Inorganic substances

A prelude to the study of descriptive inorganic chemistry

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The theoretical framework of inorganic chemistry

1.1 The scope of inorganic chemistry

Inorganic chemistry is what inorganic chemists do. The perpetuation of the traditional divisions of chemistry, and of a number of subdivisions, is related to the tribal loyalties of chemists. Just as most people are proud of their nationality, most chemists, in common with other scientists, feel the need to belong to a particular group. An inspection of the political map of the world will reveal many countries whose emergence and survival as sovereign states are difficult to understand, since they are not bounded by any obvious geographical features. Boundaries between nations are often determined, and persist, for historical reasons which have faded into relative obscurity. Likewise, chemistry has been divided for reasons thought proper at one time but which are no longer appropriate. Members of a tribe commune with each other via their writings in journals (many of which are devoted to the specialised interests of the tribe) and by meeting at conferences. The members share a common folklore and hagiology, which, together with the distinctive jargon of their subject, engender a feeling of kinship. There are movements afoot to abolish terms such as ‘inorganic chemistry’; but these are not likely to prevail in the near future.

What, then, do inorganic chemists do? An inorganic chemist is likely to be engaged in at least one of the following:

(1) The preparation and characterisation of substances other than those which fall within the domain of organic chemistry (the extent of this domain will be discussed later in this section). Characterisation of a product involves finding out what it is, and usually stops somewhere between an elemental analysis – which determines the empirical formula – and a full structure determination.

(2) The determination of the structures of inorganic substances. This requires a full description of the geometrical arrangement of
I The theoretical framework of inorganic chemistry

atoms in the substance, and the determination of all relevant bond lengths and interbond angles. Such information is usually yielded by X-ray or neutron diffraction studies of crystalline solids, and by electron diffraction or microwave spectroscopy in the case of gases. Limited, qualitative structural information can often be obtained by other physical methods, such as infra-red or NMR spectroscopy. Some inorganic chemists are completely devoted to the application of physical techniques for structure determination; but as long as their aim is to obtain structural information and to set it within the context of inorganic chemistry as a whole, they may be admitted to full membership of the tribe.

(3) The investigation of the chemical reactions of inorganic substances. This may involve detailed studies of reaction mechanisms and bring the inorganic chemist into the realms of physical chemistry and molecular physics.

(4) The investigation of the physical properties of inorganic substances. This may be undertaken with a view to exploiting practical applications, or to obtain chemically-relevant information from the physical measurements. Magnetic measurements, for example, may tell us something about the electronic structure and bonding in a coordination compound.

(5) The establishment of the theoretical principles which underlie any of the above experimental studies. Some people whose work is wholly devoted to theoretical studies still regard themselves as inorganic chemists if they feel that their work is largely of interest to other inorganic chemists, and the theory is not seen as an end in itself.

What distinguishes inorganic from organic chemistry? Organic chemistry may be defined as that area of chemistry which is directly consequent upon the unique properties of the carbon atom, viz.:

(i) Its (nearly) constant valency of 4, having four valence orbitals and four valence electrons.
(ii) The restricted number of bonding situations in which a C atom is usually found.
(iii) The relatively rigid bonding about a carbon atom, whether it be in sp, sp² or sp³ hybridisation, which entails high activation barriers to substitution, addition or elimination reactions.
(iv) The propensity of the carbon atom towards catenation, the formation of chains and rings.

There are, of course, important areas of overlap between the domains of organic and inorganic chemistry; organometallic chemistry and bio-
1.2 The role of theory in inorganic chemistry

inorganic chemistry are two which have grown very rapidly in recent decades. Even in these, however, it is often possible to distinguish between the approaches and preoccupations of organic and inorganic chemists, although the two are steadily coming together.

1.2 The role and status of theory in inorganic chemistry

According to the *Oxford English Dictionary*, a theory is a 'supposition or system of ideas explaining something, especially one based on general principles independent of the facts, phenomena etc. to be explained'. The contemporary theoretical chemist seeks to reduce a chemical problem to applied mathematics. The ultimate aim is to calculate, from first principles (the laws of physics, and universal physical constants), any experimental result which can be expressed numerically. Such *ab initio* calculations involve no simplifying assumptions, although some approximations have to be made for all but the most trivially simple systems. The mathematics may look fearsome, but 'black box' computer packages are accessible to most chemists. At the other end of the scale, we have simple, qualitative models which are based upon more rigorous, quantitative theories. Between these extremes, we have a range of methods from 'back-of-the-envelope' calculations to quite elaborate quantum-mechanical treatments in which we make some simplifying assumptions in order to economise on computing time.

A theory is rather like a Delphic oracle, an omniscient being to whom we address questions and who gives intellectually-satisfying answers; the answers may not be wholly unambiguous, and 'predictions' may be more impressive in hindsight. However, as the great theoretical chemist C. A. Coulson was wont to say, 'we like to think that the molecules are our friends'. You should be able to write vivid pen-portraits of your best friends, describing their habits and personalities; you may not always predict accurately their behaviour in certain circumstances, but you should usually be able to rationalise such behaviour after the event. So it is in theoretical chemistry.

The most elaborate and rigorous theories do not necessarily lead to the most satisfying 'explanations'. Suppose, for example, you ask a theoretical chemist the question: 'why is the H₂O molecule bent?' The theoretician will attack the problem by calculating the H–O–H angle which will minimise the total energy of the molecule. A quantum-mechanical calculation of the total energy can be performed for any assumed value of this angle, and the theoretician will be well satisfied if a plot of the total energy against the bond angle shows a minimum close to the experimental value of 104.5°. Such good agreement will satisfy the theoretician that the calculation is sound, and that any underlying approximations and assumptions are valid. But has the bent structure of the H₂O molecule
been 'explained'? The total energy of the H₂O molecule (expressed in units appropriate to the gaseous substance) is −200.758 kJ mol⁻¹; this is the energy relative to the separated nuclei and free electrons. The energy is the sum of the kinetic energies of the electrons (+200.758 kJ mol⁻¹) and the potential energy (−401.516 kJ mol⁻¹), arising from electron–nucleus attraction, electron–electron repulsion and nucleus–nucleus repulsion. The total molecular binding energy – the energy of the substance H₂O(g) relative to 2H(g) and O(g) – is 917 kJ mol⁻¹, or less than 0.5% of the total energy. The difference in energy between linear H₂O and bent (104.5°) H₂O is only about 50 kJ mol⁻¹. The potential energy term can be expressed as the sum of several thousand terms (mostly involving interelectron repulsion, and with many equalities due to symmetry). To try to 'explain' why the molecule is bent is as daunting a task as that of an accountant who is asked to explain why a company having a turnover of £600 000 per year, involving thousands of transactions large and small, has made £50 more profit in one year compared with another. Obviously, no simple explanation can be offered from such an exercise.

The reader will probably be familiar with at least one simple, qualitative 'explanation' for the shape of the water molecule (there are several). The VSEPR approach (see Section 1.4) 'predicts' that the bond angle should be somewhere between 90° and 109.5°, which is good enough for the purposes of most inorganic chemists. The fact that some of the underlying assumptions in this and other simple theories can be challenged does not necessarily vitiate the theory.

Simple, qualitative arguments are often unable to explain a single observation in isolation. They may, however, rationalise (i.e. make sense of) a large body of observations. For example, you may pose the question: 'why is H₂O a liquid at room temperature and atmospheric pressure, while H₂S is a gas?' It is a pertinent question, because the weak London attraction between molecules in condensed phases – which is often almost entirely responsible for holding them together – should increase with increasing atomic/molecular weight (see Section 3.3). A complete answer to the question would require a calculation of the enthalpies of vaporisation for both liquid water and liquid H₂S from first principles. If the calculated values are in good agreement with experiment, we can then enquire into the underlying reasons for the higher boiling point of water. Much more simply, however, we can rationalise the boiling points of binary hydrides in a qualitative way, based on considerations of hydrogen bonding as well as London forces.

To most chemists, theory means the theory of the chemical bond, or valence theory. A satisfactory theory should:

1. Describe the physical origin of chemical bonding, and explain why molecules, and non-molecular crystals, are stable with respect to the separated atoms.
1.3 The history of valency/oxidation numbers

(2) Explain (or at least rationalise) the stoichiometries of compounds, and thus guide us in the study of known compounds and in the quest for new ones.

(3) Explain the structures of molecules and crystals, e.g. why is the H₂O molecule bent, or why is SiO₂ a non-molecular crystal rather than a molecular gas like CO₂?

(4) Explain the reactivities of substances; why is X a strong acid, or why is Y a powerful oxidising agent?

(5) Provide a framework for the interpretation of, e.g., spectroscopic and magnetic data, so that such data can provide information about structure and bonding.

None of the various theories which the reader will encounter is perfect; all have their strengths and weaknesses. ‘Horses for courses’ should be the maxim of the inorganic chemist. Some theories are more firmly underpinned by experimental data and by fundamental physical laws than others. The fact that a theory ‘works’ to a useful extent does not prove that it is literally true, i.e. that it presents a physically-realistic description of the system. Conversely, the fact that some of the underlying assumptions in a theory can be shown to be unsound does not, per se, require that the theory be discarded. A simplistic approach can serve us well provided that we understand its limitations and do not take it too literally.

It is quite permissible to skip from one theory to another while discussing the same problem, just as an English-speaking person may occasionally use words and phrases from other languages in order to find le mot juste. For example, the term ‘sp² hybridisation’ properly belongs to the language of valence bond theory. You may see it appear, however, in a discussion of the molecular orbitals of a molecule such as benzene or ethylene; it provides a convenient shorthand notation to describe the σ bonding. These points should be borne in mind in reading Section 1.4 and subsequent chapters in which various theories are invoked.

1.3 Valency and oxidation numbers: a historical sketch of bonding theory prior to quantum mechanics

The historical perspective in chemistry is, alas, too often neglected in contemporary teaching. This fact is not unrelated to the confusion and infelicities which bedevil much of our nomenclature and notation (see Chapter 3). The historical reasons for the introduction of certain terminology are but dimly remembered and their validity is now highly questionable.

For some 50 years after Dalton’s atomic theory was published in the early 1800s the theory of chemical bonding made little progress. In the previous section, it was noted that one of the primary functions of
bonding theory is to rationalise stoichiometry. But the stoichiometric formulae of chemical substances were often uncertain until about 1860, despite rapid progress in analytical techniques. The determination of stoichiometry demanded a reliable table of atomic weights, the establishment of which depended, in part, on a knowledge of stoichiometry. This vicious circle was broken by the application of Avogadro’s Hypothesis – first promulgated in 1808 but not generally accepted until the 1860s – which made possible the determination of the molecular weights of gaseous substances by vapour density measurements. As the problems of stoichiometry were clarified between 1850 and 1860, the theory of valency was developed, largely by Frankland (English, 1825–99), Couper (Scottish, 1831–92) and Kekulé (Alsatan, 1829–96). The valency number of an atom (sometimes constant, but often variable) provided a numerical measure of its combining power. By about 1870, chemists were becoming familiar with ‘graphic formulae’, which depicted molecular structures with the atoms joined by straight lines; a substance would be stable if it could be represented by a molecular structure in which the usual valencies of the constituent atoms were satisfied. Some of the formulae which might have appeared in the lecture notes of a chemistry student of the 1870s would be acceptable today, e.g.:

\[
\begin{align*}
\text{H} & \quad \text{N} \quad \text{H} \\
\text{H} & \\
\text{O} & \quad \text{C} \quad \text{O} \\
\text{S} & \quad \text{O} \\
\text{Cl} & \\
\text{Cl} & \\
\end{align*}
\]

Others would, however, be unacceptable, e.g.:

\[
\begin{align*}
\text{F} & \quad \text{Ca} \quad \text{F} \\
\text{Ca} & \quad \text{O} \quad \text{S} \quad \text{O} \\
\text{O} & \quad \text{S} \quad \text{O} \\
\text{HO} & \quad \text{N} \quad \text{O} \\
\end{align*}
\]

Calcium fluoride and calcium sulphate are now known not to contain discrete molecules, and are regarded as ionic, \(\text{Ca}^{2+}(\text{F}^-)_2\) and \(\text{Ca}^{2+}\text{SO}_4^{2-}\). In the case of the nitric acid molecule, we now view pentavalent nitrogen atoms as objectionable because there are sound reasons for believing that the N atom cannot form more than four bonds, and the bonding in HNO\(_3\) can be otherwise described without violation of this rule. The experimental evidence in favour of ionic structures for solids such as CaF\(_2\) and CaSO\(_4\) did not emerge until the 1920s; and pentavalent nitrogen lingered on for a few years more.

It is important to understand that the valency number concept is based upon a *molecular* view of chemistry. Frankland was careful to warn his
1.3 The history of valency/oxidation numbers

students against the notion that his structural formulae were to be viewed as actual representations of molecular structures. Kekulé, near the end of his life, was sceptical about the real existence of atoms. These attitudes were strongly supported by the great positivist scientist-philosophers Mach (1838–1916) and Ostwald (1853–1932), who saw the atomic theory as a convenience, providing a metaphorical language in which chemistry could be expressed. However, the belief in molecules as real entities gained ground in the 1870s. Maxwell’s kinetic theory of gases depended on an explicit recognition of molecules, as did Van’t Hoff and Le Bel’s postulate of the tetrahedral carbon atom which forced organic chemists to think in terms of three-dimensional molecules.

The valency or valence of an atom in a substance is equal to the number of bonds it forms in the most satisfactory molecular formulation of the substance. This is appropriate for substances which do consist of discrete molecules; it is not without value (although liable to cause confusion) for substances which, though not molecular, can be given a plausible molecular formulation. However, the valency number concept must fail for substances which cannot be given a plausible molecular formulation. Such compounds began to attract attention in the 1870s and 1880s, just as valency theory was attaining general acceptance (the Periodic Law of Mendeleev had given it a considerable boost, since valency numbers were related to the Groups of the Periodic Table). An example of a troublesome compound was the mineral cryolite, then formulated as AlF₃.3NaF and of great technological importance because of its role in the Hall process for the extraction of aluminium (1886). It was definitely a compound and not a mixture. Given the usual valencies of 3 for Al and 1 for Na and F, it is impossible to devise a molecular structure. Such compounds were often known as ‘molecular compounds’ – the implication being that three NaF molecules were somehow bound to one AlF₃ molecule – or as ‘complexes’. We now formulate cryolite as Na₃[AlF₆], i.e. it consists of Na⁺ ions and AlF₆⁻ ions. A hundred years ago, however, the existence of ions in solids was not suspected (although their presence in solutions was gaining acceptance); and in any case the notion that an Al atom could bind six F atoms would have been dismissed by most chemists. Another class of ‘complex’ compounds were amines such as NiCl₂₆NH₃. Their molecular structures were at one time rendered by postulating chains of pentavalent nitrogen atoms, e.g. Ni(NH₃)₅-NH₃-NH₃-NH₃-Cl)₂, which preserved the usual valency of 2 for nickel. This had been superseded by about 1900 by Werner’s Coordination Theory, one of the milestones in the history of chemistry. Werner was still wedded to the molecular approach – he died in 1917, a few years before the first X-ray structures revealed the absence of discrete molecules in many inorganic compounds. However, he accepted Arrhenius’s theory of ions in solution, and made much use of it in the characterisation of complex
compounds. Werner postulated that many atoms, especially those of the transition elements, had to be assigned two valencies – primary and secondary. The former was essentially the same as the classical valency, as postulated for simple compounds (e.g. 2 for nickel). The secondary valency (commonly 6, for atoms of the 3d elements) was satisfied by groups (ligands) which were arranged in a definite geometrical figure about the central atom (an octahedron, for a secondary valency of 6). We now write \([\text{Ni(NH}_3\text{)}_6]\text{Cl}_2\) instead of \(\text{NiCl}_2.6\text{NH}_3\), i.e. the compound contains octahedral \(\text{Ni(NH}_3\text{)}^2+\) ions and \(\text{Cl}^-\) anions.

Primary and secondary valencies were later replaced by oxidation number and coordination number respectively. The oxidation number is based upon an extreme ionic view, being the charge on an atom in the most plausible ionic formulation. For many inorganic compounds this is far more satisfactory than the valency number; very often, an ionic description is possible where no molecular formulation can be devised. Indeed, coordination compounds may be historically defined as compounds whose stoichiometric formulae cannot be rationalised within the classical valency number concept. This definition is still valid. For example, it would be generally agreed that \(\text{Cs}_2\text{CuCl}_4\) falls within the purview of coordination chemistry, while the isomorphous compound \(\text{Cs}_2\text{SO}_4\) does not. The latter would have been given a molecular formulation 100 years ago:

\[
\begin{align*}
\text{Cs} & \quad \text{O} \quad \text{S} \quad \text{O} \\
\text{Cs} & \quad \text{O} \quad \text{S} \quad \text{O}
\end{align*}
\]

We now regard this formulation as inappropriate; the implication that each Cs atom is uniquely bonded to one O atom is inconsistent with the crystallographic evidence which shows that each Cs is about equidistant from eight O atoms. We prefer to regard the crystal as an assembly of \(\text{Cs}^+\) and \(\text{SO}_4^{2-}\) ions. In the case of \(\text{Cs}_2\text{CuCl}_4\), we similarly recognise the presence of discrete \(\text{CuCl}_4^{2-}\) ions. In contrast to \(\text{Cs}_2\text{SO}_4\), however, this compound could not have been given a plausible molecular structure 100 years ago, without invoking some highly unlikely valencies. This is the reason for its present-day classification as a coordination compound. Many chemists would prefer to write \(\text{Cs}_2[\text{CuCl}_4]\), to stress the presence of a discrete complex anion; but few would insist on the formulation \(\text{Cs}_2[\text{SO}_4]\) for caesium sulphate. The use of square brackets in such cases is further discussed in Section 3.4.

It should be apparent that valency number and oxidation number are two quite different concepts, not to be confused. Where it is possible to assign either a valency or an oxidation number to an atom, the two are often the same, but this is not invariably so. For example, in the \(\text{N}_2\)
molecule, the oxidation number of the N atom is zero, but its valency is 3. Unfortunately, there persists in the literature a tendency to view the two as virtually synonymous. Thus we still hear of 'the divalent (or bivalent?) state of tin', 'low-valent compounds of chromium' and 'iron in the III valence state'. (The use of 'valence state' where 'oxidation state' or 'oxidation number' is meant can be confusing, since 'valence state' has a distinct meaning in valence bond theory – see Chapter 6.) Most execrable of all is the term 'zerovalent', applied to compounds of (e.g.) nickel in the 0 oxidation state. It makes no more sense to describe the Ni atom in the molecular compound Ni(CO)$_4$ as being zerovalent than it would be to so describe the N atom in N$_2$ or C in CH$_2$Cl$_2$.

The molecular view of chemistry and its associated terminology which flourished in the second half of the nineteenth century has other legacies. If you look at almost any jar on a laboratory shelf, you will see printed on the label the 'molecular weight' of the substance therein, whether the substance is molecular or not. One of the most common sources of frustration among chemistry teachers is the deeply-ingrained belief among many students in the molecular formulation of all substances, and the tendency to use the terms 'molecule' and 'substance' as synonymous and interchangeable. This causes little difficulty in organic chemistry, nearly all of which is concerned with molecular substances. But it can cause serious problems in the teaching and study of inorganic chemistry.

The oxidation number/coordination number terminology is widely (but not universally) applicable in inorganic chemistry, and is not restricted to coordination chemistry. Valency numbers are more useful, however, for the organic chemist; it is rarely profitable to attempt the assignment of an oxidation number to a carbon atom but its (almost) constant valency of 4 is one of the cornerstones of organic chemistry. In this book, we will use valency numbers and associated terminology rather sparingly, and only in circumstances where it is clearly more appropriate than the alternative terminology. There are, of course, many situations where neither valency nor oxidation numbers can be unequivocally assigned to particular atoms. What, for example, is the oxidation number of the Rh atom in Rh$_{13}$(CO)$_{24}$H$_3^-$?

### 1.4 Contemporary theories of structure and bonding in inorganic chemistry

In this section, we survey the various theories of bonding and electronic structure which will be invoked elsewhere in the book and which will be regularly encountered by any serious student of inorganic chemistry. As pointed out in Section 1.2, it must be stressed that no one theory is wholly adequate, and the inorganic chemist must have at least a passing knowledge of several. The 'all-purpose' theory would probably
be about as useful as an all-purpose motor vehicle, Jack-of-all-trades and master of none. This section should convey to the reader the strengths and weaknesses of the various theories, and help choose the correct horse for the course.

The ionic model

In 1916, the German physicist Kossel proposed that many compounds could be described as consisting of cations and anions, so that the chemical bond was electrostatic in origin. This idea was not entirely new. Davy and Berzelius in the early nineteenth century had proposed such a theory, and its popularity for a while held back the progress of chemistry; since it could not readily accommodate molecules such as H₂, N₂ and Cl₂, followers of this 'dualistic theory' were reluctant to accept the diatomic description of these gases which followed from Avogadro's hypothesis, and this led to problems in atomic weight determination. What was new in Kossel's theory was the explicit recognition of electrons as being central to chemical bonding, and the notion that atoms tend to exchange electrons in order to attain the supposedly stable noble gas configuration. The atomic numbers of the elements had been largely determined by about 1914 (via X-ray spectroscopy), and the lack of chemical reactivity of the noble gases was established by about 1900. The Rutherford/Bohr model of the atom had gained wide acceptance by 1916, and the location of electrons at the periphery of the atom clearly suggested that the chemical bond was of electronic origin. Thus Kossel had all the information he needed to rationalise the compositions of many (although by no means all) inorganic substances. Compounds such as NaCl, CaF₂, LaI₃ etc. could all be described as containing ions having noble gas configurations. Calcium phosphate Ca₅(PO₄)₂ could be rendered as 3Ca²⁺2P⁵⁻8O²⁻. Kossel's theory led directly to the introduction of oxidation numbers.

Almost simultaneous with the publication of Kossel's paper there appeared a rival electronic theory. The American chemist Lewis introduced the idea of the covalent electron-pair bond. Like Kossel, he was impressed by the apparent stability of the noble gas configuration. He was also impressed by the fact that, apart from many compounds of the transition elements, most compounds when rendered as molecules have even numbers of electrons, suggesting that electrons are usually found in pairs. Lewis devised the familiar representations of molecules and polyatomic ions (Lewis structures, or Lewis diagrams) in which electrons are shown as dots (or as noughts and crosses) to show how atoms can attain noble gas configurations by the sharing of electrons in pairs, as opposed to complete transfer as in Kossel's theory. It was soon apparent from the earliest X-ray studies that Kossel's theory was more appropriate
for some compounds, and Lewis’s for others. Further elaboration of Kossel’s electrovalent theory led to the ionic theory in use today.

The chief merit of the ionic theory is the ease with which quantitative calculations can be performed within a simple electrostatic approach. These will be discussed in Chapter 5. Even if it could be conclusively proven that crystals such as NaCl do not contain ions, chemists would be reluctant to discard the ionic description. The model even has successes – and this should arouse suspicion – in situations where few chemists would seriously entertain the real existence of ions. For example, the 4d and 5d elements tend to exhibit high oxidation states more readily than their counterparts in the 3d series. This can be explained if we note (see Section 4.3) that the energies required to attain highly ionised states are much smaller for the heavier atoms, provided that we are prepared to believe that compounds like WF₆, ReO₃ and OsO₄ are ionic!

**Valence shell electron pair repulsion theory (VSEPR)**

The VSEPR theory has its roots in the observation prior to 1940 that isoelectronic molecules or polyatomic ions usually adopt the same shape. Thus BF₃, BO₃⁻, CO₃⁻, COF₂ and NO₃⁻ are all isoelectronic, and they all have planar triangular structures. As developed in more recent years, the VSEPR theory rationalises molecular shapes in terms of repulsions between electron pairs, bonding and nonbonding. It is assumed that the reader is familiar with the rudiments of the theory; excellent expositions are to be found in most inorganic texts.

An advantage of VSEPR is its foundation upon Lewis electron-pair bond theory. No mention need be made of orbitals and overlap. If you can write down a Lewis structure for the molecule or polyatomic ion in question, with all valence electrons accounted for in bonding or nonbonding pairs, there should be no difficulty in arriving at the VSEPR prediction of its likely shape. Even when there may be some ambiguity as to the most appropriate Lewis structure, the VSEPR approach leads to the same result. For example, the molecule HIO₃ could be rendered, in terms of Lewis theory as:

(a) ![Structure (a) violates the ‘octet rule’ of Lewis, but ‘octet expansion’ became recognised as common and acceptable for a number of heavier](image)

Structure (a) violates the ‘octet rule’ of Lewis, but ‘octet expansion’ became recognised as common and acceptable for a number of heavier
atoms such as I. In either case, five of the I atom's valence electrons are used for bonding, and there is one lone pair on the central atom. The VSEPR prediction – that the molecule will be a trigonal pyramid – is the same for either.

VSEPR theory can successfully account for many of the fine details in a structure, especially bond angles. However, we will be mainly concerned with the gross geometries of molecules and polyatomic ions. Structural minitiae are of considerable interest to most inorganic chemists, but they are important in the study of descriptive inorganic chemistry only to the extent that they may illuminate details of bonding which are relevant to the very existence of a substance, and to its reactions.

The VSEPR approach is largely restricted to Main Group species (as is Lewis theory). It can be applied to compounds of the transition elements where the nd subshell is either empty or filled, but a partly-filled nd subshell exerts an influence on stereochemistry which can often be interpreted satisfactorily by means of crystal field theory. Even in Main Group chemistry, VSEPR is by no means infallible. It remains, however, the simplest means of rationalizing molecular shapes. In the absence of experimental data, it makes a reasonably reliable prediction of molecular geometry, an essential preliminary to a detailed description of bonding within a more elaborate, quantum-mechanical model such as valence bond or molecular orbital theory.

Valence bond (VB) theory

VB theory was developed in the 1930s – mainly by Linus Pauling – as an attempt to invest the successful Lewis electron-pair bond theory with quantum-mechanical validity. An 'ordinary' single covalent bond between atoms A and B can be formed if a singly-occupied orbital on A overlaps with a singly-occupied orbital on B. A dative or coordinate covalent bond is formed by the overlap of a doubly-occupied orbital on A with an empty orbital on B. (This distinction can be removed by considering a dative bond A → B to involve the overlap between singly-occupied orbitals on A⁺ and B⁻.) The origin of the bond is best thought of as arising from the enhancement of electron–nucleus attraction in the overlap region (where electrons are within the field of both positive nuclei), overcoming the increase in interelectron and internuclear repulsion which must accompany the close approach of the atoms. 'One-electron' bonds are found only in cations such as H₃⁺, Li⁺ and Cl⁺, none of which occurs in stable substances although they can be identified spectroscopically. The pairing of electron spins in a covalent bond is a consequence of the Pauli Principle, which prohibits the occupancy of overlapping orbitals by electrons of the same spin.

The strategy for devising a VB description of the bonding in a molecule or polyatomic ion may be summarised as follows: