Bond Valences—A Simple Structural Model for Inorganic Chemistry

By I. D. Brown
INSTITUTE FOR MATERIALS RESEARCH, MCMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA L8M 4S1*

1 Introduction

In spite of the advances made in quantum chemistry during the past sixty years, organic chemists still describe many chemical structures in terms of the nineteenth century (as opposed to the twentieth century) concept of valence. In this familiar 'ball and stick' model, atoms are regarded as connected together by bonds which are either single, double, triple, or 'delocalized'. The number of bonds each atom can form is determined by its valence, an intrinsic property that is determined by the position of the atom in the periodic table. The resulting picture of a molecule not only accounts for many of its chemical properties, but also gives a description of its three-dimensional structure that is hardly less accurate than that provided by *X*-ray diffraction.

Unfortunately, the inorganic chemist has been less well served by chemical models, both those of the simple valence type and those based on electrostatic or quantum principles. Like organic compounds, inorganic compounds can be treated as atoms linked by bonds, but the bonds can vary greatly in character and their number does not correspond in any obvious way to the atomic valence. Around some atoms, notably hydrogen and the alkali metals, the bond distances vary so widely that it is often difficult to decide which neighbours are to be considered bonded and which are not. Inorganic structures can rarely be predicted with confidence in spite of the large number of accurately determined structures now known. Indeed, to give even a qualitative description of the bonding in such structures it is often necessary to use several chemical models. As a result inorganic structures are frequently described in purely geometric terms such as the packing of polyhedra or the close packing of spheres.

In this review I shall describe how the old 'ball and stick' valence model can be extended to inorganic compounds. The inorganic version differs from that used by organic chemists, but is equally powerful in accounting for structure and reactivity. The basic ideas are not new. They were described by Pauling fifty years ago,[1] but since he presented them in terms of an electrostatic model it was not

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[1] L. Pauling, *J. Amer. Chem. Soc.*, 1929, **51**, 1010.

realized how widely they could be applied.* To avoid the limitations implied by such physical models it is better to develop the theory in a purely empirical way. Only then is it profitable to compare it with the more familiar physical theories of covalence and ionicity.

2 Definition and Use of Bond Valences

We shall assume that chemical structure can be completely described as a network of bonds connecting neighbouring atoms. The network may be finite, as in the case of a molecule, or infinite, as in the case of most inorganic crystals. We shall call the number of bonds formed by an atom its *co-ordination number* and the bonding power of an atom its *valence*. The valence is determined by the position of the atom in the periodic table and can be thought of as the number of electrons that the atom uses for bonding. For the compounds considered here the valence is synonymous with the formal oxidation state. In organic compounds the valence is usually equal to or greater than the co-ordination number giving rise to single or multiple bonds, but in inorganic compounds the opposite is usually true, so that the valence to be associated with each bond is frequently less than one. We define the *valence of a bond* (s_{ij}) between atoms i and j such that

$$V_i = \sum_j s_{ij} \qquad (1)$$

for all i, where V_i is the valence of atom i. This is called *the valence sum rule*. It is the same rule which, combined with the restriction that s_{ij} is an integer, allows one to write down unique structures for organic molecules. In inorganic compounds it is not so easy to assign bond valences *a priori* since they are usually non-integral and range widely in value.

On the other hand, in inorganic compounds the bond valences correlate much better with the bond lengths than they do in organic compounds. As a result they can be accurately determined from the experimentally measured lengths. Our knowledge of the correlation between bond length (R) and bond valence (s) has increased over the past fifty years as the accuracy of crystal structure determinations has improved. The relation is of an inverse type (Figure 1) that can usually be fitted over the range of interest by one of a number of analytical expressions, the most commonly used ones being those in (2) and (3), where R_0

$$R = R_0 - A\log_{10}s \qquad (2)$$

$$s = (R/R_0)^{-N} \qquad (3)$$

is the length of a bond of unit valence and N (~ 5) and A (~ 0.8) are parameters, which determine the slope of the curve [equation (2) was proposed by Pauling[2] on the grounds that the electron density in an atom drops exponentially with distance. It has the advantage that $A = 0.85$ for many bonds. Equation (3) is

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*Pauling uses the term 'electrostatic bond strength', but the term 'bond valence' is preferred since it emphasizes the empirical nature of the concept.

[2] L. Pauling, *J. Amer. Chem. Soc.*, 1947, **69**, 542.

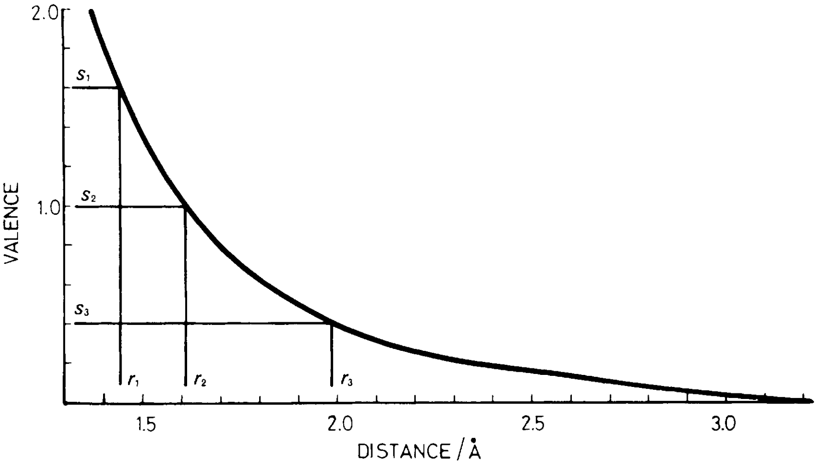

Figure 1 *Correlation between valence and distance for bonds between O and atoms of the second row*
(Composite after I. D. Brown and R. D. Shannon, *Acta Cryst.*, 1973, **A29**, 266, and G. Donnay and R. Allmann, *Amer. Miner.*, 1970, **55**, 1003)

related to the Born[3] equation with $N + 1$ being the Born exponent]. R_0 and N or A are chosen to satisfy equation (1) in a large number of accurately determined structures and, once found for a given pair of elements, can be used for any further bonds between them. Tables of R_0 and N or A for bonds between metals and oxygen have been given by Allmann using equation (2) and Brown and Wu using equation (3).[4] General methods for obtaining the parameters have been described by various authors.[4] Donnay and Donnay[5] have compared a series of different correlations and conclude that most of them work equally well. Brown and Shannon[6] have observed that the same curve (Figure 1) can be used for all the bonds between O and Na, Mg, Al, Si, P, and S, making for a great simplification in treating the structures of these important elements.

In the form of Pauling's electrostatic valence rule,[1] the bond valence model has been used for many years by mineralogical crystallographers, who have found it ideal for confirming structures that contain a complex mixture of ionic and covalent bonds. Using the present approach bond valences can be calculated directly from the observed bond lengths and can be summed around each atom to give an *experimental* measurement of the atomic valence. If this agrees with the *theoretical* valence, one has confidence that the structure has been correctly determined and correctly interpreted. In this case the bond valences give a quantitative measure of the relative strength of the various bonds and can be used to describe the structure. If the experimental and theoretical valences do not agree the cause can usually be traced to one of the following:

[3] M. Born, 'Atomtheorie des festen Zustandes', Teubner, Leipzig, 1923.

[4] R. Allmann, *Monatsh.*, 1975, **106**, 779; I. D. Brown and K. K. Wu, *Acta Cryst.*, 1976; **B32,** 1957, and references therein.

[5] G. Donnay and J. D. H. Donnay, *Acta Cryst.*, 1973, **B29**, 1417.

[6] I. D. Brown and R. D. Shannon, *Acta Cryst.*, 1973, **A29**, 266.

(i) the material is one (*e.g.* a metallic solid) to which the model does not apply,

(ii) the structure has not been correctly determined, or

(iii) the structure is correct, but has not been correctly interpreted, for example bonds have been overlooked or atoms wrongly assigned (*e.g.* the ordering of Si and Al in minerals).

These points are discussed and illustrated below.

Although the bond valence model applies to the majority of inorganic structures it does not hold universally. It clearly cannot be used for compounds such as metal alloys that do not combine according to the stoicheiometric proportions of classical valence theory and the correlation between bond length and valence does not hold well for bonds between atoms of the same element, particularly those in aromatic rings. As a general rule the model can be used for any structure or part of a structure, in which bonds only occur between atoms of the opposite formal charge.* It applies to such compounds as Na_2SO_4 and even to acetic acid, but not to the hydrazinium ion (H_2NNH_3),† nor the carbonyl complexes of transition metals.

Calcium chromium pentafluoride ($CaCrF_5$) provides a good example of the use of bond valences. The crystals contain distorted CrF_6 octahedra linked by fluorine bridges into parallel chains bonded to each other by calcium atoms as is shown schematically in Figure 2. Although the Ca—F interactions can reasonably be described as ionic, the nature of the Cr—F bonds is more difficult to divine. However, one only needs to know the bond lengths, not the bond character, in order to calculate bond valences and hence experimental atomic valences. The structure was determined by *X*-ray diffraction and refined in the space group *Cc*.[8] Since the atomic valence calculated for one of the F atoms in this structure was only 0.76 valence units (v.u.), the structure was rerefined in space group *C*2/*c*.[9] The correctness of this latter refinement was confirmed not only by an improvement in the *X*-ray diffraction agreement index (*R* factor) from 0.10 to 0.08, but also by the improved atomic valences, none of which deviated by more than 0.08 v.u. from the theoretical value. The environment of the Cr atom in the second refinement is still slightly distorted (Figure 2), but instead of the four short terminal and two long bridging bonds that might have been expected, the co-ordination around Cr contains only two short terminal bonds; the other two terminal bonds and the two bridging bonds are almost the same length. The bond valence model explains this unexpected distortion. The F atom that bonds to only two cations [F(3)] forms stronger (*i.e.* shorter) bonds than the other two, each of which forms bonds to three cations. Detailed examination of the bond valences

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*It is therefore convenient to use the terms cation and anion without necessarily implying any separation of charge.

†However it can be used for hydrazinium salts providing that the N_2H_5 group is treated as if it were a single atom.[7]

[7] S. Vilminot, M. R. Anderson, and I. D. Brown, *Acta Cryst.*, 1973, **B29**, 2628.

[8] D. Dumora, K. Von der Mühll, and J. Ravez, *Materials Res. Bull.*, 1971, **6**, 561.

[9] K. K. Wu and I. D. Brown, *Materials Res. Bull.*, 1973, **8**, 593.

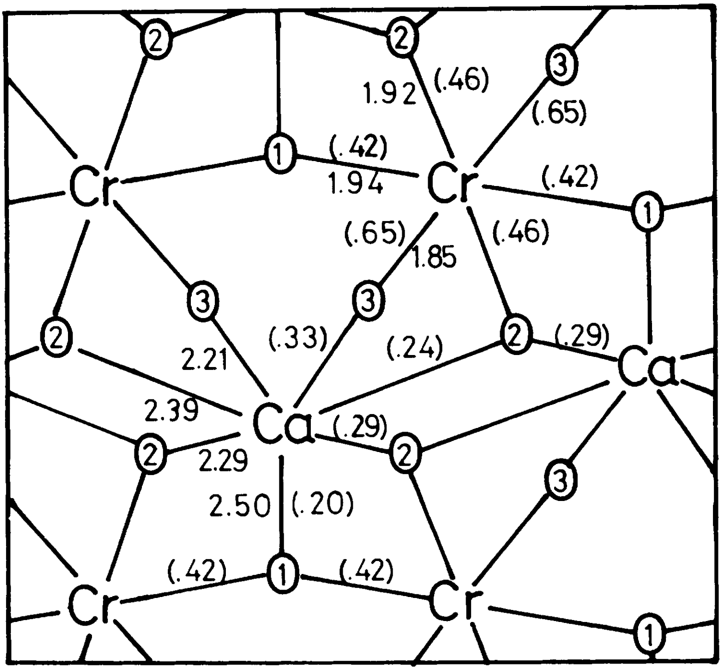
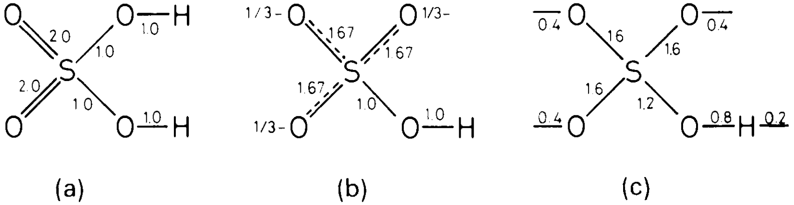


Figure 2 *Schematic diagram of the bond network in* $CaCrF_5$. *The numbered circles are* F *atoms and the* $(CrF_5)_\infty$ *chains run horizontally. Observed bond lengths are given in* Å, *bond valencies determined from these lengths are enclosed in parentheses*

in Figure 2, shows that not only can all the distortions be understood in detail but, given the bonding network, it would not have been difficult using equation (1) to estimate the bond valences *a priori.*

This kind of valence description of chemical bonding has all the advantages of the traditional valence–bond (V–B) description[10] but, by taking explicit account of the environment of the molecule or ion, it is able to give a more accurate picture of the real structure. Figure 3a shows the V–B structure of



(a) (b) (c)

Figure 3 a, *Valence-bond structure of* H_2SO_4; b, *valence-bond structure of* HSO_4^-; c, *bond valence structure of* HSO_4^-

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[10] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Second Edition, Interscience, New York, 1966, pp. 57ff.

H_2SO_4 which is the same as the bond valence structure of the isolated molecule. Removal of one H ion leads to the anion HSO_4^- whose average V–B structure is given in Figure 3b. In such a structure the environment of the ion is ignored, the unsatisfied valences on the oxygen being formally treated as residual charges. But the environment, whether it be the hydration sphere in aqueous solution or adjacent ions in crystals, has an important influence on the structure of the ion. For instance, the hydrogen atom, if not completely detached from the ion, will inevitably form a hydrogen bond to an adjacent anion or other electron donor, so that the actual valence structure will be closer to that shown in Figure 3c.* It is this structure, rather than the one implied by Figure 3b, that is found in the crystalline salts.[11]

3 Applications of Experimental Atomic Valences and Bond Valances

There are many ways in which the experimentally determined atomic valences can assist in the determination and interpretation of a crystal structure. As in the case of $CaCrF_5$ discussed above, poor agreement with the theoretical atomic valences may indicate an incorrectly determined structure. An experimental valence of 0.70 for Rb and 0.87 for two of the I atoms in $RbCdI_3$ first drew our attention to the water of crystallization in this compound.[12] Low values of the valence can also indicate that one or more bonds have been overlooked.[13] Hydrogen bonds can be reliably located by noting which anions still have unused valence after account has been taken of all the other bonds.[14]

Experimental valences are particularly useful in distinguishing between different elements with similar atomic numbers and similar crystal chemistry. Bond lengths have been used for some time to distinguish between Al and Si atoms in minerals,[15] but the distinction can be made simply and elegantly by

Table 1 *Experimental Atomic Valences in* V_4O_7[a]

V(1)	V(2)	V(3)	V(4)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)
3.47	3.63	3.28	3.53	2.00	2.02	2.01	1.86	2.04	1.97	2.01

Average experimental V valence 3.48 ± 12
V valence from stoicheiometry 3.50

[a](Structure determined by H. Horuichi, M. Tokonami, N. Morimoto, and K. Nagasawa, *Acta Cryst.*, 1972, **B28**, 1404.)

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*The structure of the hydrogen bond and the rational for splitting the valence around H in the ratio 0.8 to 0.2 are discussed in Section 6. Once the valence of this bond has been assigned, the other valences all follow from equation (1).

[11] R. J. Nelmes, *Acta Cryst.*, 1971, **B27**, 272.
[12] M. Natarajan Iyer, R., Faggiani, and I. D. Brown, *Acta Cryst.*, 1977, **33**, 129.
[13] E. Kostiner and J. R. Rea, *Inorg. Chem.*, 1973, **13**, 2876; A. D. Baranyi, M. Onyszchuk, Y. LePage, and G. Donnay, *Canad. J. Chem.*, 1977, **55**, 849.
[14] G. Donnay and R. Allmann, *Amer. Miner.*, 1970, **55**, 1003; M. Catti and G. Ferraris, *Acta Cryst.*, 1974, **B30**, 1789; F. C. Hawthorne, *Acta Cryst.*, 1976, **B32**, 2891.
[15] M. W. Phillips and P. H. Ribbe, *Contr. Miner. Petrol.*, 1973, **39**, 327.

calculating experimental cation valences, particularly as Al—O and Si—O have the same bond valence–bond length curve. If the observed valence at a particular site is 3.0 it is occupied by Al, if 4.0 it is occupied by Si and if it is 3.5 the site is occupied equally by Al and Si atoms.[16]

The method is illustrated in Table 1, which gives the experimental atomic valences of the mixed valence oxide V_4O_7. The correctness of the valence assignment at the vanadium sites is confirmed by the calculation of correct experimental oxygen valences and the excellent agreement between the average experimental vanadium valency and the average vanadium valence determined from the stoicheiometry.

Valences can be useful in predicting the structure of materials under the extremes of pressure and temperature that are found in the centre of the earth. Baur[17] has used a related technique to discuss the structure of possible unknown high pressure forms of Mg_2SiO_4 that are thought to be a major constituent of the mantle. Kahn and Hazen and Prewitt[18] have shown that the coefficient of thermal expansion of individual bonds varies inversely with their valence and have used this relationship to predict high temperature structures. Brown, Howard-Lock, and Natarajan[19] have suggested that valences might be used to predict stretching force constant and hence i.r. and Raman spectra.

4 Prediction of Structure

The bond valence concept treats a chemical compound as a network which must obey the valence sum rule [equation (1)]. This law is formally equivalent to Kirchhoff's current law in electrical network theory.[20] For compounds that have the stoicheiometry predicted by the classical valence rules there is necessarily at

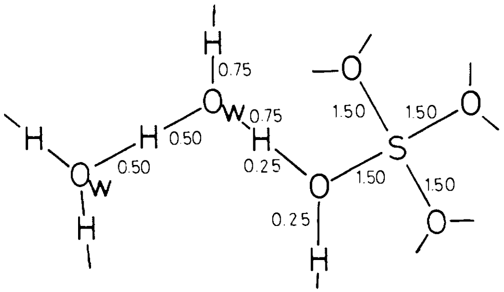

Figure 4 *Bond valence structure of* $(H_6O_2)_2SO_4$

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[16] H. D. Grundy and J. Ito, *Amer. Miner.*, 1974, **59**, 1319; M. Calleri and G. Gazzoni, *Acta Cryst.*, 1976, **B32**, 1196.
[17] W. H. Baur, *Amer. Miner.*, 1972, **57**, 709.
[18] A. A. Khan, *Acta Cryst.*, 1976, **A32**, 11; R. M. Hazen and C. T. Prewitt, *Amer. Miner.*, 1977, **62**, 309.
[19] I. D. Brown, H. E. Howard-Lock, and M. Natarajan, *Canad. J. Chem.*, 1977, **55**, 1511.
[20] A. L. Mackay and J. L. Finney, *J. Appl. Cryst.*, 1973, **6**, 284.

least one bond valence structure that obeys the valence sum rule. In cases where only one such structure is possible the predicted bond lengths are very close to those observed. Figure 4 shows the valence structure of $(H_5O_2)_2SO_4$.[21] All the S—O bonds are equivalent by crystallographic symmetry and the H_5O_2 ion lies on a crystallographic two-fold axis. The bond valences can be assigned either by dividing the valence of S ($V = 6$) equally between the four S—O bonds or the valence of the acidic proton ($V = 1$) equally between the two bonds that it forms. The other valences follow by application of the valence sum rule to the O and H atoms. The agreement between the predicted and observed bond lengths is excellent (S—O, 1.476, 1.479 Å; O—O_w 2.63, 2.66 Å; O_w—O_w 2.41, 2.43 Å respectively).

In cases where more than one valence structure can be written, one needs a second theorem. A good solution to the network can be found if one requires the valences of all the bonds formed by each atom to be as nearly equal as is consistent with the valence sum rule. An algorithm based on this condition gives predictions of bond valences that are accurate to 0.05 v.u.[22] and lengths that are generally accurate to within a few hundredths of an Ångstrom provided that the compound does not contain distortions that arise from steric or electronic effects. An alternative procedure based on the same principle has been described by Baur.[23]

The predictions made by the valence sum rule have for obvious reasons mostly been tested on crystalline structures, but the technique is expected to work equally well in amorphous networks and should therefore prove valuable in the development and testing of models of amorphous structure. Taylor and Brown[24] have used it to discuss which impurities will stabilize domain boundaries in $CaTiSiO_5$.

The effects of the non-bonding interactions are important in determining co-ordination numbers and thus in determining the structure of the network itself. In most compounds the anions are larger than the cations and the co-ordination numbers are determined by anion–anion contacts. They can be predicted following Pauling[25] by considering the ratios of the cation and anion univalent radii but such a 'hard sphere' model does not give a realistic measure of the actual O—O non-bonding distances, which are found to vary from 2.2 Å in NO_3^- to over 2.8 Å for the O atoms surrounding Na. The difference arises from the greater strength of the N—O bond (5/3 v.u.), which can pull the O atoms closer together. We can allow for this effect in the following way. We assume that for a given valence (s) of an A—O bond there exists a minimum allowed O—O distance (R_m), which is given by the relation

$$s\cos\theta = (R_m/R_0)^{-N'} \tag{4}$$

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[21] T. Kjällman and I. Olovsson, *Acta Cryst.*, 1972, **B28**, 1692.

[22] I. D. Brown, *Acta Cryst.*, 1977, **B33**, 1305.

[23] W. H. Baur, *Trans. Amer. Cryst. Ass.*, 1970, **6**, 129.

[24] M. Taylor and G. E. Brown, *Amer. Miner.*, 1976, **61**, 435.

[25] L. Pauling, 'The Nature of the Chemical Bond', Third Edition, Cornell University Press, Ithaca, 1960, pp. 543ff.

where θ is the angle between that A—O bond and the O—O vector. If the values of the constants R_0 and N' are taken to be 2.22 Å and 7.4, respectively, one gets predictions for the maximum possible co-ordination numbers for O around various cations that are as good as those of Pauling's hard sphere model but have the advantage that they involve realistic estimates of the O—O distances. This allows the model to be extended to problems of irregular co-ordination such as the bonding around hydrogen dealt with in Section 6. The best $s\cos\theta$ vR_m curve for O—O interactions is shown in Figure 8.

5 Distorted Cation Environments

The valence sum rule and the form of the bond valence–bond length correlation can be used to prove an interesting theorem concerning distorted environments, namely that any deviation of the bond lengths from their average value will increase the average bond length.[6] This can be demonstrated as follows: let a cation in regular co-ordination form bonds of length r_2 and valence s_2 (Figure 1). Suppose that the environment distorts into two equal groups of bonds with lengths r_1 and r_3 with corresponding valences s_1 and s_3. Since, by the valence sum rule $s_1 + s_3 = 2s_2$ it follows from the shape of the valence–length curve (Figure 1) that $r_1 + r_3 > 2r_2$. The effect is quite general and is well attested.[26] For example increasing the degree of distortion of VO_6 groups can increase the average V—O distance by as much as 0.1 Å. A similar distortion occurring on cooling $CaTiSiO_5$ through 220 °C is responsible for *increasing* the crystallographic *a* axis by 0.01 Å.[24]

A number of corollaries follow from this theorem. The first is that since the application of pressure tends to decrease the average bond length it will also tend to make the co-ordination more regular.

An interesting example is provided by $CuTeO_3$[27] where both cations have irregular environments. If the co-ordination number of the cations are taken as six, the range of cation–oxygen distances for both Cu and Te changes from 1.9—3.2 Å at low pressure to 1.9—2.6 Å at high pressure.

Another corollary to this theorem is that if the environment of a cation distorts in such a way that the average bond length is forced to remain constant (*e.g.* by the cation moving off centre in a rigid polyhedron of anions), then the experimental atomic valence of the cation will increase. This effect can be used to discuss the distortions found in ABO_3 crystals with a perovskite-like structure. In the ideal structure all the atom positions are fixed by symmetry and the only free parameter is the length of the cubic unit cell (Figure 5a). Since the crystals contain both A—O and B—O bonds, at least two free parameters are needed if the valence sum rule is to be obeyed. The result is generally a compromise with either the valence of A being too large and the valence of B being too small or *vice versa*. The cation with the low valence (*i.e.* that occupies a cavity that is too

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[26] R. D. Shannon, P. S. Gumerman, and J. Chenavas, *Amer. Miner.*, 1975, **60**, 714; R. D. Shannon and C. Calvo, *Acta Cryst.*, 1973, **B29**, 1338; see also ref. 6.

[27] E. Philippot and M. Maurin, *Rev. Chim. Miner.*, 1976, **13**, 162.

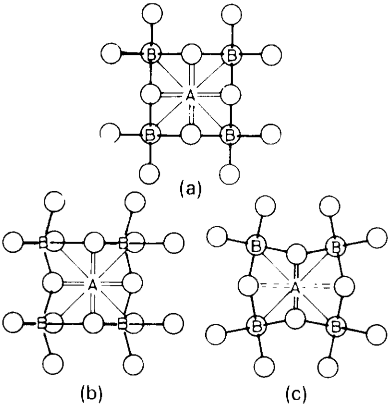

Figure 5 ABO_3 *perovskite structures:* a, *undistorted;* b, *distorted by* B *cation moving off centre in its octahedron;* c, *distorted by the collapse of the co-ordination polyhedron around* A

large for it) will tend to distort its environment to increase its valence. Two types of distortion are thus observed:

(i) when the octahedral B atom has the low valence and moves off-centre in its octahedron (Figure 5b), and

(ii) when the twelve-co-ordinated A atom has the low valence and the octahedra twist to give four shorter and four longer bonds (Figure 5c).

In both cases the valence sum rule applied to the O atoms requires that the distortions occur co-operatively in adjacent cells.[24] Figure 6 shows the deviations

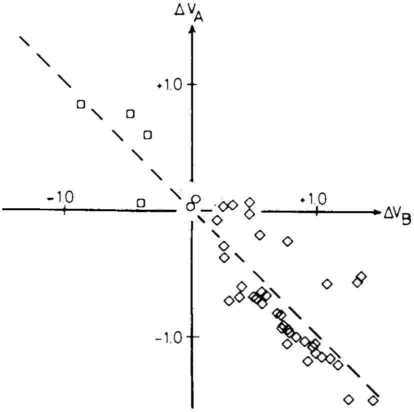

Figure 6 *A plot of the deviations between the experimental and theoretical atomic valences that would be expected for a number of* ABX_3 *compounds if they had the ideal perovskite structure. Circles denote those that have the undistorted pervoskite structure (Figure* 5a). *Squares denote structures distorted as in Figure* 5b *and diamonds structures distorted as in Figure* 5c

between the experimental and theoretical cation valences that would be expected for a number of ideal perovskite structures (Figure 5a). Only when the experimental valences of both cations are within 0.1 v.u. of the theoretical value does the ideal structure occur at room temperature. In all other cases the crystal is found to be distorted. For example, the rare earth ferrites, $LFeO_3$, have a structure like that of Figure 5c[28] with observed atomic valences within 0.05 v.u. of the expected values, even though in the ideal structure (Figure 5a) the differences would be as large as 1 v.u.

There are some distortions that cannot be predicted from the bond valence model alone since they arise from steric or electronic effects. Typical are those found around H, Cu^{II}, Sb^{III}, and Te^{IV}. Even in these cases the valence sum rule holds[29] and the bond valences calculated from the bond lengths still provide a good description of the bonding. They provide a natural interpretation of the weak secondary and bridging bonds that are such a conspicuous feature of the oxide and fluoride complexes of atoms of the series Sn^{II} to Xe^{VI},[30] providing a complementary treatment to the VSEPR approach of Gillespie and Nyholm.[31]

Brown[30] has also shown that there is a simple correlation in these compounds between the valence and the angles formed by the bonds. Similar correlations between bond angle and length have been noted in the tetrahedral oxyanions such as PO_4^{3-} [23] and SO_4^{2-}.[32] By studying the distortions found in a large number of crystals, Murray-Rust, Bürgi, and Dunitz[33] have shown that the angles in most tetrahedral groups change in the same way when one of the ligands is gradually removed. Two extreme geometries define three angles 109° (tetrahedron), 120°, and 90° (triangle with one ligand removed to infinity). Intermediate

$$\theta = 109.5 + 180\,(\Delta s/V) - 652(\Delta s/V)^2 \qquad (5)$$

values can be interpolated using equation (5), where V is the cation valence and Δs is the average deviation from V/4, the ideal valence of the four bonds defining the angle. This relation describes most of the angular distortions found in SO_4^{2-} [32] and ClO_4^- [34] groups and is expected to apply to many other tetrahedral ions where the bonding is strong.[33]

6 Hydrogen Bonds

Few bonds are more important and more difficult to describe theoretically than the hydrogen bond, the system formed by two anions linked by a hydrogen atom. Yet this bond is one that is described well by bond valences. Since the most important and best studied hydrogen bond system is the one where both anions

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[28] M. Marezio, J. P. Remeika, and P. D. Dernier, *Acta Cryst.*, 1970, **B26**, 2008.

[29] H. Mayer and G. Pupp, *Monatsh.*, 1976, **107**, 721.

[30] I. D. Brown, *J. Solid State Chem.*, 1974, **11**, 214.

[31] R. J. Gillespie, 'Molecular Geometry', Van Nostrand Reinhold Series in Inorganic Chemistry, London, 1972.

[32] I. D. Brown, *Acta Cryst.*, 1973, **29**, 1979.

[33] H-B. Bürgi, *Angew. Chem. Internat. Edn.*, 1975, **14**, 460; P. Murray-Rust, H.-B. Bürgi, and J. D. Dunitz, *J. Amer. Chem. Soc.*, 1975, **97**, 921.

[34] I. D. Brown, *Acta Cryst.*, 1976, **A32**, 786.

are oxygen, the following discussion will, for the purposes of illustration, be confined to the O—H · · · O bond but the results apply *mutatis mutandis* to other systems.

Characteristically the hydrogen bond is asymmetric with the hydrogen atom closer to one O (the donor) than the other (the acceptor). The hydrogen bond is usually characterized by its length (the O—O distance), which has been shown to correlate with the asymmetry of the bond, short hydrogen bonds (2.4 Å) being symmetric and longer ones increasingly more asymmetric. Bonds between 2.4 and 2.75 Å are essentially linear (angle O—H · · · O > 170°) but thereafter an increase in the length is accompanied by a decrease in the O—H · · · O angle.[35] It is therefore convenient to divide hydrogen bonds into two classes, short (or strong) bonds which are linear and long (or weak) bonds which are more or less bent. The linear hydrogen bond found in ice (O—O = 2.76 Å) can be taken as the dividing point. The bond valence–bond length curve for O—H bonds is shown in Figure 7*.[34,35]

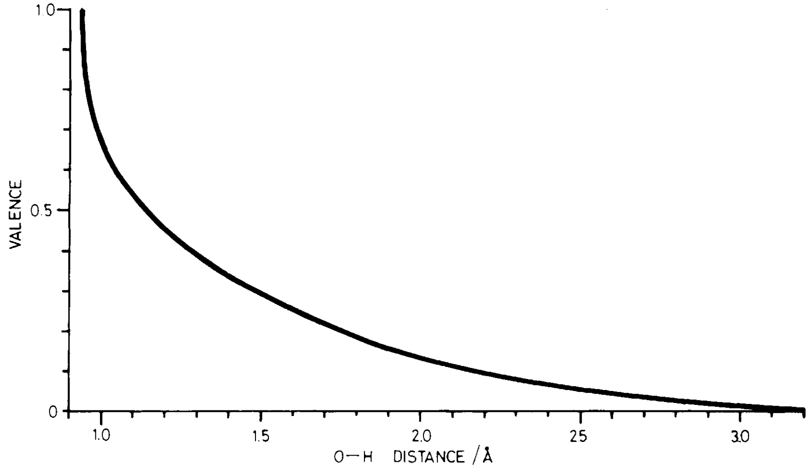

Figure 7 *Bond valence–bond length correlation for* H—O *bonds*

The asymmetry of the hydrogen bond results from the repulsion between the two O atoms.[35] According to the distortion theorem (Section 5) this repulsion can be reduced, *i.e.* the O atoms can move further apart, if the H atom moves off the centre of the bond. The increase in the O—O distance with the weakening of the hydrogen bond is indicated by the broken curve in Figure 8. The solid curve in Figure 8 is the minimum allowed non-bonded O—O distance (R_m from equation 4, in which $s\cos\theta$ is taken to be the valence of the weaker H · · · O bond recognizing that for a linear bond $\cos\theta = 1$).

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*The central section of this curve has been interpolated. If one uses the distances observed in strong bonds one obtains a curve with discontinuities at $s = 0.8$ and $s = 0.2$ v.u. The reason for this is discussed below.

[35] I. D. Brown, *Acta Cryst.*, 1976, **A32**, 24.

From Figure 8 it is seen that a linear, symmetric O—H—O bond with O—H valences of 0.5 v.u. should have a length of 2.30 Å. However, the minimum possible O—O distance is 2.42 Å. Symmetrical two co-ordination is therefore not normally possible, but by allowing the H atom to move off-centre the sum of the two O—H bond lengths is increased without increasing its atomic valence.

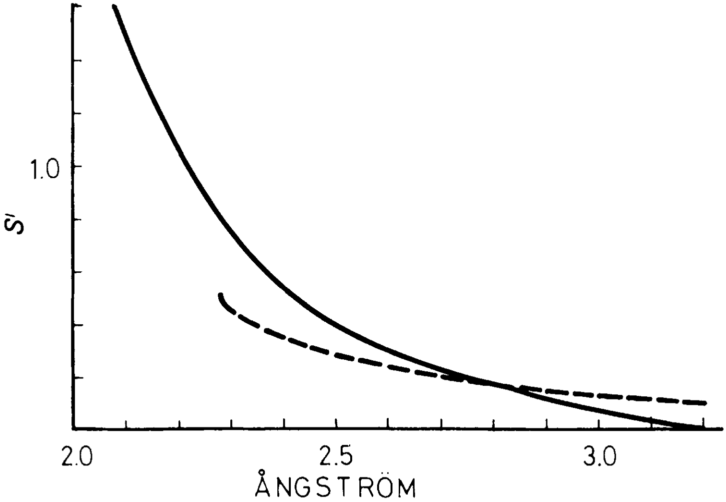

Figure 8 *Solid curve: effective valence* $s'(= s\cos\theta)$ versus R_m *equation* (4) *indicating the closest possible approach of* O *atoms when bonded to a common cation* (*e.g.* H) *by bonds of strength s. Broken curve: sum of the* O—H *and* H · · · O *distances in a hydrogen bond whose weak* H · · · O *bond has valence s'*

However, the minimum O—O distance also increases though not as rapidly, so that the two O—O distances become equal at around 2.8 Å, with valences for the two O—H bonds of 0.81 and 0.19. This is the most symmetrical bond that can normally occur and it is the type most commonly found. Shorter hydrogen bonds are formed when the donor O cannot provide 0.81 v.u., *e.g.* when it is a water molecule co-ordinated to a small highly charged cation such as H^+ or Be^{2+}. Such short hydrogen bonds have lengths that follow the $R(O—O)_{min}$ curve rather than the broken curve given in Figure 8. Less symmetrical bonds can be found either when the acceptor O cannot provide 0.19 v.u., *e.g.* when it belongs to a strong acid like ClO_4^-, or when the crystal packing requires a bent bond, since for a bent bond $R(O—H) + R(H \cdots O) > R(O—O)$, thereby forcing the bond to become more asymmetric and longer. The geometric constraints implied by Figure 8 suggest that O—H · · · O bonds will be linear for O—O distances less than 2.8 Å and generally bent for larger distances with the O—H · · · O angle determined by $R(O—H)$, $R(H \cdots O)$, and $R(O—O)_{min}$, all of which are known. The agreement between the predicted and observed geometries is shown in Figure 9.

Bond valences are particularly useful in predicting hydration structures around anions. If we assume that in neutral aqueous solution each O atom of an oxyanion

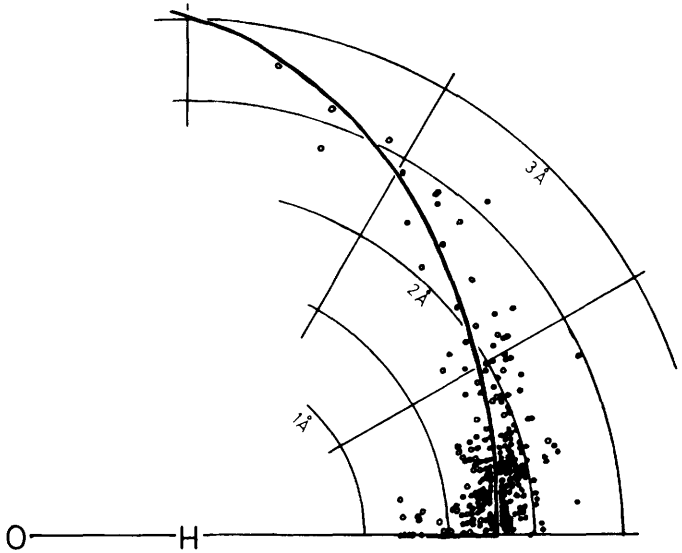

Figure 9 *Geometries of* O—H · · · O *hydrogen bonds. The circles are observed acceptor* O *positions* [*relative to the* O(*donor*)—H *bond*]. *The solid line gives the locus of predicted acceptor positions*

either accepts three hydrogen bonds or donates one and accepts one bond, and that these bonds will, where possible, be typical of those found in the adjacent water, we can predict hydration structures that agree with crystal structure studies and acid p*K* values. Figure 10 shows some of the species that are to be expected in neutral water. The hydration structure around ClO_4^- will contain hydrogen bonds that are weaker than those found in bulk water in agreement with observation,[36] but PO_4^{3-} will act as a donor to one or two hydrogen bonds so that the species HPO_4^{2-} and $H_2PO_4^-$ will be the ones found at pH 7.

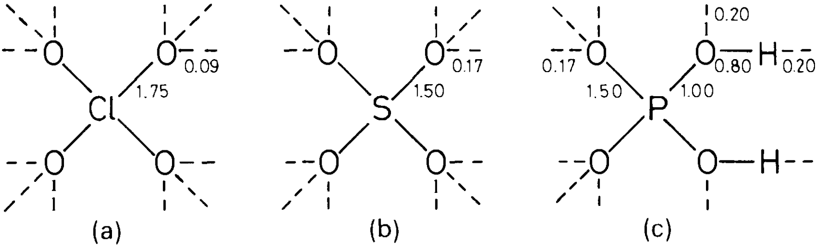

Figure 10 *Expected bond valence structures of* a, ClO_4^-; b, SO_4^{2-}; *and* c, $H_2PO_4^-$ *in aqueous solution. Broken lines indicate the weaker* (H · · · O) *end of a hydrogen bond*

Figure 11 shows the hydration structures predicted for three cations. Beryllium can co-ordinate four O atoms with bonds of 2/4 = 0.5 v.u.; Mg can co-ordinate six O atoms with bonds of 2/6 = 0.33 v.u. The difference in the strength of the

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[36] G. Brink and M. Falk, *Canad. J. Chem.*, 1970, **48**, 3019.

metal–oxygen bonds is reflected (through the action of the valence sum rule at O and H) in the differences in strength of the hydrogen bonds formed by the water molecules. These simple valence structures give predictions of bond lengths that agree within 0.02 Å with those found in crystals.[37] Experimental results for solution structures of hydrated cations are more difficult to obtain, but the agreement between the predicted and observed solution structures of hydrated Co^{3-} (Figure 11c)[38] indicates that bond valences work as well in liquids as in solids. The bond valence structure accounts for such diverse properties as the stability of the $Co(H_2O)_6{}^{3+}$ moiety (resulting from the large Co—O valence), the strong bond between the first and second hydration spheres (predicted 2.63 Å, observed 2.74 Å) and the failure of the first hydration sphere to act as a hydrogen bond acceptor.

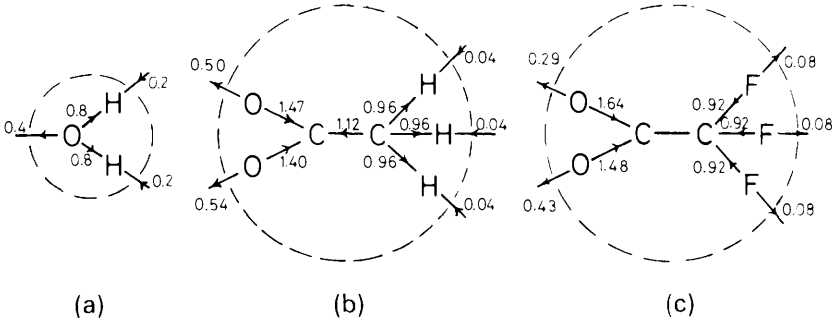

Figure 11 *Predicted bond valence structures for* a, $Be(H_2O)_4{}^{2+}$; b, $Mg(H_2O)_6{}^{2+}$; *and* c, $Co(H_2O)_6{}^{3+}$ *in aqueous solutions. Broken lines indicate the weaker* (H · · · O) *end of a hydrogen bond. Part of the second hydration sphere is shown in* c

7 Chemical Activity

For some purposes it is convenient to consider the bonds as directed from the more electronegative to the more electropositive atom. An arrow placed on the bond then indicates the direction of net electron flow into the bond as the isolated ions are brought together or as an electron donor forms a bond with an electron acceptor. This convention is particularly useful when considering the properties of atoms or groups of atoms that can act both as electron donors and electron acceptors, since the sum of the bond valences between the group and its environment (taking into account the direction of the bonds) must equal its formal charge. Thus water (Figure 12a) uses its hydrogen atoms to form two hydrogen bonds (electron acceptor bonds) with typical valences of 0.2 v.u. each and it must therefore act as an electron donor to the extent of 0.4 v.u., in order to maintain its valence neutrality. The difference in acidity between acetic acid and trifluoroacetic acid is illustrated by the observed bond valence structures given in Figures 12b and 12c. The methyl protons act as electron acceptors (0.04 v.u.), but

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[37] S. K. Sikka and R. Chidambaram, *Acta Cryst.*, 1969, **B25**, 310; G. Ferraris, D. W. Jones, and J. Yerkess, *J.C.S. Dalton*, 1973, 816.

[38] R. Caminiti, G., Licheri, G. Piccaluga, and G. Pinna, *J. Chem. Phys.*, 1976, **65**, 3134.

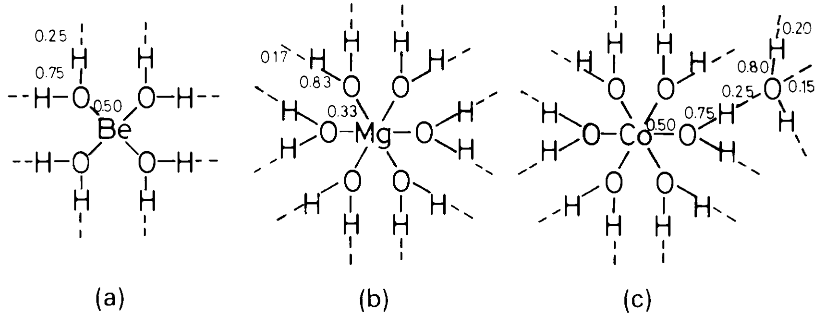

Figure 12 *Typical bond valence structure observed in crystals for* a, H_2O; b, CH_3COO^-; *and* c, CF_3COO^-

the fluorine atoms act as electron donors (0.08 v.u.). In both cases the sum of the directed bond valences around the ion is close to one, but the ability of the O atoms to bond hydrogen, as indicated by its available valence, is very different, 0.52 against 0.36 v.u. Bond valence structures of this kind not only bring out the essential similarities between ionic and charge transfer bonding, but the outwardly directed available valence of an atom provides a quantitative measure of its basicity at that site. It has been used by Rutherford and Robertson[39] to demonstrate the highly basic nature of the nitrosyl O in $O_3S(NO)SO_3{}^{3-}$. Figure 13 shows the correlation between Gutmann's electron donicity[40] for various organic bases and the available valence at the base group. In this figure the available valence has been calculated by assuming that H atoms bonded to the C adjacent to the base act as electron acceptors to the extent of 0.05 v.u., H atoms bonded to C two atoms from the base accept 0.025 v.u., all other H atoms bonded to C accept 0.01 v.u. and H atoms bonded to O or N accept 0.20 v.u.

Bond valences not only give a measure of chemical activity but can be used in the prediction of reaction mechanisms. By studying the molecular distortions found in a large number of crystals, Murray-Rust, Bürgi, and Dunitz[33] have indicated that the valence sum rule is satisfied by the series of intermediate configurations that two molecules pass through when they react. Bond valences can therefore be used to test the intermediate states of proposed reaction mechanisms.

When two ions are brought together their bonding electrons move towards the centre of the bond, so that the shorter a bond becomes the more covalent it is. Brown and Shannon[6] have shown that the valence of a typical bond between a

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[39] J. S. Rutherford and B. E. Robertson, *Inorg. Chem.*, 1975, **14**, 2537.
[40] V. Gutmann, *Angew. Chem. Internat. Edn*, 1970, **9**, 843.

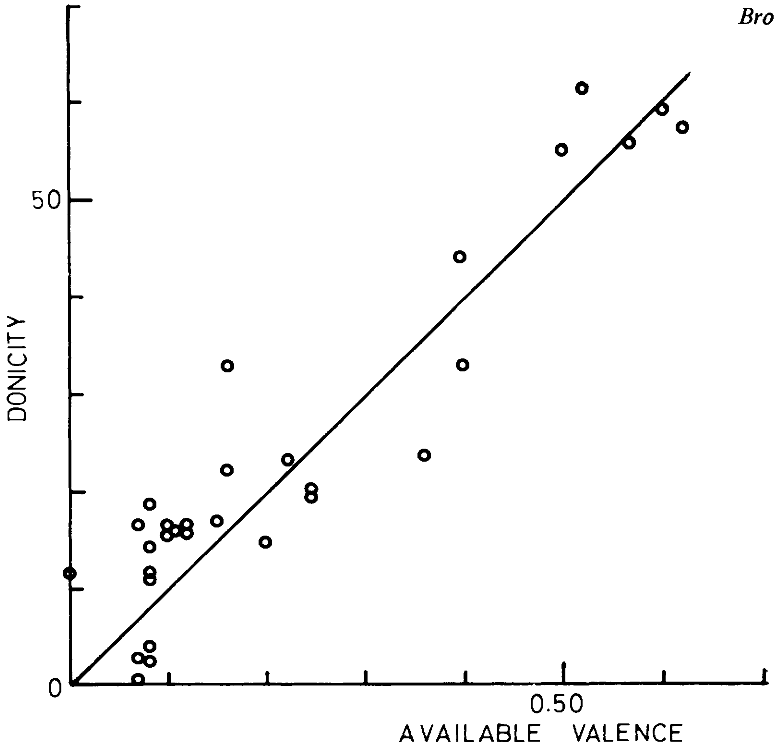

Figure 13 *Comparison of the donicity and available valence of various organic bases*

cation and O is a direct measure of its covalent character as defined by Pauling[41] and they suggest that the covalent character of an individual bond can be determined from its valence. The V—O bonds, which in the $V_{10}O_{28}{}^{6-}$ ion range from 1.593 to 2.313 Å have valences ranging from 1.82 to 0.28 v.u. and covalent characters ranging from 70% to 25%. Klemperer and Shum[42] have used the sums of covalences at the terminal O atoms in this ion to predict correctly which O atoms are most easily protonated in acid solution. All the external O atoms have the same available valence which is normally used to accept hydrogen bonds in solution, but those with the lowest covalence sum will be the most ionic, carrying the largest charge, and hence the most susceptible to electrophilic attack.

8 Conclusions

The chemical structure of inorganic compounds is at best explained only qualitatively by physical theories. The bond valence model provides a framework for discussing structural correlations without implying the physical mechanism that produces them. The ultimate understanding of chemical bonding must be sought not in simple covalent or electrostatic models but in complete quantum

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[41] L. Pauling, 'The Nature of the Chemical Bond', Second Edition, Cornell University Press, Ithaca, 1942, pp. 69ff.

[42] W. G. Klemperer and W. Shum, *J. Amer. Chem. Soc.*, 1977, **99**, 3544.

mechanical solutions. It follows that the simple empirical laws described here must be hidden within these solutions. We ought to be able to find a quantum mechanical theorem that corresponds to the valence sum rule and this theorem must be relatively rigorous at least for those structures in which the rule works. Future work should involve the extension of the empirical rules on one hand and a search for simplifying theorems of quantum mechanics on the other.

In the meantime, the bond valence model, even without a sound physical basis, is proving a powerful tool in the analysis and description of inorganic structure and, because of its simplicity, provides a useful vehicle for the teaching, understanding, and predicting of structure and reactivity in inorganic chemistry.

I would like to thank Drs. M. Falk and K. Rubenson for their helpful discussions.