short communications

Exact solution of the bond-valence sum rule for a set of coordination shells

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The calculation scheme for determining the bond-valence parameters (r_0 and b) resulting in the exact solution of the bond-valence sum rule for a given set of coordination shells is presented.

The bond-valence model (BVM) is widely used in mineralogy and structural inorganic chemistry as a powerful and convenient tool for validating newly determined crystal structures and for predicting bond lengths in structures of known chemical composition and presupposed bond-network topology (Brown, 2002, 2009). Bond valence (BV) s is defined as part of the 'classical' atomic valence shared with each bond. According to the bond-valence sum (BVS) rule, the oxidation state (atomic valence) V_A of the central ion (atom) of the $[AX_n]$ coordination shell can be calculated from the sum of the individual bond valences s_{AX}, as given by

$$V_A = \text{BVS} = \sum_n s_{AX}. \tag{1}$$

The valence of a bond (measured in 'valence units', v.u.) is considered to be a unique function of the bond length; the most commonly adopted empirical expression for the relationship between the bond valences s_{AX} and the bond lengths r_{AX} is equation (2), where r_0 and b are the empirically determined parameters (BV parameters) for a given ion (atom) pair, r_0 being the length of the conceptual bond of unit valence with $s_{AX} = 1$.

$$s_{AX} = \exp[(r_0 - r_{AX})/b] \tag{2}$$

The b parameter in (2) is commonly taken to be the 'universal constant' equal to 0.37 Å; and the r_0 parameters have been determined (directly calculated or obtained by extrapolation) for a large number (~ 1000) of ion pairs, assuming $b = 0.37$ Å (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991). In most cases, the use of the above 'universal constant' is fairly justified; but for certain ion pairs (especially for those having a wide range of coordination numbers) close approximations of the real 's_{AX} versus r_{AX}' correlations are possible only by *simultaneous* fitting of both r_0 and b (*e.g.* Krivovichev & Brown, 2001; Locock & Burns, 2004; Sidey, 2010).

The standard scheme for *direct* calculation of the BV parameters (Brese & O'Keeffe, 1991; Brown, 2002) includes:

(i) selecting the most reliable dataset of $A-X$ bond lengths for a given ion pair;

(ii) solving (1) for the ith coordination shell $[AX_n]$ by using (3), where b is usually preset to 0.37 Å;

(iii) averaging the $r_0^{(i)}$ values calculated for a given ion pair.

$$r_0^{(i)} = b \ln\left[V_A / \sum_n \exp(-r_{AX}^{(i)}/b)\right] \tag{3}$$

Intuitively, the 'standard' r_0 value (hereafter denoted as $^{st}r_0$) obtained in the above scheme by averaging the individual $r_0^{(i)}$ values is expected to give the average bond-valence sum $\langle \text{BVS} \rangle = V_A$ for the set of coordination shells considered; but rigorous mathematical examination of this scheme indicates that, in the general case, the $^{st}r_0$ value gives $\langle \text{BVS} \rangle \neq V_A$. Although at the adequately preset b value the systematic error introduced by the standard scheme is expected to be relatively small (see below), a scheme resulting in the *exact* (*i.e.*

Table 1
Comparison of the $^{st}r_0$ and $^{ex}r_0$ values calculated for the set of two coordination shells, [BO_3] of B_2O_3-(I) (Effenberger *et al.*, 2001) and [BO_4] of B_2O_3-(II) (Prewitt & Shannon, 1968).

b (Å)	$r_0^{(I)}$ (Å)	$r_0^{(II)}$ (Å)	$^{st}r_0$ (Å)	$^{st}\langle BVS\rangle$ (v.u.)†	$^{ex}r_0$ (Å)	$^{ex}\langle BVS\rangle$ (v.u.)†
0.10	1.36763	1.42546	1.39654	3.1263	1.39242	3.0000
0.20	1.36782	1.40747	1.38764	3.0148	1.38666	3.0000
0.30	1.36788	1.38205	1.37496	3.0008	1.37488	3.0000
0.3526‡	1.3678964	1.3678860	1.3678912	3.000000	1.3678912‡	3.000000
0.40	1.36791	1.35489	1.36140	3.0004	1.36135	3.0000
0.50	1.36793	1.32707	1.34750	3.0025	1.34708	3.0000
0.60	1.36794	1.29892	1.33343	3.0050	1.33244	3.0000
0.70	1.36795	1.27059	1.31927	3.0073	1.31758	3.0000
0.80	1.36795	1.24215	1.30505	3.0093	1.30258	3.0000
0.90	1.36796	1.21363	1.29079	3.0110	1.28749	3.0000

† The average BVS values calculated for the set of considered coordination shells by using the $^{st}r_0$ and $^{ex}r_0$ values, respectively. ‡ The optimum BV parameters for the set of coordination shells considered.

mathematically correct) solution of the BVS rule for a given set of coordination shells could be useful for *analytically* (Sidey, 2010) determining the high-performance BV parameters from the 'reference structure/shell sets' – to avoid accumulating the systematic errors in the final results. Thus, the main goal of this work is to present the calculation scheme developed by the author and resulting in the *exact* solution $^{ex}r_0$ of the BVS rule for a given set of coordination shells and for a given preset b value.

Equation (3) gives the *exact* solution of (1) and (2) for the *i*th coordination shell $[AX_n]$ and for a given preset b value; this equation can be easily derived by combining (1) and (2). Thus, for the *i*th shell $[AX_n]$, (1) can be rewritten as (4). Then, the required equation (3) can be obtained from the sequence of simple mathematical transformations (4) $\rightarrow$ (5) $\rightarrow$ (6) $\rightarrow$ (3).

$$V_A = \exp\left(r_0^{(i)}/b\right) \times \sum_n \exp\left(-r_{AX}^{(i)}/b\right) \quad (4)$$

$$\exp\left(r_0^{(i)}/b\right) = V_A / \sum_n \exp\left(-r_{AX}^{(i)}/b\right) \quad (5)$$

$$r_0^{(i)}/b = \ln\left[V_A / \sum_n \exp(-r_{AX}^{(i)}/b)\right] \quad (6)$$

To simplify the presentation of the mathematical formulae, hereafter the term '$\sum_n \exp(-r_{AX}^{(i)}/b)$' calculated for the *i*th coordination shell $[AX_n]$ will be denoted as '$\sum^{(i)}$'; so equation (3) for the *i*th shell can be presented as

$$r_0^{(i)} = b \ln\left[V_A / \sum^{(i)}\right]. \quad (7)$$

For a given *set* of N coordination shells $[AX_n]$ and for a given preset b value, the *exact* solution $^{ex}r_0$ of the BVS rule can be obtained by solving equation (8)

$$NV_A = N\langle BVS\rangle = \sum_n s_{AX}^{(1)} + \sum_n s_{AX}^{(2)} + ... + \sum_n s_{AX}^{(N)}. \quad (8)$$

Equation (9) can be directly obtained from (2) and (8).

$$NV_A = \exp(^{ex}r_0/b) \times \left[\sum^{(1)} + \sum^{(2)} + ... + \sum^{(N)}\right] \quad (9)$$

Then, through the sequence of simple transformations analogous to those mentioned above one can easily derive the main working formula to calculate the $^{ex}r_0$ value, equation (10).[1]

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[1] For the first time, this formula has been used by Sidey (2010), but its mathematical essence has never been discussed.

$$^{ex}r_0 = b \ln\{NV_A / [\sum^{(1)} + \sum^{(2)} + ... + \sum^{(N)}]\} \quad (10)$$

Since the term '$[\sum^{(1)} + \sum^{(2)} + ... + \sum^{(N)}]/N$' is the *arithmetic mean* of the $\sum^{(i)}$ values, $^{am}\sum^{(i)}$, equation (10) can be rewritten as

$$^{ex}r_0 = b \ln[V_A/^{am}\sum^{(i)}]. \quad (11)$$

The aforementioned 'standard' value $^{st}r_0$ obtained in the commonly used scheme is actually calculated by

$$^{st}r_0 = \langle r_0^{(i)}\rangle = \langle b \ln(V_A/\sum^{(i)})\rangle. \quad (12)$$

Taking into account the fact that the b and V_A values are constants, and using elementary mathematics, (12) can be easily rewritten as (13), where $^{gm}\sum^{(i)}$ is the *geometric mean* of the $\sum^{(i)}$ values.

$$^{st}r_0 = b \ln[V_A/^{gm}\sum^{(i)}] \quad (13)$$

Comparison of equations (11) and (13) leads to the conclusion that $^{st}r_0 \geq ^{ex}r_0$, since $^{gm}\sum^{(i)} \leq ^{am}\sum^{(i)}$. The $^{st}r_0$ and $^{ex}r_0$ values can be equal only in the exceptional case where the $\sum^{(i)}$ values are all equal and produce the arithmetic and geometric means equal to each other. In all other cases, $^{st}r_0$ is larger than $^{ex}r_0$ and, therefore,[2] gives $\langle BVS\rangle > V_A$. The error $\Delta r_0 = |^{st}r_0 - ^{ex}r_0|$ introduced by the standard scheme can be calculated from (14).

$$\Delta r_0 = b \ln[^{am}\sum^{(i)} / ^{gm}\sum^{(i)}] \quad (14)$$

It must be noted, however, that a significant difference between the $^{st}r_0$ and $^{ex}r_0$ values (*i.e.* Δr_0) is only expected if the $\sum^{(i)}$ values demonstrate rather large spread: in this case, the geometric mean $^{gm}\sum^{(i)}$ is *significantly* smaller than the arithmetic mean $^{am}\sum^{(i)}$.

Serious divergence of the arithmetic and geometric means at large spread of the considered values can be easily concluded, *e.g.* from the Latané approximation of the geometric mean (Latané, 1959; Young & Trent, 1969). According to Latané, the arithmetic mean A, the geometric mean G, and the standard uncertainty σ (the measure of spread) for a given set of values are related as in (15).

$$G^2 \simeq A^2 - \sigma^2 \quad (15)$$

It is clear from (15) that if the spread (σ) of the considered values increases, then the G value becomes smaller; conversely, a small spread of the values results in a small difference between the arithmetic and geometric means (in this case, $G \simeq A$).

On the other hand, a small spread of the $\sum^{(i)}$ [and, therefore, $r_0^{(i)}$] values is possible only if the preset b value is close to the *correct* b value for a given ion pair (Sidey, 2008). Hence, comparison of the $^{st}r_0$ and $^{ex}r_0$ values can be potentially helpful in selecting the optimum b values.

In order to illustrate the difference between the $^{st}r_0$ and $^{ex}r_0$ values, and to outline the possible uses of the calculation scheme presented here, the small set of two coordination shells, [BO_3] of B_2O_3-(I) (Effenberger *et al.*, 2001) and [BO_4] of B_2O_3-(II) (Prewitt & Shannon, 1968), has been considered. For different preset b values (0.1–0.9 Å) the $^{st}r_0$ and $^{ex}r_0$ values have been calculated and then used for calculations of the average $^{st}\langle BVS\rangle$ and $^{ex}\langle BVS\rangle$ values, respectively. The $r_0^{(I)}$ and $r_0^{(II)}$ values used to calculate the $^{st}r_0$ values were respectively obtained from the B_2O_3-(I) and B_2O_3-(II) structures. The results obtained are collected in Table 1. All calculations have been performed by means of a simple *ad hoc* program written in *BASIC*; all the numeric parameters have been taken with double precision. The bond lengths used in the calculations have been taken with the

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[2] For *any* positive b value, an increase in the r_0 parameter in equation (2) results in higher s_{AX} (and BVS) values.

precision of 0.001 Å; the superfluous precision of the values in Table 1 is used exclusively for illustrative purposes.

As seen from Table 1, the calculation scheme presented here steadily results in $^{ex}\langle BVS \rangle = V_A$, whereas the results of the standard scheme clearly demonstrate the dependence of the $^{st}\langle BVS \rangle$ value on the preset b value. However, within the limits of the b value from ~ 0.3 to ~ 0.4 Å, the difference between the $^{st}\langle BVS \rangle$ and $^{ex}\langle BVS \rangle$ values does not exceed 0.001 v.u. and virtually vanishes at the BV parameters[3] $r_0 = 1.3678912$ Å and $b = 0.3526$ Å.

Table 1 clearly suggests *two* obvious uses of the calculation scheme presented here. First, as mentioned above, this scheme could be useful for *analytically* (Sidey, 2010) determining the BV parameters from the 'reference structure/shell sets' for which the BVS rule is expected to be obeyed *exactly* (i.e. $\langle BVS \rangle = V_A$). Thus, exploring the '$r_0$ *versus* b' dependencies accurately calculated for the above sets by using this scheme [every point of such dependencies *exactly* gives $\langle BVS \rangle = V_A$ for the respective set] can help find the common or optimum solution (r_0; b) of the highest possible accuracy.

Additionally, if the correct b value for a given ion pair is hard to detect [*e.g.* if the ion pair demonstrates only *one* coordination number], this parameter might be detected by comparison of the $^{st}r_0$ and $^{ex}r_0$ (or $^{st}\langle BVS \rangle$ and V_A) values calculated for a statistically representative set of coordination shells; the best possible value of the b parameter must give the smallest difference $|^{st}r_0 - {}^{ex}r_0|$ (or $|^{st}\langle BVS \rangle - V_A|$).

However, a researcher should always bear in mind that even in very favourable cases the precision of the BV parameters is not expected to be better than 0.001 Å for b and 0.0001 Å for r_0.

Finally, it must be clearly stated that the calculation scheme presented here is just a *supplemental* tool for determining the high-performance BV parameters; as with any other related scheme, this cannot replace crystal chemical knowledge of a researcher and, therefore, should be used cautiously. Nevertheless, the author believes that the above scheme can be useful for the BVM and should be considered by a researcher if other calculation schemes supposedly fail.

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[3] Being derived from the crystalline B_2O_3 polymorphs, these BV parameters (taken with more realistic precision) can be considered as those corresponding to 'pure' B—O bonds not influenced by the 'third-party' atoms; applicability of these parameters will be discussed elsewhere.