

# Bond Valence Theory

I. David Brown

**Abstract** This chapter shows that a unified concept of a chemical bond can be derived from a theoretical picture of the atom in which the Coulomb forces are described using the electric field rather than the electric potential. The localized chemical bond and its valence arises naturally from this picture, allowing the theorems of electrostatics to be used to describe the formation and properties of any chemical structure composed of localized bonds. There is no distinction made between ionic and covalent bonds. An empirical correlation links the theoretical bond valence to the experimental bond length. The resulting picture of chemical structure predicts where bonds will form, how long they will be, and in what direction they will point. It indicates the conditions for chemical stability, suggesting which reactions a compound might undergo either in solution or at a surface. Electronic anisotropies are handled in an ad hoc manner, in which the VSEPR theory of lone pairs is extended to cases where the lone pairs are inactive or only partially stereoactive. Steric constraints leading to compressed or stretched bonds are quantified by observing the difference between the real and theoretical structures. The potential of the bond valence theory is only beginning to be exploited.

**Keywords** Bond · Bond valence · Bond valence theory · Bonding geometry · Bonding strength · Lewis acids and base strengths · Lone pairs · Steric effects · Structure prediction

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I.D. Brown (✉)  
Brockhouse Institute for Materials Research, McMaster University, Hamilton,  
ON, Canada L8S 4M1  
e-mail: [idbrown@mcmaster.ca](mailto:idbrown@mcmaster.ca)

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## 1 Introduction

The first chapter in this volume [1] describes how the bond valence theory developed over the last hundred years as an empirical research tool for analyzing inorganic crystal structures. The justification for the theory has always lain in its experimental success rather than its theoretical underpinning. This chapter attempts to rectify this lack of a theoretical basis. It starts with a simple physical picture of the atom, the core-and-valence-shell picture, from which the rules of bond valence theory are derived using the concepts of classical physics. Although a full quantum analysis is clearly essential to an understanding of the structure of the atom and its spectrum, equilibrium chemical structures involve only the ground electronic state, which greatly simplifies the theory, allowing a development in terms of classical electrostatics in which quantum effects are introduced as needed on an ad hoc basis. Apart from the obvious desirability of having a

physical picture of bond valence, putting the model on a sound theoretical basis has two particular advantages. In the first place, it allows one to appreciate the scope of the theory and to understand better how it might be extended. In the second place, a simple theory of chemical structure based on a proper physical description of bonding is ideal for introducing students to structural chemistry, a topic taken up in the Chap. 9 of this volume [2].

This chapter starts with a description of the core-and-valence-shell picture of the atom, followed by a derivation of the principal theorems of bond valence theory. The later sections of the chapter illustrate the ways in which these theorems are applied over a range of chemical bonds and structures.

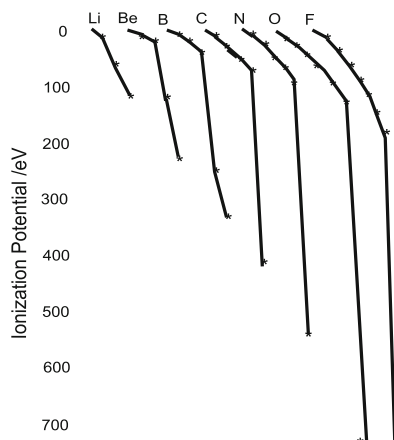
## 2 Core-and-Valence-Shell Picture of the Atom

The concept of a chemical bond as a localized interaction between two neighboring atoms has been a central part of chemistry for the past century and a half, yet our current description of chemical bonds is still empirical; it is a collage of ill-defined and largely incompatible models that are based on assumptions that do not always correspond to physical reality. The ionic and covalent models are mutually incompatible, and both the Lewis and orbital models have serious flaws [3, 4]. They do not conform to modern views of atomic structure, and consequently their predictions sometimes fail. While the bond valence theory belongs to this tradition of localized bond models, it is derived from a realistic, though simplified picture of the atom, one that is compatible with more sophisticated atomic descriptions. It can be used to derive powerful and quantitative theorems about chemical structure. The rules of both the traditional ionic and covalent models can be derived as two special cases of this model (Sects. 5 and 7.2).

What most clearly distinguishes bond models from other models of chemical structure is the centrality of the concept of valence, that is, the number of electrons that an atom uses for bonding. In order to determine the valence, we must be able to count how many valence electrons each atom contains. This is not possible in electron density models such as the quantum theory of atoms in molecules (QTAIM), where the individuality of the electron is lost as soon as it enters the atom [5]. A different picture of the atom is needed, one that tracks the *functions* of the individual electrons, rather than their *locations*.

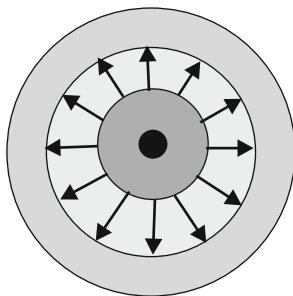
A second distinguishing feature of bond models is their treatment of the chemical bond as a localized interaction between two neighboring atoms; everything beyond the first neighbor shell is ignored. The long-range Coulomb potential, which is a central component of most other bonding models, extends well beyond the nearest neighbors, which is why the concept of a chemical bond has never been derived from models expressed in terms of the Coulomb potential, whether treated using Newtonian or quantum mechanics. Because the bonds are local, the number of bonds formed by an atom, its coordination number, is also an important quantity in bond models.

**Fig. 1** Ionization potentials of elements from the second period. Successive ionization potentials are displaced to the right



These two distinguishing features of chemical bond models, namely, the atomic valence and the bond as an interaction between neighboring atoms, point to the need for a different way of describing both the structure of the atom and the force responsible for the bond. The emphasis on the valence of an atom requires a model in which the valence electrons can be conceptually separated from the remaining (core) electrons, and the emphasis on localization requires that the long-range Coulomb potential be replaced by the electrostatic field which provides an equivalent, but complementary, description, one in which neighboring charges are linked by electrostatic flux as first suggested by Pauling [6] and Bragg [7]. In any locally neutral distribution of positive and negative charges such as are found in molecules and crystals, the Faraday lines of field, which provide an intuitive picture of this flux, always connect positive charges to their neighboring negative charges, and since the electrostatic flux (represented by the number of lines of field) is equal to the charges (valence electrons) that generate them, the concepts of valence and electric flux fuse into a picture which is both intuitive and quantitative. It is a picture from which the theorems of the bond valence theory naturally follow. This theory is completely equivalent to the traditional energy-based classical theories, but unlike the traditional models which require that all the long-range interactions be treated explicitly, valence-and-flux models are conceptually and computationally simpler because all the interactions are local, and the long-range relaxations are implicit rather than explicit.

The justification for separating the valence electrons from the core is based on the observed ionization potentials: the energies required to successively remove electrons from an atom. The large increase in ionization energy after the first few electrons have been removed allows us to separate the weakly bound electrons ( $\leq 100$  eV), namely the valence electrons, from the core electrons that are too strongly bound to the atomic nucleus to be able to take part in bonding (Fig. 1). The result is the core-and-valence-shell picture of an atom, one in which the valence electrons are conceptually distinguished from the core electrons.



**Fig. 2** The core-and-valence-shell picture of an atom. The core is shown as *dark gray*, the valence shell in *light gray*, and the nucleus is shown in *black*. The number of lines of field (electrostatic flux) is proportional to the negative charge on the valence shell as well as the positive charge on the core

The core-and-valence-shell picture of an atom is illustrated in Fig. 2. The electrons are separated into those in the valence shell (light gray) and those that remain strongly bound in the core (dark gray). Because all the electrons are held by a strong central attraction to the nucleus (black), both the core and the valence shell remain essentially spherically symmetric, even when the atom is bonded to other atoms. The justification for this assumption is that the relaxation of the electron density on bond formation is small enough ( $\sim 1\%$ ) to be ignored in this approximation. In the bond valence theory, atoms are always assumed to be electrically neutral unless otherwise stated, meaning that the core and the valence shell are not only spherically symmetric but they also carry equal and opposite charges. The small ionization energy of the electrons in the valence shell implies that this shell lies close to the surface of the atom and carries a negative charge equal to the number of electrons in the valence shell. The atomic core contains both the nucleus and the core electrons and carries a net positive charge of the same magnitude. The relative location of the valence shell and core is not relevant in this picture since the electrostatic flux linking the core to the valence shell depends only on the number of electron charges it links, not on their location. It is convenient to display them as spherical in the picture shown in Fig. 2 as this is similar to the physical distribution of electrons in the atom. The picture would be even more similar to the real atom if the core and valence shell were shown as overlapping each other, but it is more convenient to visualize them separated by a gap, since this provides room to display the lines of electrostatic field that link them.

This model explicitly does not give a picture of the true electron density since the physical location of the electrons is not relevant to the model and, indeed, cannot be derived from the model. Superimposing the valence shell and core does not yield a true physical picture of the atom because the purpose of the model is not to reproduce the true electron density, but rather to keep track of the roles played by the valence shell and core electrons. The model's validity does not depend on its ability to predict the electron density, which it is neither intended, nor is it able to do, but on its ability to predict the bonding structures in crystals and molecules. In this respect it performs at least as well as any other model and in many respects better.

### 3 Theorems of the Bond Valence Theory

#### 3.1 *The Principle of Maximum Symmetry*

The formal development of the model starts with a useful heuristic assumption that underlies the model: the *principle of maximum symmetry*:

A system in stable equilibrium adopts the highest symmetry consistent with the constraints acting on it.

(1)

The justification for this statement is that a symmetric system is always at an energy extremum with respect to any distortion that lowers its symmetry, and that the system is stable only if this extremum is a minimum. We need no further justification to explain why a compound has high symmetry. If the symmetry is lower than expected, there must be a constraint that causes the symmetry to be lost. Important constraints are those imposed by the rules of chemistry (chemical constraints) and those imposed by requirements of three dimensional space (steric constraints).

There are two atomic properties that are central to the bond valence theory: the **valence of the atom**, that is, the number of electrons the atom uses for bonding and the size of the atom, conveniently represented in bond valence theory by the atom's **coordination number**, that is, the number of bonds that it forms, as discussed in more detail below.<sup>1</sup>

The theory assumes that only the valence-shell electrons are used for bonding because these lie close to the surface of the atom where they overlap with the valence shells of other atoms on bond formation. For elements in periods two and three of the Periodic Table, the concept of a valence shell is well defined because of the large difference in ionization energy between the electrons of the valence shell and those of the core. For elements in higher periods, the gap is less well defined and the concept of a valence shell becomes more problematic, particularly for the transition metals discussed in Sect. 7.4.

#### 3.2 *Assumptions and Theorems*

We start with a formal statement of the assumptions that underlie the model. Giving these explicitly not only serves to introduce the model but also to define the range of compounds that the model describes.

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<sup>1</sup> The terms used in this theory are shown in bold type and are defined in the Glossary (Appendix 1 in this volume).

1. All atoms are assumed to be *spherically symmetric*, even when bonded to other atoms. The rationale for this assumption is that the relaxation of the electron density on bond formation is limited to a few percent. While this relaxation may be important for understanding the nature of the chemical bond and calculating its energy, it has little effect on the resulting chemical structure. The relaxation of the electron density can be ignored in modeling these structures, and the assumption of spherical symmetry places some useful constraints on the structural properties of the atoms.
2. In bond valence theory, atoms (with one exception) are always treated as *uncharged*. A bond is formed when the valence shells of two neutral atoms overlap. The electrons from the two atoms spin-pair, but they are still counted as being part of their original spherically symmetric valence shells. This assumption simplifies the description of the bond since it avoids using such elusive concepts as electron transfer, ionic character, and atomic charge. The only exception to this assumption is the ionic model which is derived from the bond valence theory in Sect. 5. Even in this case the transfer of electrons from the cation to the anion is a matter of formal bookkeeping; it does not imply any physical movement of the electrons.
3. Since a bond is formed by the pairing of electron density in the region where the valence-shells of two atoms overlap, each atom is assumed to contribute the *same number of valence electrons* to the bond. This number is known as the **bond valence**. The bond valence is therefore also equal to the number of electron pairs that constitute the bond. In general the bond valence is not an integer.
4. It is assumed that there is a large difference in the *ionization energy* between the valence shell electrons and those in the core. This allows us to ignore the core electrons and focus on those in the valence shell. This assumption holds for light main group elements, but is questionable for transition metals (Sect. 7.4) and heavy main group elements. The advantage of this assumption is that it allows us to identify clearly which atoms have well-defined valences and which atoms may not. Being able to identify why the rules may not work in a given compound makes it easier to suggest how the model might be adapted.
5. It is also assumed that all the *excited states* of the atom lie too far above the ground state to be involved in bonding. This again is valid for light main group elements, but like assumption 4 is not always valid for transition metals and heavy main group elements. Again it identifies where the model might not work and why.
6. The valence shell may contain both *bonding and nonbonding (lone pair) electrons*. The electron density of the valence shell always remains spherically symmetric (see assumption 1 above), but the way the electrons in the shell function, being either bonding or nonbonding, may result in different parts of the valence shell functioning in different ways. If the bonding and nonbonding functions are not uniformly distributed, the lone pair is said to be *stereoactive*. The properties of atoms with lone pairs are described in Sect. 7.1.

7. The bond is assumed to be *localized* between the two bonded atoms. This excludes compounds with delocalized bonding such as metals and aromatic compounds. Delocalization occurs when the valence shells of the different atoms meld into an extended band so the valence electrons are no longer constrained to remain on their own atom. Recognizing this assumption may suggest ways of extending the model to delocalized systems.

As stated above, the valence of an atom is defined as the number of electrons it uses for bonding. The valence of a bond is defined as the number of valence electrons that an atom contributes to a particular bond. From these definitions, the *valence sum rule* immediately follows.

The sum of the valences of all the bonds formed by an atom is equal to the valence of the atom.

(2)

From assumption 3 above, each of the bonded atoms contributes an equal number of electrons to the bond. This is known as the *Equal Contribution Rule*:

Each of the two terminal atoms contributes the same number of electrons to the bond that links them. This number is therefore equal to the number of electron pairs that form the bond and so is equal to the valence of the bond. It is not restricted to integers because the electron density does not consist of identifiable individual electrons.

(3)

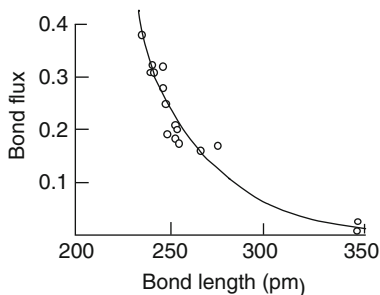
Since the flux is equal to the charges it links, the flux terminating on the electrons contributed to the bond is also equal to the valence of the bond (see Fig. 2).

It is apparent that the closer two atoms approach each other, the greater the number of electrons that lie in the **overlap region**, hence shorter bonds are expected to have larger bond valences. There is no simple way to calculate this relationship, but it can be determined empirically by comparing the predicted valence of a bond with its measured length. Even though the individual bond valences are not normally known a priori, the valences of the atoms that form the bonds are known. It is possible to determine the bond valence–bond length correlation by insuring that the bond valences determined from observed bond lengths add up to the valences of the atoms at both ends of the bond. These correlations are empirically found to be transferrable between all the bonds of the same type, i.e., all the bonds that have the same two terminal atoms in the same valence state. It is this correlation that links the theory to experiment. The problem of determining these correlations is discussed more fully in this volume by Adams [8].

The existence of a correlation between the theoretically determined bond valences and the experimentally observed bond lengths is what validates the model. Without this link, the abstract theorems of the bond valence theory developed below would have no relevance to the real world. The bond valence theory is



**Fig. 3** The correlation between bond valence (bond flux) and bond length for Ca–O bonds. The *small circles* show the bond fluxes calculated for particular compounds (Fig. 3.1 from [11] by permission of the Oxford University Press)



justified by noting that bond valences calculated from the observed bond lengths obey the theorems of the model.

The difficulty in calculating this correlation from quantum theory is not the only reason for determining it empirically. An empirical determination automatically takes into account all the factors that affect the bond length. For example, strong bonds are better able than weak bonds to draw the ligands closer to each other, but in turn the resulting repulsion between the ligands tends to stretch the bonds. With an empirically determined correlation such stretching is automatically taken into account.

Although there is no theory that predicts the algebraic form of this correlation, over a limited range of bond lengths the simple two parameter equation (4) works well [9].

$$S_{ij} = \exp \left( (R_0 - R_{ij})/b \right) \quad (4)$$

where  $R_{ij}$  is the length and  $S_{ij}$  the valence of the bond between atoms  $i$  and  $j$ , and  $R_0$  and  $b$  are the empirically determined **bond valence parameters**. Values for these parameters compiled from various sources can be found at reference [10]; their determination is discussed by Adams [8]. An example of this correlation is shown in Fig. 3.

The form of Eq. (4) gives rise to an important theorem, *the distortion theorem* (5) [12, 13]:

If some of the bonds formed by an atom are lengthened and others shortened, their bond valence sum will increase if the average bond length is held fixed, or alternatively, the average bond length will increase if the bond valence sum is held fixed.

(5)

If an atom lies at the center of a cavity that is too large, the bonds will all be longer than expected, and the atom will appear to have a valence sum that is too low. By moving the atom away from the center of the cavity some of the bonds become shorter and others longer, but the valence of the shorter bonds increases

more than the valence of the longer bonds decreases, leading to an increase in the bond valence sum. In cases where an atom occupies a large cavity, this mechanism is found to increase the bond valence sum to match the atomic valence while keeping the average bond length constant. This is effected either by the atom being displaced from the center of the cavity, or by the ligands moving to ensure that the bonds have different lengths. This theorem is central to the work described by Lufaso and Woodward in [14].

## 4 Bonding Strength and Valence Matching

The valence sum rule is not sufficient by itself to determine the valences of individual bonds, but the principle of maximum symmetry (1) implies that the bonds formed by an atom will have similar valences. In this case the valences of all the bonds in the coordination sphere are expected to be close to their average which can be calculated using Eq. (6) provided we know the number of bonds the atom forms.

$$S_{\text{average}} = V/N \quad (6)$$

where  $S$  is the valence of a bond,  $V$  is the valence of the atom, and  $N$  the number of bonds the atom forms (its coordination number).

The coordination number depends primarily on the relative sizes of the atom and ligand, but may be affected by other factors. In most cases, the coordination numbers observed for a given **atom type** (an element in a given valence state) tend to cluster around their average value. For example when sodium is bonded to oxygen, all coordination numbers between 3 and 12 are known, but 80% of the sodium atoms have coordination numbers between 4 and 7 with an average of 6.4, giving  $S_{\text{average}} = 0.16$  **valence units** (vu).

If the value of  $N$  is known or can be inferred from other considerations, this value should be used in Eq. (6). If  $N$  is not known, a standard value,  $N_{\text{O}}$ , the average of the observed coordination numbers with oxygen ligands, can be used as a best guess instead, as shown in Eq. (7) [15]. The resulting value of  $S_{\text{O}}$  is known as the **bonding strength of the atom**, since, in the absence of any better information, the bonds formed by the atom are expected to have valences close to  $S_{\text{O}}$ .

$$S_{\text{O}} = V/N_{\text{O}} \quad (7)$$

The bonding strengths of many elements in the Periodic Table are shown in Tables 1–3. The bonding strength, which is characteristic of each atom type, has two important uses. Firstly, the bonding strengths,  $S_{\text{E}}$ , of the different elements when in their highest valence state,  $V_{\text{max}}$ , i.e., when all the electrons in the

**Table 1** The Periodic Table with electronegativities and cation bonding strengths (in valence units, vu) to oxygen

1	2	3–12	13	14	15	16	17	18
H <sup>b</sup>								
0.8								
0.2								
Li	Be		B	C	N	O	F	Ne
0.20	0.50		0.87	1.35	1.67	(2.0)	(2.3)	
Na	Mg		Al	Si	P	S	Cl	Ar
0.16	0.33		0.57	1.00	1.25	(1.6)	1.75	
K	Ca	Se–Zn	G <sub>A</sub>	Ge	As	Se	Br	Kr
0.13	0.27		0.65	0.89	1.13	(1.5)	(1.5)	
Rb	Sr	Y–Cd	In	Sn <sup>a</sup>	Sb <sup>a</sup>	Te <sup>a</sup>	I <sup>a</sup>	Xe <sup>a</sup>
0.12	0.23		0.50	0.68	0.85	1.0	(1.2)	(1.3)
Cs	Ba	La–Hg	Tl <sup>a</sup>	Pb <sup>a</sup>				
0.11	0.20		0.49	0.70				

Bonding strengths are calculated using Eq. (7) (except those in parentheses which are estimated)  
<sup>a</sup>These cations are also found in lower oxidation states with one or more lone pairs  
<sup>b</sup>Hydrogen has two bonding strengths (see Sect. 8.1.1)

**Table 2** Simple anion bonding strengths (*S<sub>B</sub>*)

Col #	15	16	17
Valence	−3	−2	−1
	N	O	F
	−0.75	−0.5	−0.25
	P	S	Cl
			−0.17
		Se	Br
			(−0.10)
		Te	I
			(−0.08)

Anion bonding strengths are based on coordination numbers of 4 for N, O and F, and 6 for Cl

valence shell are bonding, follow the same ordering as their electronegativities as expressed in Eq. (8).

$$S_E = V_{\max}/N_O$$

(8)

*S<sub>E</sub>* provides a convenient scale of **electronegativity** within the bond valence theory, because even though it differs numerically from the traditional electronegativity scale, it is derived from the basic parameters of bond valence theory, namely the valence and coordination number. It is the scale used in this chapter.

Secondly the definition of bonding strength in Eq. (7) leads to an important rule for predicting structures. The equal contribution rule (3) states that the two bonded atoms should contribute the same valence to the bond, which means that a bond will only be formed if both atoms have the same bonding strength. Some latitude is

**Table 3** Complex ion bonding strengths

	Residual valence	$S_A$ or $S_B$
$\text{NH}_4^+$	1	0.12
$\text{ClO}_4$	-1	-0.1
$\text{BF}_4$	-1	-0.1
$\text{NO}_3$	-1	-0.11
$\text{HCO}_3$	-1	-0.17
$\text{SO}_4$	-2	-0.17
$\text{H}_2\text{PO}_4$	-1	-0.18
$\text{H}_2\text{O}$	0	-0.2
$\text{HPO}_4$	-2	-0.22
$\text{CO}_3$	-2	-0.22
$\text{PO}_4$	-3	-0.25
$\text{BO}_3$	-3	-0.33
$\text{SiO}_4$	-4	-0.33
$\text{OH}$	-1	-0.4

Anion bonding strengths are based on coordination numbers of 4 for N, O and F

allowed by atoms adopting different coordination numbers, but it is found that stable bonds rarely form between atoms whose bonding strengths in Tables 1, 2, and 3 differ by more than a factor of 2. This is expressed in the *valence matching rule* (9):

$$\text{Stable bonds will normally form only if } 0.5 < S_A/S_B < 2.0 \quad (9)$$

where  $S_A$  and  $S_B$  are the bonding strengths of the two bonded atoms, A and B. If the coordination number is known or can be reasonably guessed, then a better estimate of the bonding strength can be made. The bonding strength can therefore be influenced by local conditions, but it tends to lie close to the value given by Eq. (7). There are exceptions to the valence matching rule. As described in Sect. 7.1, the presence of a lone pair in the valence shell of one or both atoms provides a flexibility that removes the upper limit in the expression (9) with interesting consequences for the coordination geometry.<sup>2</sup>

If one knows which atoms are present in a compound, the inequality (9) can be used to determine which atoms will bond to each other, information that can be used to generate the **bond network**, as described in Sect. 11.2.

<sup>2</sup>Coordination numbers depend on the nature of both the bonded atoms and are sometimes different even between the same pair of atom types in different compounds.  $S_O$  is taken arbitrarily to be an atomic property, but if the bonded atom is not oxygen, a different value of  $N$  might be more appropriate. For example, carbon has a coordination number of three with oxygen, but four with hydrogen. Reducing the coordination number increases the bonding strength and this is the usual mechanism by which the bond valences of two bonded atoms can be made exactly equal.

## 5 Valence Compounds and the Ionic Model

Most bonds are formed between atoms having different electronegativities. It is convenient to call the atom having the lower electronegativity the **cation** (or A, for Lewis Acid) and the atom having the higher electronegativity the **anion** (or B, for Lewis Base). If both atoms have the same electronegativity, the choice of which is the cation and which the anion is arbitrary; either can be used. Although in traditional models cations are assumed to carry a positive charge and anions a negative charge, in bond valence theory all atoms, including cations and anions, remain electrically neutral unless otherwise stated. The terms “cation” and “anion” are used only as labels to identify which of the two atoms forming a bond has the smaller, and which the larger, electronegativity.

A **valence compound** is defined as one in which every atom is uniquely labeled as either a cation or an anion, and every bond has a cation at one end and an anion at the other, i.e., there are no bonds between two cations or between two anions.

(10)

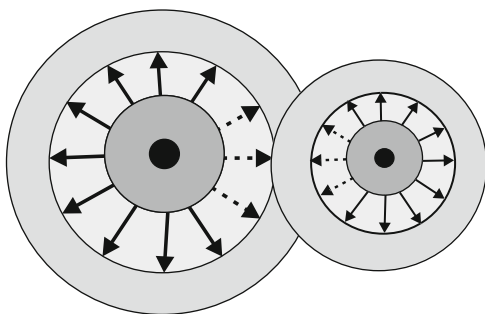
A bond network with this property is said to have a **bipartite graph**, and a corollary to this definition is that the bond network of a valence compound contains only even-membered rings since an odd-membered ring necessarily contains a **homoionic bond**.

The valence shell of the cation carries a small charge and is linked to its core by a weak electric field. Consequently it lies far from the nucleus. On the other hand, the valence shell of the anion carries a large charge and is held closer to the nucleus. As a result, the bond overlap between the cation and the anion occurs closer to the anion as shown in Fig. 4. Quantum mechanics places restrictions on the number of electrons that can be accommodated in the overlap region, and while the nature of these restrictions is complex, it is conveniently summarized by the *octet rule* (11) which states that<sup>3</sup>:

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<sup>3</sup>When the valence shells of two atoms overlap, they split into a low-energy bonding level localized in the overlap region between the atoms and a high-energy antibonding level localized behind the atoms. Because the overlap region is closer to the anion, the bonding level has more of the character of the valence shell of the anion and the antibonding level more the character of the cation. If more electrons are available for bonding than can fit into the anion-like bonding level, they must necessarily occupy the antibonding level, tending to destabilize the bond. The most stable bond is formed when the bonding level is full and the antibonding level is empty, a condition that is expressed by the octet rule. When both the bonding and antibonding levels are full, there is no bonding advantage in overlapping the valence shells, which explains the inertness of the noble gases. The repulsion that prevents the atoms from merging is provided by the electrostatic repulsion that occurs when their cores overlap (the overlap in this case providing no bonding advantage) as well as by the electrostatic repulsion between the two nuclei.

**Fig. 4** The overlap region of the bond between a cation (*left*) and an anion (*right*) occurs closer to the anion. The *dotted field lines* are those that contribute to the bond



All the valence electrons of the cations must be accommodated within the valence shells of the anions.

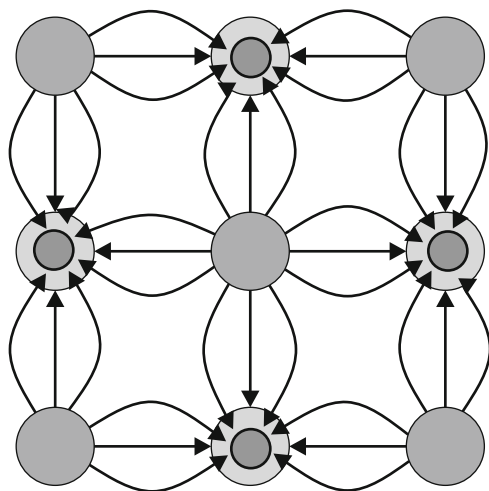
(11)

Since for many anions, particularly those in periods two and three of the Periodic Table, the valence shell is capable of holding only eight electrons; the rule (11) is known as the octet rule. The neutral anion normally has a valence shell that is more than half filled, limiting the amount of space available for the electrons of the cations. Since the equal contribution rule (3) limits the anion and cation to contributing the same number of electrons to the bond, the anion is not able to use all its valence shell electrons for bonding. For example, oxygen has six electrons and two vacancies in its valence shell. As it can accommodate only two valence electrons from the cations, it can use only two of its own valence shell electrons for bonding. The valence of oxygen when acting as an anion is only two; the remaining four electrons are nonbonding and form two nonbonding lone pairs. Thus when an atom acts as an anion it has a smaller valence than when acts as a cation, and by convention, anion valences are taken as negative as shown in Table 2 [16]. The role played by the nonbonding electrons is discussed in Sect. 7.1.

For valence compounds, the bond valence theory can be converted to the **ionic model** simply by formally reassigning the cation valence electrons to the valence shells of the anions that already accommodate them. This does not require that these electrons be physically moved from the cation to the anion, since the anion and cation-bonding electrons already occupy the same overlap region, and in any case the core-and-valence-shell model contains no information about the actual location of the electrons. Bond valence theory is only a means of keeping track of the way the electrons function; reassigning the cation valence electrons to the anion is no more than a book-keeping operation. It makes no difference to the physical description of the bond. The advantage of this approach is that it changes the way we view the bond by eliminating the need to speculate on the precise location of the bonding electrons.<sup>4</sup>

<sup>4</sup>The core-and-valence-shell diagrams, used here to illustrate the formation of bonds, are purely schematic. The pairing of electron densities that forms the bond occurs at some place where the electron density of the two atoms overlaps, but its location depends on how the atoms are defined and in any case cannot be identified experimentally.

**Fig. 5** A schematic picture showing how the lines of electrostatic field define the bonds in a neutral array of positively and negatively charged atoms. The valence electrons are shown in very *light gray* around the (negative) anion



Reassigning the cation electrons to the anion valence shell leaves the cation with the positive charge of its core which is equal to its positive valence, and the anion with a negative charge equal to its negative valence. Further the electrostatic flux that links the core of the cation to its bonding electrons (cf. Fig. 4) is still present, but as the bonding electrons are now all assigned to the anions, this flux links the cores of the positively charged cations to the valence shells of their negatively charged anion neighbors. If both ions are now shrunk to a point, one retrieves the ionic model: an array of point charges linked together by electrostatic flux, each ionic charge equal to the valence of the cation or anion it represents.

This leads to an interesting extension of the core-and-valence-shell picture. Where the valence of a bond was previously defined as the flux linking the cation core to the electrons it contributes to the bond, in the ionic model it is defined by the same flux which now links the cation to the anion. If the positions of the atoms in the array are known from experiment, this flux can be directly calculated. The calculation involves extensive computation, but Preiser et al. [17] have shown that in structures in equilibrium, the correlation between the bond flux and bond length is the same as the correlation that had previously been observed between the bond valence and bond length, showing that the electrostatic flux and bond valence are indeed the same.

It is sometimes assumed that the long range of the Coulomb potential makes it impossible to define a localized bond in the ionic model, but in fact the ionic model is the *only* model that provides a useful and unambiguous definition of a bond. Since the electrostatic flux that links two ions is equal to the valence of the bond that links them, a bond only exists between ions if they are linked by flux. A simple picture of the electrostatic field in the ionic model is provided by the lines of field that connect a cation to its first shell of anion neighbors as shown in Fig. 5.

The paradox of a localized interaction having a long-range influence can be understood by considering what happens if the valence of a particular bond is

increased. According to the valence sum rule (2), the valences of the bonds between the terminating atoms and their first neighbors must be correspondingly reduced. This in turn triggers an increase in the valence of the bonds between the first and second neighbors. In this way the bond network relaxes by means of a wave passing from one atom to the next throughout the structure. Just as the collective behavior of an ant colony is driven by the actions of each individual ant responding to its immediate environment, so the collective behavior of a molecule or crystal is driven by each atom reacting to changes in its local environment.

This derivation of the ionic model provides not only a natural definition of a bond, but it also defines the scope of the model. The assumptions on which the derivation is based show that far from being confined to compounds whose bonds have “ionic character,” the ionic model can be used for any valence compound. It can be used to describe not just NaCl but also SF<sub>6</sub>, CO<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>COOH, and O<sub>2</sub>, all of which have networks with bipartite graphs.

## 6 Geometry of Valence Compounds

### 6.1 Predicting the Bond Lengths

The ionic model can be used to derive a number of theorems that apply to valence compounds.

The first is the *electroneutrality rule* (12). Because the atoms of the core-and-valence-shell model are all electrically neutral and all the charges have been conserved during the derivation of the ionic model, the array of charged ions in the ionic model must also be electrically neutral.

In a valence compound, taking the cation valences as positive and the anion valences as negative, the sum of the valences (charges) of the atoms (ions) is zero.

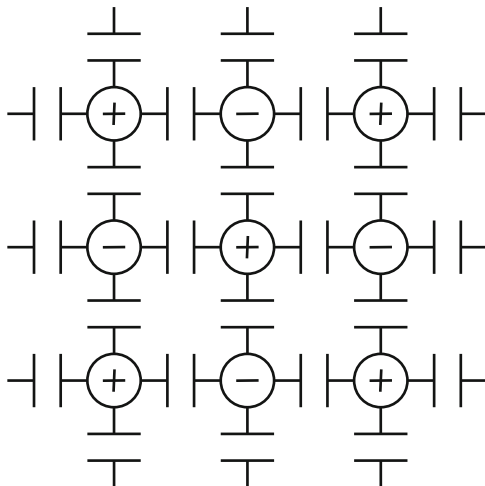
(12)

More importantly, we can use the ionic model to predict the electrostatic flux or valence of the individual bonds, and from these we can predict their lengths. If the positions of the atoms are already known, the bond flux can, in principle, be calculated using Coulomb’s law, but this is computationally intensive, and as it requires a prior knowledge of the structure, the result is not a prediction. Fortunately there is a simpler approach that requires no prior knowledge of the atomic positions. All that is required is a knowledge of the bond network, that is, which atoms are linked by bonds.

In the ionic model, a bond consists of two equal and opposite charges (ions) linked by an electrostatic field. This makes the bond an electric capacitor. Each bond in a bond network can therefore be replaced by a capacitor, converting the



**Fig. 6** The bond network shown in Fig. 5 can be represented as a capacitive electrical network



bond network into a capacitive electrical network as shown in Fig. 6 which illustrates the equivalent circuit for the bond network shown in Fig. 5.

The charges,  $Q_i$ , at each node in this circuit are the atomic valences, and the distribution of charges (equal to the bond fluxes),  $F_{ij}$ , on the plates of the capacitor linking atoms  $i$  and  $j$ , can be found by solving the set of Kirchhoff equations (13a) and (13b):

$$Q_i = \sum_j F_{ij} \quad (13a)$$

$$0 = \sum_{\text{loop}} P_{ij} \quad (13b)$$

$P_{ij}$  is the potential difference between atoms  $i$  and  $j$ . If there are  $n$  atoms, there are  $n - 1$  independent equations of the type (13a) (one equation is redundant since the total charge of the compound is zero), and if there are  $m$  bonds, there are  $m - n + 1$  independent equations of type (13b). The electric potential is related to the charge on the capacitor by the capacitor equation  $F_{ij} = P_{ij}C_{ij}$ . All that is required to solve the resulting set of equations is the capacitance,  $C_{ij}$ , of each of the  $m$  different bonds. The principle of maximum symmetry (1) implies that the values of  $C_{ij}$  will all be equal, and in practice this is found to be the case for equilibrium structures. Two types of constraint break this symmetry: anisotropies in the electronic structure of the ion, e.g., lone pairs and Jahn–Teller distortions discussed in Sect. 7, and steric stresses, e.g., atoms in cavities that are too large, such as the hydrogen atom in hydrogen bonds, as discussed in Sect. 8. In this section, we consider only those structures in which these constraints are absent.

Substituting the bond valence,  $S_{ij}$ , for the bond flux  $F_{ij}$  and the atomic valence,  $V_i$ , for the charge,  $Q_i$ , and noting that the bond capacitances, being equal, cancel out



**Fig. 7** The finite bond network corresponding to the infinite network shown in Fig. 4. *A* is the cation, *B* the anion

of the equations, one gets the **network equations** (14a) and (14b) linking the valences,  $S_{ij}$ , of the bonds to the valences,  $V_i$ , of the atoms.

$$V_i = \sum_j S_{ij} \quad (14a)$$

$$0 = \sum_{\text{loop}} S_{ij} \quad (14b)$$

Since the valence  $V_i$  is known for all the atoms, this set of  $m$  equations can be solved to give  $S_{ij}$  for each of the  $m$  bonds. This calculation is implemented in the program BONDVAL [18]. The bond valences calculated from these network equations are known as **ideal bond valences**. If they are the same as the experimental values, the assumptions of the bond valence theory are validated [17], but if they are different, they indicate that one of the additional constraints described above is present. In principle it should be possible to model these constraints by choosing suitable bond capacitances, but in practice the capacitances themselves often depend on the context in ways that are not always transparent [19].

For molecules, the bond network is finite and generating and solving the network equations (14a) and (14b) is relatively straightforward, but for non-molecular compounds the network is infinite which makes it impossible to solve the network equations unless, as in a crystal, the network is composed of identical copies of a repeating unit. In this case the infinite bond network can be reduced to a finite network by extracting one repeating unit (formula unit) from the crystal and reconnecting the broken bonds. The resulting finite network is similar to that of a molecule, except that some atoms will be connected by more than one bond. The infinite two-dimensional network of Fig. 5 reduces to the finite network, also known as the quotient graph, shown in Fig. 7. In Fig. 5, each cation *A* forms four bonds to four different anions, *B*, resulting in the two atoms of the formula unit appearing in the quotient graph (Fig. 7) being linked by four separate bonds. The local environment of each atom in the quotient graph is the same as that of the corresponding atom in the infinite network, and the network equations that solve the quotient graph give the same bond valences as they would for the infinite network. In the example shown, the network equations can be solved by inspection; if the cation has a valence of +1 and the anion a valence of −1, all the bonds have valences of 0.25 vu (valence units).

The network equations (14a) and (14b) predict the valences of the bonds based on knowing only the composition of the compound and the way the atoms are

connected. From these predicted bond valences, it is possible, using the bond valence–bond length correlation (4), to predict the lengths of each bond, and provided there are no additional electronic or steric constraints, these distances are found to differ from the observed distances by around 0.02 Å, an accuracy comparable with that achieved by other methods, both classical and quantum. Ways in which the bond network can be predicted are described in Sect. 11.2.

## 6.2 Predicting the Bond Angles

Predicting the bond angles is not as straightforward as predicting bond lengths, since they are more sensitive to steric effects which can only be taken into account once the bond network has been mapped into three-dimensional space.

If the bonds are all equivalent in the bond graph, they are expected to be uniformly distributed around the atom. The principle of maximum symmetry (1) predicts that three equivalent bonds will be arranged with threefold (triangular) symmetry as in  $\text{BF}_3$  and  $\text{CO}_3^{2-}$ , four equivalent bonds will have tetrahedral symmetry as in  $\text{CH}_4$  and  $\text{SO}_4^{2-}$ , and six will have octahedral symmetry as in  $\text{SF}_6$  and  $\text{NaCl}$ . These are the most frequently found coordination environments. The only high symmetry arrangements of five or seven bonds are planar and unlikely to be found in a three-dimensional structure. Five and seven coordination must have at least two inequivalent bonds and are notably less common than three, four, or six coordination. They are found only when a more symmetric arrangement is not possible.

Nonuniform environments occur if the ligands are different or have different environments in the bond graph so that the bonds are no longer equivalent. The symmetry may also be lost if electronic anisotropies such as stereoactive lone pairs are present (Sect. 7.1). In this section, we assume that lone pairs, if present, are not stereoactive.

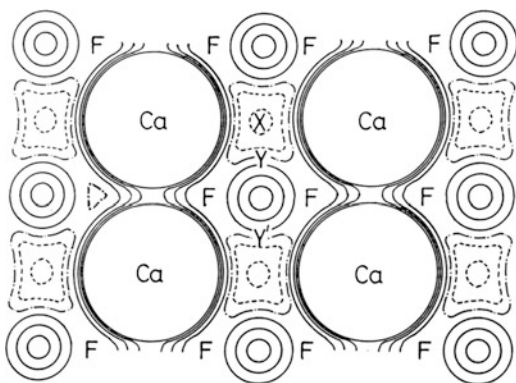
Any part of the flux linking the core of an atom to its valence shell belongs to one of the bonds formed by the atom (see Fig. 4), and because the atom is spherically symmetric, the solid angle,  $\Omega$ , subtended by this flux is a proportionate part of the total solid angle of  $4\pi$  steradians surrounding the core, leading to Eq. (15).

$$\Omega_{ij} = 4\pi S_{ij}/V_i \quad (15)$$

An approach based on this idea has been shown to work well for calculating bond angles in tetrahedral coordination, as for example around the sulfur atom in sulfates [20], and as shown in Sect. 7 it is a useful approach to exploring the extent to which lone pairs are stereoactive.

If measuring the solid angle occupied by a bond is not convenient, an alternative approach is to use the **valence vector**,  $\mathbf{S}$ . This is a vector that represents the electric flux linking the core to the overlap region. Its magnitude is equal to the magnitude of the flux and its direction is taken to be along the line connecting the two atoms as

**Fig. 8** A valence map of fluorine in a (110) plane in  $\text{CaF}_2$ . Dotted lines are negative; contours greater than 1.8 not shown. X and Y show possible sites for interstitial F (Fig. 11.8 from [11] by permission of the Oxford University Press)



an approximation to the net direction of the flux lines in the bond. Since the total flux is distributed uniformly around the core, the sum of the bond valence vectors should be zero in the absence of any perturbing influence, a condition known as the *valence vector sum rule* (16), which provides a way of expressing one of the constraints acting on the bond angles. This approach has been explored by Harvey et al. [21] and Zachara [22].

$$0 = \sum_j \mathbf{S}_{ij} \quad (16)$$

If this sum is not zero, it gives a measure of how far the bonding electrons in the valence shell deviate from spherical symmetry [23].

Another technique that is useful if the positions of most of the atoms are known, but the location of others is not, is the *valence map* [24]. Figure 8 shows the map for fluorine in  $\text{CaF}_2$ . A different representation of a valence map can be seen in Fig. 10 in Chap. 4 [14]. It is calculated by moving the fluorine atom systematically over the positions on a grid spanning the positions of the calcium atoms in the structure. At each point its bond valence sum is calculated from the distance to its neighbors. The resulting grid of bond valence sums represents a map that has high values when the fluorine atom is placed too close to the position of a calcium atom and a minimum when it is placed at the center of a cavity. In Fig. 8, the sites normally occupied by fluorine are labeled F, and possible sites for interstitial fluorine are marked X and Y.

The valence vector sum can also be treated as a field since it can be calculated for an atom placed at any point in the structure, not just the known site of an atom. Mathematically it represents the slope of the valence map,  $U(\mathbf{r})$ , at the position  $\mathbf{r}$ :

$$\sum \mathbf{S}(\mathbf{r}) = b \cdot \nabla U(\mathbf{r}) \quad (17)$$

where  $b$  is the bond valence parameter (assumed here to be the same for all the bonds). The minimum in the valence map is the point where the valence vector sum

is zero, and if the correct location of the atom is at the center of one of the cavities, the valence sum at the minimum should be the same as the valence of the atom itself. If the cavity is too small for the atom, the minimum will be larger than this, if the cavity is too large, the minimum will be smaller. If the atom does not lie at the center of the cavity, e.g., as a result of application of the distortion theorem (5), it is expected to lie on the contour whose value is equal to the valence of the atom. The position of the atom on this contour depends on which neighbor has the most deficient valence sum.

The valence map can be used for locating weakly scattering and weakly bonding atoms such as lithium in cases where it has not been detected by X-ray diffraction, but more commonly it is used for tracing possible diffusion paths in crystalline and amorphous solids as discussed in [25].

### 6.3 *Non-valence Compounds and Homoionic Bonds*

The network equations (14a) and (14b) can only be used if the graph of the bond network is bipartite, that is, if every bond has a cation at one end and an anion at the other. In inorganic compounds, and particularly in organic compounds, this condition is not always satisfied. Although this restricts the application of the bond valence theory, the core-and-valence-shell picture of the atom is still valid, as is the description of the chemical bonds this picture gives.

There are a variety of ways in which a non-bipartite bond graph can be converted to a bipartite graph, although some information is usually lost along the way.

1. The two cations, or two anions, that form the bond can be considered as a single pseudo-atom. This makes the bond graph bipartite. This solution works well for cations like  $\text{Hg}_2^{2+}$  which are traditionally described in this way. In the mercurous cation, the Hg–Hg bond is formed by an electron pair and has a valence of 1.0 vu. If the  $\text{Hg}_2^{2+}$  cation is in an asymmetric environment, the valence of the external bonds formed by the individual Hg atoms may not be the same, in which case the two mercury atoms may contribute different numbers of electrons to the Hg–Hg bond. Although this violates the equal contribution rule (3), the valence of the bond is correctly given by the average of the contributions of the two mercury atoms. Hg–Hg bonds are known in a number of mercury complexes, and not all of these are electron pair bonds, but as expected, the length of the bond is found to correlate with its valence (the number of electron pairs that form it) in the same way as any other bond [26].
2. An alternative approach to the mercurous cation is to treat the bonding electron pair as a pseudo-anion,  $\text{E}^{2-}$ . Inserting such an anion into the bond again makes the graph of the bond bipartite and does not require that the two Hg–E bonds have the same valence. Since it is not possible to locate the pseudo-anion, the individual valences of the Hg–E bonds cannot be found from their bond lengths,

but the sum of these lengths does correspond to the charge of the pseudo-anion and correlates with the Hg–Hg bond length [26].

3. In some cases an atom may act as an anion towards some of its ligands and as a cation to others. For example, in the  $\text{NO}_2^-$  ion, the oxygen atoms are the anions with a valence of  $-2$  vu and the nitrogen is a cation with a valence of  $+3$  vu. But the nitrogen is also a Lewis base and can coordinate to a transition metal to form a bond in which the nitrogen acts as the anion. In this case, the valence sum at the nitrogen is calculated by adding the bond valences having regard to their sign. For example, if the nitrite group bonds to copper, the Cu–N bond might have a valence of  $-0.4$  vu, increasing the valence of the N–O bonds from  $1.5$  to  $1.7$  vu to give a sum of  $+3.0$  around nitrogen (see Fig. 6 in [2]):

$$V_{\text{N}} = 2S_{\text{NO}} + S_{\text{CuN}} = 2 \times 1.7 - 0.4 = 3.0 \text{ vu}$$

With the N–O bonds having a valence of  $1.7$  vu, the residual valence on each of the oxygen atoms is reduced from  $-0.5$  vu in the free nitrite ion to  $-0.3$  vu and the residual valence of the nitrite group as a whole is then

$$2 \times (-0.3) + (-0.4) = -1.0 \text{ as expected.}$$

This is equivalent to splitting the nitrogen atom into two, an  $\text{N}^{2-}$  anion bonded to copper and an  $\text{N}^{5+}$  cation bonded to oxygen linked by an N–N bond of  $1.8$  vu. The N–N bond is entirely fictitious; its valence depends on the valence of the Cu–N bond but in any case is not susceptible to measurement. As in the other cases, splitting the nitrogen atom into two results in the creation of a bipartite bond graph which can be solved using the network equations (14a) and (14b).

## 7 Electronic Constraints

Electronic constraints arise from changes in the electronic structure of the atom itself. There are several ways in which these occur. Some are initiated by the atom's environment, some occur spontaneously as a result of degenerate electronic states as predicted by the Jahn–Teller theorem which states that the environment of an atom will distort if such a distortion removes the degeneracy. Electronic constraints manifest themselves as a loss of symmetry either in the bond lengths or in the bond angles. Changes in the bond lengths cause the equal valence rule (14b) to be violated, but valence sum rule (14a) continues to be obeyed. Changes in the bond angles generally do not violate the network equations (14a) and (14b), but do affect the vector valence sum (16) which is no longer expected to be zero [23].

The most common electronic constraint involves the rearrangement of nonbonding “lone pair” electrons that are found around strongly bonding main group elements as discussed in Sect. 7.1. Other constraints are found in the transition

metals, leading to the characteristic dipolar distortions found around octahedrally coordinated  $d^0$  atoms, or in the so-called Jahn–Teller quadrupolar distortion found around  $\text{Cu}^{2+}$  and  $\text{Mn}^{3+}$  described briefly in Sect. 7.2.

## 7.1 Role of Lone Pairs

All anions, and main group cations in lower oxidation states, contain lone pairs [16]. The treatment here focuses on anions, but the same principles apply to cations. In some compounds, such as  $\text{MgO}$ , the lone pairs on the oxygen anion have no effect on the bonding geometry; the cations are distributed uniformly around the anion as expected from the principle of maximum symmetry (1). But in other compounds, the lone pairs provide a constraint that destroys this symmetry; for example, the bonds formed by the oxygen atoms in the sulfate ion,  $\text{SO}_4^{2-}$ , are not uniformly distributed; there is one strong bond to sulfur and a number of weaker bonds to other cations. The different types of asymmetric bonding induced by the lone pairs in such compounds are described by the well-established valence shell electron pair repulsion (VSEPR) model [27]. The rules of this model can be carried over with little change into the bond valence theory with one difference: the underlying picture of the VSEPR model, in which the electron pairs in the valence shell are assumed to repel each other, is replaced by the more flexible core-and-valence-shell picture described in Sect. 2 [16].

The behavior of lone pairs in bond valence theory is best illustrated by an example. When oxygen acts as an anion, its valence is  $-2$  and it commonly forms between two and six bonds, so a typical coordination number can be taken as four. This gives oxygen an anion bonding strength,  $S_B$ , of  $-0.5$  vu (Table 2). According to the valence matching rule (9), oxygen should form stable compounds with any cation having a bonding strength between 0.25 and 1.00 vu. Table 4 lists the binary compounds that oxygen forms with the elements of periods two and three of the Periodic Table. For each compound listed, Table 4 gives the bonding strength,  $S_A$ , of the cation (taken from Table 1) and the ratio of the cation to anion bonding strengths,  $S_A/S_B$ . Those compounds that have  $S_A/S_B$  between 0.5 and 2.0 satisfy the valence matching rule (9) and are shown in normal type. As expected, these are all stable crystalline solids. Those compounds with ratios less than 0.5, shown in *italics*, are unstable and can be formed only with difficulty as they readily pick up water and  $\text{CO}_2$  from the atmosphere to form basic carbonates which provide a better valence match (see Tables 1, 2, and 3). Those shown in bold type have a ratio greater than 2.0 and, according to the valence matching rule, they ought not to exist. The reason they occur is attributable to the presence of the lone pairs on the oxygen atom.

According to the assumptions of the model, the electron density in the valence shell remains spherically symmetric even when the atom forms bonds. Although the electron density of the valence shell is always distributed with spherical symmetry, there is no requirement that the way this electron density functions is also uniformly

**Table 4** Oxides of atoms of rows two and three of the Periodic Table

	$S_A$ (vu)	$S_A/S_B$	State	$S_2$	Comment
<i>Li<sub>2</sub>O</i>	0.2	0.4	<i>Solid</i>	0.2	<i>Unstable, picks up water</i>
BeO	0.5	1	Solid	0.5	Stable
B <sub>2</sub> O <sub>3</sub>	0.87	1.7	Solid	0.2	Stable
<b>CO<sub>2</sub></b>	<b>1.35</b>	<b>2.7</b>	<b>Gas</b>	<b>−0.22</b>	<b>Stable but dissolves in water to give CO<sub>3</sub><sup>2−</sup></b>
<b>N<sub>2</sub>O<sub>5</sub></b>	<b>1.67</b>	<b>3.3</b>	<b>Gas</b>	<b>−0.11</b>	<b>Reactive, forms NO<sub>3</sub><sup>−</sup></b>
<i>Na<sub>2</sub>O</i>	0.16	0.33	<i>Solid</i>	0.16	<i>Unstable, picks up water</i>
MgO	0.33	0.67	Solid	0.33	Stable
Al <sub>2</sub> O <sub>3</sub>	0.57	1.14	Solid	0.43	Corundum, stable
SiO <sub>2</sub>	1	2	Solid	−0.33	Quartz, stable, forms minerals with SiO <sub>4</sub> <sup>4−</sup>
<b>P<sub>2</sub>O<sub>5</sub></b>	<b>1.25</b>	<b>2.5</b>	<b>Solid</b>	<b>−0.25</b>	<b>Reacts with water to form H<sub>3</sub>PO<sub>4</sub></b>
<b>SO<sub>3</sub></b>	<b>1.5</b>	<b>3</b>	<b>Solid</b>	<b>−0.17</b>	<b>Reacts with water to form H<sub>2</sub>SO<sub>4</sub></b>
<b>Cl<sub>2</sub>O<sub>7</sub></b>	<b>1.75</b>	<b>3.5</b>	<b>Liquid</b>	<b>−0.08</b>	<b>Reacts with water to form HClO<sub>4</sub></b>

Items in *italics* and **bold** do not obey the valence matching rule (9)

$S_A$  is the bonding strength of the cation,  $S_B$  is the bonding strength of the anion ( $= 0.5$ ), and  $S_2$  is the bonding strength of the secondary bonds, all in valence units (values in parentheses are calculated for the corresponding complex ion). Values in **bold type** refer to the corresponding complex ion.

distributed. Some parts of the valence shell may be bonding and other parts nonbonding.

In compounds with  $S_A/S_B < 1.0$ , the bonds are arranged around the anions symmetrically, as expected from the principle of maximum symmetry. The coordination is tetrahedral around oxygen in BeO and octahedral in MgO, in all cases the symmetry is as high as the constraints of three-dimensional space allow. Both the bonding and the lone pair electron density are uniformly distributed around the valence shell; each portion of the valence shell contains some electron density that is bonding some that is nonbonding (lone pair).

For compounds with  $1.0 < S_A/S_B < 2.0$ , the valence matching rule is still satisfied. The compounds are stable, but the lone pairs start to show some stereoactivity as can be seen in the structures of silica and alumina. Silica adopts various structures whose Si–O–Si angles vary from 130° to 180°. In corundum, Al<sub>2</sub>O<sub>3</sub>, two of the four bonds formed by oxygen are short (primary) and two are long (secondary) with the valence of the primary bonds being equal to the bonding strength of Al<sup>3+</sup>, 0.57 vu (1.83 Å), and the valence of the secondary bonds being equal to 0.43 vu (1.93 Å). This incidentally allows pairs of AlO<sub>6</sub> octahedra to adopt the unusual feature of sharing a face, which also happens to be a topological requirement of mapping its bond network into three-dimensional space.

If the ratio  $S_A/S_B$  is greater than 2.0, the oxygen is required to form a stronger bond to the cation than its normal bonding strength allows. If there were no lone pairs present, extra electrons would have to be brought in from other parts of the valence shell, thus destroying the spherical symmetry of its electron density. This would cost more energy than could be recovered by forming the bond, but because the oxygen anion already has nonbonding electron density in the overlap region, it



can match the bonding strength of the cation by converting lone pair electron density in the overlap region to bonding while converting an equivalent amount of bonding electron density elsewhere into lone pairs. In this way, it can reassign the function of the electron density while retaining the spherical symmetry of the valence shell.

It is only necessary to reassign enough electron density to meet the bonding requirements of the cation, resulting in an asymmetry in which the valence of the primary bonds on one side of the oxygen anion is equal to the bonding strength,  $S_A$ , of the cation, leaving a smaller residual valence to form weaker secondary bonds of valence  $S_2$  on the other side [28]. The relative strengths of the primary and secondary bonds are shown in Fig. 5 of [2]. For example, the oxygen atoms of the  $\text{PO}_4^{3-}$  ion form one strong bond (1.25 vu) to phosphorus and several weaker bonds of about 0.25 vu to other cations. In extreme cases all the bonding electron density is found on one side of the atom, leaving only lone pair electron density on the other. In  $\text{CO}_2$  the separation between the valence electrons and the lone pairs is so complete that the oxygen atoms in carbon dioxide molecules are unable to form any further bonds. Carbon dioxide remains a gas under ambient conditions.

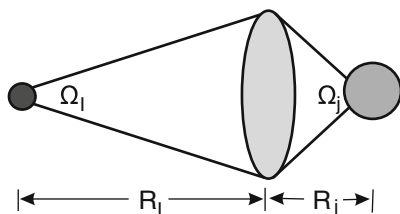
To achieve a complete separation between the valence electrons and the lone pairs as in  $\text{CO}_2$ , oxygen must form one fully saturated bond of 2.0 vu, but fluorine forms fully saturated bonds at the much small valence of 1.0 vu. Many fluorides, such as  $\text{CF}_4$ , contain saturated bonds, and since a saturated bond prevents fluorine from forming a second bond, fluorides of cations with a bonding strength of 1.0 vu or higher usually form isolated molecules with an unreactive surface. On the other hand, oxygen, because of its higher valence, rarely forms fully saturated bonds because few cations can form bonds with valences greater than 2.0 vu. Oxide molecules such as  $\text{SO}_3$  have saturated bonds, but since such molecules, unlike  $\text{CF}_4$ , have space for additional ligands in their coordination sphere, they tend to link into chains or to react with water to form  $\text{SO}_4^{2-}$  with enough bonding electrons residing on the surface of the complex to bond to weakly bonding cations such as sodium.

The core and valence shell model can be used to examine the effects of lone pairs on the bonding geometry. Because every atom has a spherically symmetric electron density, the electric field linking the core to the valence shell is also spherically symmetric. If lone pairs are present in the valence shell, some of the electrostatic flux (valence) will link to lone pair electrons and some to bonding electrons. Although the total flux is distributed symmetrically, its function as either bonding flux or lone pair flux need not be.

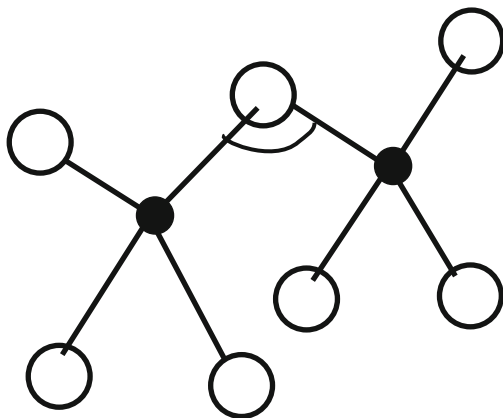
As shown in Sect. 6.2, the solid angle subtended by a bond is proportional to the valence of the bond as given in Eq. (15). The area occupied by the bonding overlap region is related to the solid angle,  $4\pi S_{ij}/V_i$ , by (18)

$$\text{area of the overlap region} = R_i^2 \Omega_i = 4\pi R_i^2 S_{ij}/V_i \quad (18)$$

**Fig. 9** The overlap region (light gray) subtends a larger angle at the anion (medium gray) than at the cation (dark gray)



**Fig. 10** An  $M_2O_7$  complex. The angle at the bridging oxygen is marked



where  $R_i$  is the distance from the overlap region to atom  $i$ . Since the overlap region is common to both bonded atoms, it defines the solid angle,  $\Omega_j$ , of the bond at the other atom  $j$  as given by Eq. (19) and shown in Fig. 9.

$$\Omega_j R_j^2 = 4\pi R_i^2 S_{ij}/V_i \quad (19)$$

The relative sizes of the two solid angles thus depend on the location of the overlap region given by  $R_i/R_j$ . The overlap region is not defined by bond valence theory, though it is expected to lie closer to the anion as can be seen in Fig. 4. We might therefore expect the solid angle subtended by the flux at the anion to be larger than the solid angle at the cation.

The presence of lone pairs gives rise to two possible extreme geometries. In the first, the lone pairs are not stereoactive and the bonding electrons and lone pairs are both distributed with spherical symmetry. The bonding flux and nonbonding flux are also uniformly distributed, and each part of the valence shell, i.e., each overlap region, contains both bonding and nonbonding electrons. Consider, for example, an  $M_2O_7$  complex composed of two  $MO_4$  tetrahedra sharing a common bridging oxygen shown in Fig. 10. The valence of the  $M-O_{\text{bridging}}$  bonds is 1.0 vu, and since this saturates the oxygen atom, if the two lone pairs of the bridging oxygen are uniformly distributed around the valence shell, the two  $M-O_{\text{bridging}}$  bonds are collinear, giving an  $M-O-M$  angle of  $180^\circ$  with the overlap regions of each bond occupying one half of the sphere.

**Table 5** Predicted and observed M–O–M angles in M<sub>2</sub>O<sub>7</sub> complexes

	Solid angle of the bond as a fraction of a sphere		M–O–M (degrees)	
	M	O	Predicted	Observed
Si <sub>2</sub> O <sub>7</sub> <sup>6−</sup>	0.25	0.45	168	140–180
P <sub>2</sub> O <sub>7</sub> <sup>4−</sup>	0.20	0.36	143	122–156
S <sub>2</sub> O <sub>7</sub> <sup>2−</sup>	0.17	0.30	127	114–121
Cl <sub>2</sub> O <sub>7</sub>	0.14	0.26	115	115

In the other extreme geometry, when the lone pairs of the oxygen atom are fully stereoactive, the bonding and nonbonding electrons are completely separated, with the four non-bonding electrons occupying two-thirds of the valence shell and the two bonding electrons occupying the remaining one-third. Each bond occupies just one-sixth of the total sphere. In this case, the lone pairs are said to be stereoactive. The most symmetric geometry of six electrons around the oxygen atom is an octahedron. If the two M–O bonds are *cis*, as expected for the dipolar valence shell of oxygen, the M–O–M angle is 90°.

In both of these extreme geometries, the fluxes of the M–O<sub>bridging</sub> bonds are 1.0 vu, but the distribution of the bonding flux and the solid angle it subtends at the nucleus depends on the degree to which the lone pairs are stereoactive. If they are completely inactive, each of the two bonds subtend a solid angle of  $(1/2) \times 4\pi$  steradians resulting in an M–O–M angle of 180°, but if they are fully active, each bond subtends an angle of only  $(1/6) \times 4\pi$  steradians and the angle between the bonds is only 90°.

The M<sub>2</sub>O<sub>7</sub> complexes with M = Si, P, S, and Cl all have geometries that are intermediate between these extremes, with the M–O–M angles decreasing as the valence of M increases from 4 to 7. All of these complexes except Cl<sub>2</sub>O<sub>7</sub> are anions, and they all have the same geometry apart from the lengths of the M–O<sub>terminal</sub> bonds and the M–O–M angle. Setting the valence of the bridging M–O bond to 1.0 vu in Eq. (19), the solid angle subtended by its overlap region at the bridging oxygen equals  $4\pi(R_M/R_O)^2/V_M$ , where  $R_O$  is the distance between the overlap region and the bridging oxygen. The factor  $(R_M/R_O)^2$  is not known a priori, but the physically reasonable value of 1.8 accounts for the decrease in the M–O–M angle as one progresses from Si to Cl as shown in Table 5. One can understand why this angle changes even though there is no change in the valence of the bridging M–O bond. As the valences of the terminal M–O bonds increase, these bonds occupy a larger portion of the solid angle around M, causing the M–O<sub>bridging</sub> bond to focus into a smaller solid angle. This leaves a larger solid angle at the bridging oxygen for the lone pairs, making them more stereoactive.

Bickmore et al. [23] have adopted an alternative approach to the description of stereoactivity by showing that the valence vector sum (Eq. 16) can be used as a measure of the stereoactivity of the lone pair, noting the correlation between vector valence sum and the valence of the shortest primary M–O bond, which as shown above is equal to the bonding strength of the cation.

In cases where the lone pairs are fully stereoactive, the VSEPR and bond valence theories make similar predictions for the bonding geometry because both models

assign the same localized regions of the valence shell to the lone pairs and the bonding electrons, but they differ in the way they make this assignment. The VSEPR model is useful for predicting the overall geometry when the lone pairs are stereoactive because it is simpler, but bond valence theory is more quantitative and can predict the extent to which the lone pairs will be stereoactive. The full power of the VSEPR model can therefore be incorporated into bond valence theory.

## 7.2 Covalent Models

The short primary bonds that are responsible for the stereoactivity of the lone pairs on anions are normally described as covalent, but bond valence theory makes no distinction between ionic and covalent bonds, since the bond valence is a variable that runs continuously across the whole spectrum of bond types. The ionic–covalent distinction does, however, reflect a marked difference between the structural chemistry of those compounds that obey the valence matching rule (9) in which the bonding is generally weak (less than about 0.8–1.0 vu), and those where the presence of anion lone pairs permits the formation of much stronger bonds by making the lone pairs stereoactive as described in Sect. 7.1. The bonds that obey the valence matching rule are those traditionally described as ionic, while bonds formed by atoms with stereoactive lone pairs are those traditionally described as covalent. Even though the bonds form a continuous series in which such a distinction is not necessary, the term covalent can be usefully applied to the primary (short) bonds formed by anions with stereoactive lone pairs.

The term “covalent” was originally applied to the bonds in the ball and stick picture of structure used in organic chemistry. It is therefore interesting to note under what conditions the ball and stick picture can be derived from bond valence theory. The concept of a bond arose in the mid nineteenth century from the study of the chemistry of carbon compounds. The original model was simple: it envisioned atoms as having a fixed number of hooks each of which could form a bond by linking to a similar hook on other atoms. This ball and stick picture, in which the balls represent the atoms and the sticks the bonds, can be derived from the bond valence theory if all the atoms have coordination numbers that are equal to their valence. Examples are silicon ( $V = N = 4$ ), molybdenum ( $V = N = 6$ ), and the two elements that form hydrocarbons: carbon ( $V = N = 4$ ) and hydrogen ( $V = N = 1$ ).<sup>5</sup>

In hydrocarbons the valence of the C–C, C–H, and H–H bonds is always 1.0 vu and since carbon and hydrogen both have the same electronegativity, these bonds are electron pair bonds and are equivalent to each other.

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<sup>5</sup>The coordination number of carbon with oxygen is three (cf., Table 1), which is also the coordination number found in elemental carbon (graphite). The coordination number of four is found only in compounds in which carbon is bonded to hydrogen or a halogen, or in compounds such as diamond that are formed under pressure. See Sect. 8.1.1 for a fuller discussion of the coordination number of hydrogen.

The consequence is that for hydrocarbons, bond valence theory reduces to the simple ball and stick model in which all the bonds are formed by a single electron pair and the coordination numbers are fixed at four for carbon and one for hydrogen. The principle of maximum symmetry (Eq. 1) requires that carbon's four bonds be directed to the corners of a tetrahedron. Carbon and hydrogen atoms are linked to each other by identical electron pair bonds to form extended networks in which hydrogen, having a coordination number of only one, always terminates the network, thus ensuring that all hydrocarbons are molecules. Double and triple bonds are formed by linking two carbon atoms by a tetrahedral edge or face, respectively. Bond valence theory does not use  $\pi$  bonds to describe these compounds but both descriptions are consistent with quantum mechanics.

This simple model is often extended to nitrogen ( $V = N = 3$ ), oxygen ( $V = N = 2$ ), and halogens ( $V = N = 1$ ), but these elements have a higher electronegativity than carbon and hydrogen. They are anionic with stereoactive lone pairs, but with sufficient residual valence to provide Lewis base sites that can act as receptors of secondary bonds such as hydrogen bonds (see Sect. 8.1.1). Although it is common to consider that the base function on oxygen is supplied by the lone pairs, lone pairs are, by definition, nonbonding. Oxygen and nitrogen act as the receptor of hydrogen bonds as the result of the ability of their bonding electrons to rearrange themselves within the valence shell in response to their environment, diverting some of the valence previously used to form the C–O or C–N bonds into accepting hydrogen bonds. When this happens, the valences of the C–C and C–H bonds will no longer be exactly 1.0 vu, and the bonds will no longer be pure electron pair bonds. The simple ball and stick model no longer strictly applies. One can treat the hydrogen bonding as a perturbation, but it is a perturbation that can significantly change the properties of the molecule. Unlike the rules of the simple ball and stick model, the rules of bond valence theory require the hydrogen bonds to be explicitly taken into account, as can be seen from the examples given in Sect. 8.1.1. Bond valence theory can predict, or at least provide limitations on, the structure and properties of many organic molecules, specifically those that have localized bonds and are valence compounds.

### 7.3 Complex Ions

Cations are Lewis acids, and anions are Lewis bases, and their respective bonding strengths are also their Lewis acid and Lewis base strengths. So far this discussion has focused on simple ions, that is, ions that consist of a single atom, in which the Lewis acid and base strengths can be calculated using Eq. (7). Complex ions are those composed of more than one atom. They differ from simple ions in that the different atoms in the complex may each have their own Lewis acid or base strength.

Each atom in a complex ion is necessarily bonded to one or more atoms within the complex to form a network of strong internal (covalent) bonds. For example, the sulfur in the sulfate anion,  $\text{SO}_4^{2-}$ , is a hexavalent cation,  $\text{S}^{6+}$ , linked by bonds

of 1.5 vu to the four oxygen anions. In the ammonium cation,  $\text{NH}_4^+$ , nitrogen is a trivalent anion,  $\text{N}^{3-}$ , linked by bonds of 0.75 vu to the four hydrogen cations. When the bonding requirements of the internal bonds are satisfied, the individual atoms forming the complex may have a residual valence that is available to form bonds external to the complex, often considered to be ionic bonds. In the sulfate ion, the oxygen uses only  $-1.5$  vu internally, leaving  $-0.5$  vu for forming external secondary bonds. In the ammonium ion, the hydrogen uses  $+0.75$  vu to form the internal bonds leaving  $+0.25$  vu for forming external bonds. The unused valence of the peripheral atoms is known as their **residual valence**. Assuming that all the oxygen atoms in the sulfate ion are equivalent and they each form four bonds, one to sulfur and three external to the complex, each oxygen has a bonding strength of  $-0.5/3 = -0.17$  vu. This is then the **Lewis base strength** of the oxygen atoms and, therefore, the Lewis base strength of the sulfate ion as a whole. Similarly, each hydrogen atom in the ammonium ion normally forms two extra bonds, so its **Lewis acid strength** is  $+0.25/2 = +0.12$  vu, similar to that of rubidium. Because the acceptor hydrogen bond normally has a valence of 0.2 vu, the ammonium ions can also bond to anions with larger bonding strengths. Since most of the atoms on the surface of a complex form more than one external bond, the Lewis acid or base strength is normally smaller than the residual valence. Complexes may be anions or cations, or neutral molecules, and any complex may contain some atoms that function as Lewis acids and others that function as Lewis bases, but in all cases the sum of the residual valences over all the atoms in a complex, taking into account their sign, is equal to the total residual valence, or formal charge, of the complex.

Neutral molecules, such as water or ammonia, if they have any chemical activity, must contain both Lewis acid and Lewis base functions, with the condition that their residual positive valence must be numerically equal to their residual negative valence. A consequence is that the Lewis acid and base functions must work together; in neutral molecules the total valence of the external bonds formed by the Lewis acid functions must equal the total valence of the external bonds formed by the Lewis base functions. It is helpful to distinguish the Lewis acid and Lewis base functions by arrows on the bonds directed from the acid to the base.

Complex ions and molecules have more flexibility in adapting to their environment than simple ions since they can redistribute their residual valence among the different atoms that form the surface of the complex ion by changing the valences of the internal bonds. Both the bonding strengths displayed by such complexes, and their internal geometries, may vary depending on what counterions are present in the compound.

## 7.4 *Transition Metals*

The valence shells of transition metals are less well defined than those of the light main group elements because the valence s–p shell of one period overlaps with the d shell of the period that lies above it in the Periodic Table. Only the

s-p shell is involved in the bonding of atoms of groups 1–3 because for these atoms the d shell lies at a higher energy and is not involved in bonding. Only the s-p shell is involved in bonding in atoms of groups 12–17 because for these atoms the d shell lies below the s-p shell; it is full and part of the core. In the remaining groups 4–11, the s-p and d shells overlap and all their electrons take part in bonding. Since the s, p, and d electrons lose their identity in the valence shell, they cannot be distinguished from each other and there is no gap in the ionization energies to define the boundary between the valence shell and the core. One consequence is that atoms in these groups can adopt a variety of different valences. Once the valence is known, the bond valence theory can be applied in the same way as it is applied to main group atoms. In some cases, there are electronic constraints that can be introduced into the bond valence theory using simple ad hoc models. These cases are discussed individually in Sects. 7.4.1–7.4.3 below. Bickmore et al. [23] have shown how the valence vector sum can be used to measure the size of the non-centrosymmetric distortions displayed by transition metals.

#### 7.4.1 Distortions Around Transition Metals with $d^0$ Configurations

The early transition metals in high-valence states show a strong aversion to being in the centrosymmetric environment of an octahedral field. They either avoid six coordination or if they adopt it, their octahedral coordination is distorted. Since the tetrahedron does not have an inversion center, it is unaffected by this distortion.

The distortion takes the form of an off-center displacement of the transition metal from the center of its octahedron, sometimes known as the Second-Order Jahn–Teller (SOJT) effect. It results from a dipole distortion that can be described using the spherical harmonics associated with the p shell. The distortion becomes stronger as one moves across the Periodic Table. Scandium(III) shows no tendency to distort its octahedral environment. Titanium(IV) usually adopts a regular octahedral coordination, but the titanium atom is easily driven off-center, for example, by occupying a cavity that is too large as in  $\text{BaTiO}_3$  (Sect. 8). Although this displacement is predicted by the distortion theorem (5), it is stabilized by the  $d^0$  electronic effect. If the ligands are topologically equivalent, as they are in  $\text{BaTiO}_3$ , the direction of displacement can be changed by application of an external electric field. The  $d^0$  distortion is best observed in vanadium in its +4 ( $d^1$ ) and +5 ( $d^0$ ) valence states. In these states, vanadium can adopt either octahedral or tetrahedral coordination, but octahedral coordination is sufficiently distorted that vanadium compounds typically adopt bond networks that support the distortion. The strongly bonded  $\text{VO}^{3+}$  group [ $s(\text{V}-\text{O}) \approx 1.80 \text{ vu}$ ] found as part of the octahedral environment of vanadium is so striking that it is sometimes called the vanadyl cation. Its strong bond is usually trans to a very weak bond which in some cases is entirely absent. In chromium(VI) the effect is so strong that  $\text{Cr}^{6+}$  is never found in an

octahedral environment, preferentially forming the tetrahedral  $\text{CrO}_4^{2-}$  anion even though chromium is large enough to accommodate six ligands.<sup>6</sup>

### 7.4.2 Jahn–Teller Distortions

The Jahn–Teller theorem states that if an atom finds itself in a degenerate ground state it will distort if such a distortion can remove the degeneracy. The theorem is very general and applies to most electronically driven distortion, but the name has become attached to a specific tetragonal distortion of the octahedral environment of certain transition metals in particular oxidation states, namely copper(II) and manganese(III). The distortion causes the two axial bonds in an octahedral environment to be longer than the four equatorial bonds. Both atoms have a degeneracy in their ground state which can be understood using a one-electron (or one hole) picture which provides a simple quantum description of the effect. Removing the degeneracy results in a quadrupolar distortion of the core electron density associated with the spherical harmonics that describe the d shell. A tetragonal distortion that makes the two axial bonds longer than the four equatorial bonds removes the degeneracy predicted for high spin  $d^4$  ( $\text{Mn}^{3+}$ ) and the  $d^9$  ( $\text{Cu}^{2+}$ ) systems.

This distortion is closely related to the observation that nickel(II), palladium(II), and platinum(II) are often found with square four coordination rather than tetrahedral configuration. This can be thought of as a more extreme distortion of the same kind in which the weakly bonded ligands are removed entirely.

### 7.4.3 Late Transition Metals in Low-Valence States

The late transition metals have nearly full d electron shells capable of back bonding, i.e., the transition metal acts as a  $\sigma$ -bonding cation towards an anionic ligand while at the same time acting as  $\pi$  bonding anion towards the same ligand acting as a cation. In the bond valence theory, these bonds are composed of two oppositely directed bonds with valences  $S_\sigma$  and  $S_\pi$ , respectively. Since  $S_\pi$  is a negative number, the valence of the bond used for calculating the valence sum is the difference in the magnitudes of the two valences:

$$S = |S_\sigma| - |S_\pi| \quad (20)$$

which results in small, possibly negative, values for the apparent valence of the bond. If the transition metal forms all of its bonds in this way, it can achieve a bond

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<sup>6</sup>The changes in the distribution of the valence electron do not mean that the atom loses its spherical symmetry. Because the core and valence shell have similar energies, the distortion in the valence shell can be compensated by the distortion of the core.



valence sum of zero. Transition metals in groups 9 and 10 sometimes have apparent atomic valences of zero.

Although the apparent valence of the bond is small and possibly zero, the bond itself can be quite strong, since both partial bonds are contributing to its strength. The total number of electrons forming the bond is given by the sum of the magnitudes of the bond valences:

$$\text{Number of valence electron pairs in the bond} = |S_{\sigma}| + |S_{\pi}| \quad (21)$$

In this way strong transition metal–ligand bonds are formed that contribute little to the atomic valence, leading to complexes in which the formal valence may even be zero. Bond lengths in these cases do not provide much information about the bond valences. There are suggestions that the bond-valence parameters in this region may depend on the ability of the ligand to accept  $\pi$  bonds, which in turn may depend on the coordination number of the ligating atom [29, 30]. This is an area where more work is needed.

## 8 Steric Constraints

Steric constraints are those that arise when a bond network cannot be mapped into three-dimensional space without straining the ideal bond lengths calculated with the network equations (14a) and (14b); some bonds may have to be stretched and others compressed. The result of these strains is that the network equations no longer give good predictions of the observed bond lengths, but the ideal bond lengths predicted by these equations provide a convenient reference which allows both the nature of the strain (either tension or compression), and its magnitude (Eq. 22), to be determined, both being useful in assessing the nature of the mechanical stresses in the bonding system.

$$\text{strain} = (R_{\text{obs}} - R_{\text{ideal}})/R_{\text{ideal}} \quad (22)$$

Here  $R_{\text{obs}}$  is the measured bond distance and  $R_{\text{ideal}}$  is the distance predicted by the network equations (14a) and (14b).

If an atom finds itself in a cavity that is too large for its bonds to adopt their ideal length, the bonds must be stretched. According to the distortion theorem (5), the environment of the atom will distort in such a way as to make the bond lengths unequal in order that the bond valence sums becomes equal to the atomic valences. As mentioned in Sect. 7.4.1, this contributes to the distortion around titanium(IV) in  $\text{BaTiO}_3$ . In many cases, such distortions are found in compounds where electronic distortions are also expected, the two effects being mutually supportive.

In all cases of steric constraint, the observed bond distances violate the equal valence rule (14b) and, in some cases, the valence sum rule (14a) as well. A simple

measure of the strain in compounds where the bond valence sum rule is violated is the global instability index,  $G$ .

$$G = \left( \sum_i \{ (V_i - \sum_j S_{ij})^2 \} / n \right)^{1/2} \quad (23)$$

where  $n$  is the number of atoms,  $i$ , in the formula unit. Experimental uncertainties in well-determined structures account for values of  $G$  around 0.05 vu. Structures with  $G$  greater than this are strained but few stable structures are found with  $G > 0.2$  vu. Examples of the use of  $G$  can be found in [14].

There are two causes of steric strain: either close contacts between nonbonded atoms (Sect. 8.1) or incommensurations in the natural spacings of different parts of the structure (Sect. 8.2). Each of these is discussed separately.

## 8.1 *Nonbonding Contacts*

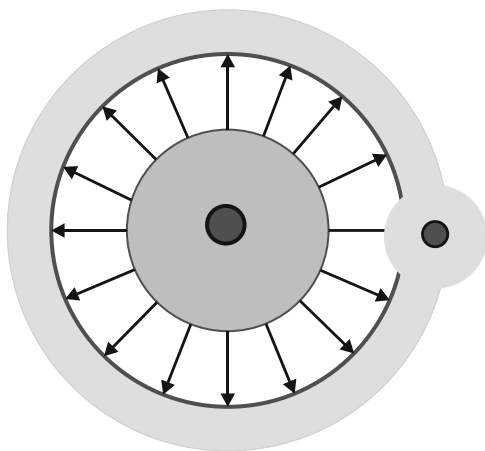
Steric effects resulting from nonbonding contacts are well-known in organic chemistry where they are invoked to explain why crowded molecules are difficult to prepare, but this kind of strain is also found in inorganic compounds, most notably in the hydrogen bond where it is the origin of the O–H...O asymmetry discussed in Sect. 8.1.1.

### 8.1.1 The Chemistry of Hydrogen and Hydrogen Bonds

Apart from the chemically inert helium, hydrogen is the only element in the first period of the Periodic Table. It differs from all other elements in having no electrons in its core and no possibility of a lone pair in its valence shell. Without a core, the nucleus is unshielded, and unlike the nuclei of other atoms, it can penetrate into the valence shell of any atom that it bonds to as shown in Fig. 11. Since the hydrogen atom continues to have spherical symmetry even when bonded to other atoms [31], its bonding electron is arranged spherically around the nucleus, allowing it to overlap completely with the valence shell of the bonded atom. Without any lone pairs to block parts of its bonding environment, hydrogen cannot use the same mechanism as other anions, such as fluorine, for terminating the bond network (Sect. 7.1). Where it does terminate the network, as in hydrocarbons, a different mechanism is used as discussed below.

When hydrogen bonds to an atom such as oxygen, the whole hydrogen atom, both nucleus and its valence electron, is drawn into the oxygen valence shell. Without a lone pair to block the formation of a second (acceptor) bond, the hydrogen nucleus can attract another anion (oxygen for example) to form a second bond. Following the principle of maximum symmetry (1), we would expect the two

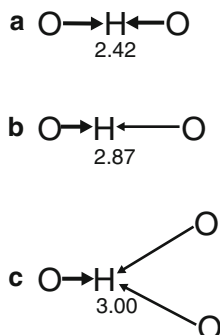
**Fig. 11** Without a core, the nucleus of the hydrogen atom can penetrate the valence shell of a bonded atom



bonds to have the same valence, 0.5 vu, and length, 1.10 Å, with the hydrogen atom lying at the midpoint between the two oxygen atoms. However, if the hydrogen atom were to lie within the valence shells of both anions, the valence shells of the two anions would have to overlap, and since both valence shells are already effectively full, this is not possible. The repulsion between the oxygen atoms causes the bond to stretch from the expected O...O distance of 2.20 to 2.42 Å, and according to the distortion theorem (5), the hydrogen atom will move from the point midway between the two oxygen atoms to increase its bond valence sum to 1.0 vu [11, p. 75ff]. Equilibrium is observed when hydrogen forms a strong bond of 0.8 vu to the oxygen atom with the larger base strength (donor) and a weak bond of 0.2 vu to the other oxygen (acceptor). For this reason, hydrogen is unusual in that it has two cation bonding strengths, 0.8 and 0.2 vu which are labeled as donor and acceptor (Table 1). Other constraints within the compound may force the hydrogen to be placed either less or more symmetrically, giving rise to three possible types of hydrogen bond. The normal O–H...O hydrogen bond has one short bond of 0.97 Å (0.8 vu) to the donor oxygen and one longer bond of 1.90 Å (0.2 vu) to the acceptor. As expected from the principle of maximum symmetry, all three atoms are collinear as shown in Fig. 12b. This geometry has the lowest energy and is the configuration most often found. More symmetric hydrogen bonds have a shorter O...O distances and are found only if the energy needed to bring the valence shells of the two oxygen atoms closer can be recovered elsewhere in the structure (Fig. 12a). For example, hydrogen phosphate ions,  $\text{HPO}_4^{2-}$ , with a bonding strength of  $-0.22$  vu, retain their tetrahedral symmetry better if they form more symmetric hydrogen bonds. A more asymmetric hydrogen bond having a longer O...O distance is found if the acceptor has a bonding strength smaller than  $-0.2$  vu (Fig. 12c). The perchlorate ion,  $\text{ClO}_4^-$ , with a bonding strength of  $-0.08$  vu forms only weak hydrogen bonds [32].

More symmetric hydrogen bonds are kept linear by the strong repulsion between the oxygen atoms. Longer hydrogen bonds are usually bent since the increased

**Fig. 12** Three types of hydrogen bond: (a) short or symmetric, (b) normal, and (c) long and bifurcated. Typical O...O distances are shown



**Table 6** Residual valences,  $V_R$ , and Lewis acid and base strengths of the second row hydrides in valence units

	Lewis acid		Lewis base		Boiling point
	$V_R$	Acid strength	$V_R$	Base strength	/K
H <sub>4</sub> C	0	0	0	0	109
H <sub>3</sub> N	0.6	0.2	-0.6	-0.6	240
H <sub>2</sub> O	0.4	0.2	-0.4	-0.2	373
HF	0.2	0.2	-0.2	-0.07	293

$V_R$  is the residual valence associated with the Lewis function

Acid strengths are calculated by assuming the hydrogen bonds have a valence of 0.2 vu and the base strengths by assuming the anions have a coordination number of 4

O...O distance relieves the stress that forces the oxygen atoms apart. For longer hydrogen bonds, the O-H...O angle decreases from 180° with the increase in asymmetry. Weak hydrogen bonds are frequently bifurcated, i.e., they involve more than one acceptor bond (Fig. 12c), so that the valence of the donor O-H bond remains close to 0.8 vu.

It is interesting to compare the properties of the hydrides formed by the anions of the second period: H<sub>4</sub>C, H<sub>3</sub>N, H<sub>2</sub>O, and HF. Their formulas are written to emphasize that in each case hydrogen is the cation, since it has the lower electronegativity. Because these are all neutral molecules, the sum of the valences of any external bonds they form must be zero. Table 6 shows the estimated Lewis acid and base strengths of these compounds.

The electronegativity difference is greatest for HF with the hydrogen atom acting as the Lewis acid and the fluorine as the Lewis base. The residual valence of the Lewis acid function (hydrogen) must equal the residual valence of the Lewis base function (fluorine), both of which are therefore determined by the intrinsic anisotropy of the hydrogen bond formed by HF. The existence of the complex F-H-F<sup>-</sup> anion with a symmetrical hydrogen bond shows that the Lewis acid strength of the hydrogen can be as large as 0.25 vu, though for most bonds it is likely smaller as assumed in Table 6.

The next largest electronegativity difference is found in water,  $\text{H}_2\text{O}$ , where it is well attested that the Lewis acid strength of the hydrogen is close to 0.2 vu. The residual bond valence contributed by the two hydrogen atoms is +0.4 vu, which means that the residual valence at oxygen must be  $-0.4$  vu. Assuming oxygen has a coordination number of four, two internal and two external bonds, this leads to water having a Lewis base strength of  $-0.4/2 = -0.2$  vu.

Ammonia,  $\text{H}_3\text{N}$ , forms three hydrogen bonds, hence the nitrogen atom with a coordination number of four is expected to form only one external bond, the other three bonds being formed internally to hydrogen. As shown in Table 6, this gives nitrogen the relatively large base strength of 0.6 vu, even though the hydrogen bonds individually have Lewis acid strengths similar to those in water. Methane,  $\text{H}_4\text{C}$ , is unique in this series in that the four hydrogen atoms saturate the coordination number of carbon, leaving no possibility for methane to have a Lewis base function, and without a Lewis base function its hydrogen atoms must have a Lewis acid strength of zero. They are unable to form hydrogen bonds and terminate the bond network.

Methane, without any Lewis acid or base function, is a gas with the lowest boiling point of the group. Water is the molecule whose Lewis acid and base strengths are ideally matched to each other, which is why water is a liquid or solid at ambient temperatures. Ammonia and hydrogen fluoride are poorly matched to themselves since their acid and base strengths differ by a factor of 3. According to the valence matching rule (9), the bonds that  $\text{H}_3\text{N}$  molecules form with themselves should not be stable. The same is true for HF, which is why both are gases and tend to react with compounds that form better hydrogen bonds. Ammonia is the strongest base, and is well-known for its ability to coordinate strongly to cations such as transition metals which typically have bonding strengths around 0.5 vu. In each case where hydrogen forms hydrogen bonds, it is bonded to its donor, N, O, or F, by a donor bond of 0.8 vu which means that the lone pairs of the donor atoms are usually stereoactive for the reasons given in Sect. 7.1. The three donor N–H bonds in ammonia are arranged pyramidally, and the two O–H bonds of water are not collinear.

When hydrogen is found in molecules and complex ions, it is usually chemically active except in pure hydrocarbons and there its lack of activity is not an intrinsic property of the hydrogen atom, but only the result of the coordination of carbon being saturated, leaving it no opportunity to act as a Lewis base. Hydrogen is left with a bonding strength of zero, but in all other compounds it forms hydrogen bonds that play a significant role in the cohesion of molecules and the formation of crystals. Where methyl groups are linked to other atoms having Lewis base functions, as in the acetate ion,  $\text{H}_3\text{CCO}_2^-$ , C–H...X bonds can be formed. Even though they are typically very weak, of the order of 0.03 vu, they can have a significant effect on structure and properties because organic compounds usually contain many hydrogen atoms. In the acetate ion C–H...O bonds are responsible for the length of the C–C bond being reduced from the single bond length of 1.54 to 1.51 Å as further described in Sect. 10.1 [11, pp. 108–9].

The ammonium ion,  $\text{NH}_4^+$ , which is isoelectronic with methane, has a residual valence of +1.0 vu, ensuring that the hydrogen atoms have a residual valence of +0.25 vu with the valence of the N–H bonds reduced to 0.75 vu. In amine groups where one ammonia hydrogen atom is replaced by an organic residue, R, the strength of the hydrogen bonds determines the valence of the N–R bond and hence the bonding strength of any Lewis base functions on R.

## 8.2 *Incommensuration*

Steric strain can also arise when two different components of a crystal structure have natural translation distances that are incommensurate with each other. Since a crystal has full translational symmetry, all its components must possess translations that are commensurate in all three dimensions. If the natural translations of the components are not equal, there are two possibilities. In the first case, the interactions within the components are larger than the interactions between components, so that each component adopts its own spacing. The result is an incommensurate crystal with two independent lattice spacings along one or more of the crystal axes, as found in  $\text{Hg}_{2.68}\text{AsF}_6$  in which the  $\text{AsF}_6^-$  anions form a lattice that contains channels occupied by linear chains of mercury atoms whose bond length is incommensurate with the spacing of the  $\text{AsF}_6^-$  lattice [33]. On the other hand, if the interaction between the two components is stronger than the interaction within one or both components, then the spacing of each component will change in order that they both adopt the same lattice spacing. This is the situation in  $\text{BaTiO}_3$  where the three-dimensional  $\text{TiO}_3^{2-}$  framework contains cavities that are too small for the barium atoms, causing the framework to expand. This requires the Ti–O bond to be stretched and the Ba–O bonds to be compressed, with a consequent deviation of these bond lengths from their ideal values. When this happens, both of the network equations (14a) and (14b) may be violated, but the loop rule (14b), being the weaker constraint, will always be violated.

$\text{BaTiO}_3$  is a member of the perovskite series of structures which provide a good illustration of this type of steric strain. With the composition  $\text{ABX}_3$ , ideal bond lengths can be calculated for both the A–X and B–X bonds, but since the structure is cubic with only one adjustable parameter, the lattice parameter, it is in general impossible to find a lattice parameter that simultaneously matches both distances. Consequently one set of bonds must be stretched and the other compressed. According to the distortion theorem (5), relaxation involves distortion of the environment of the cation with the stretched bonds, leading to structures in lower symmetry space groups. As they describe in [14], Lufaso and Woodward [34] have used bond valences in their program SPuDS to predict the distortion that will be found in a perovskite of a given composition.

## 9 Properties of Water

### 9.1 Structure

As shown in Sect. 8.1.1, water molecules have a Lewis acid strength of 0.2 vu through hydrogen and a Lewis base strength of  $-0.2$  vu through oxygen. Consequently water molecules are perfectly valence-matched to each other. It is not surprising that water is a liquid, or on cold days a solid, rather than a gas. Water is undoubtedly the most significant molecule on our planet, and although it has been extensively studied, its properties are still not fully understood.

The oxygen atom of a water molecule can form four hydrogen bonds with other water molecules, two as the hydrogen-bond donor and two as the acceptor. Since there are no other species present to exert additional constraints, the bonds in ice or liquid water are expected to be normal, i.e., they should be linear with an O...O separation of 2.87 Å, and according to the principle of maximum symmetry, the bonds are expected to be arranged tetrahedrally around each oxygen atom. This is the structure of ice, but the packing efficiency of tetrahedral structures is poor and they tend to have low densities. A denser packing can be achieved if the O-H...O bonds are bent which requires the hydrogen bonds to be longer and more asymmetric. This is possible in the liquid where the atoms are not held in a rigid framework. A range of hydrogen bond geometries is expected in liquid water. Most hydrogen bonds are normal and approximately linear, but a small number are significantly bent and more asymmetric. This picture differs from that of a commonly used model of water that assumes each hydrogen atom either forms a normal hydrogen bond or no hydrogen bond at all, with no intermediate state considered. Realistic simulations of the structure of liquid water agree well with the expectations of the bond valence theory [35].

### 9.2 Solubility

The dissolution of solids in water is a chemical reaction in which the atoms of the solid react with the surrounding water molecules and are taken into solution. Solubility is determined by whether the Lewis acid and base strengths of the cations and anions of the solid are better matched to each other than they are to the molecules of water. If they are better matched to each other, the solid is insoluble, but if they are better matched to water they will dissolve. Applying the valence matching rule (9) to the Lewis acid and base strengths of water ( $\pm 0.2$  vu), one would expect water to form stable bonds with anions and cations having bonding strengths between 0.1 and 0.4 vu. Sodium ( $S_{\text{Na}} = 0.16$  vu) and chlorine ( $S_{\text{Cl}} = -0.17$  vu) are well matched to each other, but they are also well matched to water. NaCl readily dissolves in water, but equally readily crystallizes out when the water is removed. Magnesium ( $S_{\text{Mg}} = 0.33$  vu) and carbonate

( $S_B = -0.22$  vu) are reasonably well matched to each other but both also lie within the range of solubility and can be dissolved.  $MgCO_3$  is only slightly soluble and easily crystallizes to form the familiar stalactites and stalagmites found in caves. Magnesium and sulfate ( $S_{\text{sulfate}} = -0.17$  vu) are less well matched to each other and sulfate is well matched to water.  $MgSO_4$  dissolves in water with the formation of discrete  $Mg(H_2O)_6^{2+}$  ions in solution. The Mg–O bonds of 0.33 vu result in the hydrogen atoms of the coordinated water molecules having a bonding strength of  $0.33/2 = 0.17$  vu. This allows both the sulfate and the magnesium ions to form normal hydrogen bonds with the surrounding water molecules, but recrystallizing this compound from water does not yield crystals of the original  $MgSO_4$  but rather crystals of  $Mg(H_2O)_6SO_4 \cdot (H_2O)$  in which all the valences are better matched. Any compound composed of ions with bonding strengths larger than 0.4 vu, such as silica  $SiO_2$  ( $S_{Si} = 1.0$  vu,  $S_O = -0.5$  vu), is insoluble. A revealing example of the valence matching rule is found in the fluorides of the alkaline earths which are an exception to the usual rule that the properties of elements vary monotonically as one moves down the Periodic Table. Fluorine has a bonding strength of  $-0.25$  vu, somewhat larger than that of water, the alkaline earths have bonding strengths of 0.33 vu (Mg), 0.27 vu (Ca), 0.23 vu (Sr), and 0.20 vu (Ba). The best matches for fluorine are calcium and strontium with the result that the fluorides of these two elements are less soluble than the fluorides of either magnesium or barium.

### 9.3 Solution Chemistry

Thermodynamic studies of water divide cations into those that increase the entropy during dissolution (structure breaking) and those that decrease the entropy (structure making). As one might expect, there is a close relationship between the molar entropy of solution and the bonding strength of the cation [11, p. 57]. Cations with bonding strengths less than 0.2 vu are structure breaking, those with bonding strengths in the range of 0.3–0.4 vu form complexes with a single coordination sphere of water while those with larger bonding strengths form complexes with a double coordination sphere, the outer sphere being attached to the inner sphere by hydrogen bonds with a larger valence than those normally found between water molecules. As shown in Sect. 9.2, magnesium with a bonding strength of 0.33 vu forms six bonds to water, but the  $Mg(H_2O)_6^{2+}$  complex forms 12 hydrogen bonds with a bonding strength of 0.17 vu, distributing the two valence units of magnesium over the 12 hydrogen atoms to give a complex with a bonding strength that is a good match for the solvent water. In this example, the water of the hydration sphere acts like a transformer, changing the bonding strength of magnesium from 0.33 to 0.17 vu to allow it to form normal hydrogen bonds with water. Iron(III) forms six bonds of 0.5 vu to water, resulting in the water molecules forming hydrogen bonds to the second coordination sphere of 0.25 vu. As this valence is larger than that of the hydrogen bonds in the surrounding liquid, the second coordination sphere is



**Table 7** Bonding strength of protonated orthosilicates

Complex	$V$	$V_R$	$N$	$S_B = V_R/N$
$\text{SiO}_4$	-4	-4	12	-0.33
$\text{HOSiO}_3$	-3	-3.2	10	-0.32
$(\text{HO})_2\text{SiO}_2$	-2	-2.4	8	-0.3
$(\text{HO})_3\text{SiO}$	-1	-1.6	6	-0.27
$(\text{HO})_4\text{Si}$	0	-0.8	4	-0.2

$V$  is the formal valence of the complex,  $V_R$  is its residual valence when the formation of hydrogen bonds is taken into account,  $N$  is the number of external bonds the oxygen atoms are expected to form, and  $S_B$  is the Lewis base strength of the complex ion

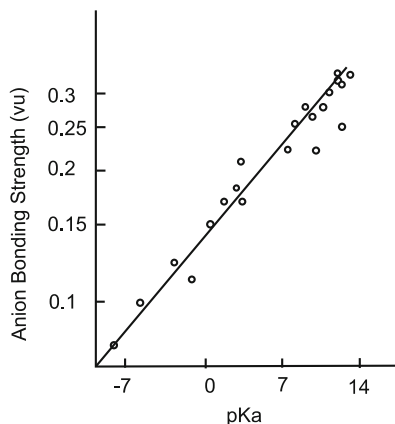
strongly attached to give  $\text{Fe}(\text{H}_2\text{O})_6(\text{H}_2\text{O})_n^{3+}$  with  $n \sim 9$ , a number that gives a bonding strength equal to that of water.

Similarly anions, such as perchlorate ( $S_{\text{perchlorate}} = -0.08$  vu), with a small bonding strengths tend to disrupt the structure of liquid water, while those such as phosphate ( $S_B = -0.25$  vu) with larger bonding strengths tend to remove the hydrogen from water to form protonated anions such as hydrogen phosphate ( $S_B = -0.22$  vu). In this way strongly bonding anions can reduce their bonding strength until it matches that of water.

Table 7 shows how the bonding strength of an orthosilicate ion,  $\text{SiO}_4^{4-}$ , changes with successive protonation. The formal ionic charge of the complex is shown in the column labeled  $V$ . This is the residual valence that would be expected in the absence of any hydrogen bonding, but since all the hydrogen atoms are expected to form external bonds of valence +0.2 vu, the protonated complexes have a Lewis acid strength of +0.2 vu as well as the expected Lewis base function acting through oxygen. While the total formal charge on the complex is  $V$ , the true residual valence,  $V_R$ , available to the Lewis base function is found by adding -0.2 vu to  $V$  for each hydrogen bond formed by the complex. The expected coordination number,  $N$ , is based on the assumption that oxygen will form three external bonds when it is terminal and one when it is part of a hydroxy group. The Lewis base strength is then the ratio of  $V_R$  to  $N$ . Increasing the degree of protonation lowers the base strength of the silicate anion, with only the fully protonated ion providing a proper match with water. All the protonated complexes have a Lewis acid strength of +0.2 vu through the hydrogen atoms, so the Lewis acid and base strengths of  $(\text{HO})_4\text{Si}$  are the same, and both are equal to those of water. Like water,  $(\text{HO})_4\text{Si}$  acts as both an acid and a base of equal strength. Adding further hydrogen atoms would turn the complex into a cation.

The ability of strong Lewis bases such as  $\text{SiO}_4^{4-}$  to abstract hydrogen atoms from water results in an excess concentration of  $\text{OH}^-$  ions, and the ability of strong Lewis acids to shed hydrogen atoms from their coordinated water molecules results in an excess concentration of  $\text{H}^+$  ions both causing changes in the pH as the respective ions dissolve. It is no surprise that one finds a linear correlation between the  $\text{p}K_a$  and the logarithm of the anion bonding strength as shown in Fig. 13 [11, p. 47].

**Fig. 13** Correlation between bond valence and  $pK_a$  (Fig. 4.3 from [11] by permission of the Oxford University Press)



## 10 Reactivity

### 10.1 Lewis Acid and Base Compounds

In the ammonia molecule,  $\text{NH}_3$ , nitrogen acts as an anion with a valence of  $-3$  vu and the hydrogen as a cation with a valence of  $+1$ . In the isolated ammonia molecule, the three  $\text{N-H}$  bonds have a valence of  $1.0$  vu with none of the atoms carrying any residual valence. As a result of the strong  $\text{N-H}$  bond, the lone pair on nitrogen is stereoactive (Sect. 7.1). However, the hydrogen atoms are expected to form hydrogen bonds. The internal donor  $\text{N-H}$  bonds would have valences of around  $0.8$  vu, which will tend to reduce the stereoactivity of the nitrogen lone pair. As shown in Table 6, this gives the ammonia complex a Lewis acid strength (at hydrogen) of  $+0.2$  vu and a Lewis base strength (at nitrogen) of  $-0.6$  vu. According to the valence matching rule (9), the nitrogen should bond to a cation with a bonding strength in the range of  $+0.3$  to  $+1.2$  vu, a range typically found in transition metals and organic compounds, which makes ammonia a good complexing agent in coordination chemistry. It also explains why ammonia reacts with  $\text{BF}_3$ . In a manner complementary to ammonia,  $\text{BF}_3$  has a Lewis acid strength of around  $0.6$  vu at boron and a Lewis base strength of around  $-0.2$  vu at fluorine, the  $\text{B-F}$  bonds having a valence of around  $0.8$  vu. However, since both  $\text{NH}_3$  and  $\text{BF}_3$  have a net residual valence of zero, the  $\text{N-B}$  bond can only be formed if the H and F atoms also form external bonds.  $\text{NH}_3\text{BF}_3$  only forms a stable compound because in the solid the molecules are linked by  $\text{N-H} \cdots \text{F}$  hydrogen bonds. This description differs from the usual explanation for the existence of this compound which calls the  $\text{N-B}$  bond a “dative bond” formed by the lone electron pair on nitrogen. While this seems a plausible explanation, it contains an inherent contradiction since a lone pair is required to be nonbonding. If it is used for bonding, the valence of nitrogen must change from  $-3$  to  $-5$ , which is forbidden by the octet rule (11). The bond valence theory provides a more realistic description by pointing

**Table 8** Bonding strengths,  $S$ , of silicate ions

Complex	$V_R$ (vu)	$N_O$	$S = V_R/N_O$ (vu)	
$\text{SiO}_4$	4	12	0.33	Isolated ion
$\text{Si}_2\text{O}_7$	6	19	0.32	Isolated dimer
$\text{SiO}_3$	2	7	0.29	Chain
$\text{Si}_2\text{O}_5$	2	4	0.14	Sheet
$\text{SiO}_2$	0	4	0	Framework

out that the base function on nitrogen can only be activated if the ammonia molecule forms hydrogen bonds which allows it to divert some of the bonding electrons from the N–H to the N–B bond. The lone pair remains nonbonding, but in  $\text{NH}_3\text{BF}_3$  it is sterically inactive.

Complex ions as well as neutral molecules can sometimes act as both a Lewis acid and a Lewis base. The acetate ion,  $\text{H}_3\text{CCO}_2^-$ , being an anion, is primarily a Lewis base with a residual valence of  $-1.0$  vu split between the two oxygen atoms to give a Lewis base strength of  $-1.00/6 = -0.17$  vu, but the methyl hydrogens can also act as weak Lewis acids, typically with a residual valence of around  $0.03$  vu. If all three hydrogen atoms form hydrogen bonds, the residual valence on the two oxygen atoms increases from  $-1.00$  to  $-1.09$  vu, and the Lewis base strength of the acetate ion increases to  $-1.09/6 = -0.18$  vu. The bonding strength of trifluoroacetate, on the other hand, is smaller ( $0.16$  vu) because the residual negative valence of  $-1.0$  vu must be shared between the oxygen and the fluorine atoms. This difference is reflected in the  $\text{p}K_a$  values of these two ions.

According to the principle of maximum symmetry, the residual anion valence of the acetate ion should be distributed equally between the two oxygen atoms, allowing it to bond to any cation with a bonding strength in the range of  $+0.09$  to  $+0.36$  vu, but it can bond to more strongly bonding cations, such as silicon ( $S_{\text{Si}} = 1.0$  vu) to form  $\text{Si}(\text{O}_2\text{CCH}_3)_4$  by distributing its residual valence unequally between the two oxygen atoms [36].

## 10.2 Stability

In a paper titled “Nonexistent silicates” Dent-Glasser [37] pointed out that no condensed silicates were known with transition metals, and no orthosilicates were known with alkali metals, an observation that is readily understood in terms of valence matching. Table 8 shows the bonding strengths of ortho- and condensed silicates. The bonding strengths of the formula units shown are equal to the residual valence of the complex,  $V_R$ , divided by the number of external bonds,  $N_O$ , that the formula unit forms. Terminal oxygen atoms are assumed to form three external bonds and bridging oxygen atoms one. The orthosilicate anion,  $\text{SiO}_4^{4-}$  has a bonding strength of  $4/12 = 0.33$  vu which matches the bonding strengths of transition metals which range from  $0.3$  to  $0.5$  vu, while condensed silicates have bonding strengths in the range of  $0.1$ – $0.2$  vu which matches the bonding strengths of alkali metals ( $0.11$ – $0.20$  vu). The known silicates are the ones that obey the valence

matching rule (9) and Dent-Glasser's nonexistent silicates include all those that do not obey this rule [11, p. 51].

Many biological compounds are required to be stable but at the same time to be sufficiently soluble that they can be assembled or disassembled under aqueous conditions at ambient temperatures. This requirement can be met if the molecule is at its stability limit with the bonding strengths of its components differing by a factor of 2. This condition is satisfied by the hydrolysis of adenosine triphosphate (ATP) into adenosine diphosphate (ADP) and phosphate, the principal method by which energy is transferred in living organisms. ATP can hydrolyze to give either  $\text{ADP}^{3-}$  and  $\text{PO}_3^{3-}$  or  $\text{ADP}^-$  and  $\text{PO}_4^{3-}$ . In calculating the bonding strength, the coordination number of the bridging oxygen is taken as two, since this reflects its actual coordination number in ATP. With this choice, the Lewis acid or base strength is equal to the residual valence on the atoms that formed the broken bond. The Lewis base strength of  $\text{ADP}^{3-}$  is  $-0.6$  vu assuming the residual valence of  $\text{ADP}^{3-}$  is distributed uniformly over all five oxygen atoms. This is to be matched with the Lewis acid strength of  $P$  in  $\text{PO}_3^{3-}$  ( $+1.25$  vu), assuming that all three  $P\text{--}O$  bonds have the same valence. For this process, the ratio  $S_A/S_B = 2.08$ . The second possible hydrolysis route yields  $\text{ADP}^-$  and  $\text{PO}_4^{3-}$  with the bridging oxygen remaining on the phosphate group. Under the same assumptions  $\text{ADP}^-$  is the Lewis acid acting through  $P$  with  $S_{\text{ADP}} = +1.4$  vu and  $\text{PO}_4^{3-}$  is the Lewis base with  $S_{\text{phosphate}} = -0.75$  vu giving  $S_A/S_B = 1.87$ . Both routes have ratios close to 2, which is the limit for bond formation, allowing ATP to form or hydrolyze with only a small change in the ambient conditions [11, pp. 201–2].

The mineral apatite,  $\text{Ca}_3(\text{PO}_4)_2$ , gives bone its strength. Its components,  $\text{Ca}^{2+}$  ( $S_{\text{Ca}} = 0.27$  vu) and  $\text{PO}_4^{3-}$ , ( $S_{\text{phosphate}} = -0.25$  vu) are well matched to each other, allowing them to form a strong material, but the bonding strengths are still within the range that matches water, ensuring that both components can be moved through the body to where they are needed, but in this case that the bone, with its better valence match, is more stable against dissolution.

## 11 Structure Analysis and Prediction

### 11.1 The Global Instability Index

There are a number of tools that are useful in validating either a measured or a proposed structure. The most widely used is the valence sum rule (2) using bond valences calculated from the observed bond lengths. Experimental uncertainties will mean that the atomic valence and bond valence sum are rarely exactly the same, but for a well-determined structure the difference is usually around  $0.05$  vu. Larger differences are often found, indicating that some bonds are compressed or stretched by the steric constraints imposed on the structure (Sect. 8). In some cases the differences can be quite large, but for a strained structure to be in equilibrium both stretched and compressed bonds must be present, which is key to verifying the presence of steric strains.

A combined measure of the steric strain over the whole structure is the **global instability index**,  $G$  defined in Eq. (23). Experience with this index shows that few stable structures have values of  $G$  greater than 0.20 vu. An observed structure with a larger value should be carefully examined to ensure that the structure determination is correct and that the bond lengths have been properly converted to bond valences. Values of  $G$  in the range 0.05–0.20 vu indicate the presence of strained bonds; the larger the value of  $G$ , the more strained the structure. Garcia-Muñoz and Rordiguez-Carvajál [38] examined an isostructural series of rare earth compounds and showed that those in which  $G$  was predicted to exceed 0.20 vu crystallized with a different structure type.

A more interesting index, but one more difficult to apply, is the **bond strain index**,  $B$ , which compares the observed and predicted bond valences by summing the squares of the deviation over all  $m$  bonds (24):

$$B = \left( \sum \{S_{\text{observed}} - S_{\text{ideal}}\}^2 / m \right)^{1/2} \quad (24)$$

This calculation requires ideal bond valences to be predicted using the network equations (14a) and (14b).  $B$  will not be zero if either electronic anisotropies (Sect. 7) or steric strains (Sect. 8) are present. It measures the deviation from the predictions of the network equations, but does not indicate the origin of these deviations, nor does it measure instability.  $B$  will always be large if hydrogen bonds are present, masking the possible presence of other effects.

## 11.2 *Predicting and Mapping the Bond Network into Euclidian Space*

In many cases the bond network can be generated from a knowledge of the bonding strengths [11, pp. 134ff]. For a given composition, the first step is to use the electronegativity (Table 1) to identify the anions and the cations while ensuring that the sum of all the atomic valences is zero. The cations and anions with the largest bonding strength are then linked by bonds to form complex ions whose bonding strengths can be matched with the remaining counterions. At each stage, the principle of maximum symmetry is used to decide between alternative choices. This approach works well for binary and ternary compounds, but packing considerations become important if many different elements are present, or if the compound contains weakly bonding cations such as alkali metals, since the number of alternative ways of constructing the network becomes large, and the spatial arrangements of the atoms impose additional constraints. If the bond network has a high symmetry, mapping into three-dimensional (Euclidean) space becomes a straightforward exercise of finding the highest symmetry space group that can accommodate the network [11, pp. 129ff].

### 11.3 Simulations

A traditional method for predicting complex chemical structure and dynamics is computer simulation, in which atoms are placed at arbitrary, though preferably favorable, positions and are moved in response to the forces acting on them, in such a way as to minimize a cost function, such as the total potential energy [39]. The cost function is usually based on a Coulomb potential, and the total energy of the system is calculated using either quantum or classical mechanics. Whichever method is used, all simulations necessarily involve simplifying assumptions and the adoption of fitted parameters to suit the particular system.

For inorganic compounds, the ionic model (Sect. 5) is the basis of both the classical two-body potential model and the bond valence theory; either can be used, separately or together, in a simulation. The two models are based on identical assumptions, the only difference being in the way in which they describe the repulsion between neighboring atoms. The two-body potential model represents this repulsion (and other factors such as polarization) by adding empirical terms to the cost function; the bond valence theory represents the repulsion through the empirical bond valence parameters,  $R_0$  and  $b$ , in Eq. (4). Unlike the repulsive potentials which are optimized for each structure, the bond valence parameters are tabulated, and as they require no special fitting, they are robust. The principal difference between the two approaches lies in the ways in which the calculations are performed: the two-body potential model minimizes a single potential energy, while the bond valence theory ensures that the bond valences obey local rules around each atom. Apart from the choice of empirical parameters, both methods should lead to the same structure. Although bond valence terms are sometimes added to the cost functions, no simulation has yet been performed using only the bond valence rules.

## 12 Epilogue

Chemical structures are too complex to be described by any single theory without drastically simplifying assumptions, and any quantitative theory requires at least some parameters to be fitted empirically. Consequently we have a variety of models or theories of chemical structure, based on different assumptions, covering different materials and designed to suit different needs, depending on whether one is looking for insights or quantitative predictions, whether one wants simplicity or an understanding of the basic physical principles.

One can identify four desirable characteristics for a theory of chemical structure:

1. It reveals the physical principles involved.
2. It applies to a wide range of compounds.
3. It offers simple insights into the factors that determine chemical structure.
4. It makes quantitative prediction of properties, preferably with simple calculations.

No existing theory meets all of these criteria, which is why structural chemistry has so many different models, but these criteria provide a standard against which each can be evaluated. Since the first pictures of chemical structure appeared in the nineteenth century, many different theories, and variations on theories, have been proposed. The bond valence theory, which is one of these, began a 100 years ago with the ionic model, took form with Pauling's electrostatic valence principle and has evolved into the relatively sophisticated model that we have today. Its ability to give simple quantitative predictions for complex structures appeals to mineralogists and materials scientists, since it provides insights which the extensive computation required by other models tends to obscure. Its greatest weakness in the past has been its apparent lack of any basis in physical theory; its only justification being its surprising success in giving a quantitative account of extended structures.

This chapter has been an attempt to rectify this weakness by taking a new look at the physical basis of the chemical bond. It shows how the rules of the bond valence theory can be derived from established physical principles by making a number of simple assumptions about the properties of atoms and developing the model using the electrostatic field. It provides many insights into chemical structure, but at the cost of losing some of the insights provided by other models. Just as the concept of a chemical bond is not found in the traditional physical models, the concepts of energy and electron density distribution are not found in the bond valence theory. If energy or electron density are important, a different approach is needed.

Even though the bond valence theory does not explain how atoms adhere to each other and its scope is limited to localized bonds, it does provide simple insights into many of the factors that determine chemical structure. It is a model which has been slow to develop, but which has a potential that is far from exhausted. It is a model that will be all the stronger for having the secure base in physical theory presented here.

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