Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

addenda and errata

On the correlations between the polyhedron eccentricity parameters and the bond-valence sums for the cations with one lone electron pair. Addendum

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Systematic variations of the bond-valence sums calculated from the poorly determined bond-valence parameters [Sidey (2008), *Acta Cryst.* B**64**, 515–518] have been illustrated using a simple graphical scheme.

Recent discussion on the reliability of the conventional bond-valence (BV) parameters, r_0 and b, determined using the 'universal constant' $b = 0.37$ Å (Krivovichev & Brown, 2001; Locock & Burns, 2004; Sidey, 2008; Wang & Liebau, 2009) has stimulated writing of this addendum to the earlier communication of the author (Sidey, 2008). The main goal of this addendum is to explain, as simply as possible, the reason for the systematic variations of the bond-valence sums (BVSs) calculated from the poorly determined BV parameters (Sidey, 2008). All the terms, symbols and abbreviations used here correspond to those used in the aforementioned original communication of the author (Sidey, 2008).

The most commonly adopted empirical expression for the relationship between the bond valences s_{ij} and the bond lengths r_{ij} (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) can be rewritten as $r_{ij} = r_0 - b \times \ln(s_{ij})$. Hence, every '$s_{ij} - r_{ij}$' curve can be uniquely represented as a straight line $y = A + Bx$ by using the '$\ln(s_{ij}) - r_{ij}$' coordinate system (Fig. 1). The mathematical slope and the y intercept of the above straight lines are equal to $-b$ and r_0, respectively. The traditional calculation scheme for determining the conventional BV parameters (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) is based on the rather rough assumption that the mathematical slopes of *all* '$\ln(s_{ij}) - r_{ij}$' straight lines are equal to -0.37 Å; so that all observed '$\ln(s_{ij}) - r_{ij}$' correlations are approximated with the *constant-slope* (conventional) straight lines $r_{ij} = r_0 - 0.37\ln(s_{ij})$. If the real value of the b constant is not 0.37 Å, then the 'optimized' conventional straight line obtained for a given ion pair merely goes through the 'gravity centre' datapoint '$\langle\ln(s_{ij})\rangle - \langle r_{ij}\rangle$'[1] of the whole observed '$\ln(s_{ij}) - r_{ij}$' dataset. As *every* well-determined coordination shell in the traditional calculation scheme is considered to be an independent 'observation' (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991), the coordinates of the above 'gravity centre' datapoint observed for a given ion pair are usually close to the '$\ln(s_{ij}) - r_{ij}$' data corresponding to the coordination shells with the most frequently occurring ('typical') coordination number(s).

Fig. 1 shows the relations between the straight lines $r_{ij} = r_0 - b \times \ln(s_{ij})$ of different slopes. The α and β straight lines represent the idealized hypothetical '$\ln(s_{ij}) - r_{ij}$' correlations with the same 'gravity centre' datapoint; the α line has $b > b$(conventional) and the β line has $b < b$(conventional). If the real '$\ln(s_{ij}) - r_{ij}$' correlation is represented by the α straight line, then the conventional straight line gives overestimated and underestimated $\ln(s_{ij})$ (and s_{ij})[2] values for the shorter (r'_{ij}) and longer (r''_{ij}) bond lengths, respectively. If the real '$\ln(s_{ij}) - r_{ij}$' correlation is represented by the β straight line, then the conventional straight line gives, in contrast, underestimated and overestimated $\ln(s_{ij})$ (and s_{ij}) values for the shorter (r'_{ij}) and longer (r''_{ij}) bond lengths, respectively. The two different types of the systematic variations of the s_{ij} values observed for the α and β straight lines can be respectively denoted as the α and β variations.

Using the scheme presented here (Fig. 1), one can easily check the quality of the BV parameters reported for a given ion pair: if these BV parameters show systematic variations of the s_{ij} (and BVS) values within the short-bond and/or long-bond range(s), then the real '$s_{ij} - r_{ij}$' correlation is approximated poorly. Detecting the type of systematic variations observed for a given ion pair (α, β) can help find the actual value of the b parameter. It is important to note that overestimating and underestimating the s_{ij} values calculated for short and long (or *vice versa*) bonds belonging to the same irregular coordination shells can compensate for each other, so that the BVS values obtained for these shells can be quite 'plausible'; therefore, only *regular* (or nearly regular) shells should be used for checking the quality of the BV parameters.

The performance of the conventional BV parameters reported for a given ion pair is critically dependent: (*a*) on the real slope of the '$\ln(s_{ij}) - r_{ij}$' correlation and (*b*) on the range of the observed bond

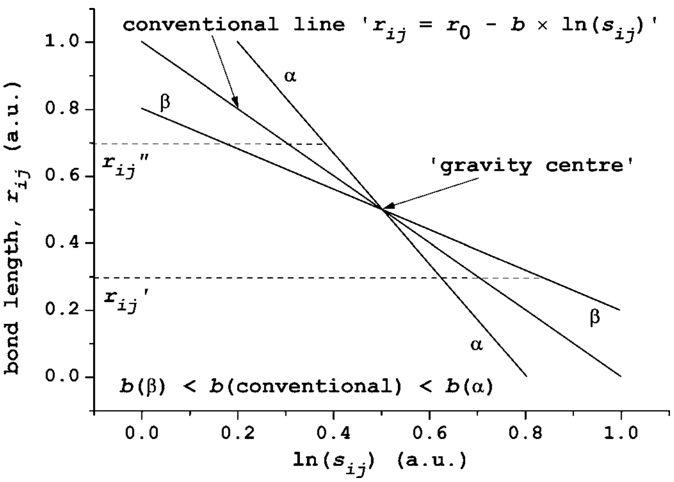

Figure 1
Typical relations between the straight lines $r_{ij} = r_0 - b \times \ln(s_{ij})$ of different slopes (for simplicity, all the values are given in arbitrary units, a.u.).

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[1] $\langle\ln(s_{ij})\rangle$ and $\langle r_{ij}\rangle$ denote the mean values for $\ln(s_{ij})$ and r_{ij}.
[2] If $\ln(a) < \ln(b)$, then $a < b$.

doi:10.1107/S0108768109008581

lengths r_{ij}. If the real mathematical slope is close to -0.37 Å and if the range of observed bond lengths is narrow, then the divergence between the real and conventional straight lines $r_{ij} = r_0 - b \times \ln(s_{ij})$ is insignificant and, therefore, the conventional BV parameters reported for a given ion pair can be used with reasonable success. Otherwise, these BV parameters can be used successfully only within the r_{ij} range near to the above 'gravity centre' datapoint (Fig. 1),[3] and must be revised. Since the coordinates of the 'gravity centre' datapoint observed for a given ion pair, $\langle \ln(s_{ij}) \rangle$ and $\langle r_{ij} \rangle$, are usually close to the '$\ln(s_{ij}) - r_{ij}$' data corresponding to the 'typical' coordination shells (see above), even poorly determined conventional BV parameters can give reasonable BVS values in most cases! However, high-quality BV parameters should give reasonable BVS values not only for 'typical' coordination shells, but also for less-common shells formed by a given ion pair in ordered, stoichiometric and stable structures determined accurately and investigated under ambient conditions. Unfortunately, this requirement was ignored for a long time and a few theories were developed based on the axiomatic use of the 'universal constant' $b = 0.37$ Å (*e.g.* O'Keeffe & Brese, 1991; Wang & Liebau, 2007). In order to be properly validated, *any* BVM related theory (including that of Wang & Liebau, 2007) ought to operate with the BV parameters of the highest possible quality. Most of the conventional BV parameters used by Wang & Liebau (2007) in their theory show the aforementioned systematic α variations of the BVS values (Sidey, 2008) and, therefore, clearly must be revised.

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[3] Within a small section near to the aforementioned 'gravity centre' datapoint, every observed '$\ln(s_{ij}) - r_{ij}$' correlation can be considered as 'well approximated'.

Acta Crystallographica Section B
Structural Science
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On the correlations between the polyhedron eccentricity parameters and the bond-valence sums for the cations with one lone electron pair

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Received 4 March 2008
Accepted 21 May 2008

Applicability of the Wang–Liebau polyhedron eccentricity parameter in the bond-valence model [Wang & Liebau (2007). *Acta Cryst.* B**63**, 216–228] has been found to be doubtful: the correlations between the values of the polyhedron eccentricity parameters and the bond-valence sums calculated for the cations with one lone electron pair are probably an artifact of the poorly determined bond-valence parameters.

In the literature on crystal chemistry, several parameters have been proposed to describe the distortion of the coordination polyhedra (Robinson *et al.*, 1971; Dollase, 1974; Lueken *et al.*, 1987; Makovicky & Balić-Žunić, 1998; Lalik, 2005; Brown, 2006), but only the eccentricity parameter $\mathbf{\Phi}_i$ proposed by Wang & Liebau (2007) explicitly indicates the degree of stereoactivity of the lone electron pair ns^2 (LEP). In this respect, the Wang–Liebau eccentricity parameter appears to be very useful for crystal chemical analysis. However, applicability of the $\mathbf{\Phi}_i$ parameter in bond-valence analysis (Brown, 2002) is currently quite doubtful, and the main goal of this communication is to avoid possible misinterpretation of the results of the statistical analyses made by Wang & Liebau (2007).

Nowadays the bond-valence model (BVM) is widely used in mineralogy and structural inorganic chemistry as a valuable tool for detecting errors in crystal structure determination and for predicting interatomic distances in the crystal structures of known chemical composition and presupposed topology (Brown, 2002). Bond valence (BV) s is defined as the classical atomic valence shared with each bond. According to the bond-valence sum rule, the oxidation state (atomic valence) V_i can be calculated from the sum of the individual bond valences s_{ij} (where i denotes an atom bonded to j), as given by

$$V_i = \sum_j s_{ij}. \tag{1}$$

Individual bond valences s_{ij} (in valence units, v.u.) can be calculated from the observed bond lengths r_{ij} using the Brown–Altermatt formula (2) or the Brown–Shannon formula (3), where r_0, b and n are the empirically determined parameters for a given ion pair (Brown & Shannon, 1973; Brown & Altermatt, 1985).

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

$$s_{ij} = (r_0/r_{ij})^n. \tag{3}$$

It should be noted, however, that the Brown–Altermatt formula (2) is used in almost all recent works describing applications of the BVM.

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 for a large number of ion pairs, assuming b = 0.37 Å (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991). Hereafter, the BV parameters determined using the 'universal constant' will be referred to as the conventional BV parameters.

In order to describe the LEP stereoactivity, Wang & Liebau (2007) introduced the so-called eccentricity parameter, $\mathbf{\Phi}_i$, which is a vector defined as

$$\mathbf{\Phi}_i = -\sum_j \boldsymbol{\varphi}_{ij}. \tag{4}$$

doi:10.1107/S0108768108015309

Table 1
Bond-valence parameters reported by Brese & O'Keeffe (1991) and by Brown & Wu (1976) for the considered ion pairs.

	Bond-valence parameters			
	Brese & O'Keeffe (1991)		Brown & Wu (1976)	
Ion pair	r_0 (Å)	b (Å)	r_0 (Å)	n
Sn^{2+}/O^{2-}	1.984	0.37	1.860	4.5
Pb^{2+}/O^{2-}	2.112	0.37	2.044	5.5
Sb^{3+}/O^{2-}	1.973	0.37	1.910	4.5
Bi^{3+}/O^{2-}	2.09	0.37	2.010	5.0
S^{4+}/O^{2-}	1.644	0.37	1.629	4.6
Se^{4+}/O^{2-}	1.811	0.37	1.796	4.0
Te^{4+}/O^{2-}	1.977	0.37	1.933	4.5
I^{5+}/O^{2-}	2.00	0.37	1.967	4.5

Table 2
Typical relations between the BVS values calculated from the Brese–O'Keeffe and Brown–Wu parameters for the coordination shells with small CNs of the considered ion pairs.

			BVS (v.u.)†	
Compound	ICSD code‡	Coordination shell§	Brese & O'Keeffe (1991)	Brown & Wu (1976)
Na_4SnO_3	49624	SnO_3	2.733 (+37%)	2.077 (+4%)
Rb_2SnO_2	24805	SnO_3	2.478 (+24%)	1.917 (−4%)
K_4PbO_3	74874	PbO_3	2.587 (+29%)	2.177 (+9%)
$K_2Pb_2O_3$	1412	PbO_3	2.530 (+27%)	2.132 (+7%)
Na_3SbO_3	23346	SbO_3	3.724 (+24%)	3.123 (+4%)
$CsSbO_2$	59329	SbO_4	3.286 (+10%)	2.936 (−2%)
Na_3BiO_3	23347	BiO_3	3.34 (+11%)	2.692 (−10%)
Rb_3BiO_3	407294	BiO_3	3.34 (+11%)	2.705 (−10%)
Na_2SO_3	4432	SO_3	4.380 (+10%)	4.318 (+8%)
K_2SO_3	60762	SO_3	4.263 (+7%)	4.189 (+5%)
H_2SeO_3	31929	SeO_4	4.046 (+1%)	3.837 (−4%)
$K_2Se_2O_5$	63508	SeO_{3-4}	4.073 (+2%)¶	3.833 (−4%)¶
K_2TeO_3	65640	TeO_3	4.598 (+15%)	3.944 (−1%)
Cs_2TeO_3	59164	TeO_3	4.274 (+7%)	3.691 (−8%)
β-$LiIO_3$	2642	IO_5	5.47 (+9%)	4.940 (−1%)
α-$RbIO_3$	2825	IO_6	5.40 (+8%)	5.042 (+1%)

† The relative BVS errors calculated as $[(BVS - V_i)/V_i] \times 100\%$ are given in parentheses. ‡ See Belsky *et al.* (2002). § The shortest distance from the central cation to another cation in a given crystal structure was assumed to be the physical limit of the coordination sphere under consideration. ¶ The mean BVS value for the Se^{4+} ions in the structure.

The $\boldsymbol{\varphi}_{ij}$ terms are the vectors pointing from the nucleus of an atom *i* to its ligands *j*. The lengths of the $\boldsymbol{\varphi}_{ij}$ vectors are scaled using

$$|\boldsymbol{\varphi}_{ij}| = \exp(-r_{ij}/0.2). \qquad (5)$$

Based on the statistical analyses, Wang & Liebau (2007) have reported the linear correlations between the $|\boldsymbol{\Phi}_i|$ values calculated for individual coordination shells of a given ion pair and the values of the conventional BV parameters r_0 and bond-valence sums (BVSs) determined for the same coordination environments.

Using elementary mathematics, one can easily conclude that the highest $|\boldsymbol{\Phi}_i|$ values are expected for coordination shells with small numbers of strong (short) bonds having approximately the same direction. Thus, the V-shaped AX_2 atomic groups and the pyramids AX_3, AX_4 and AX_5 having all the $A-X$ bonds located in one hemisphere of the coordination shell must have the highest $|\boldsymbol{\Phi}_i|$ values. However, in accordance with the Gillespie–Nyholm theory, the same coordination environments are expected for the *A* cations with one highly stereoactive LEP (Gillespie & Nyholm, 1957). Hence, the $|\boldsymbol{\Phi}_i|$ values can really be used as a measure of the LEP stereoactivity, and the highest $|\boldsymbol{\Phi}_i|$ values are expected for the coordination shells with small coordination numbers (CNs). In the coordination shells with higher CNs (if CN >> V_i), chemical bonds are much weaker (and longer, as expected from the BVM) and distributed in space more regularly; so that the $\boldsymbol{\varphi}_{ij}$ vectors are shorter and partially compensate for each other, resulting in much smaller $|\boldsymbol{\Phi}_i|$ values. In other words, there must be simple and reasonably strong correlations between the $|\boldsymbol{\Phi}_i|$ values and CNs observed for distorted coordination environments of the cations with one stereoactive LEP: the smaller the CNs the higher the $|\boldsymbol{\Phi}_i|$ values. It must be noted that all centrosymmetric and certain regular non-centrosymmetric coordination shells (triangles AX_3, tetrahedra AX_4, trigonal bipyramids AX_5, *etc.*) of the cations with one LEP are possible only if the LEP stereoactivity is fully constrained; the $\boldsymbol{\varphi}_{ij}$ vectors in these shells cancel each other, and the $|\boldsymbol{\Phi}_i|$ values of these shells are properly equal to zero, in spite of different CNs.

However, the conclusion of Wang & Liebau (2007) that the LEP stereoactivity leads to significant deviations between the V_i and BVS values is extremely important for the BVM and cannot be accepted without careful examination. Analysis of the paper of Wang & Liebau (2007) has revealed some methodological shortcomings (considering only the conventional BV parameters; ignoring the physical meaning of the r_0 values) making the aforementioned conclusion questionable (see below).

The above conclusion of Wang & Liebau (2007) was based solely on the BVS values calculated using the Brese–O'Keeffe conventional BV parameters (Brese & O'Keeffe, 1991); moreover, the attempts of other authors to refine both r_0 and b (Burns *et al.*, 1997; Krivovichev & Brown, 2001; Locock & Burns, 2004; Sidey, 2006) were discouraged by Wang & Liebau (2007). However, for some ion pairs considered by Wang & Liebau (2007) and having the highest LEP stereoactivity (Sn^{2+}/O^{2-}, Pb^{2+}/O^{2-}, Sb^{3+}/O^{2-}, Bi^{3+}/O^{2-}, S^{4+}/O^{2-}, Se^{4+}/O^{2-}, Te^{4+}/O^{2-} and I^{5+}/O^{2-}), there is an alternative set of high-quality BV parameters, r_0 and n, reported by Brown & Wu (1976) for use in the Brown–Shannon formula (3) (see Table 1).

The BVS values calculated for some coordination environments with CN $\simeq V_i$ by using the conventional and Brown–Wu parameters are given in Table 2. One can see that, in general, the BVS values calculated from the Brown–Wu parameters are much closer to the V_i values and much smaller than the BVS values calculated from the conventional parameters. Hence, strong 'overbonding' reported by Wang & Liebau (2007) for the coordination shells with small CNs (and with the high $|\boldsymbol{\Phi}_i|$ values) is not found when the Brown–Wu parameters are used.

By definition, the r_0 parameter in (2) and (3) is equal to the length of the bond of unit valence. The exact (actually, close to exact) r_0 values can be directly observed in the regular coordination shells with CN = V_i. Ideally, the r_0 parameters reported by Brown & Wu (1976) and by Brese & O'Keeffe (1991) for the same ion pairs should be equal to each other. However, analysis of the typical r_{ij} distances observed for the SbO_3 and BiO_3 pyramids (Table 3) indicates that the Brown–Wu r_0 parameters reported for the Sb^{3+}/O^{2-} and Bi^{3+}/O^{2-} ion pairs are smaller and (especially for the Sb^{3+}/O^{2-} pair) much more physically meaningful than the conventional r_0 parameters. The values of the conventional r_0 parameters reported for the Sb^{3+}/O^{2-} and Bi^{3+}/O^{2-} ion pairs are clearly overestimated and result in conventional BVSs calculated for the SbO_3 and BiO_3 pyramids which are too high. Hence, strong 'overbonding' observed for the above ion pairs is an artifact of the poorly determined conventional BV parameters.

Unfortunately, the r_0 parameters for other ion pairs considered in this paper cannot be easily observed; but the enormous 'overbonding' indicated for the stoichiometric and stable structures by using the conventional BV parameters (see Table 2) could suggest that some other conventional r_0 values collected in Table 1 (at least, the r_0

Table 3
Interatomic distances (Å) in the regular SbO_3 and BiO_3 coordination shells.

Compound	ICSD code†	Coordination shell†	$A-X$ distance
Na_3SbO_3	23346	SbO_3	1.893
K_3SbO_3	279579	SbO_3	1.923
Cs_3SbO_3	279580	SbO_3	1.928
$K_2Al_2Sb_2O_7$	280310	SbO_3	1.936
Na_3BiO_3	23347	BiO_3	2.054
K_3BiO_3	407293	BiO_3	2.063
Rb_3BiO_3	407294	BiO_3	2.052
Cs_3BiO_3	406563	BiO_3	2.036

† Footnotes as for Table 2.

values reported for the Sn^{2+}/O^{2-} and Pb^{2+}/O^{2-} ion pairs) are also strongly overestimated.

The above differences between the values of the conventional r_0 parameters and single bond lengths (as clearly observed for the Sb^{3+}/O^{2-} and Bi^{3+}/O^{2-} ion pairs and supposed for some other ion pairs considered in this work) are probably caused by simplification of the procedure for determining the BV parameters, as proposed by Brown & Altermatt (1985). Since the performances of the Brown–Shannon and Brown–Altermatt formulae in approximating the real (observed) '$s_{ij} - r_{ij}$' curves are virtually the same (Brown, 2002), the reason for the above disagreement should be sought in the procedures used for determining the Brown–Wu and conventional BV parameters.

The procedure for determining the conventional BV parameters from the structural data (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991; Brown, 2002) includes the following steps:

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

(ii) solving (1) by using (6) (where b = 0.37 Å) for every selected coordination sphere of a given ion pair

$$r_0 = b \ln\left[V_i / \sum_j \exp(-r_{ij}/b)\right]; \qquad (6)$$

(iii) averaging the r_0 values calculated for a given ion pair.

Varying the b constant to minimize the standard errors of the r_0 values, Brown & Altermatt (1985) established that the b parameter could rarely be determined to better than 0.05 Å and that a value of 0.37 Å was consistent with most of the fitted values. Since that time, the b parameter is usually considered as the 'universal constant' having a value of 0.37 Å. In other words, in approximating the real '$s_{ij} - r_{ij}$' correlations, the 'canonical' two-parameter Brown–Altermatt formula (2) was replaced by the much less-flexible monoparametric Brown–Altermatt formula

$$s_{ij} = \exp[(r_0 - r_{ij})/0.37]. \qquad (7)$$

In most cases, the use of (7) is justified; but for certain ion pairs (especially for those having a wide range of CNs) close approximations of the real '$s_{ij} - r_{ij}$' correlations are possible only by fitting of both r_0 and b. If the r_0 values calculated from (6) for different CNs of a given ion pair differ significantly [as actually observed by Wang & Liebau (2007) for the considered ion pairs], this can be a symptom of a poor description of the real '$s_{ij} - r_{ij}$' correlation with the conventional BV parameters.

In the general case, (2) and (6) include two actual variables, r_0 and b, and cannot be solved separately for one bond or one coordination sphere. Mathematically, two independent variables could be deduced only from, at least, two independent equations.

For any separately considered coordination shell formed by a given ion pair and for any fixed non-zero b value, (6) can easily be solved to give BVS = V_i. As with any other separately considered two-variable equation, this has an infinite number of solutions (r_0; b), including the solution for b = 0.37 Å. If all coordination spheres observed for a given ion pair have the same CN, then the differences between the r_0 values calculated from (6) for every separately considered coordination sphere (at the plausible b constant) are usually insignificant because of the relatively small variability of the average bond lengths r_{ij} in the chemically equivalent coordination environments AX_n. If, however, coordination shells observed for a given ion pair have different CNs, the r_0 values calculated for all the possible CNs of a given ion pair can be nearly constant only in the case of the correctly preset value of the b parameter. In this particular case only, one can state that the unique correct solution (r_0; b) showing the best agreement between the BVS and V_i values for all coordination spheres and for all CNs of a given ion pair is found. It must be noted that some variations of the r_0 values are unavoidable owing to steric and electronic constraints and/or due to experimental errors; but if the correct b value for a given ion pair is far from the preset b value, then the differences between the r_0 values calculated for different CNs of a given ion pair can be very significant (*i.e.* far beyond the variation range expected from the above constraints and experimental errors).

Since every well determined coordination sphere in the above calculation scheme is regarded as an independent 'observation', the average r_0 value determined for a given ion pair from the different interim r_0 values is closer to the r_0 values calculated for the typical coordination spheres with the most frequently occurring ('usual') CNs. Thus, the BV parameters obtained in this way can give a reasonable approximation of the real '$s_{ij} - r_{ij}$' curve within the limits corresponding to the 'usual' CNs of a given ion pair, but can fail for the less-common CNs if the correct approximation of the whole '$s_{ij} - r_{ij}$' curve is possible only by using the 'canonical' Brown–Altermatt formula (2).

The aforementioned systematic variations of the r_0 values calculated for different CNs at the wrong b constant can be illustrated using the following idealized example concerning the highly important ion pair Al^{3+}/O^{2-}. This ion pair forms the coordination polyhedra AlO_4 and AlO_6 with the typical Al—O interatomic distances of $\sim$ 1.74 and $\sim$ 1.91 Å, respectively (see, for example, Mohri, 2000). Solving (6) separately for each typical coordination polyhedron at b = 0.37 Å, one can obtain r_0 = 1.634 Å from AlO_4 and r_0 = 1.654 Å from AlO_6. The r_0 value obtained from the typical AlO_4 tetrahedron indicates significant 'underbonding' for the typical AlO_6 octahedron (BVS = 2.85 v.u.); the r_0 value obtained from the typical AlO_6 octahedron shows, in turn, significant 'overbonding' for the typical AlO_4 tetrahedron (BVS = 3.17 v.u.). If the quantities of the considered coordination polyhedra AlO_4 and AlO_6 are equal, the expected average conventional r_0 value is $\sim$1.644 Å. This value gives a better approximation of the real '$s_{ij} - r_{ij}$' curve for the Al^{3+}/O^{2-} ion pair, but still indicates some 'overbonding' (BVS = 3.09 v.u.) and 'underbonding' (BVS = 2.92 v.u.) for the typical polyhedra AlO_4 and AlO_6, respectively. The 'classical' value of the conventional BV parameter reported for the Al^{3+}/O^{2-} ion pair, r_0 = 1.651 Å (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991), is definitely optimized only for CN = 6 and cannot be successfully used for CN = 4 because it erroneously indicates BVS = 3.15 v.u. for the typical AlO_4 tetrahedron.

Solving the system of the two independent equations (2) or (6) concerning the typical polyhedra AlO_4 and AlO_6, one can easily deduce the 'correct' r_0 and b values ($\sim$ 1.62 and $\sim$ 0.42 Å, respectively) indicating the adequate BVS values for these polyhedra

(3.01 v.u. in both cases). Setting $b = 0.42$ Å in (6), one can obtain the virtually constant r_0 values for both typical polyhedra of the Al^{3+}/O^{2-} ion pair; in all other cases, the systematic variations of the r_0 values calculated for different CNs will be observed.

The above calculation of the 'correct' BV parameters for the Al^{3+}/O^{2-} ion pair should be regarded as only a rough estimation made for illustrative purposes; but the performance of the BV parameters $r_0 = 1.62$ Å and $b = 0.42$ Å can compete with the performance of the Brown–Wu parameters ($r_0 = 1.622$ Å and $n = 4.29$) that indicate BVS = 2.96 v.u. for the typical AlO_4 tetrahedron and BVS = 2.98 v.u. for the typical AlO_6 octahedron.

Methodologically, the statistical procedure developed by Brown & Shannon (1973) and then used by Brown & Wu (1976) is much more appropriate for determining the reliable BV parameters than the simplified procedure of Brown & Altermatt (1985). Brown & Shannon (1973) and Brown & Wu (1976) clearly tried to achieve the best possible approximation of the real '$s_{ij} - r_{ij}$' correlation for a given ion pair. The closest possible approximations were achieved by the weighted non-linear least-squares fitting of the r_0 and n parameters against the expected BVS values. In the above least-squares fitting, the BVS differences calculated for the less-common CNs of a given ion pair were much higher in weight; as a result, the BV parameters reported by Brown & Wu (1976) gave, in general, close approximations of the whole '$s_{ij} - r_{ij}$' curves, including the ranges corresponding to the less-common CNs. It must be noted, however, that the paucity of the structural data available for certain ion pairs in 1976 did not allow all the BV parameters reported by Brown & Wu (1976) to be determined with the same high quality.

Taking all the aforementioned facts into account, two conclusions can be made:

(i) The correlations found by Wang & Liebau (2007) for the $|\boldsymbol{\Phi}_i|$ and r_0 values can indicate systematic variations of the r_0 values calculated for different CNs using an unoptimized b constant.

(ii) Since the 'universal constant' $b = 0.37$ Å is probably not the best choice for the considered ion pairs (see above), the values of the conventional BV parameters reported for these ion pairs can give poor approximations of the real '$s_{ij} - r_{ij}$' curves, and strong 'overbonding' reported for the coordination shells with the high $|\boldsymbol{\Phi}_i|$ values and small CNs can really be an artifact of the poorly determined conventional BV parameters.

Using different calculation schemes, a few authors (Burns *et al.*, 1997; Krivovichev & Brown, 2001; Locock & Burns, 2004; Sidey, 2006; Malcherek & Schlüter, 2007; Sidey *et al.*, 2008) have simultaneously refined the r_0 and b values for use in the 'canonical' Brown–Altermatt formula (2), and have greatly improved approximations of the real '$s_{ij} - r_{ij}$' correlations for certain ion pairs. If a researcher fails to obtain good agreement using the conventional BV parameters reported for a given ion pair, the use of the alternate calculation schemes developed by the above authors for determining reliable BV parameters should always be attempted.

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