

## Historical introduction

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### 1.1 Introduction

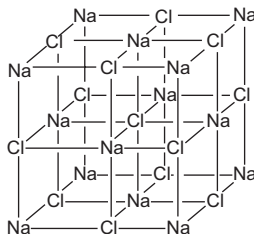
Of all the concepts used in chemistry, that of the chemical bond is one of the most useful and, at the same time, one of the most difficult. It is useful because it helps us to understand the structures of compounds and their properties, and it is difficult because it is not easy to relate it to the physical theories, such as quantum mechanics, that underlie chemistry. This is not to say that people have not attempted to find a connection between the chemical bond and quantum mechanics. The Lewis (1923) electron pair model and the orbital overlap model (Coulson 1961) are, perhaps, among the better known attempts, but all are *a posteriori* rationalizations, trying to explain the properties of the empirical nineteenth-century chemical bond in terms of twentieth-century physical concepts. It is unlikely that, left to themselves, theoretical chemists in the twentieth century would have ever created the idea of a chemical bond had not the concept already been central to the language of structural chemistry. To this day the chemical bond remains largely an empirical concept.

As an empirical concept, the chemical bond was fully developed by the end of the nineteenth century (Partington 1964, chapter 17). Even though the discovery of the electron at the turn of the century changed the way we think about bonds, it has added little to the model's predictive power. The only significant addition made during the twentieth century has been a knowledge of the actual lengths of the bonds and angles between them.

Partly because, in the twentieth century, we have insisted on interpreting the chemical bond in terms of the quantum mechanical properties of electrons, we have failed to exploit the essential simplicity of the traditional bond model. According to this model, an atom has a certain bonding power, called its valence. The atom shares its valence among the bonds that it forms, the portion received by a particular bond being regarded as a measure of the bond's strength. The relation between the strength of a bond and the valence of the atom lies at the heart of all chemical bond models such as the bond model widely used in organic chemistry and the bond valence model described in these pages.

### 1.2 Chemical bonds

Although the idea of an attractive interaction that holds the various particles of matter together can be traced back to Greek times, it was not until the early



**Fig. 1.1.** A portion of the infinite structure of NaCl (18189).

nineteenth century that the concept became usefully predictive. It derived from Dalton's atomic hypothesis (Thompson 1807), in which a limited number of types of atom were assumed to associate together to form the compounds familiar to chemists. While it soon became clear that electricity was involved in the forces by which atoms were attracted to each other, no model of chemical bonding based on Coulomb's law was possible at that time, and it was some decades before the chemical bond model as we now know it was developed (Partington 1964, chapter 16). The model treated compounds as composed of atoms connected by a network of bonds. Neither the nature of the atoms nor the nature of the bonds was known at the time, but the model proved so remarkably effective in organizing the enormous variety of known organic compounds, that by the end of the century the model could even account for stereoisomerism. This was sufficient to convince most chemists of the reality of both atoms and bonds.

In the early twentieth century, advances in atomic physics confirmed the existence of atoms, and the discovery of X-ray diffraction revealed the precise arrangements of these atoms, confirming in a striking manner the geometric predictions of the bond model in organic chemistry. However, there were a number of problems. Neither X-ray diffraction, nor any other of the techniques developed at the time were able to demonstrate the physical existence of bonds. While the theoretical developments of the twentieth century have revealed much about the nature of chemical bonding, they have been much less successful in describing this bonding in terms of the localized interactions that we call bonds. Further problems arose when the structures of inorganic crystals were examined since these did not follow the rules that worked for organic chemistry. Instead of NaCl (18189<sup>1</sup>) forming a diatomic molecule as the bond model predicted, each atom was found to be part of an infinite array of atoms lying on a cubic lattice, each atom being surrounded at equal distances by six neighbours of the opposite kind (Fig. 1.1). There was no indication of the diatomic molecule

<sup>1</sup> Each compound mentioned in this book is followed by its collection code (number) in the Inorganic Crystal Structure Database (Bergerhoff *et al.* 1983) or its refcode (letters) in the Cambridge Crystallographic Database (Allen *et al.* 1979). A reference to the original paper describing the structure of the compound is listed under this code in the literature references in Appendix 5.

predicted by the bond model. Similar results were found for other inorganic solids. The failure of the bond model that worked so well for organic chemistry to provide useful structural predictions in these cases led to its abandonment in inorganic chemistry.

### 1.3 The ionic model

There were several attempts to develop alternative bonding models for inorganic solids but none of these met with the same success as the bond model for organic compounds. Born and his colleagues (Born and Landé 1918; Madelung 1918; Born and Mayer 1932) took a physicist's approach when they proposed the *ionic model* in which the atoms were considered to be charged spheres, cations carrying positive charge and anions carrying negative charge, held together to form a solid by the electrostatic attractions between them. The potential energy,  $U$ , between any pair of atoms was expressed as the sum of two terms: an attractive Coulomb potential generated from the charges on the atoms, and a short-range, generally repulsive, potential that became important only when atoms came into contact (eqn (1.1)):

$$U = U_{\text{electrostatic}} + U_{\text{repulsive}}. \quad (1.1)$$

The correct arrangement of the atoms in the solid was assumed to be the one that minimized this potential energy summed over all pairs of atoms in the crystal. The particular virtue of this model is that the long-range attractive part of the potential can be calculated exactly using classical electrostatic theory while the unknown short-range repulsive part can be modelled empirically. Born and Landé (1918) proposed an inverse power law for  $U_{\text{repulsive}}$ , but later Born and Mayer (1932) suggested that an exponential expression was more in keeping with the predictions of the newly developed quantum mechanics.

The ionic model was able to account for many of the properties of simple salts such as the alkali metal halides, but ran into difficulties with more complex structures, partly because of the difficulty of determining the correct form of the repulsive potential, and partly because of the difficulty of summing the slowly converging electrostatic potential. The latter problem was solved for NaCl by Madelung (1918) with more general methods being subsequently developed by Ewald (1921) and Bertaut (1952). In recent years the introduction of computers has allowed both these difficulties to be overcome, and it is now possible to use the ionic model to make quantitative predictions of the properties of most inorganic compounds (Catlow 1997). However, the procedures require care in selecting the correct form for  $U_{\text{repulsive}}$  and involve extensive computer resources. While the model gives good numerical predictions, it lacks the intuitive insights that are the strength of the traditional chemical bond model.

## 1.4 Quantum mechanics

The ultimate description of chemical bonding lies in quantum mechanics and the solution of the Schrödinger equation for the crystal. Although this equation can be exactly solved only for two particles, increasingly sophisticated approximate methods have been developed which provide excellent values for both the energy and the electron density distributions in crystals. However, such calculations are cumbersome for analysing and predicting complex chemical structures. The computing requirements are even more demanding than those of the ionic model, and quantum mechanics also lacks the essential simplicity of the traditional chemical bond model.

A promising simplification has been proposed by Bader (1990) who has shown that the electron density in a molecule can be uniquely partitioned into atomic fragments that behave as open quantum systems. Using a topological analysis of the electron density, he has been able to trace the paths of chemical bonds. This approach has recently been applied to the electron density in inorganic crystals by Pendás *et al.* (1997, 1998) and Luaña *et al.* (1997). While this analysis holds great promise, the bond paths of the electron density in inorganic solids are not the same as the more traditional chemical bonds and, for reasons discussed in Section 14.8, the electron density model is difficult to compare with the traditional chemical bond models.

Other simplified quantum treatments, such as the Lewis electron pair and orbital overlap models, have proved useful in teaching and they give qualitative predictions of the structures of molecular compounds, but they become unwieldy when applied to solids. They have not proved to be particularly helpful in the description of the complex structures found in inorganic chemistry and have therefore not been widely used in this field.

## 1.5 The symmetry model

In the early years of the twentieth century, an alternative approach to understanding inorganic structure was proposed by Niggli (1918) and Shubnikov (1922), who advocated using the recently developed theory of space group symmetry. They recognized that most inorganic compounds do not form finite molecules but exist only as crystals. The translational symmetry that generates a three-dimensional crystal from a basic building block requires that every crystal must belong to one of only 230 possible space groups. Such a requirement places considerable restrictions on the arrangements of atoms that can be present in the building block.

For example, if two atoms that are related by a plane of mirror symmetry move onto that plane, they fuse to become a single atom. Thus atoms that lie on elements of symmetry (special positions) will occur less frequently in the building block than ones that lie on positions with no symmetry. The higher the

site symmetry of the atom, the smaller its multiplicity, i.e. atoms occupying sites of high symmetry appear less frequently in the building block than atoms occupying sites of low symmetry. The composition is thus determined by the multiplicities of the special positions available to the atoms. Niggli and Shubnikov argued that it should be possible to determine the structure of a compound by finding which of the 230 space groups have special positions with multiplicities that correspond to the known composition of the compound. The power of this approach was demonstrated by Niggli who used it to show that, based strictly on geometric arguments, there are only four possible cubic structures having the chemical formula  $AB$ , thus accounting for the large number of different binary compounds that adopt the NaCl (18189), CsCl (22173), sphalerite (60378) or NaTl structures. However, as in the case of the ionic model, this initial success could not be repeated with more complex structures.

Subsequent workers have explored other ways in which symmetry can be used to restrict, or at least to describe, inorganic crystal structures. Lima de Faria and Figueiredo (1975) have arranged the space groups in hierarchical order according to their symmetry and have classified inorganic structures according to where they occur in this hierarchy. Parthé (1996) and Bergerhoff *et al.* (1999) have used space group symmetry as a way of identifying isostructural compounds. While these approaches are useful in exploring the restrictions that the three-dimensional world places on possible structures, they can never provide a complete description since they are based solely on the geometric properties of space and ignore the chemistry that gives each element its distinctive properties.

## 1.6 Topological models

The mathematical theory of topology is the basis of other approaches to understanding inorganic structure. As mentioned in Section 1.4 above, a topological analysis of the electron density in a crystal allows one to define both atoms and the paths that link them, and any description of structure that links pairs of atoms by bonds or bond paths gives rise to a network which can profitably be studied using graph theory.

Graph theory has been used to explore structures, such as organic molecules and alumino-silicate minerals, in which the bonds are all of similar strength. Many minerals are built around frameworks composed of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra sharing corners. The ways in which such tetrahedra can be connected has led to attempts to enumerate and classify all possible alumino-silicate minerals. It is not difficult to show that the number of possible structures that can be made out of even a limited number of tetrahedra is extremely large, but it is the aim of this type of analysis to discover which topologies are most likely to correspond to stable structures. While such an approach is useful in rationalizing the large number of known silicate structures (Liebau 1985; Smith 1988),

it becomes awkward when different types of coordination polyhedra are present, or when the bonds differ greatly in strength.

### 1.7 Pauling's electrostatic valence model

In 1929 Pauling brought a chemist's intuitive perspective to the problem of describing the structures of inorganic compounds. In a seminal paper, Pauling (1929) lists five principles that determine the structures of complex ionic crystals. These principles are qualitative, but they summarize in a concise way much of the empirical information that was available to him about the structures of inorganic solids, particularly minerals. Because these principles have been widely used in the analysis of complex inorganic structures and since they form the starting point for the development of the bond valence model, they are worth quoting here in full:

- I. A coordinated polyhedron of anions is formed about each cation, the cation–anion distance being determined by the radius sum and the coordination number of the cation by the radius ratio.
- II. In a stable coordination structure the electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the centers of the polyhedra of which it forms a corner; that is, for each anion

$$\zeta = \sum_i z_i/v_i = \sum_i s_i$$

[ $\zeta$  = anion charge,  $z$  = cation charge,  $v$  = cation coordination number,  $s$  = (Pauling) bond strength.]

- III. The presence of shared edges, and particularly shared faces, in a coordinated structure tends to decrease its stability; this effect is large for cations with large valence and small coordination number, and is especially large in case the radius ratio approaches the lower limit of stability of the polyhedron.
- IV. In a crystal containing different cations those with large valence and small coordination number tend not to share polyhedron elements with each other.
- V. *The rule of parsimony.* The number of essentially different kinds of constituents in a crystal tends to be small.

These principles are phrased in the language of the ionic model, but they provide a simpler and more explicit description of stable structures than that given by the ionic model's energy minimization principle. Among the important ideas captured by Pauling's rules are those of local charge neutrality, the definition of electrostatic bond strength, and the rule of parsimony which is closely

related to the principle of maximum symmetry introduced in Chapter 3. The year following the publication of Pauling's rules, Bragg (1930) showed that they could be represented pictorially by Faraday's lines of electrostatic field which link the cations to their neighbouring anions. Because the energy of an electrostatic field is lowest when the lines of field are shortest, it follows that the equilibrium structure will be one which places cations and anions in intimate contact with each other.

As more accurate information became available on the structures of inorganic solids, a correlation was noticed between the length of a bond and its strength (Pauling 1947; Byström and Wilhelmi 1951; Zachariasen 1954). Donnay and Allmann (1970) showed that Pauling's second rule becomes quantitatively exact around both the cations and the anions if the electrostatic bond strengths are calculated from the bond lengths rather than from the charge and coordination number, an idea that was subsequently expanded by Brown and Shannon (1973). Donnay and Allmann coined the term *bond valence* to differentiate this new quantity from Pauling's bond strength, and since then bond valences have been extensively used in modelling and analysing crystal structures. The properties of bond valences have been summarized in a number of simple quantitative rules generally known as the *bond valence model* described in detail in Section 3.3. Recent reviews of the model have been given by Brown (1981, 2000), O'Keeffe (1989), Trömel (1992), and Urusov and Orlov (1999).

Theoretical aspects of the bond valence model have been discussed by Jansen and Block (1991), Jansen *et al.* (1992), Burdett and Hawthorne (1993), and Urusov (1995). Recently Preiser *et al.* (1999) have shown that the rules of the bond valence model can be derived theoretically using the same assumptions as those made for the ionic model. The Coulomb field of an ionic crystal naturally partitions itself into localized chemical bonds whose valence is equal to the flux linking the cation to the anion (Chapter 2). The bond valence model is thus an alternative representation of the ionic model, one based on the electrostatic field rather than energy. The two descriptions are thus equivalent and complementary but, as shown in Section 2.3 and discussed further in Section 14.1.1, both apply equally well to all types of acid–base bonds, covalent as well as ionic.

This book is divided into four parts. Part I provides a theoretical derivation of the bond valence model. The concept of a localized ionic bond appears naturally in this development which can be used to derive many of its properties. The remaining properties, those dependent on quantum mechanics, are, as in the traditional ionic model, fitted empirically. Part II describes how the model provides a natural approach to understanding inorganic chemistry while Part III shows how the limitations of three-dimensional space lead to new and unexpected properties appearing in the inorganic chemistry of solids. Finally, Part IV explores applications of the model in disciplines as different as condensed matter physics and biology. The final chapter examines the relationship between the bond valence model and other models of chemical bonding.