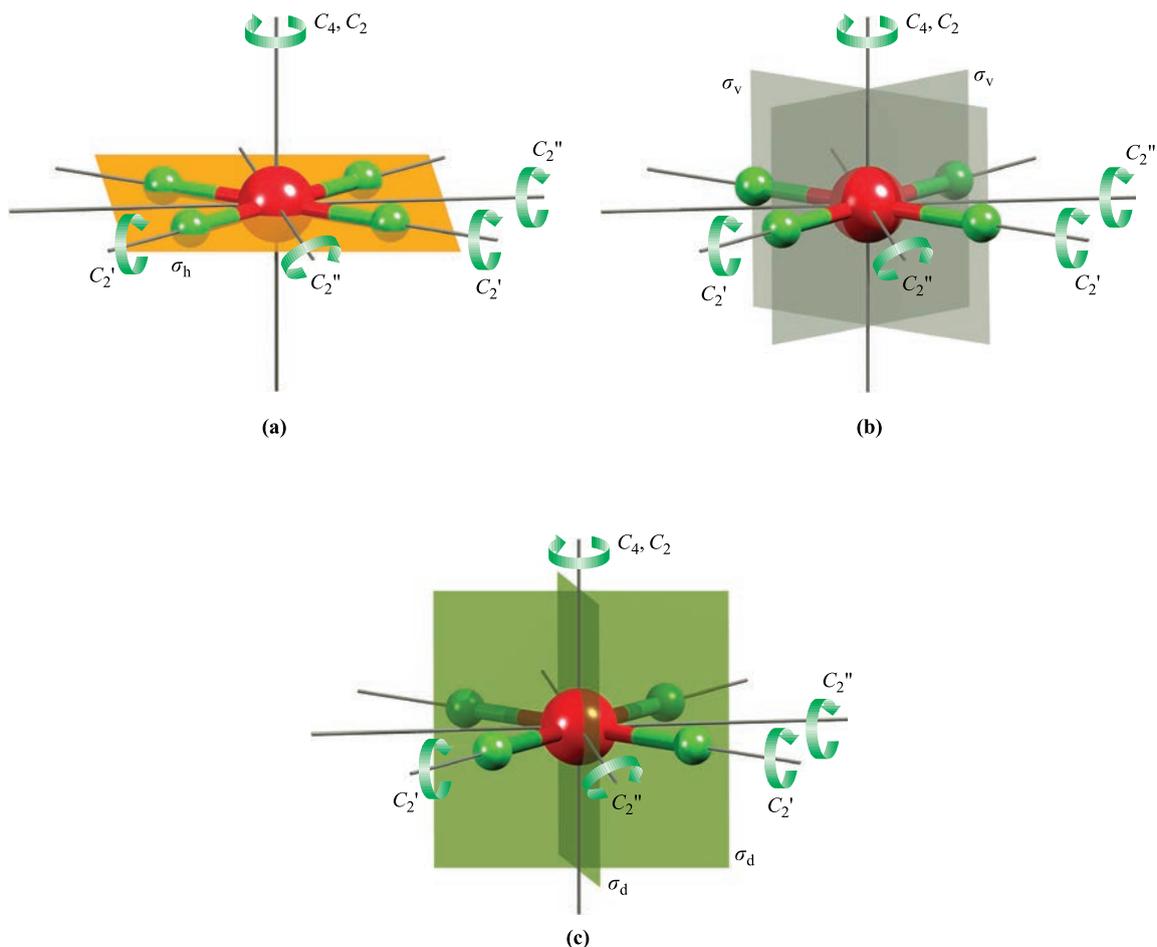
In the notation for planes of symmetry,  $\sigma$ , the subscripts h, v and d stand for horizontal, vertical and dihedral respectively.

### Self-study exercises

1.  $\text{N}_2\text{O}_4$  is planar (Fig. 15.17). Show that it possesses three planes of symmetry.
2.  $\text{B}_2\text{Br}_4$  has the following staggered structure:

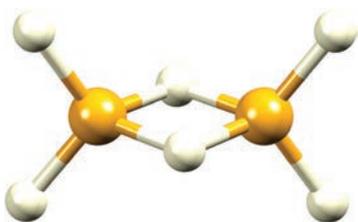


Show that  $\text{B}_2\text{Br}_4$  has one less plane of symmetry than  $\text{B}_2\text{F}_4$  which is planar.



**Fig. 3.4.** The square planar molecule XeF<sub>4</sub>. (a) One C<sub>2</sub> axis coincides with the principal (C<sub>4</sub>) axis; the molecule lies in a σ<sub>h</sub> plane which contains two C<sub>2</sub>' and two C<sub>2</sub>'' axes. (b) Each of the two σ<sub>v</sub> planes contains the C<sub>4</sub> axis and one C<sub>2</sub>' axis. (c) Each of the two σ<sub>d</sub> planes contains the C<sub>4</sub> axis and one C<sub>2</sub>'' axis.

3. Ga<sub>2</sub>H<sub>6</sub> has the following structure in the gas phase:



Show that it possesses three planes of symmetry.

4. Show that the planes of symmetry in benzene are one σ<sub>h</sub>, three σ<sub>v</sub> and three σ<sub>d</sub>.

5. Explain why BF<sub>3</sub> does *not* contain σ<sub>d</sub> planes.

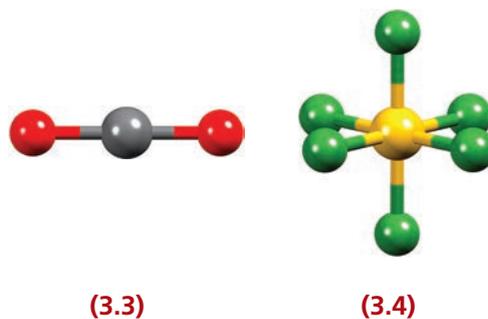
*inversion* (see also Box 2.1) and is designated by the symbol *i*. Each of the molecules CO<sub>2</sub> (3.3), *trans*-N<sub>2</sub>F<sub>2</sub> (see worked example 3.1), SF<sub>6</sub> (3.4) and benzene (3.5) possesses a centre of symmetry, but H<sub>2</sub>S (3.6), *cis*-N<sub>2</sub>F<sub>2</sub> (3.7) and SiH<sub>4</sub> (3.8) do not.

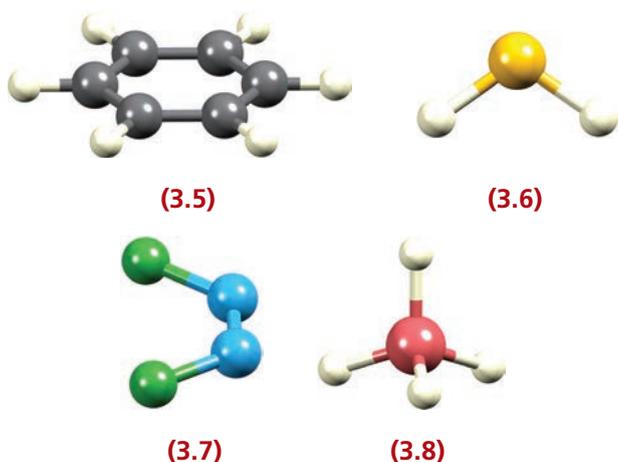
A *centrosymmetric* molecule or ion contains a centre of symmetry.

A *non-centrosymmetric* molecule or ion does not contain a centre of symmetry.

### Reflection through a centre of symmetry (inversion centre)

If reflection of *all* parts of a molecule through the centre of the molecule produces an indistinguishable configuration, the centre is a *centre of symmetry*. It is also called a *centre of*





### Rotation about an axis, followed by reflection through a plane perpendicular to this axis

If rotation through  $\frac{360^\circ}{n}$  about an axis, followed by reflection through a plane perpendicular to that axis, yields an indistinguishable configuration, the axis is an  $n$ -fold rotation–reflection axis, also called an  $n$ -fold improper rotation axis. It is denoted by the symbol  $S_n$ . Tetrahedral species of the type  $XY_4$  (all Y groups must be equivalent) possess three  $S_4$  axes, and the operation of one  $S_4$  rotation–reflection in the  $CH_4$  molecule is illustrated in Fig. 3.5.

#### Self-study exercises

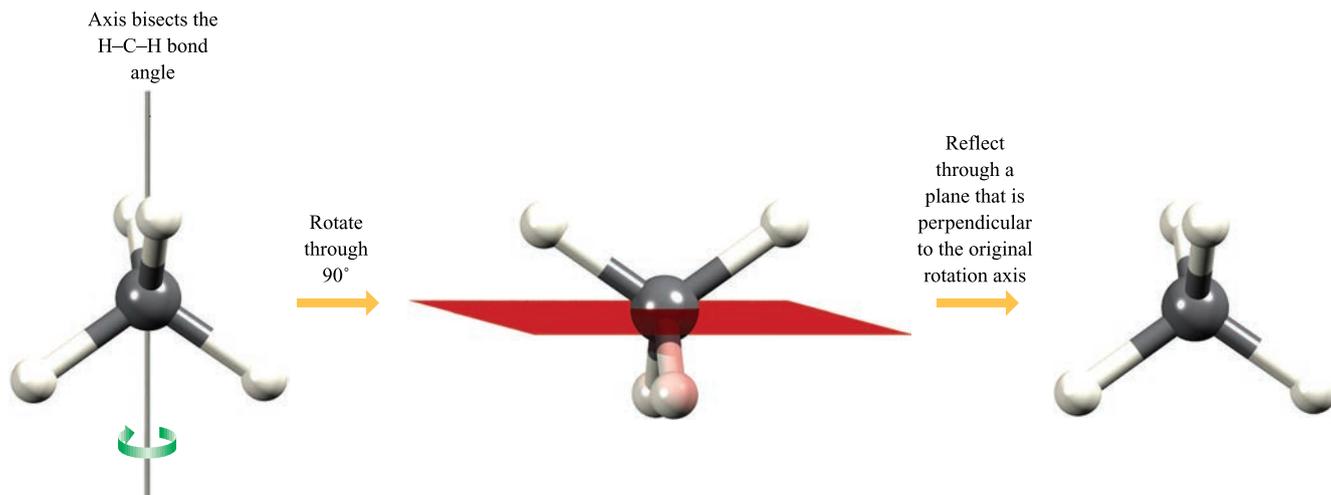
1. Draw the structures of each of the following species and confirm that each possesses a centre of symmetry:  $CS_2$ ,  $[PF_6]^-$ ,  $XeF_4$ ,  $I_2$ ,  $[ICl_2]^-$ .
2.  $[PtCl_4]^{2-}$  has a centre of symmetry, but  $[CoCl_4]^{2-}$  does not. One is square planar and the other is tetrahedral. Which is which?
3. Why does  $CO_2$  possess an inversion centre, but  $NO_2$  does not?
4.  $CS_2$  and  $HCN$  are both linear. Explain why  $CS_2$  possesses a centre of symmetry whereas  $HCN$  does not.
5. Which of the following are centrosymmetric: (a)  $BF_3$ ; (b)  $CH_2Cl_2$ ; (c)  $CCl_4$ ; (d)  $[SiF_6]^{2-}$ ; (e)  $[NO_2]^+$ ; (f)  $SO_2$ ?  
[Ans. (d), (e)]
6. Which of the following are non-centrosymmetric: (a)  $[AlCl_4]^-$ ; (b)  $CSe_2$ ; (c)  $[I_3]^-$ ; (d)  $[I_3]^+$ ; (e)  $PF_5$ ; (f)  $XeF_2$ ?  
[Ans. (a), (d), (e)]

#### Self-study exercises

1. Explain why  $BF_3$  possesses an  $S_3$  axis, but  $NF_3$  does not.
2.  $C_2H_6$  in a staggered conformation possesses an  $S_6$  axis. Show that this axis lies along the C–C bond.
3. Figure 3.5 shows one of the  $S_4$  axes in  $CH_4$ . On going from  $CH_4$  to  $CH_2Cl_2$ , are the  $S_4$  axes retained?
4. Which of the following contain  $S_n$  axes: (a)  $CHCl_3$ ; (b)  $BCl_3$ ; (c)  $SF_6$ ; (d)  $HCN$ ; (e)  $[PF_4]^+$ ; (f)  $CO_2$ ?  
[Ans. (b), (c), (e), (f)]

#### Identity operator

All objects can be operated upon by the identity operator  $E$ . This is the simplest operator (although it may not be easy to appreciate why we identify such an operator!) and effectively identifies the molecular configuration. The operator  $E$  leaves the molecule unchanged.

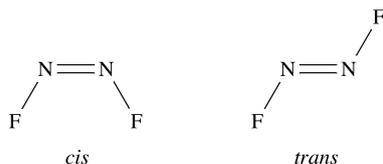


**Fig. 3.5.** An improper rotation (or rotation–reflection),  $S_n$ , involves rotation about  $\frac{360^\circ}{n}$  followed by reflection through a plane that is perpendicular to the rotation axis. The diagram illustrates the operation about one of the  $S_4$  axes in  $CH_4$ ; three  $S_4$  operations are possible for the  $CH_4$  molecule. [Exercise: where are the three rotation axes for the three  $S_4$  operations in  $CH_4$ ?]

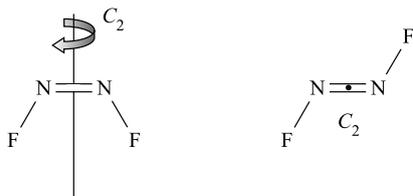
### Worked example 3.1 Symmetry properties of *cis*- and *trans*-N<sub>2</sub>F<sub>2</sub>

How do the rotation axes and planes of symmetry in *cis*- and *trans*-N<sub>2</sub>F<sub>2</sub> differ?

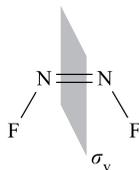
First draw the structures of *cis*- and *trans*-N<sub>2</sub>F<sub>2</sub>; both are planar molecules.



1. The identity operator  $E$  applies to each isomer.
2. Each isomer possesses a plane of symmetry which contains the molecular framework. However, their labels differ (see point 5 below).
3. The *cis*-isomer contains a  $C_2$  axis which lies in the plane of the molecule, but the *trans*-isomer contains a  $C_2$  axis which bisects the N–N bond and is perpendicular to the plane of the molecule.



4. The *cis*- (but not the *trans*-) isomer contains a mirror plane,  $\sigma_v$ , lying perpendicular to the plane of the molecule and bisecting the N–N bond:



5. The consequence of the different types of  $C_2$  axes, and the presence of the  $\sigma_v$  plane in the *cis*-isomer, is that the symmetry planes containing the *cis*- and *trans*-N<sub>2</sub>F<sub>2</sub> molecular frameworks are labelled  $\sigma_v'$  and  $\sigma_h$  respectively.

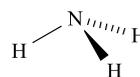
#### Self-study exercises

1. How do the rotation axes and planes of symmetry in *Z*- and *E*-CFH=CFH differ?
2. How many planes of symmetry do (a) F<sub>2</sub>C=O, (b) ClFC=O and (c) [HCO<sub>2</sub>]<sup>−</sup> possess?  
[Ans. (a) 2; (b) 1; (c) 2]

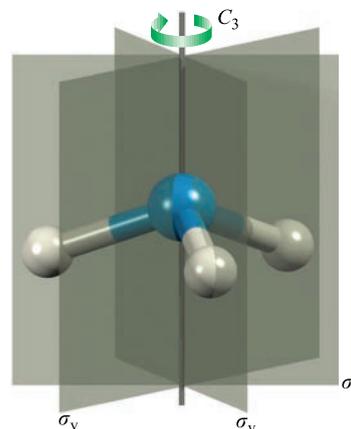
### Worked example 3.2 Symmetry elements in NH<sub>3</sub>

The symmetry elements for NH<sub>3</sub> are  $E$ ,  $C_3$  and  $3\sigma_v$ . (a) Draw the structure of NH<sub>3</sub>. (b) What is the meaning of the  $E$  operator? (c) Draw a diagram to show the symmetry elements.

- (a) The molecule is trigonal pyramidal.



- (b) The  $E$  operator is the identity operator and it leaves the molecule unchanged.
- (c) The  $C_3$  axis passes through the N atom, perpendicular to a plane containing the three H atoms. Each  $\sigma_v$  plane contains one N–H bond and bisects the opposite H–N–H bond angle.



#### Self-study exercises

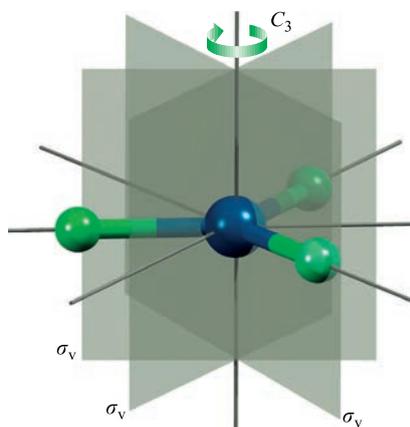
1. What symmetry elements are lost in going from NH<sub>3</sub> to NH<sub>2</sub>Cl? [Ans.  $C_3$ ; two  $\sigma_v$ ]
2. Compare the symmetry elements possessed by NH<sub>3</sub>, NH<sub>2</sub>Cl, NHCl<sub>2</sub> and NCl<sub>3</sub>.
3. Draw a diagram to show the symmetry elements of NClF<sub>2</sub>. [Ans. Show one  $\sigma$  plane; only other operator is  $E$ ]

### Worked example 3.3 Trigonal planar BCl<sub>3</sub> versus trigonal pyramidal PCl<sub>3</sub>

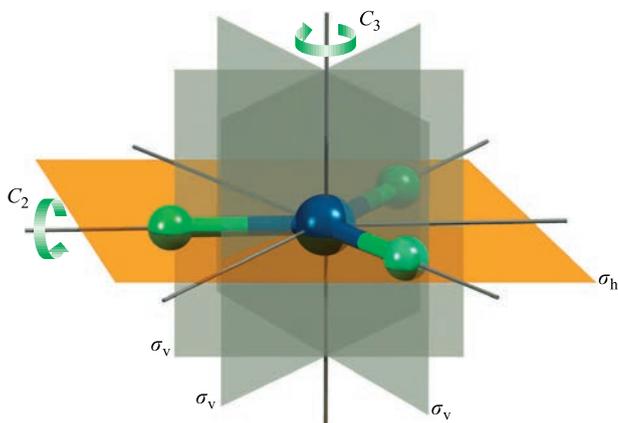
What symmetry elements do BCl<sub>3</sub> and PCl<sub>3</sub> (a) have in common and (b) not have in common?

PCl<sub>3</sub> is trigonal pyramidal (use the VSEPR model) and so possesses the same symmetry elements as NH<sub>3</sub> in worked example 3.2. These are  $E$ ,  $C_3$  and  $3\sigma_v$ .

$\text{BCl}_3$  is trigonal planar (use VSEPR) and possesses all the above symmetry elements:



In addition,  $\text{BCl}_3$  contains a  $\sigma_h$  plane and three  $C_2$  axes (see Fig. 3.2).



Rotation through  $120^\circ$  about the  $C_3$  axis, followed by reflection through the plane perpendicular to this axis (the  $\sigma_h$  plane), generates a molecular configuration indistinguishable from the first – this is an improper rotation  $S_3$ .

### Conclusion

The symmetry elements that  $\text{BCl}_3$  and  $\text{PCl}_3$  have in common are  $E$ ,  $C_3$  and  $3\sigma_v$ . The symmetry elements possessed by  $\text{BCl}_3$  but not by  $\text{PCl}_3$  are  $\sigma_h$ ,  $3C_2$  and  $S_3$ .

### Self-study exercises

1. Show that  $\text{BF}_3$  and  $\text{F}_2\text{C}=\text{O}$  have the following symmetry elements in common:  $E$ , two mirror planes, one  $C_2$ .
2. How do the symmetry elements of  $\text{ClF}_3$  and  $\text{BF}_3$  differ?  
[Ans:  $\text{BF}_3$ , as for  $\text{BCl}_3$  above;  $\text{ClF}_3$ ,  $E$ ,  $\sigma_v'$ ,  $\sigma_v$ ,  $C_2$ ]

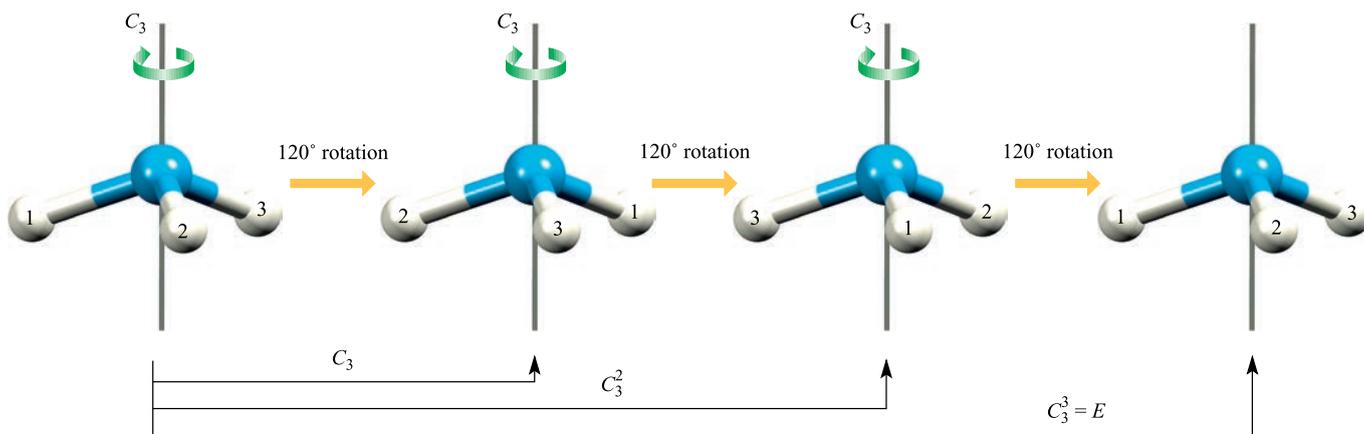
### 3.3 Successive operations

As we have seen in Section 3.2, a particular symbol is used to denote a specific symmetry element. To say that  $\text{NH}_3$  possesses a  $C_3$  axis tells us that we can rotate the molecule through  $120^\circ$  and end up with a molecular configuration that is indistinguishable from the first. However, it takes three such operations to give a configuration of the  $\text{NH}_3$  molecule that *exactly* coincides with the first. The three separate  $120^\circ$  rotations are identified by using the notation in Fig. 3.6. We cannot distinguish between the three H atoms, but for clarity they are labelled H(1), H(2) and H(3) in the figure. Since the third rotation,  $C_3^3$ , returns the  $\text{NH}_3$  molecule to its initial configuration, we can write eq. 3.2, or, in general, eq. 3.3.

$$C_3^3 = E \quad (3.2)$$

$$C_n^n = E \quad (3.3)$$

Similar statements can be written to show the combined effects of successive operations. For example, in planar  $\text{BCl}_3$ , the  $S_3$  improper axis of rotation corresponds to rotation



**Fig. 3.6.** Successive  $C_3$  rotations in  $\text{NH}_3$  are distinguished using the notation  $C_3$  (or  $C_3^1$ ),  $C_3^2$  and  $C_3^3$ . The effect of the last operation is the same as that of the identity operator acting on  $\text{NH}_3$  in the initial configuration.

about the  $C_3$  axis followed by reflection through the  $\sigma_h$  plane. This can be written in the form of eq. 3.4.

$$S_3 = C_3 \times \sigma_h \quad (3.4)$$

### Self-study exercises

1.  $[\text{PtCl}_4]^{2-}$  is square planar; to what rotational operation is  $C_4^2$  equivalent?
2. Draw a diagram to illustrate what the notation  $C_6^4$  means with respect to rotational operations in benzene.
3. Explain why  $[\text{PtCl}_4]^{2-}$  has an  $S_4$  axis.
4. Explain why  $\text{C}_6\text{H}_6$  (benzene) has both  $S_6$  and  $S_3$  axes.

## 3.4 Point groups

The number and nature of the symmetry elements of a given molecule are conveniently denoted by its *point group*, and give rise to labels such as  $C_2$ ,  $C_{3v}$ ,  $D_{3h}$ ,  $D_{2d}$ ,  $T_d$ ,  $O_h$  or  $I_h$ . These point groups belong to the classes of  $C$  groups,  $D$  groups and special groups, the latter containing groups that possess special symmetries, i.e. tetrahedral, octahedral and icosahedral.

**Table 3.1** Characteristic symmetry elements of some important classes of point groups. The characteristic symmetry elements of the  $T_d$ ,  $O_h$  and  $I_h$  are omitted because the point groups are readily identified (see Figs. 3.8 and 3.9). No distinction is made in this table between  $\sigma_v$  and  $\sigma_d$  planes of symmetry. For complete lists of symmetry elements, character tables (Appendix 3) should be consulted.

Point group	Characteristic symmetry elements	Comments
$C_s$	$E$ , one $\sigma$ plane	
$C_i$	$E$ , inversion centre	
$C_n$	$E$ , one (principal) $n$ -fold axis	
$C_{nv}$	$E$ , one (principal) $n$ -fold axis, $n$ $\sigma_v$ planes	
$C_{nh}$	$E$ , one (principal) $n$ -fold axis, one $\sigma_h$ plane, one $S_n$ -fold axis which is coincident with the $C_n$ axis	The $S_n$ axis necessarily follows from the $C_n$ axis and $\sigma_h$ plane. For $n = 2, 4$ or $6$ , there is also an inversion centre.
$D_{nh}$	$E$ , one (principal) $n$ -fold axis, $n$ $C_2$ axes, one $\sigma_h$ plane, $n$ $\sigma_v$ planes, one $S_n$ -fold axis	The $S_n$ axis necessarily follows from the $C_n$ axis and $\sigma_h$ plane. For $n = 2, 4$ or $6$ , there is also an inversion centre.
$D_{nd}$	$E$ , one (principal) $n$ -fold axis, $n$ $C_2$ axes, $n$ $\sigma_v$ planes, one $S_{2n}$ -fold axis	For $n = 3$ or $5$ , there is also an inversion centre.
$T_d$		Tetrahedral
$O_h$		Octahedral
$I_h$		Icosahedral

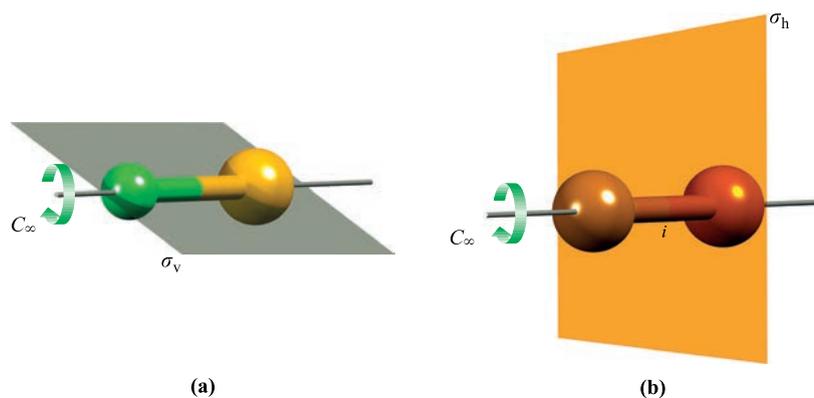
To describe the symmetry of a molecule in terms of one symmetry element (e.g. a rotation axis) provides information only about this property. Each of  $\text{BF}_3$  and  $\text{NH}_3$  possesses a 3-fold axis of symmetry, but their structures and overall symmetries are different:  $\text{BF}_3$  is trigonal planar and  $\text{NH}_3$  is trigonal pyramidal. On the other hand, if we describe the symmetries of these molecules in terms of their respective point groups ( $D_{3h}$  and  $C_{3v}$ ), we are providing information about *all* their symmetry elements.

Before we look at some representative point groups, we emphasize that it is not essential to memorize the symmetry elements of a particular point group. These are listed in *character tables* (see Sections 3.5, 5.5 and 5.6, and Appendix 3) which are widely available.

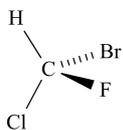
Table 3.1 summarizes the most important classes of point group and gives their characteristic types of symmetry elements;  $E$  is, of course, common to every group. Some significant points are given below.

### $C_1$ point group

Molecules that appear to have no symmetry at all, e.g. **3.9**, must possess the symmetry element  $E$  and effectively possess at least one  $C_1$  axis of rotation. They therefore belong to the  $C_1$  point group, although since  $C_1 = E$ , the rotational symmetry operation is ignored when we list the symmetry elements of this point group.



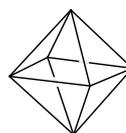
**Fig. 3.7.** Linear molecular species can be classified according to whether they possess a centre of symmetry (inversion centre) or not. All linear species possess a  $C_\infty$  axis of rotation and an infinite number of  $\sigma_v$  planes; in (a), one such plane is shown and these planes are omitted from (b) for clarity. Diagram (a) shows an asymmetrical diatomic belonging to the point group  $C_{\infty v}$ , and (b) shows a symmetrical diatomic belonging to the point group  $D_{\infty h}$ .



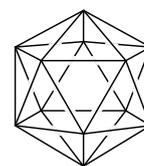
(3.9)



Tetrahedron



Octahedron



Icosahedron

**Fig. 3.8.** The tetrahedron ( $T_d$  symmetry), octahedron ( $O_h$  symmetry) and icosahedron ( $I_h$  symmetry) possess 4, 6 and 12 vertices respectively, and 4, 8 and 20 equilateral-triangular faces respectively.

### $C_{\infty v}$ point group

$C_\infty$  signifies the presence of an  $\infty$ -fold axis of rotation, i.e. that possessed by a linear molecule (Fig. 3.7); for the molecular species to belong to the  $C_{\infty v}$  point group, it must also possess an infinite number of  $\sigma_v$  planes but *no*  $\sigma_h$  plane or inversion centre. These criteria are met by asymmetrical diatomics such as HF, CO and  $[\text{CN}]^-$  (Fig. 3.7a), and linear polyatomics (throughout this book, polyatomic is used to mean a species containing three or more atoms) that do not possess a centre of symmetry, e.g. OCS and HCN.

### $D_{\infty h}$ point group

Symmetrical diatomics (e.g.  $\text{H}_2$ ,  $[\text{O}_2]^{2-}$ ) and linear polyatomics that contain a centre of symmetry (e.g.  $[\text{N}_3]^-$ ,  $\text{CO}_2$ ,  $\text{HC}\equiv\text{CH}$ ) possess a  $\sigma_h$  plane in addition to a  $C_\infty$  axis and an infinite number of  $\sigma_v$  planes (Fig. 3.7). These species belong to the  $D_{\infty h}$  point group.

### $T_d$ , $O_h$ or $I_h$ point groups

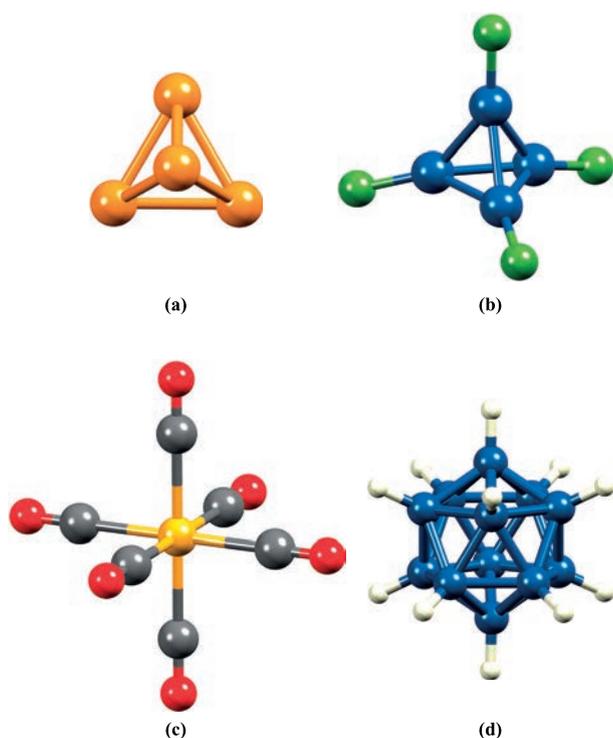
Molecular species that belong to the  $T_d$ ,  $O_h$  or  $I_h$  point groups (Fig. 3.8) possess many symmetry elements, although it is seldom necessary to identify them all before the appropriate point group can be assigned. Species with tetrahedral symmetry include  $\text{SiF}_4$ ,  $[\text{ClO}_4]^-$ ,  $[\text{CoCl}_4]^{2-}$ ,  $[\text{NH}_4]^+$ ,  $\text{P}_4$  (Fig. 3.9a) and  $\text{B}_4\text{Cl}_4$  (Fig. 3.9b). Those with octahedral symmetry include  $\text{SF}_6$ ,  $[\text{PF}_6]^-$ ,  $\text{W}(\text{CO})_6$  (Fig. 3.9c) and  $[\text{Fe}(\text{CN})_6]^{3-}$ . There is no centre of symmetry

in a tetrahedron but there is one in an octahedron, and this distinction has consequences with regard to the observed electronic spectra of tetrahedral and octahedral metal complexes (see Section 20.7). Members of the icosahedral point group are uncommon, e.g.  $[\text{B}_{12}\text{H}_{12}]^{2-}$  (Fig. 3.9d).

### Determining the point group of a molecule or molecular ion

The application of a *systematic* approach to the assignment of a point group is essential, otherwise there is the risk that symmetry elements will be missed with the consequence that an incorrect assignment is made. Figure 3.10 shows a procedure that may be adopted; some of the less common point groups (e.g.  $S_n$ ,  $T$ ,  $O$ ) are omitted from the scheme. Notice that it is *not* necessary to find all the symmetry elements (e.g. improper axes) in order to determine the point group.

We illustrate the application of Fig. 3.10 in four worked examples, with an additional example in Section 3.8. Before assigning a point group to a molecule, its structure must be determined by, for example, microwave spectroscopy, or X-ray, electron or neutron diffraction methods (see Section 4.11).

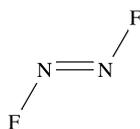


**Fig. 3.9.** The molecular structures of (a) P<sub>4</sub>, (b) B<sub>4</sub>Cl<sub>4</sub> (the B atoms are shown in blue), (c) [W(CO)<sub>6</sub>] (the W atom is shown in yellow and the C atoms in grey) and (d) [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> (the B atoms are shown in blue).

### Worked example 3.4 Point group assignments: 1

#### Determine the point group of *trans*-N<sub>2</sub>F<sub>2</sub>.

First draw the structure.



Apply the strategy shown in Fig. 3.10:

#### START ⇒

Is the molecule linear? No  
 Does *trans*-N<sub>2</sub>F<sub>2</sub> have T<sub>d</sub>, O<sub>h</sub> or I<sub>h</sub> symmetry? No  
 Is there a C<sub>n</sub> axis? Yes; a C<sub>2</sub> axis perpendicular to the plane of the paper and passing through the midpoint of the N–N bond

Are there two C<sub>2</sub> axes perpendicular to the principal axis? No  
 Is there a σ<sub>h</sub> plane (perpendicular to the principal axis)? Yes

⇒ STOP

The point group is C<sub>2h</sub>.

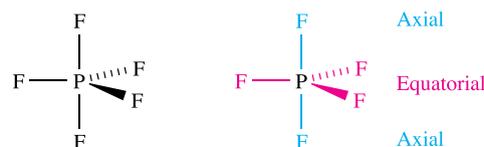
### Self-study exercises

1. Show that the point group of *cis*-N<sub>2</sub>F<sub>2</sub> is C<sub>2v</sub>.
2. Show that the point group of *E*-CHCl=CHCl is C<sub>2h</sub>.

### Worked example 3.5 Point group assignments: 2

#### Determine the point group of PF<sub>5</sub>.

First, draw the structure.



In the trigonal bipyramidal arrangement, the three equatorial F atoms are equivalent, and the two axial F atoms are equivalent.

Apply the strategy shown in Fig. 3.10:

#### START ⇒

Is the molecule linear? No  
 Does PF<sub>5</sub> have T<sub>d</sub>, O<sub>h</sub> or I<sub>h</sub> symmetry? No  
 Is there a C<sub>n</sub> axis? Yes; a C<sub>3</sub> axis containing the P and two axial F atoms

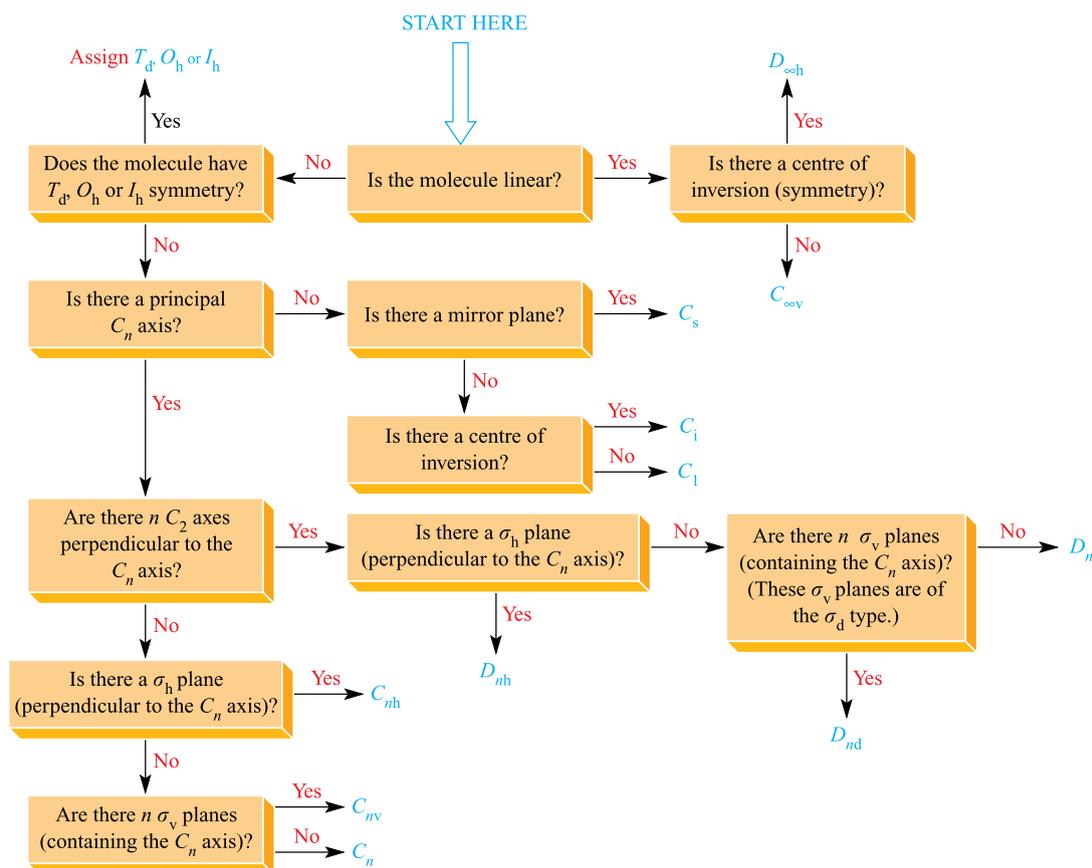
Are there three C<sub>2</sub> axes perpendicular to the principal axis? Yes; each lies along an equatorial P–F bond  
 Is there a σ<sub>h</sub> plane (perpendicular to the principal axis)? Yes; it contains the P and three equatorial F atoms.

⇒ STOP

The point group is D<sub>3h</sub>.

### Self-study exercises

1. Show that BF<sub>3</sub> belongs to the D<sub>3h</sub> point group.
2. Show that OF<sub>2</sub> belongs to the C<sub>2v</sub> point group.
3. Show that BF<sub>2</sub>Br belongs to the C<sub>2v</sub> point group.
4. Confirm that SO<sub>2</sub> belongs to the C<sub>2v</sub> point group, but that XeF<sub>2</sub> does not.
5. Confirm that NF<sub>3</sub> belongs to the C<sub>3v</sub> point group, but that AlF<sub>3</sub> does not.

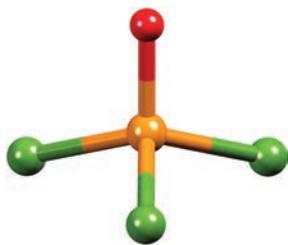


**Fig. 3.10.** Scheme for assigning point groups of molecules and molecular ions. Apart from the cases of  $n = 1$  or  $\infty$ ,  $n$  most commonly has values of 2, 3, 4, 5 or 6.

### Worked example 3.6 Point group assignments: 3

#### To what point group does $\text{POCl}_3$ belong?

The structure of  $\text{POCl}_3$  is:



Apply the strategy shown in Fig. 3.10:

#### START $\Rightarrow$

Is the molecule linear? No  
 Does  $\text{POCl}_3$  have  $T_d$ ,  $O_h$  or  $I_h$  symmetry? No (although this molecule is tetrahedral in shape, it does *not* possess  $T_d$  symmetry)  
 Is there a  $C_n$  axis? Yes; a  $C_3$  axis running along the O–P bond

Are there three  $C_2$  axes perpendicular to the principal axis? No  
 Is there a  $\sigma_h$  plane (perpendicular to the principal axis)? No  
 Are there  $n$   $\sigma_v$  planes (containing the principal axis)? Yes; each contains the one Cl and the O and P atoms  $\Rightarrow$  **STOP**

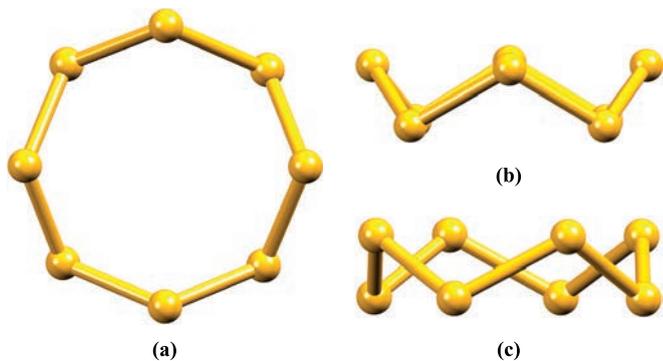
The point group is  $C_{3v}$ .

#### Self-study exercises

- Show that  $\text{CHCl}_3$  possesses  $C_{3v}$  symmetry, but that  $\text{CCl}_4$  belongs to the  $T_d$  point group.
- Assign point groups to (a)  $[\text{NH}_4]^+$  and (b)  $\text{NH}_3$ .  
[Ans. (a)  $T_d$ ; (b)  $C_{3v}$ ]
- In trigonal bipyramidal  $\text{PCl}_4\text{F}$ , the F atom is in an axial site. Confirm that  $\text{PCl}_4\text{F}$  belongs to the  $C_{3v}$  symmetry.
- Trigonal bipyramidal  $\text{PCl}_3\text{F}_2$  belongs to the  $D_{3h}$  point group. Show that the F atoms must be in axial sites.

### Worked example 3.7 Point group assignments: 4

Three projections of the cyclic structure of  $S_8$  are shown below, and the structure can also be viewed in 3D on the accompanying website. All S–S bond distances are equivalent, as are all S–S–S bond angles. To what point group does  $S_8$  belong?



Follow the scheme in Fig. 3.10:

#### START $\Rightarrow$

Is the molecule linear?	No
Does $S_8$ have $T_d$ , $O_h$ or $I_h$ symmetry?	No
Is there a $C_n$ axis?	Yes; a $C_4$ axis running through the centre of the ring; perpendicular to the plane of the paper in diagram (a)
Are there four $C_2$ axes perpendicular to the principal axis?	Yes; these are most easily seen from diagram (c)
Is there a $\sigma_h$ plane (perpendicular to the principal axis)?	No
Are there $n$ $\sigma_d$ planes (containing the principal axis)?	Yes; these are most easily seen from diagrams (a) and (c)

$\Rightarrow$  STOP

The point group is  $D_{4d}$ .

#### Self-study exercises

1. Why does the  $S_8$  ring not contain a  $C_8$  axis?
2. Copy diagram (a) above. Show on the figure where the  $C_4$  axis and the four  $C_2$  axes lie.
3.  $S_6$  has the chair conformation shown in Box 1.1. Confirm that this molecule contains a centre of inversion.

Earlier, we noted that it is not necessary to find all the symmetry elements of a molecule or ion to determine its point group. However, if one needs to identify all the operations in a point group, the following check of the total number can be carried out:<sup>†</sup>

- assign 1 for  $C$  or  $S$ , 2 for  $D$ , 12 for  $T$ , 24 for  $O$  or 60 for  $I$ ;
- multiply by  $n$  for a numerical subscript;
- multiply by 2 for a letter subscript (s, v, d, h, i).

For example, the  $C_{3v}$  point group has  $1 \times 3 \times 2 = 6$  operations, and  $D_{2d}$  has  $2 \times 2 \times 2 = 8$  operations.

### 3.5 Character tables: an introduction

While Fig. 3.10 leads you to a point group assignment using diagnostic symmetry elements, it may be necessary to establish whether any additional symmetry elements are exhibited by a molecule in a given point group.

Each point group has an associated *character table*, and the character table for the  $C_{2v}$  point group is shown in Table 3.2. The point group is indicated at the top left-hand corner and the symmetry elements possessed by a member of the point group are given across the top row of the character table. The  $H_2O$  molecule has  $C_{2v}$  symmetry and when we looked at the symmetry elements of  $H_2O$  in Fig. 3.3, we labelled the two perpendicular planes. In the character table, taking the  $z$  axis as coincident with the principal axis, the  $\sigma_v$  and  $\sigma_v'$  planes are defined as lying in the  $xz$  and  $yz$  planes, respectively. Placing the molecular framework in a convenient orientation with respect to a Cartesian set of axes has many advantages, one of which is that the atomic orbitals on the central atom point in convenient directions. We return to this in Chapter 5.

Table 3.3 shows the character table for the  $C_{3v}$  point group. The  $NH_3$  molecule possesses  $C_{3v}$  symmetry, and worked example 3.2 illustrated the principal axis of rotation and planes of symmetry in  $NH_3$ . In the character table, the presence of three  $\sigma_v$  planes in  $NH_3$  is represented by the notation ' $3\sigma_v$ ' in the top line of the table. The notation ' $2C_3$ ' summarizes the two operations  $C_3^1$  and  $C_3^2$  (Fig. 3.6). The operation  $C_3^3$  is equivalent to the identity operator,  $E$ , and so is not specified again.

**Table 3.2** The character table for the  $C_{2v}$  point group. For more character tables, see Appendix 3.

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$

<sup>†</sup> See O.J. Curnow (2007) *J. Chem. Educ.*, vol. 84, p. 1430.

**Table 3.3** The character table for the  $C_{3v}$  point group. For more character tables, see Appendix 3.

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$		
$A_1$	1	1	1	$z$	$x^2 + y^2, z^2$
$A_2$	1	1	-1	$R_z$	
$E$	2	-1	0	$(x, y) (R_x, R_y)$	$(x^2 - y^2, xy) (xz, yz)$

Figure 3.4 showed the proper axes of rotation and planes of symmetry in the square planar molecule  $\text{XeF}_4$ . This has  $D_{4h}$  symmetry. The  $D_{4h}$  character table is given in Appendix 3, and the top row of the character table that summarizes the symmetry operations for this point group is as follows:

$D_{4h}$	$E$	$2C_4$	$C_2$	$2C_2'$	$2C_2''$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$
----------	-----	--------	-------	---------	----------	-----	--------	------------	-------------	-------------

In Fig. 3.4 we showed that a  $C_2$  axis is coincident with the  $C_4$  axis in  $\text{XeF}_4$ . The  $C_2$  operation is equivalent to  $C_4^2$ . The character table summarizes this information by stating ' $2C_4 C_2$ ', referring to  $C_4^1$  and  $C_4^3$ , and then  $C_4^2 = C_2$ . The operation  $C_4^4$  is taken care of in the identity operator  $E$ . The two sets of  $C_2$  axes that we showed in Fig. 3.4 and labelled as  $C_2'$  and  $C_2''$  are apparent in the character table, as are the  $\sigma_h$ , two  $\sigma_v$  and two  $\sigma_d$  planes of symmetry. The symmetry operations that we did not show in Fig. 3.4 but that are included in the character table are the centre of symmetry,  $i$  (which is located on the Xe atom in  $\text{XeF}_4$ ), and the  $S_4$  axes. Each  $S_4$  operation can be represented as  $(C_4 \times \sigma_h)$ .

The left-hand column in a character table gives a list of *symmetry labels*. These are used in conjunction with the numbers, or *characters*, from the main part of the table to label the symmetry properties of, for example, molecular orbitals or modes of molecular vibrations. As we shall see in Chapter 5, although the symmetry labels in the character tables are upper case (e.g.  $A_1, E, T_{2g}$ ), the corresponding symmetry labels for orbitals are lower case (e.g.  $a_1, e, t_{2g}$ ). Symmetry labels give us information about degeneracies as follows:

- $A$  and  $B$  (or  $a$  and  $b$ ) indicate non-degenerate;
- $E$  (or  $e$ ) refers to doubly degenerate;
- $T$  (or  $t$ ) means triply degenerate.

In Chapter 5, we use character tables to label the symmetries of orbitals, and to understand what orbital symmetries are allowed for a molecule possessing a particular symmetry.

Appendix 3 gives character tables for the most commonly encountered point groups, and each table has the same format as those in Tables 3.2 and 3.3.

### 3.6 Why do we need to recognize symmetry elements?

So far in this chapter, we have described the possible symmetry elements that a molecule might possess and, on the

basis of these symmetry properties, we have illustrated how a molecular species can be assigned to a particular point group. Now we look at some of the reasons why the recognition of symmetry elements in a molecule is important to the inorganic chemist.

Most of the applications of symmetry fall into one of the following categories:

- constructing molecular and hybrid orbitals (see Chapter 5);
- interpreting spectroscopic (e.g. vibrational and electronic) properties;
- determining whether a molecular species is chiral.

The next two sections introduce the consequences of symmetry on observed bands in infrared spectra and with the relationship between molecular symmetry and chirality. In Chapter 20, we consider the electronic spectra of octahedral and tetrahedral  $d$ -block metal complexes and discuss the effects that molecular symmetry has on electronic spectroscopic properties.

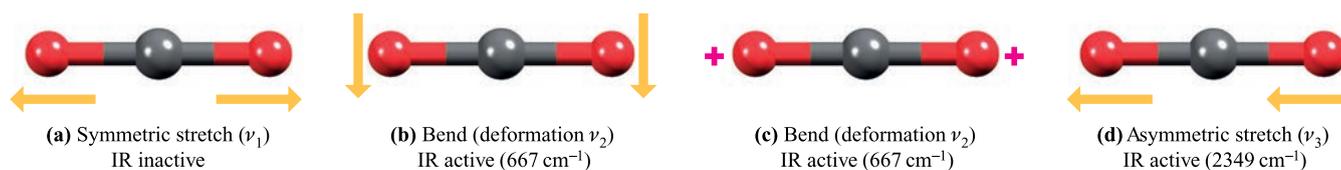
## 3.7 Vibrational spectroscopy

Infrared (IR) and Raman spectroscopies (see also Section 4.6) are branches of *vibrational spectroscopy* and the former technique is much the more widely available of the two in student teaching laboratories. The discussion that follows is necessarily selective and is pitched at a relatively simplistic level. We derive the number of vibrational modes for some simple molecules, and determine whether these modes are infrared (IR) and/or Raman active (i.e. whether absorptions corresponding to the vibrational modes are observed in the IR and/or Raman spectra). We also relate the vibrational modes of a molecule to its symmetry by using the character table of the relevant point group. A rigorous group theory approach to the normal modes of vibration of a molecule is beyond the scope of this book. The reading list at the end of the chapter gives sources of more detailed discussions.

### How many vibrational modes are there for a given molecular species?

Vibrational spectroscopy is concerned with the observation of the *degrees of vibrational freedom*, the number of which can be determined as follows. The motion of a molecule containing  $n$  atoms can conveniently be described in terms of the three Cartesian axes. The molecule has  $3n$  *degrees of freedom* which together describe the *translational, vibrational* and *rotational* motions of the molecule.

The translational motion of a molecule (i.e. movement through space) can be described in terms of three degrees of freedom relating to the three Cartesian axes. If there are



**Fig. 3.11.** The vibrational modes of  $\text{CO}_2$  ( $D_{\infty h}$ ). In the vibrational mode shown in (a), the carbon atom remains stationary. Vibrations (a) and (d) are stretching modes. Bending mode (b) occurs in the plane of the paper, while bend (c) occurs in a plane perpendicular to that of the paper; the + signs designate motion towards the reader. The two bending modes require the same amount of energy and are therefore *degenerate*.

$3n$  degrees of freedom in total and three degrees of freedom for translational motion, it follows that there must be  $(3n - 3)$  degrees of freedom for rotational and vibrational motion. For a *non-linear molecule* there are three degrees of rotational freedom, but for a *linear molecule*, there are only two degrees of rotational freedom. Having taken account of translational and rotational motion, the number of degrees of vibrational freedom can be determined (eqs. 3.5 and 3.6).<sup>†</sup>

Number of degrees of vibrational freedom for a *non-linear* molecule =  $3n - 6$  (3.5)

Number of degrees of vibrational freedom for a *linear* molecule =  $3n - 5$  (3.6)

For example, from eq. 3.6, the linear  $\text{CO}_2$  molecule has four *normal modes of vibration* and these are shown in Fig. 3.11. Two of the modes are *degenerate*; i.e. they possess the same energy and could be represented in a single diagram with the understanding that one vibration occurs in the plane of the paper and another, identical in energy, takes place in a plane perpendicular to the first.

*Degenerate modes of vibration* possess the same energy.

### Self-study exercises

- Using the VSEPR model to help you, draw the structures of  $\text{CF}_4$ ,  $\text{XeF}_4$  and  $\text{SF}_4$ . Assign a point group to each molecule. Show that the number of degrees of vibrational freedom is independent of the molecular symmetry. [Ans.  $T_d$ ;  $D_{4h}$ ;  $C_{2v}$ ]
- Why do  $\text{CO}_2$  and  $\text{SO}_2$  have a different number of degrees of vibrational freedom?
- How many degrees of vibrational freedom do each of the following possess:  $\text{SiCl}_4$ ,  $\text{BrF}_3$ ,  $\text{POCl}_3$ ? [Ans. 9; 6; 9]

<sup>†</sup> For further detail, see: P. Atkins and J. de Paula (2014) *Atkins' Physical Chemistry*, 10th edn, OUP, Oxford, p. 514.

### Selection rules for an infrared or Raman active mode of vibration

One of the important consequences of precisely denoting molecular symmetry is seen in IR and Raman spectroscopy. For example, an IR spectrum records the frequency of a molecular vibration, i.e. bond stretching and molecular deformation (e.g. bending) modes. However, not all modes of vibration of a particular molecule give rise to observable absorption bands in the IR spectrum. This is because the following *selection rule* must be obeyed:

For a mode of vibration to be *infrared (IR) active*, it must give rise to a change in the molecular electric dipole moment.

A different selection rule applies to Raman spectroscopy:

For a mode of vibration to be *Raman active*, it must give rise to a change in the polarizability of the molecule. *Polarizability* is the ease with which the electron cloud associated with the molecule is distorted.

In addition to these two selection rules, molecules with a centre of symmetry (e.g. linear  $\text{CO}_2$ , and octahedral  $\text{SF}_6$ ) are subject to the *rule of mutual exclusion*:

For centrosymmetric molecules, the *rule of mutual exclusion* states that vibrations that are IR active are Raman inactive, and vice versa.

Application of this rule means that the presence of a centre of symmetry in a molecule is readily determined by comparing its IR and Raman spectra. Although Raman spectroscopy is now a routine technique, it is IR spectroscopy that remains the more accessible of the two for everyday compound characterization. Hence, we restrict most of the following discussion to IR spectroscopic absorptions. Furthermore, we are concerned only with *fundamental* absorptions, these being the dominant features of IR spectra.

The transition from the vibrational ground state to the first excited state is the *fundamental* transition.

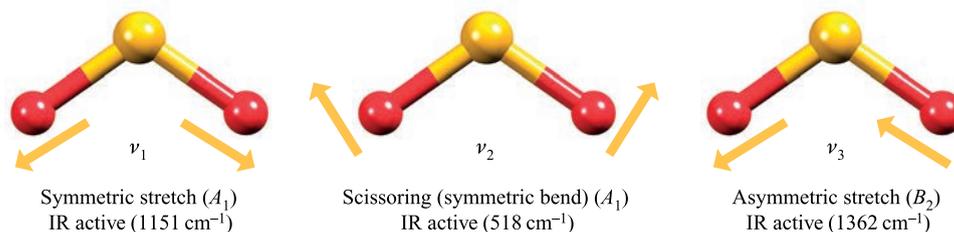


Fig. 3.12. The vibrational modes of  $\text{SO}_2$  ( $C_{2v}$ ). In each mode, the S atom is also displaced from the position shown.

### Linear ( $D_{\infty h}$ or $C_{\infty v}$ ) and bent ( $C_{2v}$ ) triatomic molecules

We can readily illustrate the effect of molecular symmetry on molecular dipole moments, and thus on IR active modes of vibration, by considering the linear molecule  $\text{CO}_2$ . The two C–O bond distances are equal (116 pm) and the molecule is described as being ‘symmetrical’. Strictly,  $\text{CO}_2$  possesses  $D_{\infty h}$  symmetry. As a consequence of its symmetry,  $\text{CO}_2$  is non-polar. The number of degrees of vibrational freedom is determined from eq. 3.6:

$$\begin{aligned} \text{Number of degrees of vibrational freedom for } \text{CO}_2 \\ = 3n - 5 = 9 - 5 = 4 \end{aligned}$$

The four fundamental modes of vibration are shown in Fig. 3.11. Although both the asymmetric stretch and the bend (Fig. 3.11) give rise to a change in dipole moment (generated transiently as the vibration occurs), the symmetric stretch does not. Thus, only two fundamental absorptions are observed in the IR spectrum of  $\text{CO}_2$ .

Now consider  $\text{SO}_2$  which is a bent molecule ( $C_{2v}$ ). The number of degrees of vibrational freedom for a non-linear molecule is determined from eq. 3.5:

$$\begin{aligned} \text{Number of degrees of vibrational freedom for } \text{SO}_2 \\ = 3n - 6 = 9 - 6 = 3 \end{aligned}$$

The three fundamental modes of vibration are shown in Fig. 3.12. In the case of a triatomic molecule, it is simple to deduce that the three modes of vibration are composed of two stretching modes (symmetric and asymmetric) and a bending mode. However, for larger molecules it is not so easy to visualize the modes of vibration. We return to this problem in the next section. The three normal modes of vibration of  $\text{SO}_2$  all give rise to a change in molecular dipole moment and are therefore IR active. A comparison of these results for  $\text{CO}_2$  and  $\text{SO}_2$  illustrates that vibrational spectroscopy can be used to determine whether an  $\text{X}_3$  or  $\text{XY}_2$  species is linear or bent.

Linear molecules of the general type  $\text{XYZ}$  (e.g.  $\text{OCS}$  or  $\text{HCN}$ ) possess  $C_{\infty v}$  symmetry and their IR spectra are expected to show three absorptions: the symmetric stretching, asymmetric stretching and bending modes are all IR active. In a linear molecule  $\text{XYZ}$ , provided that the atomic masses

of X and Z are significantly different, the absorptions observed in the IR spectrum can be assigned to the X–Y stretch, the Y–Z stretch and the XYZ bend. The reason that the stretching modes can be assigned to individual bond vibrations rather than to a vibration involving the whole molecule is that each of the symmetric and asymmetric stretches is dominated by the stretching of one of the two bonds. For example, absorptions at  $3311$ ,  $2097$  and  $712 \text{ cm}^{-1}$  in the IR spectrum of  $\text{HCN}$  are assigned to the H–C stretch, the  $\text{C}\equiv\text{N}$  stretch and the  $\text{HCN}$  bend, respectively.

A *stretching mode* is designated by the symbol  $\nu$ , while a *deformation* (bending) is denoted by  $\delta$ . For example,  $\nu_{\text{CO}}$  stands for the stretch of a C–O bond.

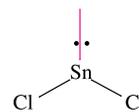
### Worked example 3.8 IR spectra of triatomic molecules

**The IR spectrum of  $\text{SnCl}_2$  exhibits absorptions at 352, 334 and  $120 \text{ cm}^{-1}$ . What shape do these data suggest for the molecule, and is this result consistent with the VSEPR model?**

For linear  $\text{SnCl}_2$ ,  $D_{\infty h}$ , the asymmetric stretch and the bend are IR active, but the symmetric stretch is IR inactive (no change in molecular dipole moment).

For bent  $\text{SnCl}_2$ ,  $C_{2v}$ , the symmetric stretching, asymmetric stretching and scissoring modes are all IR active.

The data therefore suggest that  $\text{SnCl}_2$  is bent, and this is consistent with the VSEPR model because there is a lone pair in addition to two bonding pairs of electrons:



### Self-study exercises

- The vibrational modes of  $\text{XeF}_2$  are at  $555$ ,  $515$  and  $213 \text{ cm}^{-1}$  but only two are IR active. Explain why this is consistent with  $\text{XeF}_2$  having a linear structure.
- How many IR active vibrational modes does  $\text{CS}_2$  possess, and why? [*Hint*:  $\text{CS}_2$  is isostructural with  $\text{CO}_2$ .]

- The IR spectrum of  $\text{SF}_2$  has absorptions at 838, 813 and  $357\text{ cm}^{-1}$ . Explain why these data are consistent with  $\text{SF}_2$  belonging to the  $C_{2v}$  rather than  $D_{\infty h}$  point group.
- To what point group does  $\text{F}_2\text{O}$  belong? Explain why the vibrational modes at 928, 831 and  $461\text{ cm}^{-1}$  are all IR active. [Ans.  $C_{2v}$ ]
- The IR spectrum of FNO shows three bands at 520, 766 and  $1844\text{ cm}^{-1}$  arising from vibrational modes. What shape is FNO? Confirm that FNO belongs to the  $C_s$  point group.

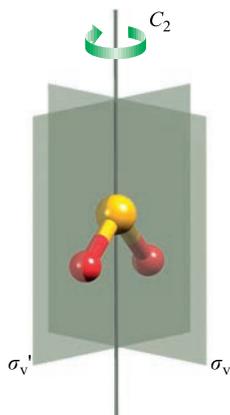
### Bent molecules $\text{XY}_2$ : using the $C_{2v}$ character table

The  $\text{SO}_2$  molecule belongs to the  $C_{2v}$  point group, and in this section we look again at the three normal modes of vibration of  $\text{SO}_2$ , but this time use the  $C_{2v}$  character table to determine:

- whether the modes of vibration involve stretching or bending;
- the symmetry labels of the vibrational modes;
- which modes of vibration are IR and/or Raman active.

The  $C_{2v}$  character table is shown below, along with a diagram that relates the  $\text{SO}_2$  molecule to its  $C_2$  axis and two mirror planes. The  $z$  axis coincides with the  $C_2$  axis, and the molecule lies in the  $yz$  plane.

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$



In a molecule, stretching or bending modes can be described in terms of changes made to the bond vectors or bond angles, respectively. Let us first consider vibrations involving bond stretching in  $\text{SO}_2$ . (Since a triatomic molecule is a simple case, it is all too easy to wonder why we need the following exercise; however, it serves as an instructive example before we consider larger polyatomics.) Without thinking about the relative directions in which the bonds may be stretched, consider the effect of each symmetry operation of the  $C_{2v}$  point group on the bonds in  $\text{SO}_2$ . Now ask the question: how many bonds are left *unchanged* by each symmetry operation? The  $E$  operator leaves both S–O bonds unchanged, as does reflection through the  $\sigma_v'(yz)$  plane. However, rotation about the  $C_2$  axis affects both bonds, and so does reflection through the  $\sigma_v(xz)$  plane. These results can be summarized in the row of characters shown below, where ‘2’ stands for ‘two bonds unchanged’, and ‘0’ stands for ‘no bonds unchanged’:

$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
2	0	0	2

This is known as a *reducible representation* and can be rewritten as the sum of rows of characters from the  $C_{2v}$  character table. Inspection of the character table reveals that summing the two rows of characters for the  $A_1$  and  $B_2$  representations gives us the result we require, i.e.:

$A_1$	1	1	1	1
$B_2$	1	-1	-1	1
Sum of rows	2	0	0	2

This result tells us that there are two non-degenerate stretching modes, one of  $A_1$  symmetry and one of  $B_2$  symmetry. For a bent  $\text{XY}_2$  molecule, it is a straightforward matter to relate these labels to schematic representations of the stretching modes, since there can be only two options: bond stretching in-phase or out-of-phase. However, for the sake of completeness, we now work through the assignments using the  $C_{2v}$  character table.

The modes of vibration of  $\text{SO}_2$  are defined by vectors which are illustrated by yellow arrows in Fig. 3.12. In order to assign a symmetry label to each vibrational mode, we must consider the effect of each symmetry operation of the  $C_{2v}$  point group on these vectors. For the symmetric stretch ( $\nu_1$ ) of the  $\text{SO}_2$  molecule, the vectors are left unchanged by the  $E$  operator and by rotation about the  $C_2$  axis. There is also no change to the vectors when the molecule is reflected through either of the  $\sigma_v(xz)$  or

$\sigma_v'(yz)$  planes. If we use the notation that a '1' means 'no change', then the results can be summarized as follows:

$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
1	1	1	1

Now compare this row of characters with the rows in the  $C_{2v}$  character table. There is a match with the row for symmetry type  $A_1$ , and therefore the symmetric stretch is given the  $A_1$  symmetry label. Now consider the asymmetric stretching mode ( $\nu_3$ ) of the  $\text{SO}_2$  molecule (Fig. 3.12). The vectors are unchanged by the  $E$  and  $\sigma_v'(yz)$  operations, but their directions are altered by rotation about the  $C_2$  axis and by reflection through the  $\sigma_v(xz)$  plane. Using the notation that a '1' means 'no change', and a '-1' means 'a reversal of the direction of the vector', we can summarize the results as follows:

$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
1	-1	-1	1

This corresponds to symmetry type  $B_2$  in the  $C_{2v}$  character table, and so the asymmetric stretching mode is labelled  $B_2$ .

Now recall that  $\text{SO}_2$  has a total of  $(3n - 6) = 3$  degrees of vibrational freedom. Having assigned two of these to stretching modes, the third must arise from a bending (or scissoring) mode. The bending mode ( $\nu_2$ ) can be defined in terms of changes in the O-S-O bond angle. To assign a symmetry label to this mode of vibration, we consider the effect of each symmetry operation of the  $C_{2v}$  point group on the bond angle. Each of the  $E$ ,  $C_2$ ,  $\sigma_v(xz)$  and  $\sigma_v'(yz)$  operations leaves the angle unchanged and, therefore, we can write:

$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
1	1	1	1

The scissoring mode is therefore assigned  $A_1$  symmetry.

Finally, how can we use a character table to determine whether a particular mode of vibration is IR or Raman active? At the right-hand side of a character table, there are two columns containing functions  $x$ ,  $y$  and/or  $z$ , or products of these functions (e.g.  $x^2$ ,  $xy$ ,  $yz$ ,  $(x^2 - y^2)$ , etc.). We will not detail the origins of these terms, but will focus only on the information that they provide:

If the symmetry label (e.g.  $A_1$ ,  $B_1$ ,  $E$ ) of a normal mode of vibration is associated with  $x$ ,  $y$  or  $z$  in the character table, then the mode is **IR active**.

If the symmetry label (e.g.  $A_1$ ,  $B_1$ ,  $E$ ) of a normal mode of vibration is associated with a product term (e.g.  $x^2$ ,  $xy$ ) in the character table, then the mode is **Raman active**.

The  $\text{SO}_2$  molecule has  $A_1$  and  $B_2$  normal modes of vibration. In the  $C_{2v}$  character table, the right-hand columns for the  $A_1$  representation contain  $z$  and also  $x^2$ ,  $y^2$  and  $z^2$  functions. Hence, the  $A_1$  modes are *both* IR and Raman active. Similarly, the right-hand columns for the  $B_2$  representation contain  $y$  and  $yz$  functions, and the asymmetric stretch of  $\text{SO}_2$  is both IR and Raman active.

The most common bent triatomic molecule that you encounter daily is  $\text{H}_2\text{O}$ . Like  $\text{SO}_2$ ,  $\text{H}_2\text{O}$  belongs to the  $C_{2v}$  point group and possesses three modes of vibration, all of which are IR and Raman active. These are illustrated in Fig. 3.13a which shows a calculated IR spectrum of gaseous  $\text{H}_2\text{O}$ . (An experimental spectrum would also show rotational fine structure.) In contrast, the IR spectrum of liquid water shown in Fig. 3.13b is broad and the two absorptions around  $3700\text{ cm}^{-1}$  are not resolved. The broadening arises from the presence of hydrogen bonding between water molecules (see Section 10.6). In addition, the vibrational wavenumbers in the liquid and gas phase spectra are shifted with respect to one another.

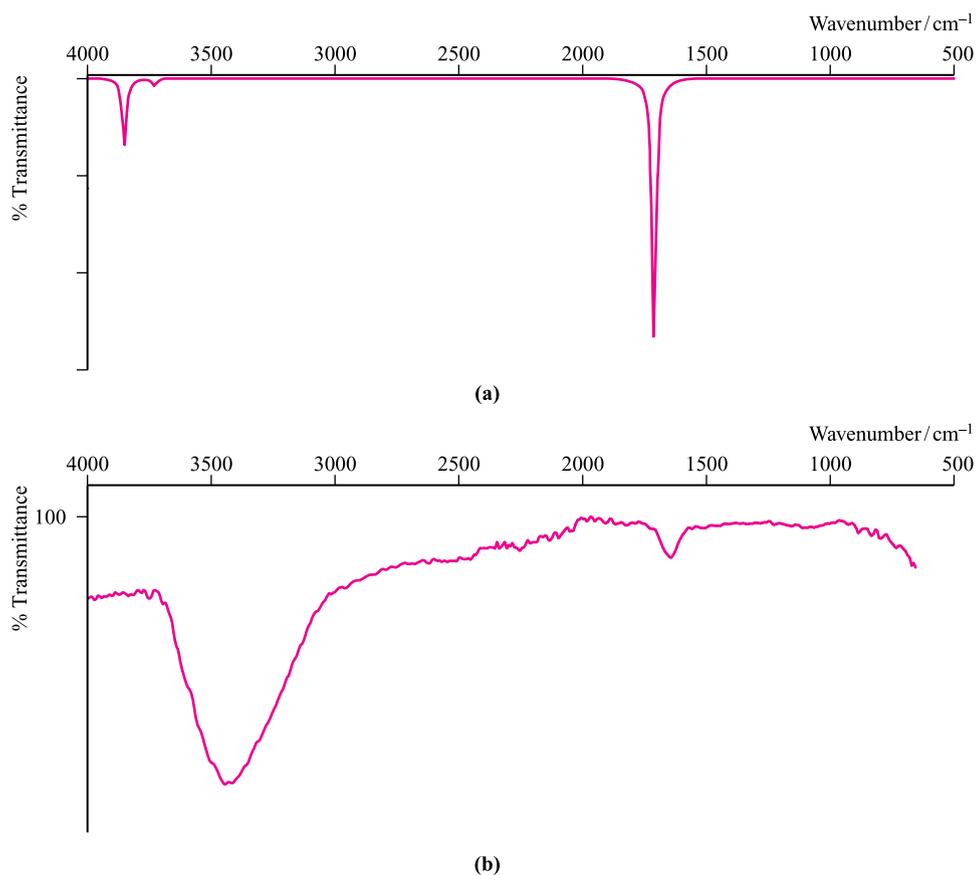
### Self-study exercises

- In the vibrational spectrum of  $\text{H}_2\text{O}$  vapour, there are absorptions at  $3756$  and  $3657\text{ cm}^{-1}$  corresponding to the  $B_2$  and  $A_1$  stretching modes, respectively. Draw diagrams to show these vibrational modes.
- The symmetric bending of the non-linear  $\text{NO}_2$  molecule gives rise to an absorption at  $752\text{ cm}^{-1}$ . To what point group does  $\text{NO}_2$  belong? Explain why the symmetric bending mode is IR active. Why is it assigned an  $A_1$  symmetry label?

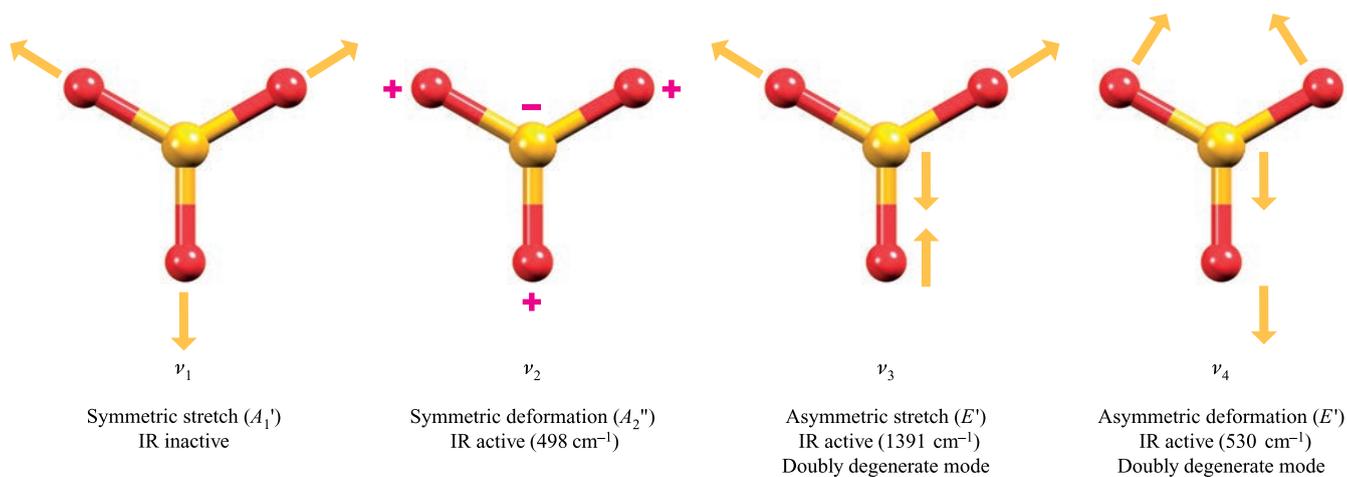
### $\text{XY}_3$ molecules with $D_{3h}$ symmetry

An  $\text{XY}_3$  molecule, irrespective of shape, possesses  $(3 \times 4) - 6 = 6$  degrees of vibrational freedom. Let us first consider planar  $\text{XY}_3$  molecules belonging to the  $D_{3h}$  point group. Examples are  $\text{SO}_3$ ,  $\text{BF}_3$  and  $\text{AlCl}_3$ , and the six normal modes of vibration of  $\text{SO}_3$  are shown in Fig. 3.14. The symmetries of the stretching modes stated in the figure are deduced by considering how many bonds are left *unchanged* by each symmetry operation of the  $D_{3h}$  point group (refer to Fig. 3.2, worked example 3.3 and Table 3.4). The  $E$  and  $\sigma_h$  operators leave all three bonds unchanged. Each  $C_2$  axis coincides with one X-Y bond and therefore rotation about a  $C_2$  axis leaves one bond unchanged; similarly for reflection through a  $\sigma_v$  plane. Rotation about the  $C_3$  axis affects all three bonds. The results can be summarized in the following row of characters:

$E$	$C_3$	$C_2$	$\sigma_h$	$S_3$	$\sigma_v$
3	0	1	3	0	1



**Fig. 3.13.** (a) Calculated IR spectrum of gaseous  $\text{H}_2\text{O}$  (Spartan '14 v.1.1.8, ©Wavefunction Inc. 2013, Density Functional level, B3LYP) showing the three fundamental absorptions. Experimental values are 3756, 3657 and 1595  $\text{cm}^{-1}$ . (b) IR spectrum of liquid  $\text{H}_2\text{O}$ .



**Fig. 3.14.** The vibrational modes of  $\text{SO}_3$  ( $D_{3h}$ ); only three are IR active. The + and – notation is used to show the ‘up’ and ‘down’ motion of the atoms during the mode of vibration. Two of the modes are doubly degenerate, giving a total of six normal modes of vibration.

If we rewrite this reducible representation as the sum of rows of characters from the  $D_{3h}$  character table, we can determine the symmetries of the vibrational modes of the planar  $\text{XY}_3$  molecule:

$A_1'$	1	1	1	1	1	1
$E'$	2	-1	0	2	-1	0
Sum of rows	3	0	1	3	0	1



For the  $C_{2v}$  molecules  $\text{ClF}_3$  (3.10) or  $\text{BrF}_3$ , there are six normal modes of vibration, approximately described as equatorial stretch, symmetric axial stretch, asymmetric axial stretch and three deformation modes. All six modes are IR active.

### Self-study exercises

1. The IR spectrum of  $\text{BF}_3$  shows absorptions at 480, 691 and  $1449\text{ cm}^{-1}$ . Use these data to decide whether  $\text{BF}_3$  has  $C_{3v}$  or  $D_{3h}$  symmetry. [Ans.  $D_{3h}$ ]
2. In the IR spectrum of  $\text{NF}_3$ , there are four absorptions. Why is this consistent with  $\text{NF}_3$  belonging to the  $C_{3v}$  rather than  $D_{3h}$  point group?
3. The IR spectrum of  $\text{BrF}_3$  in an argon matrix shows six absorptions. Explain why this observation confirms that  $\text{BrF}_3$  cannot have  $C_{3v}$  symmetry.
4. Use the  $C_{3v}$  character table to confirm that the symmetric deformation mode of  $\text{NH}_3$  (Fig. 3.15) has  $A_1$  symmetry.

### $\text{XY}_4$ molecules with $T_d$ or $D_{4h}$ symmetry

An  $\text{XY}_4$  molecule with  $T_d$  symmetry has nine normal modes of vibration (Fig. 3.16). In the  $T_d$  character table (see Appendix 3), the  $T_2$  representation has an  $(x,y,z)$  function, and therefore the two  $T_2$  vibrational modes are IR active. The character table also shows that the  $T_2$  modes are Raman active. The  $A_1$  and  $E$  modes are IR inactive, but Raman active. The IR spectra of species such as  $\text{CCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{OsO}_4$ ,  $[\text{ClO}_4]^-$  and  $[\text{SO}_4]^{2-}$  exhibit *two* absorptions (see Table 4.2).

There are nine normal modes of vibration for a square planar ( $D_{4h}$ )  $\text{XY}_4$  molecule. These are illustrated for  $[\text{PtCl}_4]^{2-}$  in Fig. 3.17, along with their appropriate symmetry labels. In the  $D_{4h}$  character table (see Appendix 3), the  $A_{2u}$

and  $E_u$  representations contain  $z$  and  $(x,y)$  functions, respectively. Therefore, of the vibrational modes shown in Fig. 3.17, only the  $A_{2u}$  and  $E_u$  modes are IR active. Since  $[\text{PtCl}_4]^{2-}$  contains an inversion centre, the rule of mutual exclusion applies, and the  $A_{2u}$  and  $E_u$  modes are Raman inactive. Similarly, the  $A_{1g}$ ,  $B_{1g}$  and  $B_{2g}$  modes that are Raman active, are IR inactive. Among compounds of the  $p$ -block elements,  $D_{4h}$   $\text{XY}_4$  structures are rare; the observation of absorptions at  $586$ ,  $291$  and  $161\text{ cm}^{-1}$  in the IR spectrum of  $\text{XeF}_4$  is consistent with the square planar structure predicted by the VSEPR model.

### Self-study exercises

1. Use the  $D_{4h}$  character table in Appendix 3 to confirm that the  $A_{1g}$ ,  $B_{1g}$  and  $B_{2g}$  modes of  $[\text{PtCl}_4]^{2-}$  are IR inactive, but Raman active. Why does this illustrate the rule of mutual exclusion?
2. The IR spectrum of gaseous  $\text{ZrI}_4$  shows absorptions at  $55$  and  $254\text{ cm}^{-1}$ . Explain why this observation is consistent with molecules of  $\text{ZrI}_4$  having  $T_d$  symmetry.
3. The  $[\text{PdCl}_4]^{2-}$  ion gives rise to three absorptions in its IR spectrum ( $150$ ,  $321$  and  $161\text{ cm}^{-1}$ ). Rationalize why this provides evidence for a  $D_{4h}$  rather than  $T_d$  structure.
4.  $\text{SiH}_2\text{Cl}_2$  is described as having a tetrahedral structure;  $\text{SiH}_2\text{Cl}_2$  has eight IR active vibrations. Comment on these statements.

### $\text{XY}_6$ molecules with $O_h$ symmetry

An  $\text{XY}_6$  molecule belonging to the  $O_h$  point group has  $(3 \times 7) - 6 = 15$  degrees of vibrational freedom. Figure 3.18 shows the modes of vibration of  $\text{SF}_6$  along with their symmetry labels. Only the  $T_{1u}$  modes are IR active; this can be confirmed from the  $O_h$  character table in Appendix 3.

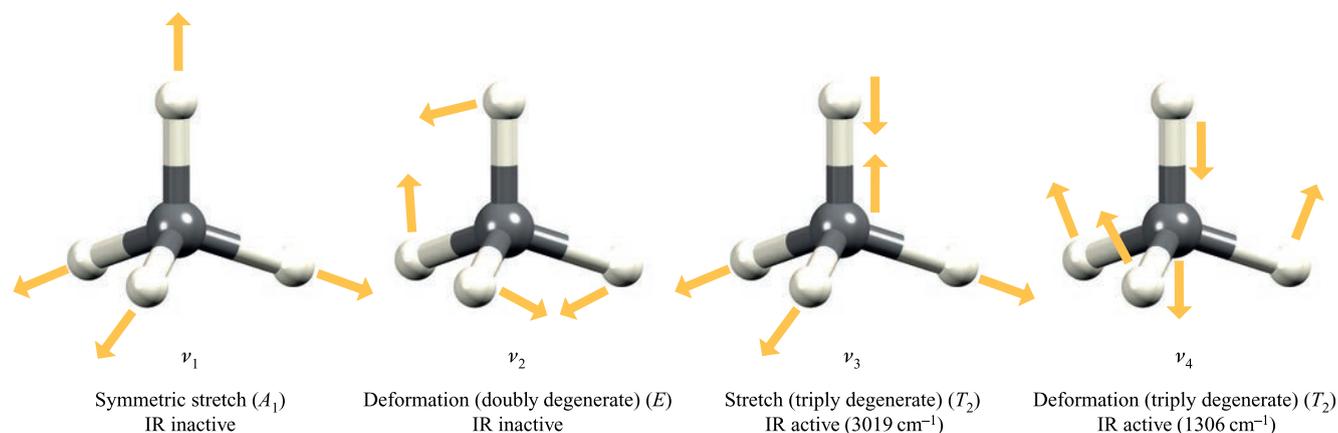
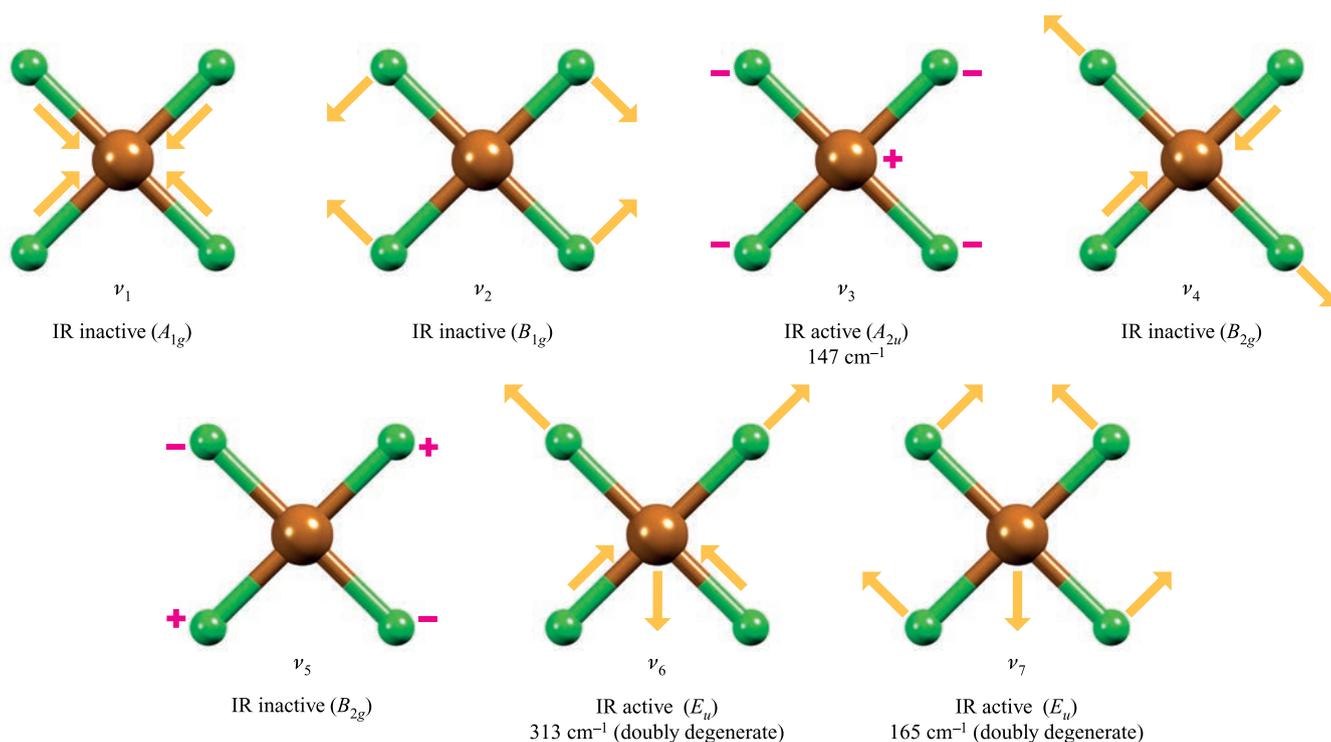


Fig. 3.16. The vibrational modes of  $\text{CH}_4$  ( $T_d$ ), only two of which are IR active.



**Fig. 3.17.** The vibrational modes of  $[\text{PtCl}_4]^{2-}$  ( $D_{4h}$ ); only the three modes (two of which are degenerate)  $\nu_3$ ,  $\nu_6$  and  $\nu_7$  are IR active. The + and – notation is used to show the ‘up’ and ‘down’ motion of the atoms during the mode of vibration.

Since the S atom in  $\text{SF}_6$  lies on an inversion centre, the  $T_{1u}$  modes are Raman inactive (by the rule of mutual exclusion). Of the  $T_{1u}$  modes shown in Fig. 3.18, one can be classified as a stretching mode ( $939\text{ cm}^{-1}$  for  $\text{SF}_6$ ) and one a deformation ( $614\text{ cm}^{-1}$  for  $\text{SF}_6$ ).

### Metal carbonyl complexes, $\text{M}(\text{CO})_n$

Infrared spectroscopy is especially useful for the characterization of metal carbonyl complexes  $\text{M}(\text{CO})_n$  since the absorptions arising from C–O bond stretching modes ( $\nu_{\text{CO}}$ ) are strong and easily observed in an IR spectrum. These modes typically give rise to absorptions close to  $2000\text{ cm}^{-1}$  (see Section 24.2) and these bands are usually well separated from those arising from M–C stretches, M–C–O deformations and C–M–C deformations. The  $\nu_{\text{CO}}$  modes can therefore be considered separately from the remaining vibrational modes. For example,  $\text{Mo}(\text{CO})_6$  belongs to the  $O_h$  point group. It has  $(3 \times 13) - 6 = 33$  modes of vibrational freedom, of which 12 comprise four  $T_{1u}$  (i.e. IR active) modes:  $\nu_{\text{CO}}$   $2000\text{ cm}^{-1}$ ,  $\delta_{\text{MoCO}}$   $596\text{ cm}^{-1}$ ,  $\nu_{\text{MoC}}$   $367\text{ cm}^{-1}$  and  $\delta_{\text{CMoC}}$   $82\text{ cm}^{-1}$ . The other 21 modes are all IR inactive. A routine laboratory IR spectrometer covers a range from  $\approx 400$  to  $4000\text{ cm}^{-1}$  and, therefore, only the  $\nu_{\text{CO}}$  and  $\delta_{\text{MoC}}$  modes are typically observed. We can confirm why an  $O_h$   $\text{M}(\text{CO})_6$  species exhibits only one absorption in the C–O stretching region by comparing it with  $\text{SF}_6$  (Fig. 3.18). The set of six C–O bonds in  $\text{M}(\text{CO})_6$  can be considered analogous to the set of six S–F bonds in  $\text{SF}_6$ . Therefore,

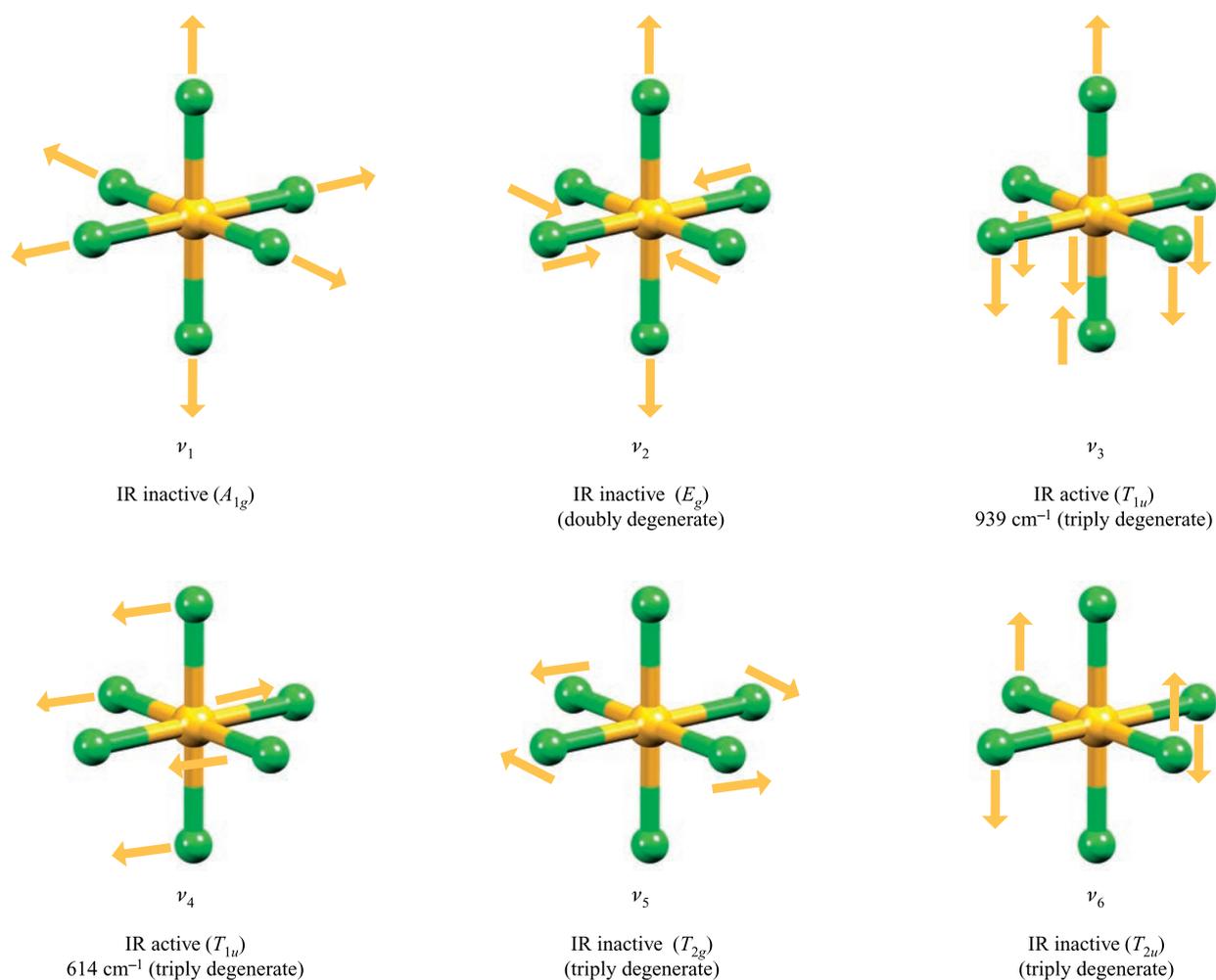
an  $O_h$   $\text{M}(\text{CO})_6$  molecule possesses  $A_{1g}$ ,  $E_g$  and  $T_{1u}$  carbonyl stretching modes, but only the  $T_{1u}$  mode is IR active.

### Self-study exercises

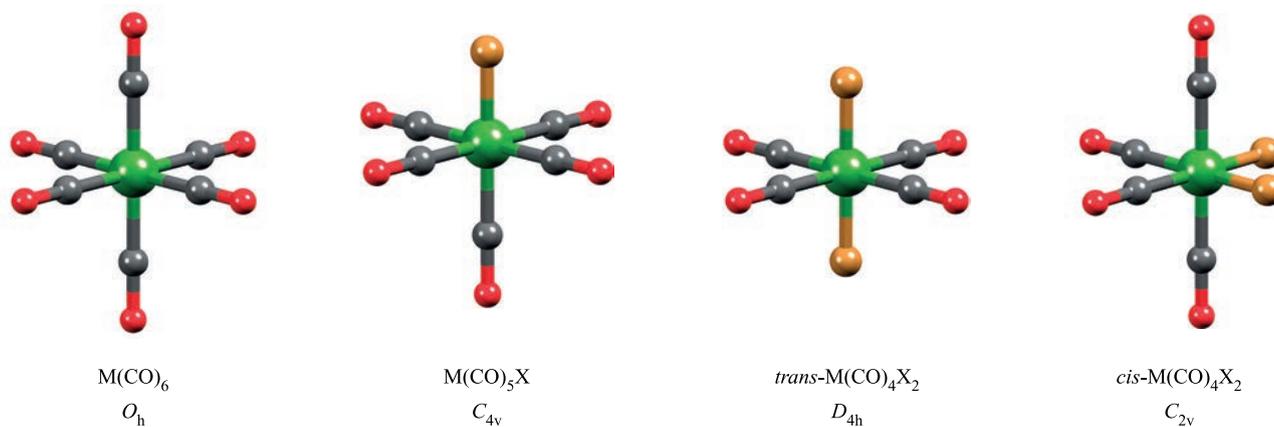
- By considering only the six CO groups in  $\text{Cr}(\text{CO})_6$  ( $O_h$ ), sketch diagrams to represent the  $A_{1g}$ ,  $E_g$  and  $T_{1u}$  stretching modes. Use the  $O_h$  character table to deduce which modes are IR active.  
[Ans. See Fig. 3.18; each C–O acts in the same way as an S–F bond]
- In its IR spectrum,  $\text{W}(\text{CO})_6$  exhibits an absorption at  $1998\text{ cm}^{-1}$ . Sketch a diagram to show the mode of vibration that corresponds to this absorption.  
[Ans. Analogous to the IR active  $T_{1u}$  mode in Fig. 3.18]

### Metal carbonyl complexes $\text{M}(\text{CO})_{6-n}\text{X}_n$

In this section, we illustrate the relationship between the numbers of IR active  $\nu_{\text{CO}}$  modes and the symmetries of  $\text{M}(\text{CO})_{6-n}\text{X}_n$  complexes. The metal carbonyls  $\text{M}(\text{CO})_6$ ,  $\text{M}(\text{CO})_5\text{X}$ , *trans*- $\text{M}(\text{CO})_4\text{X}_2$  and *cis*- $\text{M}(\text{CO})_4\text{X}_2$  are all described as being ‘octahedral’ but only  $\text{M}(\text{CO})_6$  belongs to the  $O_h$  point group (Fig. 3.19). We saw above that an  $O_h$   $\text{M}(\text{CO})_6$  complex exhibits one absorption in the CO stretching region of its IR spectrum. In contrast,  $C_{4v}$



**Fig. 3.18.** The vibrational modes of  $\text{SF}_6$  ( $O_h$ ). Only the  $T_{1u}$  modes are IR active.

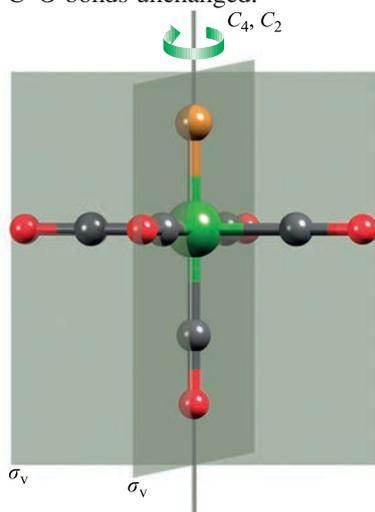


**Fig. 3.19.** Point groups of octahedral metal carbonyl complexes  $\text{M}(\text{CO})_6$ ,  $\text{M}(\text{CO})_5\text{X}$ , *trans*- $\text{M}(\text{CO})_4\text{X}_2$  and *cis*- $\text{M}(\text{CO})_4\text{X}_2$ . Colour code: metal M, green; C, grey; O, red; group X, brown.

$\text{M}(\text{CO})_5\text{X}$  shows three absorptions, e.g. in the IR spectrum of  $\text{Mn}(\text{CO})_5\text{Br}$ , bands are observed at 2138, 2052 and 2007  $\text{cm}^{-1}$ . The origins of these bands can be understood by using group theory. Consider how many C–O bonds in the  $\text{M}(\text{CO})_5\text{X}$  molecule (Fig. 3.19) are left *unchanged* by each symmetry operation ( $E$ ,  $C_4$ ,  $C_2$ ,  $\sigma_v$  and  $\sigma_d$ ) of

the  $C_{4v}$  point group (the  $C_{4v}$  character table is given in Appendix 3). The diagram on the next page shows the  $C_4$  and  $C_2$  axes and the  $\sigma_v$  planes of symmetry. The  $\sigma_d$  planes bisect the  $\sigma_v$  planes (look at Fig. 3.4). The  $E$  operator leaves all five C–O bonds unchanged, while rotation around each axis and reflection through a  $\sigma_d$  plane leaves

one C–O bond unchanged. Reflection through a  $\sigma_v$  plane leaves three C–O bonds unchanged.



The results can be summarized in the following row of characters:

$E$	$C_4$	$2C_2$	$\sigma_v$	$\sigma_d$
5	1	1	3	1

This representation can be reduced to rows of characters from the  $C_{4v}$  character table:

$A_1$	1	1	1	1	1
$A_1$	1	1	1	1	1
$B_1$	1	-1	1	1	-1
$E$	2	0	-2	0	0
Sum of rows	5	1	1	3	1

The vibrational modes of  $M(CO)_5X$  therefore have  $A_1$ ,  $B_1$  and  $E$  symmetries and the  $C_{4v}$  character table shows that only the two  $A_1$  and the  $E$  modes are IR active, consistent with the observation of three absorptions in the IR spectrum.

A similar strategy can be used to determine the number of IR active modes of vibration for *cis*- and *trans*- $M(CO)_4X_2$ , as well as for other complexes. Table 3.5 gives representative examples.

### Self-study exercises

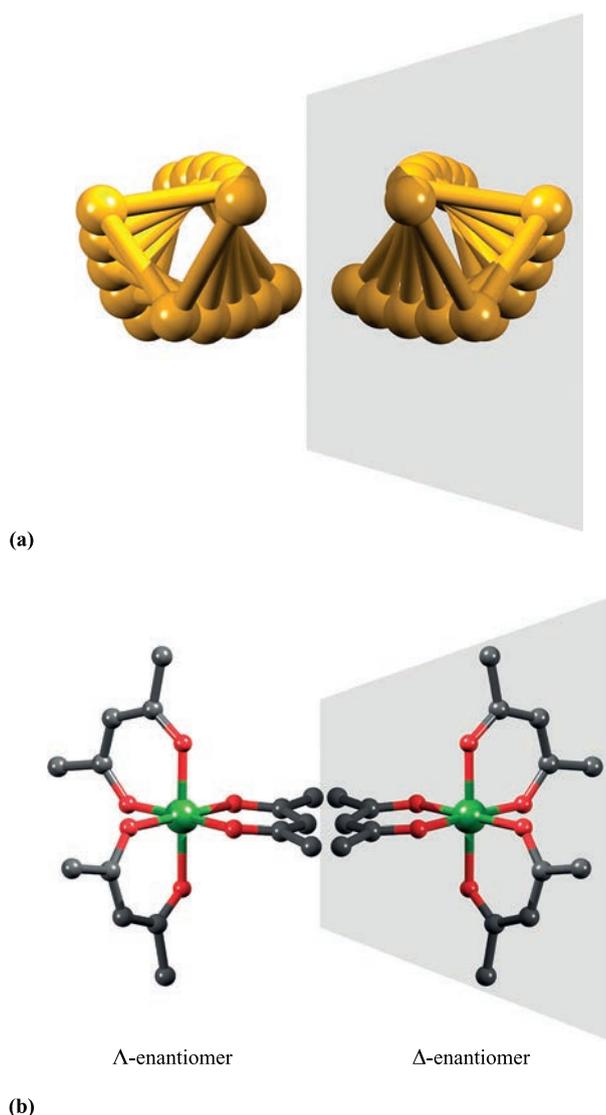
1. Draw a diagram to show the structure of *fac*- $M(CO)_3X_3$ . Mark on the  $C_3$  axis and one of the  $\sigma_v$  planes.
2. Using the  $C_{3v}$  character table (Appendix 3), confirm that the CO stretching modes of *fac*- $M(CO)_3X_3$  have  $A_1$  and  $E$  symmetries. Confirm that both are IR active.
3. Rationalize why the IR spectrum of *fac*- $[Fe(CO)_3(CN)_3]^-$  has two strong absorptions at 2121 and 2096  $\text{cm}^{-1}$ , as well as two weaker bands at 2162 and 2140  $\text{cm}^{-1}$ .  
[Ans. See: J. Jiang *et al.* (2002) *Inorg. Chem.*, vol. 41, p. 158.]

### Observing IR spectroscopic absorptions

In this section we have focused on how to establish the number of vibrational degrees of freedom for a simple molecule with  $n$  atoms, how to deduce the total number of normal modes of vibration for the molecule and how to determine the number of absorptions in its IR spectrum. We expand the discussion at a practical level in Section 4.5.

**Table 3.5** Carbonyl stretching modes ( $\nu_{CO}$ ) for some families of mononuclear metal carbonyl complexes; X is a general group other than CO.

Complex	Point group	Symmetries of CO stretching modes	IR active modes	Number of absorptions observed in the IR spectrum
$M(CO)_6$	$O_h$	$A_{1g}, E_g, T_{1u}$	$T_{1u}$	1
$M(CO)_5X$	$C_{4v}$	$A_1, A_1, B_1, E$	$A_1, A_1, E$	3
<i>trans</i> - $M(CO)_4X_2$	$D_{4h}$	$A_{1g}, B_{1g}, E_u$	$E_u$	1
<i>cis</i> - $M(CO)_4X_2$	$C_{2v}$	$A_1, A_1, B_1, B_2$	$A_1, A_1, B_1, B_2$	4
<i>fac</i> - $M(CO)_3X_3$	$C_{3v}$	$A_1, E$	$A_1, E$	2
<i>mer</i> - $M(CO)_3X_3$	$C_{2v}$	$A_1, A_1, B_1$	$A_1, A_1, B_1$	3



**Fig. 3.20.** A pair of enantiomers consists of two molecular species which are mirror images of each other and are non-superposable. (a) Helical  $\text{Se}_\infty$  has either right- or left-handedness. (b) The 6-coordinate complex  $[\text{Cr}(\text{acac})_3]$  contains three identical bidentate, chelating ligands; the labels  $\Lambda$  and  $\Delta$  describe the absolute configuration of the molecule (see Box 19.3).

### 3.8 Chiral molecules

A molecule is *chiral* if it is non-superposable on its mirror image.<sup>†</sup>

Helical chains such as  $\text{Se}_\infty$  (Fig. 3.20a) may be right- or left-handed and are chiral. 6-Coordinate complexes such as  $[\text{Cr}(\text{acac})_3]$  ( $[\text{acac}]^-$ , see Table 7.8) in which there are three bidentate chelating ligands also possess non-superposable mirror images (Fig. 3.20b). Chiral molecules can rotate the plane of plane-polarized light. This property is

<sup>†</sup> This definition is taken from ‘Basic terminology of stereochemistry: IUPAC recommendations 1996’ (1996) *Pure Appl. Chem.*, vol. 68, p. 2193.

known as *optical activity* and the two mirror images are known as *optical isomers* or *enantiomers*. We return to this in Chapter 19.

The importance of chirality is clearly seen in, for example, dramatic differences in the activities of different enantiomers of chiral drugs.<sup>‡</sup>

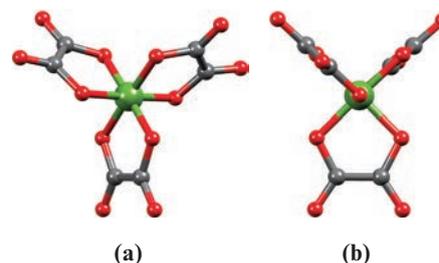
A helical chain such as  $\text{Se}_\infty$  is easy to recognize, but it is not always such a facile task to identify a chiral compound by attempting to convince oneself that it is, or is not, non-superposable on its mirror image. Symmetry considerations come to our aid:

A *chiral* molecule lacks an improper ( $S_n$ ) axis of symmetry.

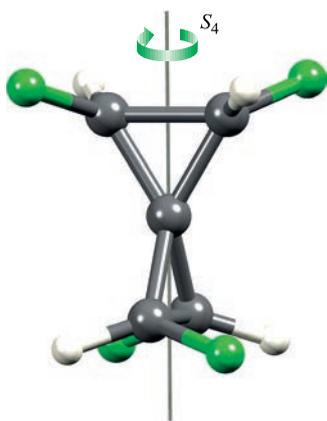
Another commonly used criterion for identifying a chiral species is the lack of an inversion centre,  $i$ , and plane of symmetry,  $\sigma$ . However, both of these properties are compatible with the definition given above, since we can rewrite the symmetry operations  $i$  and  $\sigma$  in terms of the improper rotations  $S_2$  and  $S_1$  respectively. (See end-of-chapter problem 3.35.) A word of caution: there are a few species that are non-chiral (achiral) despite lacking an inversion centre,  $i$ , and plane of symmetry,  $\sigma$ . These ‘problem’ species belong to an  $S_n$  point group in which  $n$  is an even number. An example is the tetrafluoro derivative of spiro-pentane shown in Fig. 3.21. This molecule does not contain an inversion centre, nor a mirror plane, and might therefore be thought to be chiral. However, this conclusion is incorrect because the molecule contains an  $S_4$  axis.

#### Worked example 3.9 Chiral species

The oxalate ligand,  $[\text{C}_2\text{O}_4]^{2-}$ , is a bidentate ligand and the structure of the complex ion  $[\text{Cr}(\text{ox})_3]^{3-}$  is shown below. The view in the right-hand diagram is along one O–Cr–O axis. Confirm that the point group to which the ion belongs is  $D_3$  and that members of this point group are chiral.



<sup>‡</sup> Relevant articles are: E. Thall (1996) *J. Chem. Educ.*, vol. 73, p. 481 – ‘When drug molecules look in the mirror’; H. Caner *et al.* (2004) *Drug Discovery Today*, vol. 9, p. 105 – ‘Trends in the development of chiral drugs’; M.C. Núñez *et al.* (2009) *Curr. Med. Chem.*, vol. 16, p. 2064 – ‘Homochiral drugs: a demanding tendency of the pharmaceutical industry’; F. Arnesano *et al.* (2015) *Coord. Chem. Rev.*, vol. 284, p. 286 – ‘Effect of chirality in platinum drugs’.



**Fig. 3.21.** A tetrafluoro derivative of spiropentane which belongs to the  $S_4$  point group. This is an example of a molecule that contains no inversion centre and no mirror plane but is, nonetheless, achiral.

Using the scheme in Fig. 3.10:

**START**  $\Rightarrow$

Is the molecular ion linear?	No
Does it have $T_d$ , $O_h$ or $I_h$ symmetry?	No
Is there a $C_n$ axis?	Yes; a $C_3$ axis; perpendicular to

Are there three $C_2$ axes perpendicular to the principal axis?	Yes; one runs vertically, in the plane of the paper through the Fe centre in diagram (b)
Is there a $\sigma_h$ plane (perpendicular to the principal axis)?	No
Are there $n$ $\sigma_d$ planes (containing the principal axis)?	No

$\Rightarrow$  **STOP**

The point group is  $D_3$ .

No centre of symmetry or planes of symmetry have been identified and this confirms that molecular species in the  $D_3$  point group are chiral.

### Self-study exercise

By referring to the character table (Appendix 3) for the  $D_3$  point group, confirm that the symmetry elements of the  $D_3$  point group do not include  $i$ ,  $\sigma$  or  $S_n$  axis.

## KEY TERMS

The following terms have been introduced in this chapter. Do you know what they mean?

- |  |   |   |
|--|---|---|
| <input type="checkbox"/> symmetry element  | <input type="checkbox"/> improper rotation axis ( $S_n$ ) | <input type="checkbox"/> selection rule for an IR active mode   |
| <input type="checkbox"/> symmetry operator   | <input type="checkbox"/> point group                      | <input type="checkbox"/> selection rule for a Raman active mode |
| <input type="checkbox"/> identity operator ( $E$ )                                     | <input type="checkbox"/> translational degrees of freedom | <input type="checkbox"/> rule of mutual exclusion               |
| <input type="checkbox"/> rotation axis ( $C_n$ )                                       | <input type="checkbox"/> rotational degrees of freedom    | <input type="checkbox"/> fundamental absorption                 |
| <input type="checkbox"/> plane of reflection ( $\sigma_h$ , $\sigma_v$ or $\sigma_d$ ) | <input type="checkbox"/> vibrational degrees of freedom   | <input type="checkbox"/> chiral                                 |
| <input type="checkbox"/> centre of symmetry or inversion centre ( $i$ )                | <input type="checkbox"/> normal mode of vibration         | <input type="checkbox"/> enantiomer (optical isomer)            |
|  | <input type="checkbox"/> degenerate modes of vibration    |   |

## FURTHER READING

### Symmetry and group theory

- P.W. Atkins, M.S. Child and C.S.G. Phillips (1970) *Tables for Group Theory*, OUP, Oxford – A set of character tables with useful additional notes and symmetry diagrams.
- R.L. Carter (1998) *Molecular Symmetry and Group Theory*, Wiley, New York – An introduction to molecular symmetry and group theory as applied to chemical problems including vibrational spectroscopy.
- M.E. Cass, H.S. Rzepa, D.R. Rzepa and C.K. Williams (2005) *J. Chem. Educ.*, vol. 82, p. 1736 – ‘The use of the free, open-source program Jmol to generate an interactive web site to teach molecular symmetry’.
- F.A. Cotton (1990) *Chemical Applications of Group Theory*, 3rd edn, Wiley, New York – A more mathematical treatment of symmetry and its importance in chemistry.
- G. Davidson (1991) *Group Theory for Chemists*, Macmillan, London – An excellent introduction to group theory with examples and exercises.
- S.F.A. Kettle (2007) *Symmetry and Structure*, 3rd edn, Wiley, Chichester – A detailed, but readable, account of symmetry and group theory.
- R. McWeeny (2002) *Symmetry: An Introduction to Group Theory and its Applications*, Dover Publications, New York – A well-tested book on group theory.
- K.C. Molloy (2011) *Group Theory for Chemists: Fundamental Theory and Applications*, 2nd edn, Woodhead Publishing, Oxford – A well-organized coverage of symmetry, group theory and its applications in spectroscopy and bonding.
- J.S. Ogden (2001) *Introduction to Molecular Symmetry*, OUP, Oxford – A concise introduction to group theory and its applications.