

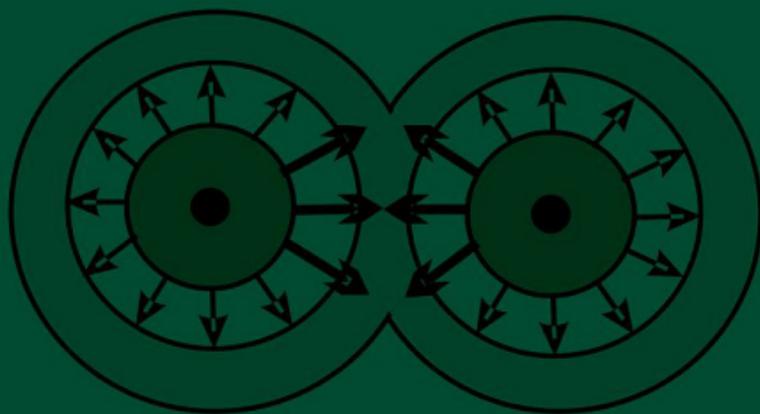
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# The Chemical Bond in Inorganic Chemistry

The Bond Valence Model

**Second Edition**

I. DAVID BROWN



INTERNATIONAL UNION OF CRYSTALLOGRAPHY

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The Chemical Bond in  
Inorganic Chemistry  
The Bond Valence Model

*2nd Edition*

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# Preface to the Second Edition

Since publication of the first edition, the bond valence model has been advanced in a number of ways. The identification of the chemical bond with the electrostatic flux linking two-bonded atoms, which was reported in the first edition, has now been developed into a formal physical theory of the chemical bond with theorems that can be derived directly from classical electrostatics. The flux theory underlies all the empirical models of localized bonds: the ionic, the covalent ball-and-stick and VSEPR models. It shows how the properties of a localized bond relate to the distribution of the charge surrounding the nucleus and it defines the scope of the traditional bond models while revealing their limitations. When combined with the empirical correlation between the bond flux and bond length, the flux theory yields the rules of the bond valence model described in this work. It is a model that applies to all localized bonds, covalent as well as ionic, but it is particularly well-suited to describing the structure and properties of inorganic compounds.

In the 14 years since the appearance of the first edition, the techniques of the bond valence model have been extended by the introduction of bond valence vectors and methods for estimating bond angles. Existing techniques have been applied to new systems and the complex relationship between the bond valence and bond energy has been clarified. New examples of the applications of bond valences to the structures of crystals, glasses, liquids and surfaces are included. The final chapter, on the implications of the model, has been rewritten to illustrate the correspondence between the concepts of the flux theory of the chemical bond and those of the Quantum Theory of Atoms In Molecules (QTAIM), representing two complementary approaches to the description of chemical bonding.

This edition is dedicated to my late wife, Mariana, in recognition of the support she gave me throughout our marriage.

25 December 2015

I.D.P.

# Preface to the First Edition

This book describes the bond valence model, an increasingly popular description of acid–base bonding, particularly in fields such as materials science and mineralogy where solid-state inorganic chemistry is important. The text is aimed at two groups of readers; those who are teaching chemical bonding in acid–base systems, and those who are researching in fields, ranging from physics to molecular biology, in which such bonding is involved. The model derives from Pauling’s concept of electrostatic valence which in recent years, has evolved into a simple but highly predictive model. It is essentially empirical. Its theorems have not yet been derived from quantum mechanics, but its presentation of chemical bonding is complementary to the quantum mechanical approaches. The essential simplicity of the model makes it useful in situations that are too complex to be adequately treated by more fundamental theories.

The reader is advised to avoid bringing too many preconceptions about the nature of chemical bonding to a reading of this work. While there are rather too many models of chemical bonding in existence, the bond valence model represents their common features reduced to their simplest mathematical form. The model should be judged on its own terms: how well does it predict acid–base chemistry and how effective are the insights it provides? Attempts to formulate the model in terms of the traditional concepts of chemistry, covalent *versus* ionic bonding, resonance Lewis structures, or electronic orbitals (except as discussed in Chapter 8), only make it more complex and less predictive. The model works best when it is kept simple. I have, therefore, only introduced concepts where they are needed to account for the observed phenomena, and the concepts are all precisely defined. The result is a simple but quantitatively rigorous model that describes many of the phenomena of inorganic and other acid–base bonding. It requires a minimum of computing (a pocket calculator, pencil and paper usually suffice) and the basic concepts can readily be grasped by secondary-school students.

The model itself is developed in Part I and its applications to inorganic chemistry are described in Part II. Part III is devoted to an analysis of inorganic solids, showing how the unique character of solid state chemistry derives from the conflict between the constraints of chemistry and those of three-dimensional space. Part IV surveys the wide range of problems to which the model has been applied, from condensed matter physics, through mineralogy and soil science, to catalysis and molecular biology. The book ends with a comparison between the bond valence model and other descriptions of chemical bonding, and includes a discussion of why such a simple model works so well.

This book started as a series of lectures which Prof. Schenk invited me to give to the Chemistry Department of the University of Amsterdam in 1994. Many

people have helped in developing the ideas presented in this book, often in lively discussions over midmorning cups of coffee. These people are too numerous to list here, but I thank them all for their contributions which are referred to at the appropriate places in the text. I would particularly like to acknowledge three people whose influence was instrumental in introducing me to the important ideas described in these pages. They are my research supervisor, Jack Dunitz, whose unconventional, but always correct, approach to research has inspired many besides myself, Bob Shannon, who introduced me to Pauling's electrostatic valence principle, and Hans Burzlaff who convinced me of the importance of symmetry and spatial restrictions to an understanding the chemistry of solids. To these three I wish to dedicate this work.

11 April 2001

I.D.B.



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# 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 has not been easy to relate it to any of 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 is mostly treated as an empirical concept, though this book shows that all the rules of the various chemical bond models can be derived directly from the properties of the negative charge surrounding the nucleus (Chapters 2 and 3).

As an empirical concept, the chemical bond was fully developed by the end of the nineteenth century (Partington 1964, Ch. 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 the angles between them.

Partly because in the twentieth century we insisted on interpreting the chemical bond in terms of the quantum mechanical properties of electrons, we 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 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, Ch. 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

<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; Groom and Allen 2014). A reference to the original paper describing the structure of the compound is listed under this code in Appendix 3.

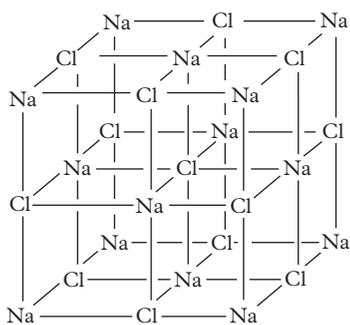


Fig. 1.1 A portion of the infinite structure of NaCl (18189).

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 predicted by the bond model. Similar results were found for other inorganic solids. The failure of the bond model, which worked so well for organic chemistry, to provide useful structural predictions in crystals led to it being abandoned 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 they 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 only be exactly solved for two particles, increasingly sophisticated approximate methods have been developed that provide excellent values for both the energy and the distribution of negative charge in crystals. However, such calculations require *a priori* knowledge of the arrangement of the positive nuclei in order to define the potential energy that shapes the negative charge distribution. The computing requirements are even more demanding than those of the ionic model, and consequently quantum mechanics also lacks the essential simplicity of the traditional chemical bond model.

Bader (1990) has shown that the charge density in a molecule can be partitioned into atomic fragments and that it is possible to trace bond paths that link them. This approach has been applied to the charge density in inorganic crystals by, e.g. Pendás *et al.* (1997, 1998) and Luaña *et al.* (1997) and, while the atomic fragments and bond paths bear some resemblance to the classical concepts of atoms and bonds, they do not have the same properties and cannot be used to derive the empirical rules of the successful bond models (Section 13.2).

Other simplified quasi-quantum treatments, such as the Lewis electron pair and orbital overlap models, have been widely used in teaching, but they are poor descriptions of the physics of bond formation; their predictive power is marginal and their link to quantum mechanics is tenuous.

### 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 repeating 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 (Chapter 9).

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. 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; that is, 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 (105169) 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, a topological analysis of the charge density in a crystal allows one to define both the 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 that 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 aluminosilicate 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 centres of the polyhedra of which it forms a corner; that is, for each anion

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

[ $\zeta$  = anion charge,  $z$  = cation charge,  $\nu$  = 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 that is closely related to the principle of maximum symmetry (eqn 2.1). 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 that 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). The term *bond valence* was coined to differentiate this new quantity from Pauling's bond strength and since the 1980s 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 Chapters 2 and 3. Recent reviews of the model have been given by Brown (1981, 2000, 2002a, 2009b, 2014a), O'Keeffe (1989), Trömel (1992), Urusov and Orlov (1999), Brown and Poeppelmeier (2014) and a brief history of the model can be found at Brown (2014b).

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 electrostatic 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, an idea explored further in Chapter 2, which outlines the flux theory of the chemical bond. The bond valence model is thus an alternative representation of the ionic model based on the electrostatic field rather than the energy. The electrostatic field and electrostatic potential provide

equivalent and complementary descriptions of the same theory, and as shown in Section 2.3.4 both apply equally well to covalent as well as ionic bonds.

The work starts with a description of the flux theory of the chemical bond in which the concept of a localized bond appears naturally (Chapter 2). This theory is then used to derive the theorems of the bond valence model (Chapter 3) and provide a natural approach to understanding inorganic chemistry (Chapters 4 to Chapters 8). The limitations of three-dimensional space lead to new and unexpected properties appearing in the inorganic chemistry of solids (Chapters 9 to Chapters 11). Chapter 12 explores applications of the bond valence model in disciplines ranging from condensed matter physics to biology, while Chapter 13 explores a number of more general features of the flux theory and its relationship to other models, particularly those based on the analysis of charge density.

# 2

## The Flux Theory of the Chemical Bond

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### 2.1 Introduction

The chemical bond is a localized interaction that depends only on the two neighbouring atoms that it links; all other interactions are ignored. That all the longer interactions can be ignored is surprising, given that the cohesion between atoms is mediated by the Coulomb potential whose influence is known to extend well beyond nearest neighbours, but this did not cause the nineteenth-century chemists any grief. They had discovered the usefulness of the bond model long before the electrical nature of the atom was understood.

The chemical bond was first proposed in the mid-nineteenth century as an empirical model designed to explain the large variety of structures found in organic chemistry. It was so successful that by the time quantum mechanics appeared it was accepted that compounds were composed of atoms linked to their neighbours

by bonds. The quantum nature of the atom was quickly established, but the many attempts to reconcile the classical bond picture with quantum theory have only served to confuse the original bond concept. Rather than revealing the physical character of the bond as was expected, these attempts have decorated the empirical model with a layer of quantum jargon that disguises its essential simplicity. A century of quantum mechanics has yielded no physical theory from which we can derive even the simplest of the empirical rules of the various chemical bond models in use today.

Solutions of the Schrödinger equation are effectively limited to calculating the energy and the distribution of negative charge surrounding a proposed arrangement of atomic nuclei. They provide no evidence for the traditional concept of a bond as an interaction that involves only neighbouring atoms. Further, quantum calculations, being computer intensive, provide few insights into the factors that determine chemical structure. In an attempt to simplify the quantum picture of the atom, the charge density is sometimes described as being composed of individual electrons each occupying its own spatially defined orbital so that bonds are formed when the orbitals of neighbouring atoms overlap, but there is no experimental or theoretical evidence for the physical existence of either orbitals or, indeed, of individual electrons in atoms. Such views present a false picture of the physics of the bonding process and often lead to incorrect predictions of structure and geometry. An alternative popular approach is to assume that a bond consists of some admixture of ionic and covalent character, but covalency and ionicity are ill-defined and mutually incompatible. Even if it were possible to define ionic and covalent character, there would be no way to measure how much of each is present in a bond. Attempts to do so are always speculative. The language currently used to describe chemical bonds is confused and full of contradictions.

In spite of this confusion, there are a number of simple and well-tried empirical models that provide sound quantitative predictions even if their physical foundations are weak or non-existent. These models are devoid of quantum jargon, using only a classical picture of atoms and bonds. The original ball-and-stick model, in which the atoms are represented by the balls and the bonds by the sticks that link them, gives a remarkably fruitful and precise description of the structures of organic compounds, if one ignores the weak interactions between molecules. However, it lacks any theoretical justification. The ionic model, in the form of the two-body potential model, uses a classical force field to make good predictions of the structures of the condensed phases of inorganic compounds (Catlow 1997), but it is based on a model in which the atoms carry unphysically large charges, and the long-range Coulomb potential used in the force field provides no hint of a localized chemical bond. The Valence Shell Electron Pair Repulsion (VSEPR) model (Gillespie and Hargittai 1991) provides a simple explanation of the asymmetric bonding geometries adopted by many electron-rich atoms, but it is qualitative and its range of applications is limited. The bond valence model, the subject of this work, is a simple bond description of inorganic compounds not

unlike the ball-and-stick model of organic chemistry, and like the ball-and-stick model, its rules have been developed empirically.

The rest of this chapter describes the *flux theory of the chemical bond*, a physically correct description of the way atoms form bonds, from which the rules of all of these successful empirical bond models can be derived. It is a classical theory that avoids the conflicting concepts popularly used to describe chemical bonding and replaces them with a simple picture that emphasizes the physical origins of the bond. It identifies the chemical bond with the electrostatic flux (the number of Faraday lines of field) that link two neighbouring atoms. The flux theory can be used to derive the rules of both the covalent (ball-and-stick) and the ionic (bond valence) models. The rules of the VSEPR model can be derived from the directional properties of the flux linking the valence shell of an atom to its core.

Like other theories of bonding, the flux theory assumes that an atom consists of a diffuse negative charge surrounding a small positively charged nucleus. The negative charge is traditionally treated as a collection of electrons, but it is more correctly described as a negatively charged matter-wave resonating within the cavity to which the charge is confined by its attraction to the nucleus. The different quantum states of the atom correspond to the natural harmonics of the wave resonating in the cavity. Bonds are formed when the charge waves of two atoms overlap. The theory is developed using a picture of the atom in which the negative charge wave of the ground state can be conceptually divided into a core and a valence shell, a picture that is in all essential respects a correct physical description of the real atom.

The classical flux theory of the bond, augmented by a few simple *ad hoc* rules to accommodate certain quantum restrictions, is used to derive a variety of theorems or rules about chemical bonds that can be translated into experimentally measurable properties through an empirical correlation between the bond flux and bond length (Section 3.2).

In Chapter 3, the flux theory is used to derive the rules of the bond valence model. The remaining chapters show how these rules lead to a consistent picture of chemical bonding, structure, and properties such as stability and reactivity.

## 2.2 Theoretical Foundation

### 2.2.1 The Structure of the Atom

Bohr described an atom as consisting of negatively charged electrons travelling in orbits around a central positively charged nucleus, much as the planets in our Solar System orbit the Sun. This simple and appealing picture accounts quantitatively for the atomic spectrum of the hydrogen atom, but it fails to explain the spectra of any of the other elements, nor does it lead naturally to a theory of the chemical bond. The wave picture proposed later by Schrödinger was able to explain the spectra of all the elements and provide a better physical picture

of the atom. According to Schrödinger, the negative charge of the atom is confined to a small volume by its electrostatic attraction to the nucleus, and being a wave, it resonates at one of the characteristic wavelengths of the volume to which it is confined. The fundamental mode represents the ground state and the higher harmonics correspond to the excited states of the atom. The atomic spectrum arises from the emission or absorption of a photon of energy as the charge wave changes from one harmonic resonance to another. While the frequency of the spectral lines measures the energy difference between resonant states, the intensity of the resonating matter wave corresponds to the spatial distribution of the charge (Boeyens 2013). For the ground state, this distribution is readily measured by X-ray diffraction. It can also be calculated using the Schrödinger equation.

Somewhat perversely, chemists have largely rejected this simple wave picture of the atom in favour of a hybrid view in which the charge is composed of a collection of electrons that are not waves but small particles. The density of the charge wave merely represents the probability that an electron will be found at a given location. In an effort to explain the formation of bonds, these electrons are further assumed to be localized in ‘orbitals’ represented by the spherical harmonics into which the charge density can be resolved. This model has many problems. The obvious question—‘what determines the trajectories followed by the electrons within the probability envelope?’—is one for which there is no answer, and while the charge density can be both calculated and measured, there are many equivalent ways in which this density can be decomposed into spherical harmonics (orbitals). The choice between these different representations is arbitrary. Further, it is impossible either by experiment or theory to identify and locate the individual electrons within the charge wave. Treating the negative charge as a wave rather than as a collection of electrons is not only physically more realistic, but also gives better chemical predictions.

An electron is the smallest quantum of charge that can have an independent existence, but the free electrons that are attracted to a nucleus in order to form a neutral atom cease to exist the moment they are captured by the nucleus. They are absorbed into the charge wave and, like Lewis Carroll’s (1865) Cheshire Cat that disappears leaving only its smile behind, the electron disappears bequeathing only its conserved properties: charge, mass and spin, to the charge wave surrounding the nucleus. The electron’s charge and mass are added to the charge and mass of the wave, while the spin, being a vector, is added vectorially in a way that keeps the net spin small. Because electrons obey Fermi–Dirac statistics, they also occupy a finite amount of space and this space is also bequeathed to the atom. In a formal way this is expressed as the rule that no two electrons enter the atom with the same set of the four quantum numbers  $(n, l, m, s)$ . The numbers  $n, l$  and  $m$  are related to the spherical harmonics of three-dimensional space and  $s$  to relativistic time. They are subject to the limitations  $l < n, -l \leq m \leq +l$  and  $s = \pm 1/2$ . The charge tends to accumulate in spherical shells surrounding the nucleus, each shell identified with a different value of  $n$  and able to hold  $2n^2$  electron units of charge. These shells are barely visible in the charge density, but for the lighter

atoms they are readily identified by the differences in the ionization energies required to remove charge from the atom in successive electron quanta. For the heavier elements the shells tend to overlap, resulting in a more complex structural chemistry discussed in Chapter 7 and briefly in Section 3.5. Since charge can only be added to or removed from an atom in electron quanta, the total negative charge surrounding the nucleus is always an integral number of electron units, which is why atomic valences are usually integers. This restriction does not apply to the charge that forms the bonds since the bonding charge is not physically removed from the atom.

In principle, all the properties of an atom or molecule can be calculated using the Schrödinger equation, though in practice there are many impediments to such a calculation. Firstly, the Schrödinger equation is relativistic with real (spatial) and imaginary (temporal) components, but it can only be solved if these components are separated, thereby reducing relativistic space-time to classical space and time coordinates. The solution to the real part of the equation does give the amplitude of the wave, from which one can derive the charge density, but the Schrödinger equation can only be solved if one knows the electric potential that shapes the charge wave. For a single atom this is the potential field of the nucleus which is known but the potential field of a molecule or crystal requires a knowledge of the positions of all the nuclei. This makes it impossible to write down the Schrödinger equation without a prior knowledge of the structure. The structure must be either determined experimentally or predicted using, for example, the empirical ball-and-stick model.

Even though the information available from the Schrödinger's wave equation is limited, it does offer a physical picture of the atom that can be used to calculate many different properties. It also serves as the starting point for the flux theory of the chemical bond. At any given time, the negative charge surrounding the nucleus exists in one of the atom's resonant states. Since most of the energy released in the transitions from excited states lies in the ultra-violet and X-ray regions of the spectrum, these transitions mostly require energies that are too large to be involved in chemical reactions. Excited states are normally ignored when discussing chemical structure, particularly for the elements lighter than argon. Heavier elements often have low-lying excited states that can affect the chemistry since changing the environment of an atom may change the relative energies of the different states, converting an excited state to the ground state and *vice versa*. Approximate quantum calculations can be helpful in such cases. Alternatively, the bonding geometry can be treated empirically, sometimes assisted by a simplified quantum picture as described in Chapter 7.

The intensity of the charge wave of a free atom is shaped only by the potential well of the nucleus, which is spherically symmetric; hence the charge wave itself is also spherically symmetric, a condition that will prove useful in determining bond angles as discussed in Sections 2.3.7 and 3.4.7. The charge density is largest at the nucleus and decreases more or less exponentially with increasing distance from the nucleus, the different shells appearing as small ripples. The outer shell, known as

the *valence shell*, lies closest to the surface of the atom and contains the charge used for bonding since it is the most exposed to interactions with other atoms. In most atoms the valence shell is only partially filled; its total charge is found by noting the number of electrons having significantly smaller ionization energies than those in the core. The filling of the valence shell can also be calculated from the position of the atom in the Periodic Table. If the atom is electroneutral, the magnitude of the negative charge in the valence shell is equal to the positive charge of the *core* that contains the nucleus and the remainder of the negative charge. The *atomic valence* is the total amount of charge the atom uses to form bonds. All of the bonding (valence) charge is found in the valence shell, but not all the charge in valence shell is necessarily used for bonding. The role of any non-bonding valence shell charge (known as ‘lone pairs’) is discussed in Section 7.3. Unless otherwise stated, in this chapter we assume that all the charge in the valence shell is used for bonding.

### 2.2.2 Electrostatic Theory

The success of the nineteenth-century bond model in predicting the structure and properties of many chemical compounds lies in its implied origin in the classical theory of electrostatics. The original simple picture can be recovered and expanded if we identify the chemical bond with the electrostatic flux linking two atoms. Here we review the essential elements of electrostatic theory.

The properties of the electrostatic flux can be derived from Maxwell’s equations of electromagnetism, but Faraday’s lines of field provide a simple graphical, though no less rigorous, representation. Faraday’s lines of electrostatic field have the following properties:

1. They start on positive charges and end on negative charges.
2. The number of lines of field is proportional to the size of the charge from which they emanate and on which they terminate. It is called the *electrostatic flux* and has the dimensions of charge. By a suitable choice of the constant of proportionality, the unit of flux used here is the charge of one *electron unit* ( $1.60 \times 1.0^{-19}$  C), which in chemistry is referred to as the *valence unit* (vu). A more formal definition of the electrostatic flux,  $\Phi_{ij}$ , that links two charges  $i$  and  $j$  is given by eqn 2.1:

$$\Phi_{ij} = \int \mathbf{E} \cdot d\mathbf{A} \quad (2.1)$$

where the integration is taken over any cross-sectional area,  $\mathbf{A}$ , threaded by the field,  $\mathbf{E}$ . However, the Faraday lines of field that provide a graphical representation of this equation are all that is needed to understand the flux theory of the chemical bond.

3. Lines of electrostatic field follow the direction of steepest slope in the electric potential. This means that they cannot cross and tend to avoid each other, two simple rules that allow one to visualize the spatial arrangement of these lines for a given array of charges.
4. At any given point, the direction of a line of field is the direction of the electrostatic field and the density of the lines is proportional to the magnitude of the field.

Some consequences that follow from these definitions are:

1. The positive and negative charges linked by flux must have the same magnitude, which is also the magnitude of the flux. The flux is thus equal to the size of each of the two charges it links. It is measured in electron units, which are the same as valence units.
2. In any arrangement of charges that is locally neutral, such as the interpenetrating arrays of cations and anions of the ionic model, the lines of field link each positive charge only to its neighbouring negative charges and *vice versa* (c.f. Fig. 2.6). This follows from the rule that lines of field cannot cross.
3. While the direction of the lines of field linking two charges depends on where the charges are located, their number (the flux) depends only on the size of these charges. The flux contains no information about the distribution of charge density within the atom.

This last property of the flux is critical for the flux theory of the chemical bond, because it means that if one is independently able to determine the flux linking two charges, one does not need to know where the charges are located. The emphasis in the flux theory is thus on the *function* of the charge rather than its *location*. This explains why quantum mechanics, with its concern for how the charge is distributed, has failed to find evidence for the localized chemical bond; quantum mechanics also has no way to identify how much charge is used to form the bond.

### 2.2.3 The Role of Symmetry

While the function of the negative charge surrounding the nucleus is important to the understanding of chemical bonding, equally important is the role of symmetry. A powerful predictor of structure and geometry is the *principle of maximum symmetry* (rule 2.1), which states that:

*A system in stable equilibrium will adopt the highest symmetry that is consistent with the constraints acting on it.*

Rule 2.1

The justification for this principle is that the energy of any system is at an extremum with respect to any distortion that removes an element of its symmetry and if the system is in stable equilibrium, that extremum must be a minimum. For example, the potential energy of an atom in stable equilibrium lying on a mirror plane is necessarily increased if the atom is displaced from the mirror plane in any direction. Consequently, a system will tend to have the lowest energy when it has the highest possible symmetry.

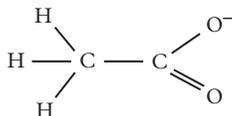


Fig. 2.1 *The bond graph of an acetate ion.*

This principle is useful whenever a choice is to be made between two or more equivalent structures. For example, in the ball-and-stick model the carboxylate group of the acetate ion (ACETAC),  $\text{H}_3\text{C}-\text{COO}^-$ , is formally shown with one single  $\text{C}-\text{O}^-$  and one double  $\text{C}=\text{O}$  bond as in Fig. 2.1. Without knowing anything about the structure in which this ion appears, there is no way to decide which of the two  $\text{C}-\text{O}$  bonds is the double bond. The solution suggested by the principle of maximum symmetry is that both bonds must be identical, each having a bond of order 1.5 and each oxygen atom carrying a formal charge of  $-0.5$  electron units. This is the configuration one expects to find unless there is a constraint that forces one of the  $\text{C}-\text{O}$  bonds to have a bond order less than 1.5 which necessarily results in the other  $\text{C}-\text{O}$  bond having an order greater than 1.5 (Brown 1980b).

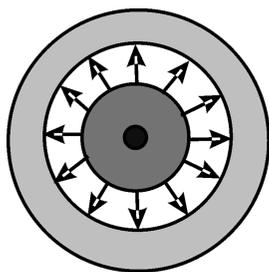
A corollary of the principle of maximum symmetry is rule 2.2:

*The failure of any system to adopt a potentially higher symmetry implies the presence of a physical constraint that prevents the higher symmetry from being achieved.*      Rule 2.2

If a potential symmetry is found to be broken, it is worth enquiring what constraint is responsible.

#### 2.2.4 **The Core-and-Valence-Shell Picture of the Atom**

Because the flux does not depend on the location of the charge, but only on whether or not the charge is used to form a bond, the flux theory is concerned with the function of the charge, not with its location. The picture of an atom that matches this theory is one that separates the charge by function into the bonding charge of the valence shell and the non-bonding charge of the core. It is impossible to make the separation by inspecting their physical locations in the real atom because there is no natural boundary between these functions, but in the flux theory the physical location is irrelevant, so we are free to place the charge wherever it is most convenient for developing the theory. We can design our own atomic picture that separates the charge according to its function.



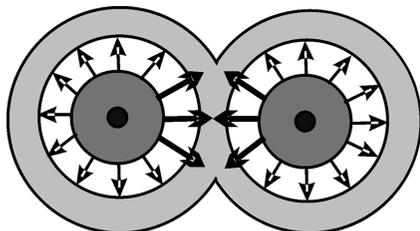
**Fig. 2.2** *The core-and-valence-shell model of an atom. The core is shown in dark grey with the nucleus in black; the valence shell is shown in light grey. The arrows show the lines representing the electrostatic flux linking the core to the valence shell.*

In the core-and-valence-shell picture the atom has a positively charged core consisting of the nucleus and the filled inner shells, surrounded by a negatively charged valence shell. According to the principle of maximum symmetry (rule 2.1), in the absence of any perturbing influence the atom is spherical. If the atom is also electrically neutral, the magnitude of the negative charge of the valence shell is equal to the magnitude of the positive charge of the core and the two are linked by an electrostatic flux of the same magnitude. Since the charge has spherical symmetry, the flux distribution (the electrostatic field) is also spherically symmetric. This core-and-valence-shell picture of an electrically neutral atom is shown in Fig. 2.2. It is a simple picture but it has all the ingredients needed to derive most of the rules of structural chemistry. Like the real atom, the core-and-valence-shell atom is spherically symmetric. It differs from the real atom only in the radial distribution of the charge; the core-and-valence-shell displays the charge according to its function, the real atom displays it according to its location.

## 2.3 The Chemical Bond

### 2.3.1 The Neutral Atom Model

When two atoms come into contact their valence shells overlap as shown in Fig. 2.3. The charge in the overlap region attracts both cores and draws the atoms closer together. This attraction is countered by two forces, the repulsion of the positive nuclei as they become increasingly exposed to each other, and more importantly, the repulsion caused by the overlapping of the cores, which places more charge in the region where the cores overlap than can, according to Fermi–Dirac



**Fig. 2.3** *A bond is formed when the valence shells of two atoms overlap and the lines of field (flux) shown by the thick arrows link the cores to the valence shell charge that each atom contributes to the bond.*

statistics, be accommodated by their already full shells. An equilibrium is reached when the attractive and repulsive forces are equal. The equilibrium bond length is therefore determined by the sizes of the cores and the amount of bonding charge in the overlap region. The more charge in this region, the greater the flux that links the bonding charges to their cores (shown by the thick arrow in Fig. 2.3). It should be no surprise then that as the flux increases the atoms are drawn closer together. The correlation between the length of the bond and its flux cannot be determined classically from first principles but it is readily determined empirically as described in Section 3.2.

When two atoms overlap to form a bond, there is some rearrangement of the charge density, but the size of this deformation is only a few percent (Section 13.3); the strong central potential of the nucleus dominates even after bond formation. It is a good approximation to treat atoms as having the same charge density as the free atom even when they are bonded. This is called the *promolecule* or *procrystal* model (Sections 2.3.7 and 13.3). In this model, the charge densities of the individual atoms never change even as the atoms are moved around. However, the charge density of the molecule or crystal as a whole will change since moving the atoms closer together, for example, increases the overlap, hence also the charge density in the bond. Gibbs *et al.* (2014) show that this increase correlates with the bond length in the same way as the flux (Section 13.2).

The charge in the overlap region that forms the bond belongs equally to both atoms and, for bookkeeping purposes, it can be assigned to either of the two bonded atoms or it can be divided in some manner between them. Because the flux does not depend on the location of the charge, which of these descriptions one chooses is arbitrary and depends on the use to which the theory is to be put. The choice does not depend on the location of the physical charge nor does a particular choice imply that the charge can be found in any particular location. There are two obvious choices, each of which leads to a different model with its own advantages and disadvantages. The simplest choice is to divide the charge between the atoms in a way that ensures that both atoms remain electrically neutral as suggested by the principle of maximum symmetry (rule 2.1). This is the *neutral atom model*. Since all the atoms remain electrically neutral in this model, its advantage is that there are no atomic charges to keep track of. An alternative choice, in which all the bonding charge is associated with just one of the bonded atoms, yields the *ionic model* in which each atom carries a charge equal to its valence. This model is developed in Section 2.3.4.

It is an experimental observation that:

*the two atoms forming a bond normally contribute equal charges to the bonding (or overlap) region.*<sup>1</sup>

Rule 2.3

<sup>1</sup> This is usually explained as a result of the pairing of the spins associated with the two contributions. Here, it is treated as an observation. There are some exceptions discussed in Section 3.4.5.

This rule means that the fluxes linking the overlap region to the cores of the two bonded atoms are equal since they are each equal to the charges that their respective atoms contribute to the bond (Fig. 2.3). In terms of the traditional electron-pair models, the fluxes are also equal to the number of electron pairs forming the bond, though this number is not restricted to an integer. This measure of the strength of the bond is called the *bond flux*, which in the bond valence model is also known as the *bond valence*. In the covalent bond model it is called the *bond order*. These three terms all refer to the same concept and should therefore be equal, even though they have different definitions.

### 2.3.2 Coordination Numbers

Since every bond lowers the total potential energy of a compound, every atom is expected to bond to as many other atoms (known as *ligands*) as possible. The full set of ligands around an atom is known as its *coordination sphere*. The number of atoms in this sphere is known as the *coordination number*. The most important of the various constraints that determine the coordination number (Chapter 4) is the physical size of the atom; the larger the central atom and the smaller the ligands, the larger the coordination number. For this reason, the coordination number can be used as a convenient measure of the effective size of the atom. Since the same element is sometimes found with different coordination numbers, it is convenient to identify a *typical coordination number*,  $\langle N \rangle$ , as a measure of the size of the atom, and because of the widespread presence of oxygen in inorganic chemistry, the typical coordination number is defined as the average coordination number observed with oxygen ligands (Brown 1988a). Average coordination numbers with other ligands may be different but they tend to follow the same trends. The typical coordination numbers of the main group elements are shown in italics in Table 2.1. The same information for some transition metals is given in Table 7.5 (see also Table 2.3). Some of the practical problems of determining the coordination numbers used in calculating  $\langle N \rangle$  are discussed in Section 3.3.

### 2.3.3 Bond Networks

It is possible to represent the structure of a molecule or a crystal as a network of bonds (Beever and Schwarz 1935). In topology theory, a network consists of an array of nodes that are connected by links. Translated into chemical terms, a *bond network* consists of an array of atoms connected by bonds. The important chemical properties of this network are the *valences* of the atoms and the *fluxes* of the bonds.<sup>2</sup> These, combined with a knowledge of the topology of the network,

<sup>2</sup> In the mathematical theory of networks, the 'valence' of a node is defined as the number of links it forms, and it was in this sense that the term was introduced into chemistry. However, chemists were later forced to distinguish between a chemical valence (bonding power of an atom) and a coordinative valence (number of neighbours to which it is bonded). They chose to keep the term 'valence' for the chemical valence and introduced the term 'coordination number' for the coordinative valence. This