1

Some Aspects of Structure and Bonding in Main Group Chemistry

Aims

By the end of this chapter you should understand:

- The concepts of ionization energy and electronegativity in surveying the periodic trends in the properties of the oxides, chlorides and hydrides of the main group elements
- The use of valence shell electron pair repulsion theory (VSEPR) in predicting molecular shapes, and basic molecular orbital (MO) theory for describing the bonding in diatomic molecules

1.1 Introduction

As a prelude to discussion of the chemistry of the main group elements, this chapter aims to introduce aspects of the structure and bonding of main group compounds. It is assumed that the reader has a basic understanding of atomic structure and bonding. We will start by discussing the concepts of ionization energy, electron affinity and electronegativity, which provide a framework for a brief overview of the chemistry of the main group elements, setting the scene for the detailed chemistry described in subsequent chapters. Valence shell electron pair repulsion theory (VSEPR), a powerful but simple theory for predicting and rationalizing the shapes adopted by main group compounds, is then discussed. The concept of molecular orbital theory will then be briefly covered.

More correctly, ionization energies and electron affinities should be referred to as **ionization enthalpies** and **electron attachment enthalpies**, respectively, though energies are commonly used.

1.2 Ionization Energy, Electron Affinity and Electronegativity

When an element forms a chemical compound, electrons are either lost, gained or shared with other atoms. These tendencies can be assessed by the parameters of **ionization energy** (IE), **electron affinity** (EA) and **electronegativity**. Prediction of bond types as either ionic or covalent allows prediction of the chemical and physical properties of chemical substances.

Ionization energies (kJ mol^{-1})

Element	K	Al
First IE	+425	+584
Second IE	+3058	+1823
Third IE	+4418	+2751

IE refers to the loss of an electron from a gaseous atom or ion (equation 1.1). Successive loss of electrons from an atom becomes increasingly difficult (because the resulting positive ion holds on to its remaining electrons even more strongly), so, for example, third IEs are always higher than second IEs, which in turn are higher than first.

$$M^{n+}_{(g)} \rightarrow M^{(n+1)+}_{(g)} + e^- \qquad (1.1)$$

First IEs (kJ mol^{-1})

Li	+526
Na	+502
K	+425
Rb	+409
Cs	+382

Going down a group, IEs decrease. Atoms increase in size and the electron to be removed is further from the nucleus; although the nuclear size is much increased, outer electrons are shielded by completed, filled, inner shells, so the **effective nuclear charge** felt by an outer electron is much less.

Crossing the Periodic Table, first IEs increase because extra protons are being added to the nucleus, and electrons are being added to the same electron shell (Figure 1.1). These electrons are not very efficient at screening each other from the nuclear charge, so they are attracted more strongly by the nucleus and are harder to ionize. Removal of an elec-

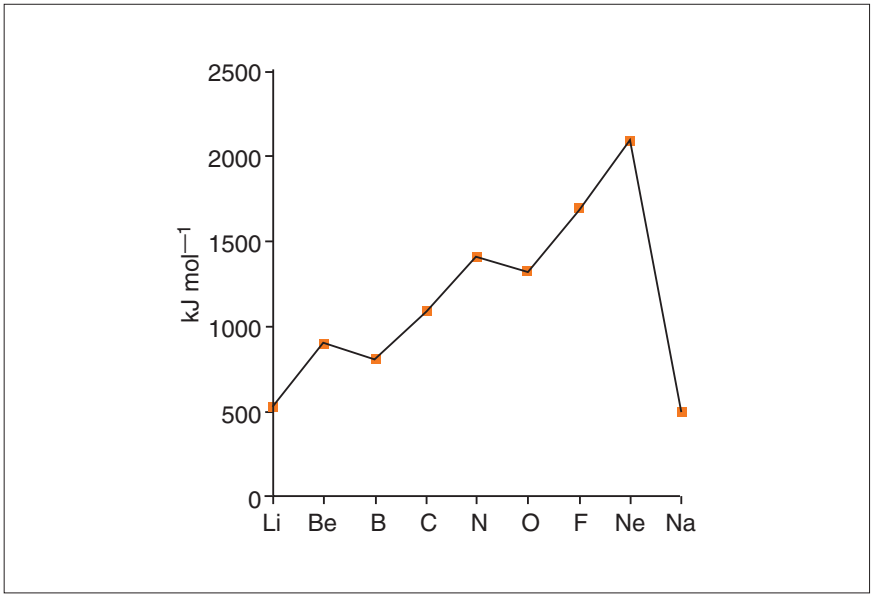
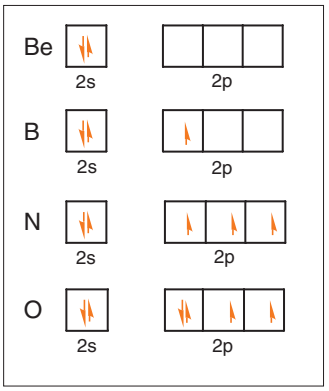


Figure 1.1 First ionization energies for the elements Li to Na

tron from a filled shell requires a large amount of energy: the first IE of neon is very high in comparison to the next element, sodium, where loss of an electron will leave a filled shell; Group 1 metals therefore have low first IEs but very high second IEs.

Superimposed on the general trend of increased IE with atomic number within a period, are 'kinks' at boron and oxygen. For beryllium, the 2s level is filled, so going to boron involves adding an electron to one of the 2p orbitals. Despite the increase in nuclear charge there is a decrease in IE because of the relatively efficient shielding of the 2p electron by the 2s electrons. At nitrogen, the three 2p orbitals each contain one electron (Hund's rule), so going to oxygen involves pairing an electron in one of the 2p orbitals. The two electrons in the same orbital repel each other, so the first IE of oxygen is lower than that of nitrogen, because loss of one of the paired electrons is assisted by electron–electron repulsions.



Worked Problem 1.1

Q Figure 1.2 shows the variation in second ionization energy for the elements Li to Na. Comment on the shape of the graph by comparison with first ionization energies of the same elements (Figure 1.1).

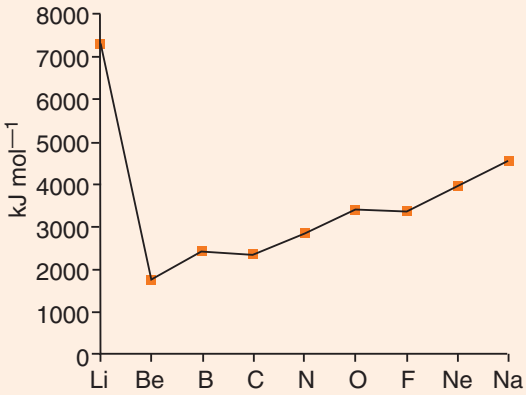


Figure 1.2 Second ionization eneergies for the elements Li to Na

A The same general trend is observed, with a general increase in second IE with increasing atomic number; for a given element the second IE is much higher than the first IE because it involves removal of an electron from a positive ion. The lowest second IE is for Be, since this involves the loss of the second 2s electron,

leaving a filled $1s^2$ shell, and the highest second IE is for Li, since this involves loss of one of the 1s electrons (the sole 2s electron is lost in the first IE of Li). The kinks in the graph of second IE are similar of those in the first IE graph, except that the 'pattern' is shifted one element to the right. Thus, the decrease in first IE which occurs from N to O occurs in the second IE graph from O to F, because the process involves the loss of the same electrons.

Electron affinity (EA) is defined as the energy change on addition of an electron to a gaseous atom or ion (equation 1.2).

$$X^{n-}_{(g)} + e^- \rightarrow X^{(n+1)-}_{(g)} \qquad (1.2)$$

First electron affinities (kJ mol^{-1})

F	–322
Cl	–349
Br	–325
I	–295

EAs are most negative for elements in the top right of the Periodic Table (*i.e.* the halogens), while second and higher EAs are always positive because it is more difficult to add an electron to an already negatively charged ion. EAs also become positive on adding electrons to a new shell, so the first EAs of oxygen, fluorine and neon are –141, –322 and +29 kJ mol^{-1}, respectively. Trends in EA are generally less simple than trends in IE.

When we consider IEs and EAs together, elements in the bottom-left corner of the Periodic Table have low IEs and EAs and readily lose electrons to form cations, whereas elements in the top-right corner (the halogens, oxygen and sulfur) have high IEs and large negative EAs and readily gain electrons to form anions. Elements in the middle (particularly the lighter elements) have intermediate IEs and EAs and generally form covalent bonds in their compounds. However, unequal electron sharing results in polar bonds, and this is best discussed in terms of atom electronegativities.

Electronegativity refers to the tendency of an atom, *in a molecule*, to attract electrons to itself. A scale of electronegativity was devised by Linus Pauling, based on bond energies. While several other electronegativity scales have been developed, the one by Pauling is still widely used. The most electronegative elements are in the top right of the Periodic Table, with fluorine being the most electronegative with the maximum value of 4.0 on the Pauling scale.

Some electronegativities (Pauling scale)

F	4.0
Cl	3.0
O	3.5
N	3.0
S	2.5
C	2.5
H	2.1
B	2.0
Na	0.9

Electronegativity is a useful general parameter for predicting the general chemical behaviour of an element, and gives good indications of bond types. In general terms, two elements with a large electronegativity difference will tend to form ions, though smaller electronegativity differences are needed when one of the compounds is a highly electropositive metal (*e.g.* of Group 1). Two elements with similar and intermediate electronegativities (around 2.5) will tend to form covalent

compounds. This is illustrated by C and H, which form an extensive range of covalently bonded organic compounds.

1.3 Periodic Trends among the Main Group Elements

The main group elements, and their chemical compounds, cover a wide range of bonding types, from ionic, through polymeric, to molecular. In this section we will survey the general features of the chemistry of the main group elements and selected compounds, using the variation in electronegativity of the elements as a qualitative tool for rationalizing the features. The compounds surveyed are the hydrides, oxides and chlorides, which are some of the most important compounds, and which illustrate the general features very well. More detailed discussion of individual compounds can be found within the appropriate chapter.

1.3.1 The Elements

Main group elements can be roughly classified as metals with an electronegativity <2, and as non-metals with electronegativities >2.2.

It is noteworthy that the p block is the only part of the Periodic Table to contain non-metallic elements. There is a general trend from metallic elements at the bottom left of the Periodic Table (the s-block metals) to non-metallic elements at the top right of the Table (the halogens and noble gases) (Figure 1.3). This correlates very well with the electronegativities of the elements. Metals are good conductors of heat and electricity, and in solid metals the electrons are extensively delocalized over the whole material. Non-metallic elements are insulators and have no delocalized bonding, instead being formed from localized covalent bonds. In the centre of the p block, there are also so-called **metalloid** elements such as boron and silicon, which show intermediate electronegativities; they also show relatively low electrical conductivity (compared to metals), but it increases with temperature.

The change in properties is nicely illustrated by looking at the first long period, Na to Ar. Na and Mg are both electropositive metals; the next element, aluminium, is a metal, but shows several characteristics of non-metals in forming many covalent compounds. In Group 14, silicon is a metalloid, the element being a semiconductor, and has compounds which show characteristics of both metal compounds and non-metal compounds. By the time we get to phosphorus in Group 15, we are truly in the domain of non-metals; phosphorus exists in several elemental forms, all of which contain covalent P–P bonds. In Groups 16 (sulfur) and 17 (chlorine) the elements are also true non-metals, sulfur existing as covalent S_8 rings (and other forms), and chlorine forming diatomic, covalently bonded molecules. Argon exists as a monoatomic gas under ambient conditions, and does not participate in chemical bonding owing

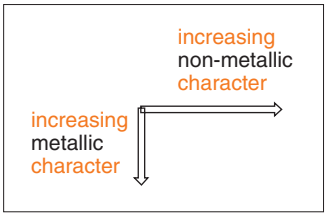


Figure 1.3 Variation in metallic and non-metallic character in the Periodic Table

to the filled valence shell of electrons, and high ionization energy.

Going down any of the main groups, elements become more metallic in character, paralleled by a decrease in electronegativity.

1.3.2 Main Group Element Hydrides

The chemistry of hydrides is discussed in Section 2.4.

The properties of the main group element hydrides range from ionic (for the s-block metals, with the exception of beryllium), through polymeric (AlH_3), to molecular covalent hydrides for the elements of Groups 14–17.

In Groups 1 and 2, the metals are less electronegative than hydrogen (Pauling scale electronegativities: Na 0.9, H 2.1), so the bonding in the hydrides of these metals is predominantly ionic, as M^+H^-; these hydrides react violently with water, generating H_2 gas. For boron and beryllium, the electronegativity diference between the element and hydrogen is small. BeH_2 is covalent and boron hydrides are covalent clusters. In Group 14 the hydrides are all covalent molecular species, typified by CH_4. Continuing across the Periodic Table, to Groups 15, 16 and 17, the hydrides are all molecular covalent species, with acidity in aqueous solution increasing on moving to the right, as the electronegativity difference between the element and hydrogen increases and the H–X bond becomes more polarized: $H^{\delta+}$–$X^{\delta-}$. This has a marked effect on the physical properties (*e.g.* boiling points) of the hydrides of electronegative elements, as described in Section 2.6.1.

Worked Problem 1.2

Q Predict the properties of the hydrides formed by elements with electronegativities of (a) 0.9 and (b) 3.5.

A (a) An element with an electronegativity of 0.9 is a metal; it will probably form an ionic hydride which will react with water, giving hydrogen and a basic solution of the hydroxide. (b) This element is a non-metal, and the hydride will be covalent with a polar H–X bond and will dissolve in water, probably giving a neutral to acidic solution.

1.3.3 Main Group Element Chlorides

Like the hydrides, the properties of the chlorides follow a broadly similar pattern, with chlorides of metals being ionic and of non-metals being covalent molecular in structure. Thus, for the Group 1 and 2 metals (except beryllium) the chlorides are ionic solids which form neutral solu-

tions in water. The chlorides of small, highly polarizing metal ions such as beryllium, aluminium, gallium and some other elements are polymeric in the solid state. The majority of the chlorides of the Groups 14 and 15 elements, and BCl_3, are molecular covalent species. The chlorides of the p-block elements and beryllium generally give acid solutions in water, because they react with it rather than simply dissolving. It is noteworthy that CCl_4, unlike $SiCl_4$, does not react with water to give an acidic solution; this is purely a kinetic effect, and is discussed in Section 6.5.1.

1.3.4 Main Group Element Oxides

For main group oxides, there is a similar trend from ionic oxides for the bottom left elements, through polymeric oxides in the centre (many of which are **amphoteric**), to molecular covalent oxides for the elements of higher electronegativity on the right-hand side of the p block.

An amphoteric oxide dissolves in both acidic and basic (alkaline) solutions.

Oxygen is the second most electronegative element, so in combination with (low electronegativity) Group 1 and 2 metals at the left-hand side of the Periodic Table, the resulting oxides are ionic. Examples include Na_2O and CaO. Such oxides are basic oxides, giving highly alkaline solutions in water (equation 1.3). On moving to the right, to Group 13, the oxides such as B_2O_3 and Al_2O_3 are polymeric and Al_2O_3 is amphoteric. In Group 14 the oxides of the lightest element, carbon, such as CO and CO_2, are molecular oxides; in marked contrast, SiO_2 is a polymeric oxide. CO_2 is an example of an acidic oxide, since it dissolves in water giving an acidic solution (see Section 6.7.1). In Groups 15 and 16 the oxides of nitrogen are all molecular covalent species, many of which are acidic, while those of sulfur (SO_2 and SO_3) are both acidic oxides (equation 1.4). Likewise, in Group 17, and for xenon in Group 18, the oxides are molecular species.

$$Na_2O_{(s)} + H_2O_{(l)} \rightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} \quad (1.3)$$

$$SO_{3(s)} + H_2O_{(l)} \rightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)} \quad (1.4)$$

1.4 Valence Shell Electron Pair Repulsion Theory

1.4.1 Introduction

A cursory inspection of the compounds formed by the p-block elements in subsequent chapters reveals that many structures are observed. Even for a certain fixed number of groups around a central atom, there are often different geometrical ways of arranging these; for example, five-coordinate species may be either trigonal bipyramidal or square pyramidal.

The shape of a molecule is described by the spatial arrangement of the atoms, disregarding the positions of any **lone pairs** (often called **non-bonding pairs**). Thus, ammonia, NH_3, is pyramidal, even though the N has four pairs of electrons in its valence shell, arranged approximately tetrahedrally.

The simplest and most widely practised method for shape prediction is **valence shell electron pair repulsion theory (VSEPR)**, originally developed in the 1960s, and recently redeveloped by Gillespie.[1] Prediction (or ideally knowledge) of molecular shapes is important for prediction of properties dependent on molecular shape, for example boiling points. The knowledge of bond polarity, determined using the concept of electronegativity, is also important.

1.4.2 Basic Principles of VSEPR

The basic premise of VSEPR is that *pairs of electrons* in the *valence shell* of the central atom of a molecule *repel* each other and take up positions as far apart as possible. The core electrons, which cannot easily be polarized, are conveniently ignored. The shape of a molecule thus condenses to a simple geometrical 'points-on-a-sphere' model, and the basic shapes adopted by molecules with between two and six pairs of electrons on the central atom are given in Table 1.1. In order to predict the *basic* shape of a molecule or ion by VSEPR, the general procedure in Box 1.1 should be followed. It is important to note that the shape of a molecule or ion can be predicted without knowing anything about the bonding in that species (see Section 1.5).

Table 1.1 Shapes of molecules and ions

Number of central atom electron pairs	*Bonding pairs*	*Non-bonding pairs*	*Shape*	*Example*
2	2	0	Linear	$BeCl_2$
3	3	0	Triangular	BF_3
3	2	1	Bent	$SnCl_2$
4	4	0	Tetrahedral	CCl_4
4	3	1	Pyramidal	NH_3
4	2	2	Bent	H_2O
5	5	0	Trigonal bipyramidal (tbp)	PF_5
5	4	1	Pseudo-tbp	BrF_4^+, SF_4
5	3	2	T-shaped	BrF_3
5	2	3	Linear	XeF_2
6	6	0	Octahedral	SF_6, PF_6^-
6	5	1	Square pyramidal	IF_5
6	4	2	Square planar	XeF_4, IF_4^-

Box 1.1 Predicting the Shapes of Molecules and Ions using VSEPR

1. Draw a simplified Lewis structure for the molecule, noting the presence of any formal double, triple and dative bonds. The presence of a charge on the central atom should also be identified; if the charge is not on the central atom, then it can be ignored.
2. Count electrons on the central atom, taking the central atom as a neutral atom. An atom in Group 14 will have four valence electrons, an atom in Group 15 will have five, *etc.*
3. Add one electron for every atom σ-bonded to the central atom, but two electrons from any dative bonds from other atoms.
4. Subtract one electron for every π-bond present involving the central atom.
5. If the central atom has a positive charge, subtract the appropriate number of electrons, or add the appropriate number of electrons if it has a negative charge.
6. Thus obtain the number of *electron pairs* on the central atom. By consulting Table 1.1, the basic shape of the molecule can then be determined.

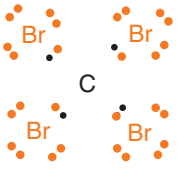
Worked Problem 1.3

Q Predict the shape of carbon tetrabromide, CBr_4.

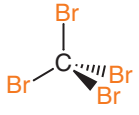
A Carbon is in Group 14, and has four valence electrons; σ-bonds to four Br atoms contribute a total of four electrons. The central atom has no charge, so there are eight electrons, or four pairs, on the carbon. There are four bonding pairs and four Br atoms to be bonded, so the shape is therefore a regular tetrahedron.

The bond angles in a regular tetrahedron are all 109.5°.

Lewis structure:



Shape:



(tetrahedral)

Box 1.2 Hybridization

The concept of hybridization is used to combine atomic orbitals on an atom to generate suitable orbitals which point in the directions required. The hybridization of a carbon 2s-orbital with three carbon 2p-orbitals generates four equivalent sp^3 hybrid orbitals, which point towards the vertices of a regular tetrahedron, so the carbon in CBr_4 can be considered to be sp^3 hybridized. Similarly, for bond angles of 120° or 180°, sp^2 or sp hybrids can be used, while in a trigonal bipyramid sp^3d hybrids, and in an octahedron sp^3d^2 hybrids, point in the required directions, and so can accommodate the electron pairs identified in the VSEPR analysis.

The role of hybridization must be kept in perspective: it is a mathematical means of generating orbitals pointing in the required directions.

1.4.3 Molecules containing Non-bonding Pairs of Electrons

A bonding pair is shared by *two atoms* whereas a lone pair is only held by *one atom*. A lone pair therefore occupies more space in the valence shell of the atom to which it belongs, and it will exert a larger repulsive influence on the other pairs of electrons on that atom. Therefore, in general terms:

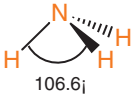
lone pair–lone pair repulsion > lone pair–bonding pair repulsion > bonding pair–bonding pair repulsion

This is best illustrated by two worked examples: ammonia, NH_3, and water, H_2O.

Worked Problem 1.4

Q Predict the shape of the ammonia molecule.

A Nitrogen has five valence electrons; three σ-bonds to H contribute three electrons. Thus there is a total of eight electrons, or four pairs, and therefore the *distribution of electron pairs* is **tetrahedral**. Since there are four pairs of electrons and three hydrogens, there is a lone pair. Hence the *shape of the molecule* is described as **trigonal pyramidal**. The lone pair will occupy more space in the valence shell of N, so the N–H bonds will be pushed towards each other slightly, decreasing the H–N–H bond angle from that of a regular tetrahedron.

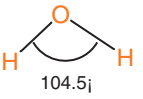


xperimentally determined shape of ammonia

Worked Problem 1.5

Q Predict the shape of water.

A The oxygen of water also has four pairs of valence electrons. The geometry of the water molecule is now described as **bent**, and since there are two lone pairs on oxygen, these try to repel each other slightly more, and so the hydrogens are pushed slightly closer, reducing the H–O–H angle from that in a regular tetrahedron even further.



erimentally determined shape of water

1.4.4 Molecules with Multiple Bonds

A double bond contains both σ and π components. For the purposes of VSEPR, both can be considered to point in the same direction, and we can thus treat a double or triple bond as one 'superpair' of electrons, the effect of which is rather similar to that of a lone pair. As an example, consider the molecule COF_2. The molecule will be trigonal, but the greater space occupied by the double bond will make the fluorine atoms move closer together, decreasing the F–C–F bond angle.

1.4.5 Molecules with Five Electron Pairs

In a tetrahedron or octahedron, all of the vertices are identical; however, this is not the case for a trigonal bipyramid, where there are two different types of vertex: **axial** and **equatorial**. This is best illustrated by an example, that of PCl_5 in the gas phase, shown in Figure 1.4. The molecule is a regular trigonal bipyramid.

The P–Cl(axial) bond length (214 pm) of PCl_5 is slightly longer than the P–Cl(equatorial) bond length (202 pm) (where 1 pm = 1 picometre = 10^{-12} m).

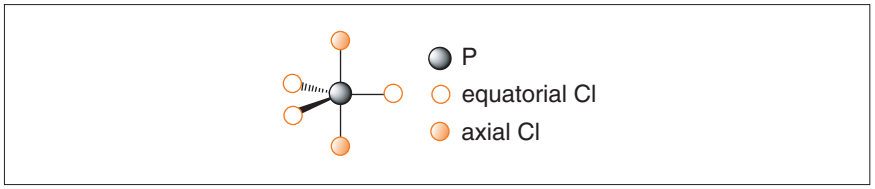


Figure 1.4 The structure of gas-phase PCl_5, showing the presence of Cl atoms in axial and equatorial positions

This has implications for molecules which contain five electron pairs, with one or more lone pairs, since there will be a choice of putting the lone pair(s) in axial or equatorial positions. However, on considering the various repulsions in such species, it can be concluded that: *lone pairs of electrons, or multiple bonds, always adopt equatorial positions in trigonal bipyramids, owing to the greater space occupied in the valence shell of the central atom.* This can be illustrated by species such as SF_4, BrF_4^+, ClF_3 and XeF_2.

Worked Problem 1.6

Q Predict the shape of SF_4.

A S has six valence electrons and the four fluorines contribute four electrons, giving 10 electrons or five pairs. The experimentally determined shape of SF_4 is a 'see-saw' shape, sometimes called a *pseudo* trigonal bipyramid (Figure 1.5). The effect of the sulfur lone pair can be clearly seen, pushing the fluorines towards each other. The molecule SOF_4 has a very similar shape, with the (double bonded) oxygen replacing the sulfur lone pair.

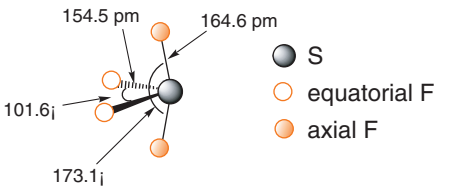


Figure 1.5 The structure of gas-phase SF_4, showing the presence of F atoms in axial and equatorial positions. The strong repulsing effect of the equatorial lone pair is clearly shown

1.4.6 Molecules and Ions with Seven or More Electron Pairs

When seven electron pairs are present in the valence shell of the central atom, the shape is more difficult to predict; there are often a number of different arrangements with similar energies. The three most important regular shapes are the monocapped octahedron, the monocapped trigonal prism and the pentagonal bipyramid, shown in Figure 1.6.

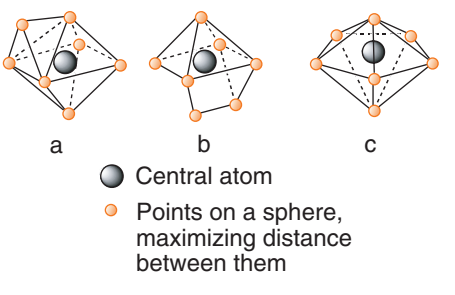


Figure 1.6 Common shapes adopted by seven-electron pair species: (a) monocapped octahedron; (b) monocapped trigonal prism; (c) pentagonal bipyramid

In certain cases, for the heavy p-block elements such as selenium, tellurium, bromine and bismuth, lone pairs occupy spherical s-orbitals, which do not influence the geometry of the species. As an example,

$TeCl_6^{2-}$ has one lone pair and six Cl atoms, but it is a regular octahedron; $SeCl_6^{2-}$ and BrF_6^- are also octahedral for the same reason.

An example of a species with eight electron pairs is XeF_8^{2-}, which has a square antiprism shape, shown in Figure 1.7.

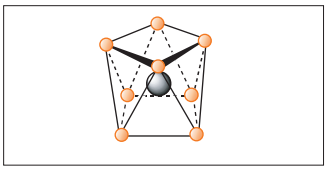
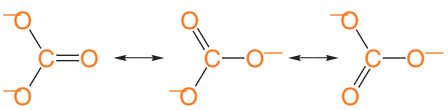


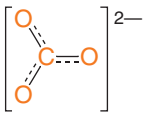
Figure 1.7 The square antiprismatic arrangement of eight fluorines around a central xenon atom in the ion XeF_8^{2-}. (A square antiprism can be derived from a cube by rotation of one of the square faces through 45°)

1.4.7 Resonance

When there are two or more **resonance forms** for a molecule or ion, it is essential that these are considered before predictions of bond angles are made. This can be illustrated by the example of the carbonate ion, CO_3^{2-}. This ion has six electrons (three pairs) around the carbon atom, and so is trigonal. As shown in Scheme 1.1, there are three resonance hybrids of the carbonate ion, so the true structure is a blend of all three, structure **1.1**, and all of the O–C–O bond angles are exactly 120°. If *one* of the resonance forms was taken in isolation, with a C=O double bond and two C–O single bonds, it would be (incorrectly) predicted that the O=C–O bond angles would be >120° and the O–C–O bond angle <120°. The importance of considering all resonance forms before predicting bond angles can be clearly seen.



Scheme 1.1



1.1

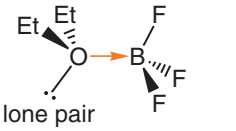
1.4.8 Dative Bonds

A dative bond is fundamentally identical to a 'normal' two-electron covalent bond except that in our electron 'book-keeping' we consider both electrons in the bond to originate from the same atom.

Worked Problem 1.7

Q Predict the shape of $Et_2O{\rightarrow}BF_3$ (Section 5.5.1).

A In this species, both electrons in the O–B bond come from the oxygen. There are two central atoms (O and B): for the B, we add two electrons to the count, both coming from O, whereas for the O, zero electrons are provided from the B. Thus:



The structure of $Et_2O—BF_3$

For B:	For O:
B has three valence electrons	O has six valence electrons
3F provides three electrons	Two Et groups provide two electrons
Dative bond provides two electrons	B provides 0 electrons (dative bond is from O to B)
Total eight electrons (four pairs)	Total eight electrons (four pairs)

Thus the geometry about B is tetrahedral, while around O it is trigonal pyramidal (with one non-bonding pair).

1.4.9 Atom Electronegativities

Electronegativity: see Section 1.2.

In an A–X bond between atoms A and X, as the atom X becomes more electronegative, the bonding pair occupies less space in the valence shell of atom A. In practice, this means that in a related series of compounds, bond angles of the type F–A–F are typically smaller than Cl–A–Cl or Br–A–Br angles, as illustrated in Figure 1.8. The greater size of a Cl atom compared to an F atom also contributes to the widening of the Cl–A–Cl angle.

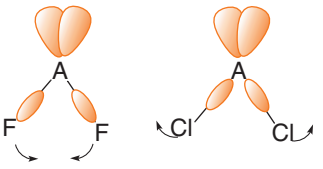


Figure 1.8 Effect of atom electronegativity on bond angle

Worked Problem 1.8

Q Explain why the X–P–X bond angles for the series of POX_3 molecules decrease from X = Br (104.1°) to X = Cl (103.3°) to X = F (101.3°).

A Fluorine is the most electronegative halogen, so it will draw electron density in the P–F bond away from the P atom; repulsion of the P–F bonding pairs will be less than repulsion of P–Cl and P–Br bonding pairs, so the F–P–F bond angle will be the smallest.

Worked Problem 1.9

Q Which of H_2O and F_2O will have the larger X–O–X bond angle?

A F is more electronegative than H; therefore the space occupied by the O–H bonding pair in the O valence shell will be greater. Hence, H_2O will have the larger bond angle

The H–O–H and F–O–F bond angles in H_2O and F_2O are 104.5° and 103.1°, respectively.

CH_4 and CF_4 have regular tetrahedral shapes, but CF_2H_2 is a distorted tetrahedron with the F–C–F bond angle smaller than the H–C–H angle. Following the same logic as in worked problems 1.8 and 1.9, this is because the electronegative fluorines attract electrons in the C–F bonds, decreasing the space they occupy in carbon's valence shell, causing the F–C–F angle to decrease.

Box 1.3 Bent's Rule

Bent's rule[2] states: *More electronegative substituents 'prefer' hybrid orbitals having less s-character, and more electropositive substituents 'prefer' orbitals having more s-character.*

The bond angles in CH_4, CF_4 and CH_2F_2 can be explained using Bent's rule. While a carbon atom in CH_4 or CF_4 uses four identical sp^3 hybrids in bonding, in CF_2H_2 the hybrids used are not identical. The C–F bonds are formed from sp^{3+x} hybrids, with slightly more p-character and less s-character than an sp^3 hybrid, and the hydrogens are bonded by sp^{3-x} hybrids, with slightly less p-character and slightly more s-character. Increasing the amount of p-character in the C–F bonds decreases the F–C–F bond angle, because for bonding by pure p-orbitals the bond angle would be decreased to 90°.

Recall that the three p-orbitals, p_x, p_y and p_z, point at 90° to each other along the *x*, *y* and *z* axes.

1.5 Molecular Orbital Theory

In **molecular orbital (MO) theory**, rather than having localized orbitals which form bonds between pairs of atoms, we construct molecular orbitals which extend over all atoms in a molecule. Space prevents more than a brief summary of the MO treatment of bonding, and in this section it is intended to illustrate the application of MO theory to main group molecules. The discussion will be illustrated by considering the properties of various O_2 species (O_2^+, O_2, O_2^- and O_2^{2-}).

We will start by looking at a very simple molecule: dihydrogen, H_2. Each H atom has a 1s atomic orbital (AO) available for bonding, and

these can interact in two ways. In-phase interaction gives a bonding MO, σ, while out-of-phase interaction gives an antibonding MO, σ*, as shown in Figure 1.9. The bonding MO is symmetrical about the centre of the molecule, and there is an increase in electron density in the internuclear region compared to the two H 1s orbitals; the bonding MO σ therefore has a lower energy than the energy of the hydrogen 1s atomic orbital. In contrast, the antibonding MO σ* has a decrease in electron density

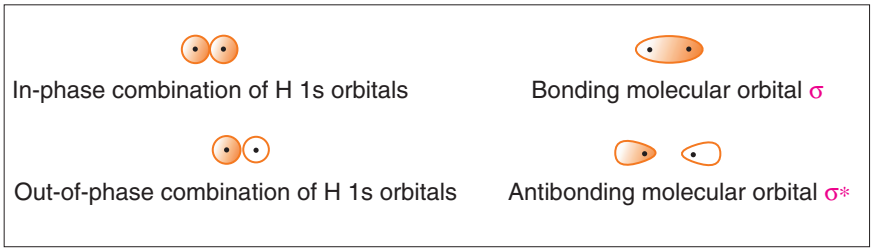


Figure 1.9 Molecular orbitals of H_2. The small black dots indicate the nucleus; these are omitted on subsequent diagrams

An antibonding MO is denoted by the * symbol.

in the internuclear region (when occupied by electrons), and is higher in energy than the 1s atomic orbitals. Figure 1.10 shows an energy level diagram for the H_2 molecule. The two electrons (one from each hydrogen atom) enter the bonding MO σ, corresponding to a net H–H single bond. If two more electrons are added to H_2, the antibonding MO σ* becomes filled. In this case, equal numbers of electrons are present in bonding and antibonding MOs, there is no net bonding, and H_2^{2-} is unfavoured relative to its dissociation product, two H^- (hydride) anions.

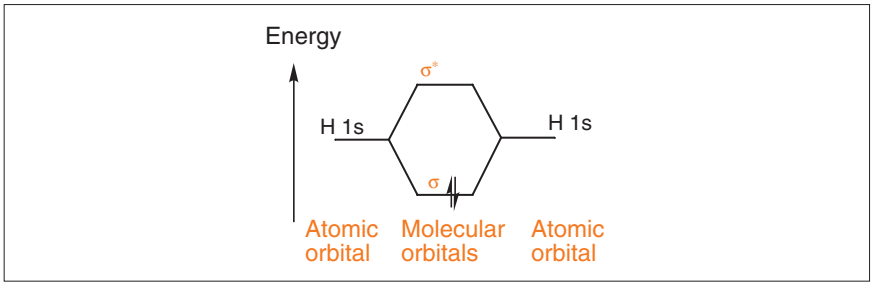


Figure 1.10 MO energy level diagram for H_2

In dioxygen species O_2, the MO scheme is slightly more complex because each O atom has both 2s and 2p AOs available for bonding. The MO energy level diagram is shown in Figure 1.11. Similar to H_2, the 2s AOs of the oxygen atoms interact to form bonding σ_1 and antibonding σ_2* MOs. The p_z orbitals point towards each other (the molecular axis is defined as the z axis) and can interact to form σ bonding (σ_3) and antibonding (σ_4*) MOs. The p_x orbitals on each oxygen can interact in a side-on manner, to form π bonding (π_1) and antibonding (π_2*) MOs, respectively. In the same way, the p_y orbitals interact to form π bonding (π_1) and antibonding (π_2*) MOs which are **degenerate** with the p_x-derived π MOs. The MO diagram in Figure 1.11 can be used to describe

Degenerate orbitals are ones with the same energy.

the bonding in O_2^+, O_2, O_2^- and O_2^{2-}. As with atoms, electrons enter MOs from the lowest energy levels first, and if there are degenerate orbitals, electrons initially singly occupy each with parallel spins.

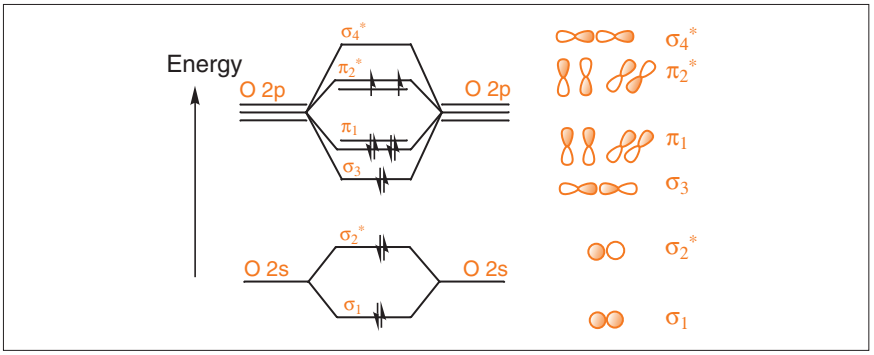


Figure 1.11 MO energy level diagram for dioxygen, O_2

For O_2 it can be seen that the π_2^* MO contains two unpaired electrons, and hence O_2 is predicted to be paramagnetic and attracted by a magnetic field. This fits very well with the physical properties of O_2, which is indeed paramagnetic. It is important to note that a simple valence bond description of O_2 (as O=O) does not predict any unpaired electrons, and this therefore represents one of the major triumphs of MO theory. The total **bond order** for O_2 from the MO diagram is 2, in accordance with the simple valence bond description of O=O.

Bond order is defined as ½ × [electrons in bonding MOs minus electrons in antibonding MOs].

The oxygenyl cation, O_2^+, has one less electron in the antibonding π_2^* MO, so the bond order is 2.5. Similarly, O_2^- and O_2^{2-} have respectively one and two more electrons in π_2^*, so the bond orders are 1.5 and 1, respectively. The predicted bond orders correlate very well with the experimental bond lengths, with a larger bond order giving a shortened bond, as shown in Table 1.2. Similarly, O_2^+, O_2 and O_2^- contain unpaired electrons and are paramagnetic, while O_2^{2-} has no unpaired electrons and is diamagnetic.

Table 1.2 Bond lengths of some dioxygen species[a]

Species	*Name*	*Bond order*	*Bond length* (pm)
O_2^+	Oxygenyl	2.5	112.3
O_2	Dioxygen	2.0	120.7
O_2^-	Superoxide	1.5	128
O_2^{2-}	Peroxide	1.0	149

[a] Refer to Chapter 8 for further details on the chemistry of these species.

Worked Problem 1.10

Q Identify the following orbital interactions as bonding, non-bonding or antibonding:

A (a) This interaction has in-phase (end-on) overlap of an s-orbital with a p-orbital, and so it is a bonding interaction. (b) This interaction is non-bonding, because although there is a bonding interaction, it is cancelled out by an equal antibonding interaction.

(a) 

(b) 

Summary of Key Points

1. The *overall chemistry* of the main group elements can be classified using the principles of ionization energy and electronegativity. Elements at the bottom left of the main group show strong metallic properties, forming basic oxides and hydrides and neutral halides. Non-metals in the top right of the p-block have high ionization energies and electron affinities, and form acidic oxides, hydrides and halides.

2. Valence shell electron pair repulsion theory (VSEPR) is a simple, powerful method for predicting the *molecular shapes* of main group species. While VSEPR can be used to predict shapes, it says nothing about the bonding in main group compounds.

3. Molecular orbital (MO) theory can be used to predict the *bonding* and properties of many species, and the discussion has centred around dioxygen species as an example.

Problems

1.1. Which of the following species will have the larger first ionization energy: (a) Li or Be; (b) N or O; (c) C or N; (d) Se or Se^+; (e) K or Rb.

1.2. Predict the shapes of the following molecules or ions: (a) SF_6; (b) SeF_2; (c) HCO_3^-; (d) $XeOF_4$; (e) PF_3Cl_2; (f) $[SF_2Cl]^+$; (g) $[S_2O_4]^{2-}$.

1.3. Which of the following molecules has a bond angle greater than 109.5°: (a) SF_2; (b) CF_4; (c) BF_3; (d) PF_3; (e) H_2S.

1.4. Using the MO diagram in Figure 1.9, predict the bond order of the species O_2^{2+}. With which common molecule is it isoelectronic?

1.5. Classify the following orbital interactions as bonding, nonbonding or antibonding:

(a) 

(b) 

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