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Semi-Empirical Groundwork of the Bond-Valence Model

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Abstract

The bond-valence model (BVM) which relates the length R of a bond to its bond valence s is a widely used empirical approach to the interpretation and prediction of atomic arrangements in crystals. However, a theoretical foundation of the BVM appears to be fairly inadequate so far. In this paper derivations of the main expressions of $R(s)$ for both versions of the BVM (in inverse-power and exponential forms) are reproduced and refined by the use of various semi-empirical potentials for interatomic interactions that are appropriate for ionic, covalent and intermediate ionic-covalent bonding, respectively.

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Independence of the BVM from bonding character is the result of such a treatment. Interrelations between both versions of the BVM are also analyzed. Much attention is given to the question of transferability of the single bond-length parameter and to the special role of bond-specific values of the softness parameter. The latter is proved to be a simple function of the ionization potentials of bonded atoms. In turn, this explains the strong linear correlations between the single bond lengths from cations to a pair of anions and the relation between single bond lengths and atom sizes (sum of the covalent radii). It is demonstrated that a correction related to electronegativity difference is involved in this consideration. In general, one might conclude that the BVM becomes soundly based from both the empirical and semi-empirical viewpoints.

Introduction

The simple concept of the dependence of a bond length on its bond order (or bond strength) is known to be ill-defined, but extremely fruitful in inorganic crystal chemistry. The method has a very long history. For predominantly ionic crystals, Pauling (1929) was the first to introduce the notion of electrostatic bond strength $s_{ij} = z_i/v_{ij}$, where z_i is the charge (valence) and v_{ij} is the coordination number of atom i with respect to atom j . The valence sum rule (Pauling's second rule) is defined as follows

$$\sum s_{ij} = z_j, \quad (1)$$

where z_j is the valence of atom j connecting i – j bonds with all neighboring i atoms. The use of rule (1) is straightforward if the coordination polyhedron around atom i is regular and the valences (or formal oxidation states) could be immediately determined from stoichiometry and the position of the element in the periodic table. However, the situation becomes much more complicated if the coordination configuration is irregular or the valence states of the atoms are uncertain. In such cases a certain relation is employed between the bond strength value s and the corresponding bond length R , which is at the heart of the method of interest.

Recall that the evidence of a similar dependence came from the chemistry of carbon compounds. Indeed, the length of the single bond C—C is 1.544 Å, the double bond C=C is 1.330 Å ($\Delta R_1 = -0.214$ Å) and the triple bond C≡C is 1.204 Å ($\Delta R_2 = -0.340$ Å). The value $\Delta R_1/\Delta R_2 = 0.629$ is nearly equal to $\ln 2/\ln 3 = 0.630$. This observation was used by Pauling (1947) in order to propose an empirical relation between the bond length R_{ij} and the bond order n_{ij}

$$R_{ij} = R_1 - b \ln(n_{ij}), \quad (2)$$

where R_1 is the length of a single bond ($n_{ij} = 1$), $b = 0.31$ Å. Taking into account the fractional C—C bonds in graphite ($n = 1.33$, $R = 1.420$ Å) and benzene ($n = 1.50$, $R = 1.378$ Å), the value of the constant was estimated as $b = 0.26$ Å. Pauling considered this value of b as equally suitable for both covalent and metallic crystals.

In organic compounds a typical atomic valence is usually equal to or even greater than the coordination number, *i.e.* $n \geq 1$. On the other hand, in inorganic compounds and metals the opposite is more often true. This is why most inorganic crystal chemists prefer to use the bond strength s instead of the bond order n in (2). In place of the term 'bond strength', other terms were proposed for s : 'valence strength' (Zachariasen, 1963), 'bond valence' (Donnay & Donnay, 1973) or 'valence strength of a bond' (Pyatenko, 1972). Although all these terms may be considered as synonyms, we will use in this paper the terms 'bond valence' (BV) and 'bond-valence model' (BVM), which appear to be the most acceptable by contemporary investigators (*e.g.* Brown, 1992).

As shown empirically for almost 1000 various bonds in inorganic crystals (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991), the value of parameter b in (3)

$$R_{ij} = R_1 - b \ln(s_{ij}) \quad (3)$$

can normally be taken as a 'universal' constant equal to 0.37 Å. This point will be of particular importance for further discussion.

The other well known expression for the relation between s_{ij} and R_{ij} has the following form

$$s_{ij} = (R_{ij}/R_1)^{-N}, \quad (4)$$

where R_1 and N are adjustable parameters. For a given type of anion (for instance, oxygen), the value of N is a function of electronegativity (Pyatenko, 1972), the number of electrons (Brown & Shannon, 1973), size (Allmann, 1975) or the typical coordination number ν of a cation (Brown & Wu, 1976).

Equations (3) and (4) both give similar results (Donnay & Donnay, 1973; Allmann, 1975). However, due to the above-mentioned 'universality' of b , (3) has an advantage over (4). Using the optimized value of $b = 0.37$ Å and the Inorganic Crystal Structure Database

(Bergerhoff, Hundt, Sievers & Brown, 1983), the empirical values of the only fitted parameter R_1 were determined for different pairs of atoms in a variety of crystal structures (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991). For most reliable values of R_1 the estimated standard deviation is less than 0.01 Å.

Many crystallographers have used the BVM outlined above for many years with great success, not only to interpret observed bond lengths but also to predict expected values in crystals (Baur, 1970; Brown, 1977, 1978). This simple approach allows to distinguish atoms close in atomic number (Donnay & Allman, 1970), to locate the positions of light atoms, including hydrogen bonds (Brown, 1978), to indicate the sites of an element with variable valences [for instance, Cu in high-temperature superconductors (O'Keeffe & Hansen, 1988; Brown, 1989)] and to foresee order-disorder behavior in crystals (Brown, 1988).

It is evident from the characterization of the BVM that it is soundly based as a purely empirical model which has very useful crystal chemical applications. This is the reason for the problem of theoretical substantiation of the BVM becoming highly relevant (Brown, 1992; Burdett & Hawthorne, 1993). Such an attempt will be undertaken in the following sections.

Independence of the main expressions of the BVM from the bonding character

It seems reasonable to begin the successive analysis of the problem with a purely ionic approach. Indeed, years ago Brown & Shannon (1973) used the Born-Landé-type interaction potential

$$U(R_{ij}) = Az_i z_j / R_{ij} + B/R_{ij}^n = -Az_i z_j / R_{ij} + \nu_{ij} \beta / R_{ij}^n, \quad (5)$$

where A is the so-called Madelung constant, B and n are the parameters of the repulsion term; B is set proportional to the coordination number ν_{ij} so that β is kept constant for a given bond from one crystal to another. After application of the equilibrium condition $(dU/dR_{ij})_{R_0} = 0$, they obtained

$$S_{ij} = (\beta n / Az_j) R_{ij}^{1-n}, \quad (6)$$

where $s_{ij} = (z_i / \nu_{ij})$ is the i - j bond valence. For a given value of z_j and a certain structure type (so that A is constant), (6) can be written as

$$S_{ij} = \text{const } R_{ij}^{1-n}. \quad (7)$$

Within the same constraints, (7) is equally true for a single bond ($s_{ij} = 1$, $R_{ij} = R_1$), that is

$$\text{const } R_1^{1-n} = 1. \quad (8)$$

Obviously, from (7) and (8) it follows that

$$s_{ij} = (R_{ij}/R_1)^{-(n-1)}. \quad (9)$$

This result is identical to (4), providing $N = n - 1$. Remember that the values of n vary in the range 5–12, increasing with the number of electrons in the ion, *i.e.* the larger the ion, the greater the value of n . An average value of n usually accepted is 9. The typical values of N in (4) vary for a number of oxides in the range 4–8 (Brown & Wu, 1976) and tend to increase with increasing size and coordination number of the cation. The average value of N is *ca* 6, being less than the expected value (8).

There are at least two reasons for such divergence between the predicted ($n - 1$) and the observed (N) values of the power of R . The first is the van der Waals contribution to the short-range interaction, which involves an R_7^{-6} term omitted in (5). This term corresponds to the fifth power of R_{ij} and R_1 neglected in (7) and (8). The second possible source of the disagreement is due to the above-mentioned assumption of proportionality between the repulsion parameter B and the first coordination number ν . In fact, this parameter is proportional to the lattice sum $S_n = \sum_j^n v_{ij}/k_{ij}^n$, where $k_{ij} = R_{ij}/R_0$ (R_0 is the shortest interatomic distance), which is a function of n and usually somewhat greater than ν (*e.g.* Shanker & Agrawal, 1984). Thus, for the NaCl structure type $\nu = 6$, but $S_6 = 6.5952$ and $S_8 = 6.1457$, for the CsCl and CaF₂ structure types $\nu = 8$, but $S_6 = 8.7088$ and $S_8 = 8.1575$, for the ZnS structure type $\nu = 4$, but $S_6 = 4.3544$ and $S_8 = 4.0787$ *etc.* Therefore, one must substitute z_i/S_n for s_{ij} on the left side of (9). From the inequalities $s_{ij} > z_i/S_n$ and $R_{ij}/R_1 > 1$, it follows that $n - 1 > N$. In other words, the BVM accounts empirically for some effects of the short-range and long-range interactions which were rejected in (5).

The Born–Mayer parametrization of the lattice energy of an ionic crystal

$$U(R_{ij}) = -Az_i z_j / R_{ij} + v_{ij} \gamma \exp(-R_{ij}/\rho) \quad (10)$$

was recently used (Jansen Chandran & Block, 1992) to substantiate the empirical relation (3) of the BVM. The repulsion term in (10) is assumed to be proportional to the first coordination number, $1/\rho$ is the so-called hardness parameter (ρ is the softness). Considering the equilibrium state of a static crystal, the authors found the following expression

$$s_{ij} = \text{const}(R_{ij}^2/\rho) \exp(-R_{ij}/\rho), \quad (11)$$

where $\text{const} = \gamma A z_j$. In order to present this relation in form (3), rewritten as

$$s_{ij} = \exp[R_1 - R_{ij}/b],$$

the authors assumed the validity of the following relation for the length of a single bond

$$R_1/\rho = \ln(\text{const} \rho) + 2 \ln(R_{ij}/\rho) \quad (12)$$

and equated the parameter b in (3) and the softness

parameter ρ in (10). Jansen *et al.* (1992) emphasized that the ‘universal’ value of $b = 0.37 (\pm 0.05) \text{ \AA}$ is in fact very close to the average value of ρ for alkali halide crystals (0.33 \AA).

Now let us continue the above consideration in another way. For a single bond one has, from (11),

$$1 = \text{const}(R_1^2/\rho) \exp(-R_1/\rho). \quad (13)$$

It is easily seen from (11) and (13) that

$$(R_1/R_{ij})^2 = s_{ij}^{-1} \exp(-\Delta R/\rho), \quad (14)$$

where $\Delta R = R_{ij} - R_1$. Denoting $\Delta R/R_1 = \delta$, we have logarithmically

$$\rho \ln(s_{ij}) = -\Delta R + 2\rho \ln(1 + \delta). \quad (15)$$

When this result is compared with the initial equation (3), it is apparent that

$$b = \rho[1 - 2 \ln(1 + \delta)/\ln(s_{ij})]. \quad (16)$$

It is not difficult to estimate the second term in the brackets, keeping in mind that $\delta \ll 1$,

$$b \simeq \rho(1 + 2\rho/R_1). \quad (17)$$

The correction term $2\rho/R_1$ is usually no more than 0.2. This explains the fact that the empirical value of b (0.37 \AA) is greater than the typical (average) value of the softness parameter ρ for ionic crystals ($0.30\text{--}0.34 \text{ \AA}$). In other words, a bond is likely to be somewhat softer than the crystal as a whole.

The foundations of the BVM described above were based on a purely ionic model. However, it is well known that the BVM is equally suitable for metallic, covalent and predominantly covalent crystals. Therefore, one needs to find a more general explanation of the common utility of the BVM.

A semi-empirical approach to solving the problem for covalent molecules (and crystals) was used by Bürgi & Dunitz (1987). They described the interatomic interaction by the modified Morse potential function

$$V(\Delta R) = D_0 \{ \exp[-2\sigma(\Delta R)] - 2n_{ij}^{2p} \exp[-\sigma(\Delta R)] \}, \quad (18)$$

where $\Delta R = R_{ij} - R_1$, R_1 corresponds to the length of a single bond, D_0 is the dissociation energy of a single bond, σ is the hardness parameter, n_{ij} is the bond order and $2p$ is a number close to unity ($0.8\text{--}1.1$ for various types of bond).

Minimization of (18) with respect to ΔR yields

$$R_{ij}(n_{ij}) = R_1 - p\sigma^{-1} \ln(n_{ij}). \quad (19)$$

Equation (19) has the same form as (3) and coincides with it if $b = \rho = p\sigma^{-1}$ and $n_{ij} = s_{ij}$. Indeed, for a wide variety of diatomic molecules the empirical value of p is *ca* 0.5 and σ is *ca* 2 \AA^{-1} (Bürgi & Dunitz, 1987), *i.e.*

$\rho\sigma^{-1} \simeq 0.25 \text{ \AA}$. This estimate is in accordance with the parameter b in (3), which is, for example, equal to 0.26 \AA for the fractional C—C bonds.

Thus, the origin of the main empirical relations of the BVM becomes clear for the two extreme types of chemical bond – ionic and covalent. Now let us attempt to explain the independence of these relations from bond type. Consider a universal characterization of cohesion energy, namely, atomization energy $E(R_{ij})$, instead of lattice energy, $U(R_{ij})$, given by (5) and (10). The semi-empirical expression of the atomization energy can be used in the simplified form (Urusov, 1975)

$$E(R_{ij}) = -Az_i z_j f_{ij}^2 / R_{ij} - v_{ij} d_{ij} \exp(-\sigma R_{ij}) + v_{ij} b_{ij} \exp(-R_{ij}/\rho) + \Delta E(f_{ij}). \quad (20)$$

Here, f_{ij} denotes the ionicity of the i — j bond ($0 \leq f_{ij} \leq 1$), so that $z_i f_{ij} = q_i$ and $z_j f_{ij} = q_j$ are the so-called effective charges of the atoms. The second term in (20) describes the covalent attraction between the nearest neighbors i and j , the third term is due to repulsion between them and the fourth term is the charge-transfer energy. The latter depends only on the ionicity parameter f_{ij} and energetic properties of free atoms in their valence states. The parameters d_{ij} and b_{ij} are, in principle, functions of f_{ij} also. However, it is not sufficient in this context to involve any explicit forms of such dependencies, if one assumes that the value of f_{ij} does not change with relatively small variations of R_{ij} . Note that (20) becomes a purely ionic potential at $f_{ij} = 1$ and a covalent one at $f_{ij} = 0$ and $\rho = 0.50\sigma^{-1}$. The latter corresponds to the usual empirical observation, mentioned above, that the value of 2ρ in the Morse function (18) is close to unity. Then, using the equilibrium condition, we have

$$\rho R_{ij}^{-2} = \text{const } s_{ij}^{-1} \exp(-R_{ij}/\rho),$$

i.e. a result which is not distinguishable from the previous one (11), except for a different constant value. Therefore, all further considerations remain valid and (12)–(17) are equally true. This indicates that the BVM is, in fact, not constrained by bonding character. However, there are some strong constraints originating in such electronic effects as Jahn–Teller distortion and the stereochemical role of lone pairs of electrons (Brown, 1992).

Interrelations between two different versions of BVM

As mentioned above, the two main schemes of the correlation between bond valence and bond length, expressed by (3) and (4), correspondingly give similar results over the range of interest. This indicates that some simple connections exist between the parameters of both these versions of the BVM.

Since the slope of the curves R_{ij} versus s_{ij} is given by N or b , these two parameters were supposed to be

approximately related (Brown & Wu, 1976) by

$$N \simeq \bar{R}/b, \quad (21)$$

where \bar{R} is an average observed bond length, at which the slopes of the two curves are set equal.

It can be shown that a relation of type (21) is valid if the other parameters of the BVM, namely single bond lengths R_1 , are equal in both the variants of the BVM. Indeed, we have from (3)

$$\ln(s_{ij}) = (R_1 - R)/b,$$

and from (4)

$$\ln(s_{ij}) = -N \ln(R/R_1).$$

If R_1 is set equal to R_1' , then

$$N \simeq R_1/b, \quad (22)$$

or, a little more accurately (Burdett & Hawthorne, 1993),

$$N + [N(N + 1)]^{1/2} \simeq 2R_1/b.$$

In fact, for many cation–oxygen bonds (Brown & Wu, 1976) the average ratio R_1'/N is equal to $0.33 (\pm 0.03 \text{ \AA})$, which is very close to the best empirical value of b ($0.37 \pm 0.05 \text{ \AA}$). Besides, the empirical values of R_1 in both approaches are strikingly similar. Let us quote as an example the two series of R_1 for various Mn—O bonds (\AA): Mn^{II}—O 1.798 (1.790), Mn^{III}—O 1.769 (1.760), Mn^{IV}—O 1.774 (1.753), Mn^{VII}—O 1.780 (1.79) \AA . The values of ‘exponential’ R_1 from recent work (Brese & O’Keeffe, 1991) are given in parentheses for comparison with the values of ‘inverse-power’ R_1 (Brown & Wu, 1976). It is worth noting that the bond-valence parameters R_1 are significant to an accuracy of *ca* 0.02 \AA , although data for many oxides and fluorides justify higher precision (Brese & O’Keeffe, 1991).

Now consider the slopes of the two curves $s_{ij}(R_{ij})$ more generally. By differentiation one obtains from (9)

$$ds_{ij}/dR_{ij} = (1 - n)R_{ij}^{-1} s_{ij}, \quad (23)$$

and from (11)

$$ds_{ij}/dR_{ij} = (2/R_{ij} - 1/\rho)s_{ij}. \quad (24)$$

Hence, it follows that

$$n + 1 = R_{ij}/\rho. \quad (25)$$

As $N \simeq n - 1$ and $\rho = b - 2\rho^2/R_1$, we may write

$$N + 2 = (R_1 + \Delta R)/(b - 2\rho^2/R_1). \quad (26)$$

A little algebra gives (if we use unity as a good approximation for the square of the ratio ρ/b)

$$N \simeq R_1/b,$$

in agreement with (22).

The distortion theorem

Inasmuch as the BVM tends to explain and predict the deviations of atomic arrangements from regular polyhedral packing, the distortion theorem plays an especially important role. This theorem is stated as follows (Brown, 1992): 'Any deviations of the lengths of the bonds formed by an atom from their average length will increase the average length providing the average bond valence remains constant'. The reverse statement is equally true. The distortion theorem derives from the concave shape of the bond valence–bond length correlation (Brown, 1978; 1992). Let us now attempt to prove this theorem analytically.

First consider the subsystem of two equivalent bonds $X-M-X$ (linear or angular). This can be a fragment of any regular polyhedron with a given number of X vertices around the M atom at its center. Let the bond valence of each $X-M$ bond be s and the bond length be R . Then allow both bonds to change their bond valences and, therefore, their bond lengths, providing the total bond valence $2s + \Delta s_1 + \Delta s_2$ remains constant and equals $2s$, so that $\Delta s = \Delta s_1 = -\Delta s_2$. Hence

$$\begin{aligned} s_1 &= s + \Delta s & R_1 &= R + \Delta R_1, \\ s_2 &= s - \Delta s & R_2 &= R + \Delta R_2. \end{aligned}$$

For the sake of definition, let Δs be positive, then $\Delta R_1 < 0$ and $\Delta R_2 > 0$. Going to the finite differences, one obtains from (23)

$$\begin{aligned} \Delta s &= [(s + \Delta s)/(R + \Delta R_1)]\Delta R_1(1 - n), \\ -\Delta s &= [(s - \Delta s)/(R + \Delta R_2)]\Delta R_2(1 - n). \end{aligned} \quad (27)$$

The summation of these two equations yields

$$\begin{aligned} (s + \Delta s)[(\Delta R_1/R)(1 + \Delta R_1/R)] \\ + (s - \Delta s)[(\Delta R_2/R)(1 + \Delta R_2/R)] \\ = 0. \end{aligned} \quad (28)$$

If the squares of the small ratios $\Delta R_1/R$, $\Delta R_2/R$ can be taken as negligible quantities, corresponding to the substitution of the curve $R(s)$ by a polygonal line, then

$$\Delta R_1 + \Delta R_2 = -(\Delta s/s)(\Delta R_1 - \Delta R_2), \quad (29)$$

in good approximation. Keeping in mind that $\Delta s/s > 0$ and $\Delta R_1 - \Delta R_2 < 0$, we conclude that $\Delta R_1 + \Delta R_2 > 0$. It follows that the average bond length will increase and thus the distortion theorem is proved. The reverse statement is easily proved in an analogous way, because (23) is symmetric in relation to s and R .

Transferability of a single bond length

One of the most striking features of the BVM is the constancy and transferability of a single bond length R_1 . This sole parameter (in the exponential version) depends

only on the individuality of a pair of bonded atoms, but does not depend on any structural properties. For instance, one has to apply the same value of $R_1(\text{Mg}-\text{O}) = 1.69 \text{ \AA}$ (Brese & O'Keeffe, 1991) to explain or predict the Mg–O bond lengths in such different crystal structures as spinel MgAl_2O_4 ($Fd\bar{3}m$) or okermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ($P42_1m$), with $\nu_{\text{Mg}} = 4$, periclase MgO ($Fm\bar{3}m$) or forsterite Mg_2SiO_4 ($Pnma$) with $\nu_{\text{Mg}} = 6$, and garnet (pyrope) $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ($Ia\bar{3}d$) or silicate perovskite MgSiO_3 ($Pnma$) with $\nu_{\text{Mg}} = 8$. Note that the observed Mg–O bond distances vary in these crystals over a wide range: from 1.92 to 2.20 Å.

In order to explain this remarkable property of the parameter R_1 let us consider the following expression for the site potential of an i ion in a crystal structure (e.g. Urusov, 1975)

$$\varphi_i(R_{ij}) = -\alpha z_i R_{ij}^{-1} + \nu_{ij} \beta R_{ij}^{-n}. \quad (30)$$

Here α is the so-called 'partial' Madelung constant characterizing the electrostatic potential at the ion site (Hoppe, 1970). In contrast with the 'total' Madelung constant A in (5) and (10), which is strongly structure- and stoichiometry-dependent, the values of α vary in a relatively narrow interval: from 1.3 to 1.8 (Urusov, 1975; O'Keeffe, 1981).

The condition of equalization of attractive and repulsive forces in a stable crystal structure yields

$$d\varphi_i/dR_{ij} = \alpha z_i - \nu_{ij} \beta R_{ij}^{1-n} = 0.$$

This can be rewritten in the appropriate form

$$s_{ij} = z_i/\nu_{ij} = (n\beta/\alpha)R_{ij}^{1-n},$$

from which it follows for a single bond length R_1 ($s_{ij} = 1$)

$$R_1 = (n\beta/\alpha)^{1/n-1}.$$

Thus, the value of R_1 for a given pair of atoms will be a constant if $n\beta/\alpha$ is a constant. The product $n\beta$ is characteristic of atomic properties and could be considered, to a good approximation, as almost independent of crystal structure. The same is also true for the partial Madelung constant α , as shown by O'Keeffe (1979) for many cation–oxygen pairs. O'Keeffe found empirically that the electrostatic potential at the oxygen ion site is expressed by

$$\varphi_i = -1.77 z_i R^{-1},$$

where R is the cation–oxygen bond length which is appropriate for six-coordination. This remarkable result bears testimony to the dependence of the potential at that ion site only on the size of the counter ion and an absence of its dependence on structure, or even on the charge on the counter ion. In other words, the value of R_1 is actually a unique bond-valence parameter for bonds between a given pair of atoms transferable within a variety of observed crystal and molecular structures.

With the exponential repulsive term instead of the inverse-power term in the site potential $\varphi_i(R_{ij})$ it follows that

$$R_1 = \rho B(1 + A), \quad (31)$$

where $B = \ln(\gamma\rho/\alpha)$, $A = \ln[(R_1/\rho)^2/\ln(\gamma\rho/\alpha)]$. Both parameters A and B are almost constant for a given pair of atoms. This assumption is a close approximation to the truth because the product $\gamma\rho$ is characteristic of atomic properties and $R_1/\rho (\simeq N)$ appears to be dependent only on the number of electrons in the electronic shells of bonded atoms.

Another estimation of R_1 originates from (22) and (17)

$$R_1 = \rho N(1 + 2\rho/R_1)$$

or

$$R_1 \simeq \rho N(1 + 2/N - 4/N^2 + \dots). \quad (32)$$

Comparing (31) and (32), one could conclude that B is proportional to N and A is inversely proportional to the corresponding N value. Further, it is evident from (32) that the length of a single bond is a function of short-range forces. This supports the corresponding postulate by Gibbs & Finger (1985).

Bond-specific softness parameters

The approximate identity of b in the BVM [see equation (3)] and the softness parameter ρ in the Born–Mayer repulsion potential [see equation (10)] makes it possible to ascribe a specific value of b to a given bond. It is worth bearing in mind that such a rejection of the commonly accepted ‘universality’ of the b value ($0.37 \pm 0.05 \text{ \AA}$) has more of a theoretical than a practical significance.

It has long been known that the softness parameter ρ displays relatively moderate but quite noticeable changes from one crystal to another. For instance, Table 1 presents the values of ρ for the alkali halide crystals with the NaCl-type structure derived empirically with two different input data: from compressibilities ρ_1 and from transverse optic mode frequencies ρ_2 (Singh & Shanker, 1981). It is seen that the individual values of ρ vary from 0.29 to 0.38 \AA . It should also be emphasized that the variations of values of ρ refer mainly to the anion species: for fluorides $\rho_1 = 0.29\text{--}0.31 \text{ \AA}$, for chlorides $\rho_1 = 0.33\text{--}0.35 \text{ \AA}$, for bromides $\rho_1 = 0.34\text{--}0.36 \text{ \AA}$ and for iodides $\rho_1 = 0.36\text{--}0.38 \text{ \AA}$.

On the other hand, in 1931 it was shown (Zener, 1931) with the aid of quantum-mechanical calculations that the repulsion of closed-shell atoms can be expressed as an exponential function of the distance

$$\varphi_{\text{rep}} = b \exp(-R_{ij}/\rho_{ij}), \quad (33)$$

where the short-range interaction constant ρ_{ij} is related to the ionization potentials I_i and I_j of the interacting ions

Table 1. Values of softness parameter ρ (\AA) for alkali halide crystals

Crystal	ρ_1	ρ_2	ρ_3
LiF	0.290	0.296	0.286
LiCl	0.351	0.356	0.312
LiBr	0.348	0.383	0.321
NaF	0.293	0.276	0.287
NaCl	0.333	0.332	0.315
NaBr	0.345	0.352	0.325
NaI	0.364	0.369	0.337
KF	0.311	0.285	0.297
KCl	0.345	0.322	0.326
KBr	0.358	0.336	0.336
KI	0.376	0.344	0.348
RbF	0.312	0.294	0.299
RbCl	0.345	0.328	0.328
RbBr	0.360	0.343	0.338
RbI	0.379	0.349	0.351

through

$$1/\rho_{ij} = 2^{1/2}(I_i^{1/2} + I_j^{1/2}). \quad (34)$$

Here I is in atomic units ($1 \text{ a.u.} = 27.212 \text{ eV}$).

It has also long been known from molecular quantum chemistry (Mulliken, 1955) that the repulsion between bonded atoms is, to a good approximation, proportional to the square of the overlap integral $S^2 = (\int \varphi_A \varphi_B d\tau)^2$. If the valence atomic orbitals φ_A and φ_B are represented by the Slater-type functions $\varphi(r) = Nr^{n-1} \exp(-\xi r)$, then the main contribution to S^2 is converted into the following form

$$S^2 = \lambda \exp[-2(\xi_A + \xi_B)R_{AB}], \quad (35)$$

where ξ are the so-called orbital exponents and λ preserves an almost constant value within the interval of interatomic R_{AB} distances of interest.

In its turn, it has been demonstrated (Urusov, 1962) that the orbital exponent $\xi = Z^*/n^*$ (Z^* and n^* are the effective nuclear charge and principle quantum number, respectively) could be well estimated by the simple relation

$$\xi = I^{1/2}/2^{1/2}.$$

Taking this into account, a comparison of (33) and (35) testifies to the validity of relation (34). Thus, a semi-empirical estimate of the repulsion parameter ρ_3 is given by

$$\rho_3 = 1.85(\sum I^{1/2})^{-1}, \quad (36)$$

where the factor 1.85 converts ρ_3 into \AA , if I is expressed in eV. As shown in Table 1, the values of ρ_3 are in excellent agreement with ρ_1 and ρ_2 : the average deviation is of the order of the experimental uncertainty.

Another confirmation of relation (36) comes from the measurements of high-energy elastic scattering of atoms, molecules and ions (Radzig & Smirnov, 1985). The repulsion potentials derived from these data are described by a function of type (33). Indeed, the correlation between such empirical estimates of values of ρ_4 for

collisions between atoms of inert gases, inert gases and H,F,O, inert gases and ions of alkali metals and the corresponding $I^{1/2}$ is found to be

$$\rho_4 = 1.82(\pm 0.29)(\sum I^{1/2})^{-1} + 0.07(\pm 0.04)$$

(correlation coefficient 0.63). Obviously, the multiplier 1.82 is very close to 1.85 in (36) and the second term is almost equal to zero.

The anticorrelation between ρ and $\sum I^{1/2}$ obtained above indicates that the softness ρ increases when the values of ionization potentials I decrease. This explains the results listed in Table 1: the values of ρ for iodides [$I(\text{I}) = 10.45$ eV] are the highest (*ca* 0.37 Å) and the values of ρ for fluorides [$I(\text{F}) = 17.42$ eV] are the lowest (*ca* 0.30 Å). The first ionization potential of oxygen [$I(\text{O}) = 13.62$ eV] is very close to that of chlorine [$I(\text{Cl}) = 12.97$ eV] and one could predict a proximity between the softness parameters of chlorides and oxides. Indeed, the average value of the softness parameters of *ca* 40 oxides derived recently from calculations by the modified electron gas (MEG) method (Freeman & Catlow, 1992) is 0.35 Å, a value which is very close to the average ρ for chlorides in Table 1 (*ca* 0.34 Å).

An explanation of linear relationships between single bond lengths

Equation (31) indicates that the value of R_1 is a linear function of the softness parameter ρ . If the hypothesis that the bond softness can be expressed by a constant value of $\rho = b = 0.37$ Å is valid, then it becomes rather difficult to understand why each bond is characterized by a specific value of the parameter R_1 . It is a serious problem for isoelectronic series of molecules and crystals. On the other hand, it has recently been shown (Brese & O'Keeffe, 1991) that there are strong linear correlations between the parameters R_1 for bonds from cations to pairs of anions. The equation of the line is

$$R_{ij} = a_{jk} + b_{jk} R_{ik}. \quad (37)$$

Here, R is a single bond length, subscript i denotes a certain type of cation and subscripts j and k refer to a pair of the 12 anions, so that the empirical parameters a_{jk} and b_{jk} are characteristic of a given anion pair jk . Equation (37) yields an excellent fit for a set of 66 jk pairs (Brese & O'Keeffe, 1991).

With the purpose of explaining the origin of expression (37) and making some predictions of the values of the parameters a_{jk} and b_{jk} , let us consider the relation between R_{ij} and R_{ik} , as follows from the estimation (31)

$$R_{ij} = (\rho_{ij}/\rho_{ik})(B_{ij}/B_{ik})R_{ik} + \Delta A,$$

where $\Delta A = \rho_{ij}B_{ij}(A_{ij} - A_{ik})$. If the anions j and k belong to the same row of the periodic table, then it is reasonable to assume that $B_{ij} \simeq B_{ik}$ and $A_{ij} \simeq A_{ik}$. Therefore, one can

simplify the previous relation

$$R_{ij} \simeq (\rho_{ij}/\rho_{ik})R_{ik} + \Delta A, \quad (38)$$

where ΔA is set close to zero. With the aid of the estimates of ρ [see equation (33)], one obtains finally

$$R_{ij} = (1 + \delta)R_{ik} + \Delta A, \quad (39)$$

where $\delta = (I_k^{1/2} - I_j^{1/2})/(I_i^{1/2} + I_j^{1/2})$. By comparing this result with the empirical correlation (34), one readily sees that

$$1 + \delta = b_{jk} \quad \text{and} \quad \Delta A = a_{jk}.$$

Using definition (31), one obtains an approximation

$$a_{jk} \simeq 2\rho \ln(R_{ij}/R_{ik}) \simeq 2\rho \ln(N_{ij}/N_{ik}).$$

Since the first ionization potentials change nonmonotonically across a row in the periodic table (for instance, $I_{\text{N}} = 14.53$, $I_{\text{O}} = 13.62$, $I_{\text{F}} = 17.42$ eV), it is better to use the multiplet-averaged one-electron energies of valence p -electrons, ε_p , rather than the corresponding ionization potentials, I_p (Allen, 1989). For the same examples the experimental values of ε are: $\varepsilon_{\text{N}} = 13.17$, $\varepsilon_{\text{O}} = 15.84$ and $\varepsilon_{\text{F}} = 18.14$ eV.

Let us suppose approximately that an average one-electron energy for a typical i cation, ε_i , is close to 6 eV. With the aid of relation (39) one could then easily find the following values of the parameters b_{jk} : $b_{\text{FO}} = 0.95$, $b_{\text{NO}} = 1.06$. The corresponding empirical values of the same parameters ($b_{\text{FO}} = 0.942$, $b_{\text{NO}} = 1.077$) are in good agreement with these estimates. Further, one can verify our assumption that $a_{jk} = \Delta A \simeq 0$ in these examples. In fact, $a_{\text{FO}} = 0.016$ and $a_{\text{NO}} = -0.006$ Å. Thus, the intercepts in (37) are very close to zero. Moreover, as follows from our assumption that B is proportional to N and A is inversely proportional to N , $a_{jk} > 0$ if $b_{jk} < 1$ and $a_{jk} < 0$ if $b_{jk} > 1$. These predictions are also in accordance with the observed signs of a_{jk} .

It is much more difficult to make similar quantitative estimates for bonds to the pairs of anions from different rows of the periodic table. Nevertheless, one could expect that the values of $b_{\text{F}k}$ will always be smaller than 1, since $\varepsilon_{\text{F}} > \varepsilon_k$ ($k = \text{O, S, Se, Te, Cl, Br, I, N, P, As, H}$). As shown empirically (*cf.* Table 1; Brese & O'Keeffe, 1991), it is actually true in all cases but one ($b_{\text{FTe}} = 1.007$). Moreover, the smaller the value of ε_k the smaller the value of $b_{\text{F}k}$ (for instance, $b_{\text{FCl}} = 0.927$, $b_{\text{FBr}} = 0.911$, $b_{\text{FI}} = 0.895$). Estimates given by the procedure described above yield the following results: $b_{\text{FCl}} = 0.91$, $b_{\text{FBr}} = 0.88$, $b_{\text{FI}} = 0.85$. Evidently, these estimates are still in semi-quantitative agreement with the observations.

On the other hand, the values of $b_{\text{N}k}$ are nearly always larger than 1. The only exception is for the case of $k = \text{H}$, but generally the main discrepancies were observed for hydrides (Brese & O'Keeffe, 1991).

As to the values of intercepts a_{jk} of the line (37), one could predict from the above analysis that a_{jk} will be positive if the k anion is lighter (and smaller) than the j anion. In addition, from the estimate that $a_{jk} \approx 2\rho \ln(N_{ij}/N_{ik})$, one could conclude that the greater the difference in Z between the anions j and k , the larger will be the positive value of the intercept a_{jk} . This prediction corresponds to the observed facts (Brese & O'Keeffe, 1991), for instance: $a_{\text{SO}} = 0.361$, $a_{\text{SeO}} = 0.560$, $a_{\text{TeO}} = 0.910 \text{ \AA}$.

In any case, the lightest anions ($k = \text{H, N, O}$) are characterized by negative values of a_{jk} (with the only exception for $a_{\text{FN}} = 0.007$) and the heaviest ($k = \text{Te, I}$) have positive values of a_{jk} (with the exception of $a_{\text{Te}} = -0.411$ and $a_{\text{TeI}} = -0.553 \text{ \AA}$, *i.e.* for the anion pair itself).

Atom sizes and single bond lengths

The values of single bond lengths R_1 being transferable from one crystal to another clearly account for the sizes of bonded atoms. Indeed, these values decrease gradually across a row (*e.g.* from 1.91 \AA for Ca—O to 1.68 \AA for Ni—O at an almost constant value of $N = 5.2\text{--}5.5$; Brown & Wu, 1976) and increase down a column (*e.g.* from 1.36 \AA for Li—F to 2.33 \AA for Cs—F ; Brese & O'Keeffe, 1991). Similarly, the values of R_1 smoothly decline from La—O (2.172 \AA) to Lu—O (1.971 \AA) (Brese & O'Keeffe, 1991), reflecting the well known effect of 'lanthanide contraction'.

An earlier systematic study (Brown & Altermatt, 1985) has shown a definite relation between R_1 values and the sums of the ionic radii. However, ionic radii must be adapted for changes in coordination number and/or valence. In contrast, single bond lengths exhibit significant dependence on neither coordination number nor valence. Besides the example of $\text{Mn}^{\text{II-VII}}\text{—O}$ bonds cited above, another instance is: $R_1(\text{Cr}^{\text{II}}\text{—Cl}) = 2.09$, $R_1(\text{Cr}^{\text{III}}\text{—Cl}) = 2.08$ and $R_1(\text{Cr}^{\text{VI}}\text{—Cl}) = 2.12 \text{ \AA}$ (Brese & O'Keeffe, 1991). Note that the values of R_1 slightly increase from Cr^{II} to Cr^{VI} , whereas the ionic radii sharply decrease in the same direction: from 0.80 (Cr^{2+}) to 0.44 \AA (Cr^{6+}) for six-coordination (Shannon, 1976). This tendency is quite typical for many transition elements, although R_1 is not very different for different oxidation states in general, except for Cu—O , Cu—F , Ag—O and Ag—F (Brese & O'Keeffe, 1991). These observations argue for a relation between the values of R_1 and the sums of covalent radii rather than ionic radii.

Such an assumption was recently examined by O'Keeffe & Brese (1991). These authors have emphasized that in order to express single bond lengths as sums of radii, a correction for electronegativity differences of the bonded atoms should be applied. They considered the well known Schomaker–Stevenson formula (Schomaker & Stevenson, 1941) and several other empirical expressions, of which the simplest was

$$R_{ij} = r_i + r_j - (c_j r_i - c_i r_j)/(c_i + c_j) \\ = (c_i r_i + c_j r_j)/(c_i + c_j), \quad (40)$$

where r_i is the 'size' parameter and c_i is an empirical parameter that may be related to electronegativity.

The best expression found was one derived originally by Ray, Samuels & Parr (1979)

$$R_{ij} = r_i + r_j - r_i r_j (c_i^{1/2} - c_j^{1/2})^2 / (c_i r_i + c_j r_j). \quad (41)$$

O'Keeffe & Brese (1991) used 600 values of R_1 for bonds to as many as 16 different 'electronegative' elements and found the best values of c and r which minimized the squared deviation of the calculated and observed values of R_1 for 75 elements. The c parameters of all except the electronegative elements were fixed at the Allred–Rochow values (Allred & Rochow 1958). The derived c parameters for the electronegative elements, except H, are found to correlate well with the Allred–Rochow electronegativity scale.

For bonds between atoms with close electronegativities the correction term in (41) is generally less than the expected uncertainty in R_1 and may be ignored. It is also very interesting that the values of r quite successfully predict interatomic distances in metals, although no data for metallic compounds have been used in deriving the set of r_j . Therefore, one might consider the size parameters r as a covalent or metallic single bond radii. However, for bonds between atoms of very different electronegativities, *i.e.* for ionic bonds, the correction term is important and can amount to tenths of \AA . Thus, the maximum value of the correction is 11% (-0.30 \AA) for the Cs—F bond.

Building on our previous analysis, there is an opportunity to take an alternative approach to the problem outlined above. Using (31), let us write the following expressions for single bond lengths for bonds between different (R_{ij}) and like (R_{ii} and R_{jj}) atoms

$$R_{ij} = 1.85 (I_i^{1/2} + I_j^{1/2})^{-1} C_{ij}, \\ R_{ii} = 1.85 (2I_i^{1/2})^{-1} C_{ii}, \quad (42) \\ R_{jj} = 1.85 (2I_j^{1/2})^{-1} C_{jj},$$

where $C = B(1 + A)$. Obviously, the covalent single bond radii r_i and r_j will be defined as follows

$$r_i = R_{ii}/2 = 1.85 (2I_i^{1/2})^{-1} (C_{ii}/2), \\ r_j = R_{jj}/2 = 1.85 (2I_j^{1/2})^{-1} (C_{jj}/2).$$

One then obtains, using the assumption commonly accepted in a similar context, that $C_{ij} \approx (C_{ii} + C_{jj})/2$,

$$R_{ij} = r_i + r_j + 1.85 [C_{ij}(I_i^{1/2} + I_j^{1/2})^{-1} \\ - (C_{ii}/2)(2I_i^{1/2})^{-1} - (C_{jj}/2)(2I_j^{1/2})^{-1}] \\ \approx r_i + r_j + [(I_i^{1/2} - I_j^{1/2})/(I_i^{1/2} + I_j^{1/2})](r_i - r_j). \quad (43)$$

The last term in (43) yields a tentative estimate of the electronegativity correction to the sum of the covalent radii. For instance, let us compare the following pairs of correction term values: B—F = -0.04 (-0.06), Na—Cl = -0.08 (-0.14), Mg—O = -0.10 (-0.10), Zn—S = -0.00 Å (-0.01). The correction values derived by the use of (41) are given in parentheses. Despite a satisfactory agreement between these two estimates, it is evident that in using the new equation (43) a little recalibration of the covalent radii scale is needed to obtain a better fitting. However, our aim is to explain rather than to revise available sets of the BVM data.

Concluding remarks

It now seems clear that the wide applicability of the BVM has, indeed, a serious basis. It is worth emphasizing in conclusion that the intuition of many crystal chemists has received, once again, further support through the systematic semi-empirical study presented here. The BVM, therefore, can be actively recommended for the purpose of predictions and explanations of atomic arrangements in crystals. It may be considered as the first stage of the computer modelling of crystal structures and properties, a topic which has progressed rapidly in recent years.

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