From bond strength to charge distribution: modern developments of the empirical analysis of crystal structures
Massimo Nespolo

To cite this version:
Massimo Nespolo. From bond strength to charge distribution: modern developments of the empirical analysis of crystal structures. Physical Sciences Reviews, 2022, 10.1515/psr-2019-0074. hal-03938666

HAL Id: hal-03938666
https://hal.univ-lorraine.fr/hal-03938666
Submitted on 13 Jan 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
From Bond Strength to Charge Distribution: modern developments of the empirical analysis of crystal structures

Massimo Nespolo¹

¹Université de Lorraine, CNRS, CRM2, Nancy, France. massimo.nespolo@univ-lorraine.fr

Abstract

A brief review of the empirical analysis of chemical-bond topology in crystal structures is presented, from the pioneering work of Pauling to the most recent development represented by the Charge Distribution analysis. The strengths and limitations of the various methods are briefly discussed.

1. Introduction

A real crystal differs from its idealized model for the presence of static and dynamic defects. Among the formers, we can cite vacancies, interstitials, impurities, precipitates, dislocations and the surface itself. Among the dynamic defects we have individual and collective atomic vibrations. A classical X-ray diffraction experiment gives a space- and time-average structure which justifies adopting an essentially idealized model of the crystal structure, where the deviations from the ideal model are accounted for in terms of disordered occupation of atomic sites and a finite volume assigned to each atomic position, most often in the shape of an ellipsoid that represents the atomic displacement during the diffraction experiment.

The stability of a crystalline edifice is governed by its thermodynamics. The calculation of the free energy of a crystal is a complex task (Jacucci and Quirke, 1984; Vasileiadis, 2013), not suitable for a routine screening of large samples. A rougher, empirical estimation is in most cases sufficient to rationalize known crystal structures and to predict what type of environment an atom may have in a crystal. This type of considerations constitutes the rationale behind approaches like the crystal field theory (Burns, 1993) or the Madelung Part of the Lattice Energy (Hoppe, 1970a; 1995). The former is well-known among the readers, whereas the latter has found more limited applications, possibly because of the problems related to the convergence of lattice sums in Madelung’s constants (Borwein et al., 1985).

Pauling (1929) introduced the well-known empirical rules that today bring his name to estimate the stability of ionic crystals. These rules are based on the description of crystal structures as compact packing of hard spheres bringing a charge that corresponds to the valence of the atoms they represent. The interatomic distance corresponding to a chemical bond is interpreted as the sum of the ionic radii, and the type of coordination, including the coordination number, is governed by the ratio of these radii. The strength of the bond is therefore estimated as the ratio between the charge of the cation centring the coordination polyhedron and its coordination number, i.e. the number of anions occupying the corners of that polyhedron. Under the very drastic assumption of a uniform coordination polyhedron (i.e. a polyhedron in which all the
cation-anion bond distances have the same length), Pauling’s bond strength possesses a significant prediction power, expressed by the second rule, which states that the sum of the bond strengths about a given anion is equal to the formal charge of that anion:

\[ q(A_j) = \sum s_i, \quad s_i = q(C_i)/N_i \]  

(1)

where \( q \) is the charge, \( A_j \) and \( C_i \) are the \( j \)-th anion and \( i \)-th cation respectively, \( N_i \) is the coordination number of \( C_i \), \( s_i \) is the bond strength and the summation is performed over the \( A_j-C_i \) bonds. Within the conditions used to define Pauling’s bond strength, Eq. (1) can be used to predict the number of cations bonded to a given anion but also as a very simple rationale behind empirical observations like Loewenstein’s rule (Loewenstein, 1954), for which today we dispose of more sophisticated interpretations (Larin, 2013).

Whereas the sphere packing model still plays an important role in the description and interpretation of non-molecular structures, at least as the aristotype from which a large number of real structures can be obtained as substitution-distortion hettotypes (Umayahara and Nespolo, 2018), the assumption of ionic bonding is quite restrictive on the type of structures that can be studied. For example, simple structures corresponding to important aristotypes, like cuprite, \( \text{Cu}_2\text{O} \), do not fit Pauling’s scheme, because the sum of the ionic radii of \( \text{Cu}^+ \) and \( \text{O}^{2-} \) (0.96 and 1.40 Å respectively: Pauling radii) is much larger than the actual bond distance (about 1.85 Å), and the ratio, 0.69, suggests a tetragonal antiprism coordination for copper, which instead occurs as linear \( \text{O-Cu-O} \) coordination. When non-ionic bonds are involved, availability of orbitals, rather than the ratio of cation and anion radii, governs the coordination (Brown, 1988; Chiari, 1988).

In this context, the terms “cation” and “anion” have to be interpreted as a handy term for “electropositive atom” and “electronegative atoms” respectively.

Even more severe is the assumption of uniform coordination polyhedra. Pauling’s bond strength does not include any dependence on the bond length but assigns a unique bond strength to a cation bonded to a given number of anions of the same chemical species (“homoligand polyhedra”: Mohri, 2000). This assumption becomes less and less realistic the more a coordination polyhedron undergoes deformation. Small polyhedra centred on hard ions\(^1\) like Si-centred tetrahedra in aluminosilicates present a small range of scattering of bond lengths which justifies a description in terms of Pauling’s bond strength as a first approximation. In contrast, soft cations like the larger alkali metals usually occur in the cavities of a structure and their interaction with the surrounding anions is spread over a large interval of bond lengths; no net separation appears between a first and a second coordination sphere, so that the coordination number is hardly identified (Chiari, 1990; Balić Žunić & Makovicky, 1996; Makovicky & Balić Žunić, 1998). In this type of coordination environment, the bond strength decreases almost asymptotically: not only assigning a unique bond strength gives a completely unrealistic picture; one also needs some criterion to assign the coordination number.

Finally, the possibility of heteroligand polyhedra (Mohri, 2000), i.e. coordination polyhedra in which the atoms at the centre of the polyhedra are bonded to chemically different atoms at the corners, is not even

\(^1\) By the terms “hard” and “soft” ions we make reference to the well-known HSAB theory (Pearson, 1968).
considered in Pauling’s approach, which explains the lack of duality in his definition of bond strength. In
fact, whereas in ionic solids a cation is often, although not always, bonded to a single chemical species of
anion, that anion is usually bonded to different types of cations. Now, heteroligand polyhedra around cations
do also occur: a cation can for example be bonded at the same time to oxygen, halogens, sulphur etc. This
type of polyhedra, non-uniform by definition, cannot be analysed in terms of Pauling’s bond strength.

Different generalisations of Pauling’s approach have been introduced, which all have in common the
consideration of the dependence of the bond strength from the bond distance. After a very brief critical
account of some of them, we concentrate on the Charge Distribution approach, which is the most recent
development of Pauling’s original ideas.

2. Bond strength as a function of bond lengths

The dependence of the bond strength from the bond length can be modelled by a function relating the
former to the latter and a series of empirical parameters:

\[ s_i = f(d_i, p) \]  

where \( s_i \) and \( d_i \) are the bond strength and the bond length of the \( i \)-th interatomic distance between two given
chemical elements, and \( p \) is a vector containing a certain number (usually up to three) of empirical
parameters. Baur (1970, 1971) showed a linear dependence of the bond length from the bond strength
received by each anion (cf. also Ferraris and Catti, 1973). Several functions \( f \) have been proposed by various
authors, where the bond strength decreases in a more or less exponential way with the increase of the bond
length. These functions are often called “R-s curves” (Donnay and Allman, 1970; Pyatenko, 1973; Brown
1985; Urusov, 1995), where \( R \) is the bond length (we use \( d \) instead of \( R \) for consistency of notation with
other approaches). The bond strength computed from Eq. (2) is called bond valence, shortened to BV
hereafter (Donnay and Allman, 1970); the coordination number is obtained as the number of anions after
which \( s_i \) is close to zero (Brown, 1978) but it has been set \( a \text{ priori} \) in the group of structures used for
determining the empirical parameter. By replacing Pauling’s definition of bond strength with a curve of type
(2), Eq. (1) becomes much more general and the restrictions to uniform or homoligand coordination
polyhedra are removed. Furthermore, bonds between the same type of atom become in principle treatable,
provided that a suitable and reliable set of parameters \( p \) is available for the pairs of atoms involved in the
chemical bond, under the experimental conditions in which the structure was solved and refined. These
parameters are obtained by a fit on a large set of reliably refined structures and are frequently redefined and
re-refined (Bosi, 2014a,b; Gagné & Hawthorne, 2015) so that the same crystal structure gives different
results when analysed with the same type of curve but with a different set of empirical parameters.

Brown (1977, 1978) developed the theory of bond valence as a method of predicting bond lengths in
inorganic crystals. In case of very distorted distributions, however, the results are poor; for the case of \( V^{5+} \)
Gopal (1972) reported that “V-O bond lengths can be predicted with some accuracy for systems where the
range of bond lengths are not too great (~ 10%). Several extensions have been proposed with different
goals, such as: 1) to treat bonds which occur with a wide range of lengths (Brown, 1987); 2) to introduce the
effect of the lone-pairs on the geometry of the coordination polyhedra (Wang & Liebau, 1996a,b); 3) to take
into account zero and negative oxidation states (Naskar et al., 1997); 4) to correlate bond strength and
electron density distribution (Gibbs et al., 1998); 5) to treat compounds with heteroligand polyhedra (Mohri,
2000). All these extensions are based on a more or less complex power-law relationship between the bond
length and the bond valence and do not have any internal criterion to evaluate whether the method itself is
applicable or not to a given structure. Therefore, when a significant deviation from the expected bond
valences occurs, the investigator should evaluate independently, and before drawing any conclusion from the
bond valence analysis, whether the quality of the refinement of the structure model is reliable, and whether
the type of structure (type and pattern of bonding) is suitable for such analysis. A ‘blind’ application without
critical inspection may otherwise result into a discussion in terms of bond valences without solid ground.

Extensions in a different direction were proposed in terms of graph-theoretical approaches. Boisen et al.
(1988) considered all the Lewis structures that can be associated with a given compound, and defined the
resonance bond number (RBN) as the weighted average of the bond order over the Lewis structures. This
method ignores the periodicity of the crystalline structures and omits any non-nearest-neighbour interaction:
the calculation requires $10^7$ or $10^8$ Lewis graphs per atom and the resonance bond numbers obtained in this
way are close or identical to the bond valences, but the method has the advantage of being applicable to
amorphous as well as to crystalline solids (Rutherford, 1991; 1998).

Hoppe (1970b; 1979) criticized the common definitions and applications of the concepts on which bond
valence theory is based, namely:

1) the coordination number, which can be hardly identified in those cases in which no net separation
appears between a first and a second coordination sphere;

2) the ionic radius, which is far from being uniquely defined, because the interatomic distances cannot
always be described as sum of ionic radii, the variation depending partly on geometrical constraints
on the crystal structure and especially on the overall connectivity of the atoms in the structure
(Rutherford, 1991).

To generalize the concepts of coordination number and ionic radius, Hoppe (1979) introduced the
definitions of FIR (Fictive Ionic Radii), MEFIR (MEan Fictive Ionic Radii) and ECoN (Effective
Coordination Number), and Hoppe et al. (1989) applied ECoN to the calculation of the distribution of
charges in crystalline structures. This “charge” actually has a strict correspondence with the BV, as defined
by Brown (1978). Hoppe et al. (1989) showed that the charge distribution method systematically gives better
results than BV when applied to oxide compounds. Despite a large and increasing number of publications
where this approach has shown its power, it still remains underestimated with respect to bond valence,
possibly because of its more demanding computation requirements. In the following sections we present a
systematic analysis of the approach originally developed by Hoppe and a critical comparison with the bond

3. FIR, MEFIR and EcOn

Atoms in a non-molecular crystal structure can be classified in “polyhedron-centring atoms” (PC-atoms) and “vertex (corner) atoms” (V-atoms). The assignment of cations (“electropositive atoms”) or anions (“electronegative atoms”) to each of the two categories can be done interchangeably. The majority of non-molecular structures are described as corner, edge or, more rarely, face sharing of polyhedra centred on cations, but anion-centred polyhedra represent an alternative, and sometimes preferable description in a number of cases (Krivovichev, 2009; Krivovichev et al., 2013).

In the following sections, PC-atoms and V-atoms are indicated as PC\(_{(ij)}\) and V\(_{(rs)}\) respectively, where \(i\) and \(r\) identify the atomic site (i.e. the chemical element in absence of isomorphic substitution; otherwise, a statistical mix of chemical elements), \(j\) and \(s\) the crystallographic type. The latter indices, \(j\) and \(s\), are necessary when atoms of the same chemical element are not all symmetrically equivalent but two or more occur in the asymmetric unit. The formal charges (which become weighted average charges in case of isomorphic substitutions) are indicated as \(q_{(ij)}\) and \(q_{(rs)}\) and depend on \(j\) or \(s\) through the site occupation factor (sof): for sof = 1, all the PC-atoms with the same \(i\), as well as all the V-atoms with the same \(r\), have the same \(q\). Similarly, the multiplicity of the Wyckoff position is indicated as \(h_{(ij)}\) and \(h_{(rs)}\). A bond between the atoms PC\(_{(ij)}\) and V\(_{(rs)}\) is indicated as \(ij \rightarrow rs\), the corresponding distance as \(d_{(ij \rightarrow rs)}\). The \(L\)-th bond length between PC\(_{(ij)}\) and V\(_{(rs)}\) is then indicated as \(d_{(ij \rightarrow rs)}\)\(_{L}\). For computational purposes, the bond lengths are ordered in increasing length with respect to \(i\), \(j\) and \(r\), where \(d_{(ij \rightarrow rs)}\)\(_{1}\) is the shortest one and \(s\) a sort of dummy index at this stage.

Pauling’s (1929) statement that in ionic compounds the distance between two bonded ions with charges of opposite sign should be nearly identical to the sum of the ionic radii \(R_{(i)}\) and \(R_{(r)}\) was generalised by Hoppe (1979), with the introduction of the Fictive Ionic Radii FIR\(_{(ij \rightarrow rs)}\)\(_{L}\) concept, defined as:

\[
\text{FIR}_{(ij \rightarrow rs)} = d_{(ij \rightarrow rs)} \cdot \frac{R_{(i)}}{R_{(i)} + R_{(r)}}.
\]  

In case of uniform coordination polyhedra, all the \(d_{(ij \rightarrow rs)}\)\(_{L}\) are identical and the same holds for FIR\(_{(ij \rightarrow rs)}\); if the crystal is ionic, \(d_{(ij \rightarrow rs)} = R_{(i)} + R_{(r)}\) so that FIR\(_{(ij \rightarrow rs)}\) should correspond to \(R_{(i)}\). Deviations from the ionic radius may be read as a measure of the departure from the pure ionic character of the bond. For non-uniform polyhedra, instead, the concept of ionic radius is less well defined; accordingly, a different Fictive Ionic Radius is assigned to each bond, which is then used to compute a weighted average, called the MEan Fictive Ionic Radius (MEFIR). Concretely, an ion at the centre of a uniform polyhedron can be described as a sphere whose dimension, FIR, is directly related to the ionic radius, \(R_{(i)}\). For non-uniform polyhedra, instead, the ionic radius shows a dependence on the direction, which leads to a polyhedral shape for the atomic basins (Pendás et al., 1998). The computation of MEFIR corresponds to assigning to the ion a...
spherical basin whose radius is a weighted average of the ionic radius for each direction. MEFIR is calculated through a convergent iterative process:

\[
\text{MEFIR}(ij \rightarrow r) = \sum \sum \exp \left( -\frac{\text{FIR}(ij \rightarrow rs)}{n\text{MEFIR}(ij \rightarrow r)} \right) / \sum \sum \exp \left( -\frac{\text{FIR}(ij \rightarrow rs)}{n\text{MEFIR}(ij \rightarrow r)} \right)
\]

(4)

where \( n \) is the number of iterations and where the starting value, \( \text{MEFIR}(ij \rightarrow r) \), is simply \( \text{FIR}(ij \rightarrow rs) \). The exponential term is responsible for the asymptotic decrease of the contribution of each FIR with the increase of the bond distance. MEFIR gives a quantitative meaning to the rule of mutual influence (Beck, 2014) of different cations on their seeming size and polarity, according to which the size of an ion depends on the chemical relations with its neighbours. A global \( \text{MEFIR}(ij) \) for each PC-atom can also be defined, because \( \text{MEFIR}(ij \rightarrow r) \) does not change significantly as a function of \( r \):

\[
\text{MEFIR}(ij) = \sum \sum \sum \exp \left( -\frac{\text{FIR}(ij \rightarrow rs)}{n\text{MEFIR}(ij \rightarrow r)} \right) / \sum \sum \sum \exp \left( -\frac{\text{FIR}(ij \rightarrow rs)}{n\text{MEFIR}(ij \rightarrow r)} \right)
\]

(5)

The concepts of FIR and MEFIR have been introduced for ionic bonds but they do apply as well to polar bonds. According to Pauling's (1960) classification, chemical bonds can be divided into ionic, polar and non-polar depending on the electronegativity difference of the bonded atoms, this difference being respectively higher than 1.7, between 0.4 and 1.7, and lower than 0.4. For polar bonds, one could simply use covalent radii instead of ionic radii in Eq. (3): \( \text{FIR}(ij \rightarrow rs) \) would then correspond to the covalent radius for bond order 1, or be smaller than it for higher bond orders.

FIR and MEFIR clearly aim at treating atoms as spherical although they are not necessarily spherical. The purpose is to keep the description of a crystal structure as simple as possible, with nevertheless some consideration of the effect of the environment in which each atom is embedded. In the same line, the classical definition of the coordination number of an atom as “the number of other atoms directly linked to that specified atom” (IUPAC, 1997) becomes less and less satisfactory with the distribution of bond distances over a large interval, from uniform polyhedra to cavities which can hardly be recognized as polyhedra, like in the typical example of alkaline metals showing a very irregular coordination. These considerations led Hoppe (1970) to call the coordination number an “inorganic chameleon” and generalise it to a function of the weighted average of bond distances which he called the Effective Coordination Number, ECoN (Hoppe, 1979). ECoN is computed as a normalised sum of bond strengths defined as function of the bond lengths to which a weight is associated that decreases with the increase of the bond length. The approach is therefore somehow similar to that behind Eq. (2), with however a fundamental difference: instead of using empirical parameters which depend on the pair PC-V, like in the Bond Valence approach, the function is based on the
ratio of experimental bond distances in each polyhedron; the bond strength computed in this way is called

*bond weight*, shortened to BW hereafter.

The first step in the computation of the bond weight is the calculation of a weighted mean distance

\[ ^*d(ij \rightarrow r) \]

through a convergent iterative process similar to that used to obtain *MEFIR:

\[
{^*d(ij \rightarrow r) = \frac{\sum \sum \exp \left[ 1 - \frac{d(ij \rightarrow rs)}{^*d(ij \rightarrow r)} \right]}{\sum \sum \exp \left[ 1 - \frac{d(ij \rightarrow rs)}{^*d(ij \rightarrow r)} \right]}}
\]

(6)

with \(^*d(ij \rightarrow r) = d(ij \rightarrow rs)\). The weighted average \(^*d(ij \rightarrow r)\) is actually simply MEFIR scaled by the ratio \([R(i) + R(r)]/R(i)\); in fact, solving Eq. (3) for \(d(ij \rightarrow rs)\), we rewrite Eq. (6) at step \(n = 1\) as follows:

\[
{^*d(ij \rightarrow r) = \sum \sum \frac{FIR(ij \rightarrow rs)}{R(i)} \cdot \frac{R(i) - R(r)}{R(i)} \cdot \exp \left[ 1 - \frac{FIR(ij \rightarrow rs)}{FIR(ij \rightarrow rs)} \right]}
\]

\[
\sum \sum \exp \left[ 1 - \frac{FIR(ij \rightarrow rs)}{FIR(ij \rightarrow rs)} \right]}
\]

(7)

and by iteration we obtain \(^*d(ij \rightarrow r) = ^*MEFIR(ij \rightarrow r)\cdot[R(i) + R(r)]/R(i)\).

The shortest PC-V distance in each polyhedron is used as *normalising parameter* at the zero-th stage of

the iteration, to be replaced by the weighted average until convergence is reached. This exponential term,

which acts as a weight applied to each bond length, is precisely the *bond weight*

\[ ^*w(ij \rightarrow rs) \]

\[
^*w(ij \rightarrow rs) = \exp \left[ 1 - \frac{d(ij \rightarrow rs)}{^*d(ij \rightarrow r)} \right] = \exp \left[ 1 - \frac{FIR(ij \rightarrow rs)}{^*MEFIR(ij \rightarrow r)} \right].
\]

(7)

The sum over the bond weights gives *ECoN(ij \rightarrow r)*:

\[
^*ECoN(ij \rightarrow r) = \sum \sum ^*w(ij \rightarrow rs),
\]

(8)

Because \(^*w(ij \rightarrow rs)\) is equivalently defined in terms of FIR/\(^*MEFIR\) and of \(^*d\)/\(^*d\) (Eq. 7), ECoN too is
equivalently defined in terms of MEFIR (as in Hoppe, 1979) and of $d(\text{i} \to \text{r})$ (as in Hoppe et al., 1989). Eq. (6) can therefore be rewritten as:

$$d(\text{i} \to \text{r}) = \frac{\sum_j d(\text{i} \to \text{rs}_j \text{w}(\text{i} \to \text{rs}))}{\sum_j \sum_k \text{w}(\text{i} \to \text{rs}_k)}$$  

(6')

MEFIR is the only variable that depends, through FIR, on the ionic radii. BW, ECoN, and the computed ‘charges’, defined and illustrated in the next section, which are a function of ECoN, do not depend on the ionic radii. For homoligand polyhedra $^\text{ECoN}(\text{i} \to \text{r})$ is actually $^\text{ECoN}(\text{i})$, because $r$ takes only a single value for each coordination polyhedron. Instead, for heteroligand polyhedra, $^\text{ECoN}(\text{i} \to \text{r})$ defined simply as the sum of $^\text{ECoN}(\text{i} \to \text{r})$ results from $r$ coordination shells corresponding to each type of anion.

ECoN, as a generalisation of the classical coordination number, is a real number that has to become equal to the integer coordination number for uniform polyhedra. This is the condition imposed to obtain the contraction parameter 6 in the definition of the bond weights. It was in fact obtained by finding the highest value giving an ECoN equal to the number of first neighbours in the structure of simple metals, where a clear separation between a first and a second coordination sphere exists (Hoppe, 1979). One exception was later found, for which the contraction parameter had to be modified. In the case of hydrogen bonds, the ratio of two short distances (donor-H and H-acceptor) with a high relative gap makes the weight $^\text{w}(\text{i} \to \text{rs})$ for the second bond (hydrogen-acceptor bond) negligible so that its presence is not taken into account in the iterative calculation. A revised contraction parameter of 1.6 was then introduced (Nespolo et al., 2001).

Although Eq. (7) can be equally expressed in terms of $^\text{d}(\text{i} \to \text{r})$ or of $^\text{MEFIR}(\text{i} \to \text{r})$, the results significantly differ in the case of heteroligand polyhedra. If $r$ takes only one value (homoligand polyhedra), the two expressions give exactly the same result. If instead $r$ takes multiple values, Eq. (7) has to be computed separately for each $r$ when using $^\text{d}(\text{i} \to \text{r})$ so that each heteroligand polyhedron is divided into homoligand subpolyhedra, treated independently, while this is not the case when it is computed in terms of $^\text{MEFIR}(\text{i} \to \text{r})$. In fact, by using the bond lengths one automatically selects a different normalising parameter (minimal distance) for each type of V-atom: it would make no sense to normalise bond lengths of a V-atom with respect to the shortest bond length of a different V-atom having in general a different size. It would also make no sense to define a unique weighted mean distance $^\text{d}(\text{i})$ by making $r$ in $^\text{d}(\text{i} \to \text{r})$ variable over all the V-atoms coordinated by the same PC-atom because the corresponding bond distances can be significantly different so that global average would over-estimate bonds with smaller V-atoms and under-estimate bonds with larger V-atoms. Accordingly, $^\text{ECoN}(\text{i} \to \text{r})$, Eq. (8), is defined unambiguously for each homoligand subpolyhedron, and the resulting $^\text{ECoN}(\text{i} \to \text{r})$ are then summed up to obtain $^\text{ECoN}(\text{i})$:

$$^\text{ECoN}(\text{i}) = \sum_{\text{r}} ^\text{ECoN}(\text{i} \to \text{r}) = \sum_{\text{r}} \sum_{\text{i}} ^\text{w}(\text{i} \to \text{rs})$$  

(9)

ignoring thus the effect of the size of the different V-atoms at this stage.
3.1. Examples

Table 1 shows the example of a regular octahedron with six PC-V distances of 2.000 Å, undergoing three gradual deformations of bond distances, which however do not affect the arithmetic average, kept constant at 2.000 Å. With increasing distortion, the weighted average distance $d(\text{ij} \rightarrow \text{r})$ (Eq. 6') decreases with respect to the arithmetic average. This is a normal effect of the exponential decay of the bond weights. When two distances $d_1$ and $d_2$ depart from the value $d_{\text{uni}}$ corresponding to a uniform polyhedron by the same amount but in the opposite sense ($d_1 = d_{\text{uni}} - \Delta; d_2 = d_{\text{uni}} + \Delta$), the increase of the bond weight of $d_1$ is larger than the decrease of the bond weight of $d_2$. This leads to a shortening of the weighted average distance and a reduction of ECoN, which is no longer equal to the classical value of the coordination number. Accordingly, the smaller ECoN becomes, the more distorted is the polyhedron. In this example, ECoN decreases slowly for the two first distortions, but for the third distortion is only 4.73, and the distribution of the bond weights shows that the coordination is closer 4+2 than to 6 (Figure 1).

Table 2 shows the example of KNaTiO$_3$, which contains three types of cation (Ti, K, Na; one crystallographic type each) and one type of anion (O; two crystallographic types: O1 and O2). The index $i$ runs from 1 to 3, and for each of them $j$ takes the only value 1 ($ij = 11$: Ti; $ij = 21$: K; $ij = 31$: Na). The index $r$ takes the only value 1 and the index $s$ runs from 1 to 2 ($rs = 11$: O1; $rs = 12$: O2). Na. where K is in contact with twelve oxygen atoms (six pairs of distances), Ti and Na with five. The K-O distances increase in a more or less continuous way, until a jump is observed after the eighth distance. FIR has a parallel behaviour and the bond weight decreases. The contribution of the last four oxygen atoms is almost negligible (lower than 0.01) and the value of ECoN is practically 8. Only the first eight oxygen atoms contribute significantly to the coordination of K. The opposite occurs for Na, where the contribution of each to the five bonds to ECoN is comparable, leading to ECoN practically 5. An intermediate situation occurs for Ti, which makes five bonds with oxygen atoms but ECoN is only 4.56.

Table 3 shows the results for $\alpha'$-Ba$_2$TiO$_4$. This orthorhombic polymorph of Ba$_2$TiO$_4$ crystallizes in $P2_1nb$, which is an unconventional setting of $Pna2_1$ (space-group type No. 33). It is a Bieberbach-type of space group (Nespolo et al. 2018), which does not contain any special Wyckoff position; the multiplicity of the general Wyckoff position is 4. For this compound $Z = 12$, so that the unit cell contains 24 barium atoms (six sites), 12 titanium atoms (three sites) and 48 oxygen atoms (twelve sites). The six polyhedra centred on barium have eight to ten bond contacts whereas the three titanium atoms are all in tetrahedral coordination. ECoN from the three titanium atoms is 3.99, showing that the distortion is minimal. On the other hand, for barium ECoN spans a large interval, from 5.54 to 7.69. The minimal value corresponds to Ba1, with eighth Ba-O contacts, of which seven are bonding contacts, whereas the last two contribute for less than 2% to ECoN ($0.069 + 0.035 = 0.104$, i.e. 1.9 % of 5.54) and can therefore be considered negligible. The discrepancy between ECoN and the number of oxygen atoms bonded to Ba (6) is a measure of the degree of distortion of the polyhedron. Ba2 has nine bond contacts, none of which can be considered negligible. The bond weights span however a very large interval, which explains why the nine contacts correspond to ECoN.
of only 6.16. Ba3 presents a similar situation, the tenth Ba-O distance having a bond weight negligible. The last three barium polyhedra are less deformed: with eight Ba-O bonds each, their ECoN goes from 7.43 to 7.69.

4. Charge Distribution Analysis of homoligand polyhedra

ECoN\((ij \rightarrow r)\) computed through Eq. (8) can be distributed among all the bonds around the PC-atom defining a homoligand (sub)polyhedron, obtaining in this way the fractional contribution by each V-atom to ECoN itself.

\[
\Delta \text{ECoN}(ij \rightarrow rs) = \sum \frac{w(ij \rightarrow rs)}{\text{ECoN}(ij \rightarrow r)}. \tag{10}
\]

If one sums up \(\Delta \text{ECoN}(ij \rightarrow rs)\), one gets obviously 1 (cfr. Eq. 8):

\[
\sum \Delta \text{ECoN}(ij \rightarrow rs) = \sum \frac{w(ij \rightarrow rs)}{\text{ECoN}(ij \rightarrow r)} = \frac{\text{ECoN}(ij \rightarrow r)}{\text{ECoN}(ij \rightarrow r)} = 1.
\]

Each bond \(ij \rightarrow rs\) connects a PC-atom with formal charge \(q(ij)\) and a V-atom with formal charge \(q(rs)\). We can read this network of bonds as a graph along which the formal charge \(q(ij)\) is transferred (“distributed”) from the PC-atom to the V-atoms bonded to it, exactly like Pauling’s scheme in Eq. (1). Instead of using a single bond strength calculated as \(q/N\), which does not take into account the variation of bond strength with bond lengths, we use \(\Delta \text{ECoN}(ij \rightarrow rs)\) as a factor to distribute the formal charge of the PC-atom. Because the result is entirely dependent on the geometry of the coordination polyhedron, the distribution scheme is usually read the other way round, saying that the formal charge \(q(ij)\) is used as a scaling parameter applied to \(\Delta \text{ECoN}\), providing the contribution by each PC-V bond to the distributed ‘charge’:

\[
\Delta q(ij \rightarrow rs) = \Delta \text{ECoN}(ij \rightarrow rs)q(ij). \tag{11}
\]

Finally, by summing the \(\Delta q(ij \rightarrow rs)\) on the PC-atoms around a V-atom, one should obtain the expected ‘charge’ of the V-atom itself:

\[
Q(rs) = -\sum \sum \Delta q(ij \rightarrow rs) \frac{h(ij)}{h(rs)}. \tag{12}
\]

where \(q\) is the input charge (formal oxidation number) and \(Q\) is the charge computed as a function of the distribution of ECoN. The ratio of the multiplicities of the respective Wyckoff positions, \(h(ij)/h(rs)\), is introduced to avoid counting multiple contributions when a bond connects atoms on Wyckoff positions with different multiplicities. Eq. (12) is the extension of Pauling’s second rule (Eq. 1) to general coordination polyhedra.

A similar distribution is repeated the other way round and summed up on the V-atoms about a PC-atom. This time, however, instead of using \(q(rs)\) as scaling parameter, in a perfectly symmetrical way, the ratio \(q(rs)/Q(rs)\) for the V\((rs)\) bonded to PC\((ij)\) is used:
\[
Q(y) = \left[ \sum \sum \text{ECoN}(ij \rightarrow rs) \frac{q(rs)}{Q(rs)} \right] q(y) = \sum \sum \text{ECoN}(ij \rightarrow rs) \frac{q(rs)}{Q(rs)}.
\]

(13)

If \(q(rs)/Q(rs) = 1\) for each \(r\) and \(s\), i.e. if the distributed charge and formal charge are identical, then the bracket in Eq. (13) goes to 1 (it becomes the sum of the fractions of ECoN about each PC-atom) and thus \(Q(ij) = q(ij)\). This shows that in a structure correctly solved and perfectly valence-balanced the distribution of ECoN scaled by the formal charges gives back those charges. On the other hand, when a structure has developed some structural strains, its V-atoms may not be perfectly balanced; nevertheless, the distribution of this unbalance, measured by the ratio \(q(rs)/Q(rs)\), should give back the expected formal charges on the PC-atoms, otherwise the whole set of coordination polyhedra would be unbalanced and the structure would be unstable. In other words, CHARDI possesses an internal criterion to evaluate the quality of its analysis: the ratio \(q(ij)/Q(ij)\) for the PC-atoms. When this ratio is reasonably close to 1 for all the PC atoms, then the analysis of the connectivity can be approached by the study of the \(Q(rs)\), which diverge from \(q(rs)\) proportionally to the structural strains inside the structure. One speaks of over-under-bonding (OUB) effect.

Now, because the core of the method is a distribution of ECoN scaled by the formal charges (oxidation numbers), in the trivial case of a structure containing only one type of V-atom, when there is nothing to distribute, \(Q(rs)\) is identical to \(q(rs)\) and the CHARDI analysis simply does not give any information.

Tables 4 and 5 and Figures 2 and 3 show the Charge Distribution analysis for KNaTiO\(_3\) and \(\alpha\)'-Ba\(_2\)TiO\(_4\), whose ECoN analysis was presented in Tables 2 and 3. The same tables provide the Bond Valence Sums (BVS hereafter) as well. The results of the CHARDI analysis are closer to the formal charges (oxidation numbers) than the BVS. The two approaches are fundamentally different: whereas CHARDI, as its name says, distributes the charges and sums back those distributions, BVS computes the charges. With CHARDI it is therefore impossible to get charges that are globally lower (or higher) than the oxidation numbers, as it occurs instead with BVS (i.e. both crystallographic types of oxygen in KNaTiO\(_3\) have a BVS lower, as absolute value, than the formal oxidation numbers, whereas with CHARDI the slight excess of one oxygen is compensated by the slight deficit of the other, once the site multiplicity is taken into account). However, because these figures are often used for structure validation, it is evident that the conclusions drawn from BVS are subject to criticism in the spotlight of the better agreement one gets from CHARDI. As a matter of fact, when the method does apply (on the basis of the internal validation criterion \(q(ij)/Q(ij)\)), the results are usually better than those obtained with BVS.

5. Charge Distribution Analysis of heteroligand polyhedra

Eq. (5) allows treating all the PC-V distances in a polyhedron at once; this however leads to neglecting the differences between the various V-atoms. In other words, it corresponds to replacing each V-atom with a dimensionless charged point. While this does make sense in the calculation of ECoN(\(ij\)), which simply gives a measure of the number of coordinated V-atoms weighted by the respective bond distances, it would prevent any charge distribution analysis. In fact, although every V-atom retains its charge, the relation between the
bond distance and the strength of the bond would be lost. There is however one aspect in which the use of
FIR and MEFIR instead of the individual and average distances presents a clear advantage.

In a structure built on homoligand polyhedra, every PC($ij$) is bonded to V($1s$) for some $s$ and the minimal
PC-V distance, $d(\text{j} \rightarrow 1\text{s})$, obviously corresponds to a chemical bond between the two atoms. Every PC-atom
distributes its charge to all the V-atoms bonded to it, in an inverse proportion to the bond length. On the other
hand, in a structure containing heteroligand polyhedra not all the PC($ij$) are necessarily bonded to every
V($rs$); this results in two types of problems.

1. $d(\text{j} \rightarrow \text{rs})$, for some $r$ may correspond to a non-bonded contact. If the distances are used directly, then
$d(\text{j} \rightarrow \text{rs})$, is scaled to itself in the first step of the calculation of the average distance, $d(\text{j} \rightarrow \text{r})$, and to
avoid considering non-bonded contacts as chemical bonds one needs an external criterion, like the
sum of the radii scaled by an expansion factor to allow some tolerance. If FIR and MEFIR are used
instead, each polyhedron is treated as homoligand at this stage and the risk of counting non-bonded
contacts as chemical bonds is avoided. Concretely, in the analysis of the coordination polyhedra, a
first step is performed in terms of FIR and MEFIR, to discriminate between bonding and non-bonding
contacts; then, the calculation is repeated by using the distances to treat each coordination
sub-polyhedron separately.

2. Each PC-atom distributes a fraction of its charge to each homoligand subpolyhedron. This fraction
depends on the relative distances: V-atoms closer to the PC-atom receive a larger fraction than V-
atoms farther from it. The problem is how to define this fraction. This is straightforward for
structures which are built by homoligand polyhedra in one of the two possible descriptions (cation-
centred or anion-centred), while it requires a convergence algorithm when a structure is built by
heteroligand polyhedra in both descriptions.

The treatment slightly differs depending on whether the structure under investigation contains only
homoligand polyhedra in one description (either cation-centred or anion-centred) or not. Numerous examples
have been presented and discussed in Nespolo (2016), which we do not repeat here for lack of space.

5.1. Structures built by homoligand polyhedra in one description

If a structure contains only one chemical species of cation or of anion, the calculation is straightforward.
The single-type of element (cation or anion) is first assigned to V-atoms ($r = 1$) and the computation
described above is performed. Next, the fraction of $Q(\text{ij})$ coming from each V-atom is calculated by a simple
modification of Eq. (13):

$$
\Delta Q_i \rightarrow 1s = \sum_j \Delta q_j \rightarrow 1s \frac{q_j(1s) f(j)}{h_j(1s)} = \sum_j \frac{\DeltaECoN(\text{j} \rightarrow 1s) q_j(1s) f(j)}{Q(1s) h_j(1s)}.
$$

(14)

The summation is here over $j$, i.e. the crystallographic type of PC-atom, instead than $r$ and $s$. The result is
thus the fraction of the formal charge that each V-atom (identified by their crystallographic type $s$) shares
with the $i$-th chemical species of PC-atoms. The role of PC-atoms and V-atoms is then swapped so that Eq.
(14) gives in the next step the fraction that each PC-atom (V-atom in the previous step) shares with each chemical species of V-atom (PC-atom in the previous step):

$$\Delta Q(1j \rightarrow r) = -\Delta Q(i \rightarrow 1s).$$  \hspace{1cm} (15)

This corresponds to re-labelling the contribution $\Delta Q$ so that the only chemical species of V atom ($r = 1$) becomes the only chemical species of PC-atom ($i = 1$); the index on the crystallographic type is also relabelled from $s$ to $j$. Finally, the index on the chemical species of PC-atoms ($i$) is relabelled as index on the chemical species of V-atoms ($r$). In the case of KNaTiO$_3$ discussed in section 3.1 as cation-centred homoligand cation-centred polyhedra, we had $ij = 11$: Ti, $ij = 21$: K, $ij = 31$: Na, $rs = 11$: O1 and $rs = 12$: O2.

In the anion-centred description, the two oxygen-centred polyhedra become heteroligand; $ij = 11$: O1; $ij = 12$: O2; $rs = 11$: Ti; $rs = 21$: K; $rs = 31$: Na.

$\Delta Q(ij \rightarrow r)$ is then used instead of $q(ij)$ in Eq. (13), which is replaced by Eq. (16):

$$Q(ij) = \sum \sum \Delta E \cdot CoN(\langle ij \rightarrow rs \rangle) \cdot \frac{q(rs)}{Q(rs)} \cdot \Delta Q(\langle ij \rightarrow r \rangle).$$  \hspace{1cm} (16)

### 5.2. Structures built by heteroligand polyhedra in both descriptions

When a structure contains heteroligand polyhedra in both descriptions, we miss the starting point to compute Eq. (14). The problem is solved with an iterative procedure in which the starting value of $\Delta Q(\langle ij \rightarrow r \rangle)$ in Eq. (15) is assigned as a function of $ECoN(\langle ij \rightarrow r \rangle)/ECoN(ij)$:

$$\Delta Q(\langle ij \rightarrow r \rangle) = q(ij) \cdot \frac{ECoN(\langle ij \rightarrow r \rangle)}{ECoN(ij)}.$$  \hspace{1cm} (15')

Eq. (15') corresponds to Pauling's definition of bond strength, Eq. (1) applied to each sub-polyhedron. From the second step Eq. (14) and (15) can be used directly and the role of PC and V-atoms is swapped back and forth between cations and anions until the same values of $\Delta Q(\langle ij \rightarrow r \rangle)$ are obtained in each description, meaning that convergence has been obtained.

### 6. Comparison of Charge Distribution and Bond Valence approaches

The concept of bond strength has its roots in the XIX century theory of valence and is based on the idea that the total bond valence received by each atom is equal to its atomic valence. Charge Distribution and Bond Valence are both expressions of strengths, but they differ in the way they describe a crystal structure. The expected outcomes of the two approaches also do not fully overlap, although both methods can be used for structure validation.

Bond Valence assigns a strength (valence) to each bond on the basis of some empirical parameters. These parameters are far from being established once for all and indeed in the literature these parameters are often re-refined or redefined. If a reliable and optimised set of parameters is available, then the Bond Valence approach is potentially able to predict the geometry of polyhedra and molecules in a crystal structure (Brown, 2014). However, the empirical parameters depend, in general, on the conditions under which the set
of crystal structures used to obtain these parameters have been solved and refined. As a matter of fact, bond lengths do depend on the temperature, pressure, electromagnetic field or other external constraints to which the structure is subjected; empirical parameters that have been optimized for ambient conditions are less adapted to describe structures under conditions in which the bond lengths are significantly shrunk or elongated. Furthermore, bond lengths are also affected by the spin state of the atoms: for example, the Fe-N distance can change as much as 10% following a high-spin to low-spin transition (Legrand et al., 2007). However, the spin state does not normally enter in the definition of the Bond Valence parameters. Attempts have been made to relate the Bond Valence parameters to electron density (Adams, 2014), although doubts can be reasonably expressed on the ground on which simple empirical parameters can bear information related to quantum mechanics. Finally, Bond Valence lacks an internal criterion to evaluate whether the results of the analysis can be considered correct or not.

Charge Distribution fundamentally differs from Bond Valence in being essentially a geometric analysis of the coordination polyhedra exploiting the observed distances only, rather than comparing them with some ‘standard values’. Atoms are replaced by point charges in a Madelung-type scheme and the bond weight is a purely geometric concept which quantitatively tells how strongly the presence of a V-atom at the corner of a polyhedron is felt by the PC-atom at the centre of it. The bond weight is not directly related with the electron density of the bond and the charge is distributed, rather than computed, among each bond. The equivalent of the Bond Valence Sum strictly applies to computed charges of the PC-atoms, not to those of the V-atoms, the two quantities bringing different information: a measure of the OUB effects for latter, the evaluation of the applicability – including structure reliability – for the former.

Despite the Madelung-type approach, CHARDI has proven to be able to treat a wide range of structures with a large chemical heterogeneity, although some types of compounds still remain outside its possibilities. Apart from these rare exceptions, CHARDI can bring important information not always easily obtained from experimental data:

• a structure validation based only on internal criteria, without the reference to empirical parameters;
• the presence of structural anomalies;
• the site-occupancy factor of incompletely occupied sites;
• the most likely oxidation state of atoms with multiple valences;
• the most likely oxidation state of an atomic site in compounds presenting isomorphic substitutions, which gives a clear indication of the fractional occupancy by each type of atom: this information may be difficult to obtain from conventional X-ray diffraction experiments in case of heterovalent substitutions involving atoms of close atomic number or atoms with different valence states;
• the most likely positions of missing light atoms (like hydrogen), who are hidden by the presence of relatively heavy atoms.

CHARDI does not possess the same predictive power as Bond Valence, because it cannot treat single bond lengths separated from the others in the same coordination polyhedron. This difficulty could in
principle be overcome in the seek for missing atoms by computing a CHARDI map reminding the Fourier difference map routinely used in the refinement of crystal structures. Such a development is not available to date and one may reasonably question whether the computational effort would be justified, considering the simplified, Madelung-type description of the structure.

A computationally economical approach could use Bond Valence to predict the bond lengths between an already located atoms and missing atoms. The likely positions could then be estimated from the expected coordination geometry and the chemical good sense. This estimation can then be verified with CHARDI, whose results are normally in better agreement with the expected charges than those provided by the BVS. A few trial-and-error cycles can provide a reasonable estimation of the most likely atomic position.

**Figure captions**

**Figure 1.** A regular octahedron with six distances $d(ij \rightarrow rs)$ all equal to 2.000 Å (a) undergoing increasing deformation of bond distances (b) to (d), while preserving the arithmetic average of 2.000 Å. The weighted average distance decreases as does ECoN too. Values in the figures are bond distances in Ångströms. Figure drawn with VESTA (Momma and Izumi, 2011).

**Figure 2.** Graphical representation of the Charge Distribution (CHARDI) and Bond Valence Sum (BVS) for the structure of KTiNO$_3$. ΔQ shows the departure from the ideal value of the compute charges (valences). The higher departure calculated for BVS might suggest a more important over-under bonding effect, whereas this actually comes from the limits of the method itself, as shown by the significantly lower departure calculated for CHARDI.

**Figure 3.** Graphical representation of the Charge Distribution (CHARDI) and Bond Valence Sum (BVS) for the structure of $\alpha'$-Ba$_2$TiO$_4$. Same interpretation as for Figure 1.

**References**


Alphabetical Index

bond strength........................................................................................................... 2 ff., 6 f., 10, 13, 16
Bond strength......................................................................................................... 3
Bond Strength........................................................................................................... 1
bond valence........................................................................................................... 3 f., 13, 16 ff.
Bond valence........................................................................................................... 16
Bond Valence.......................................................................................................... 6, 11, 13 ff.
Bond weight........................................................................................................... 7 ff., 14
charge distribution.................................................................................................. 4, 11
Charge distribution.................................................................................................. 16 f.
Charge Distribution.................................................................................................. 1, 3, 10 f., 13 ff., 17
coordination polyhedron........................................................................................ 1 f., 8, 10, 15
ECoN......................................................................................................................... 4 ff., 13, 15, 17 f.
Effective coordination number.............................................................................. 17 f.
Effective Coordination Number............................................................................... 4, 6
Fictive Ionic Radius................................................................................................ 4 f., 17 f.
FIR......................................................................................................................... 4 f.
heteroligand.................................................................................................................. 2 ff., 8, 11 ff., 17
homoligand.................................................................................................................. 2 f., 8, 10, 12 f.
MEan Fictive Ionic Radius.............................................................................................. 4 f.
MEFIR............................................................................................................................ 4 f.
resonance bond number............................................................................................... 4
Resonance bond number............................................................................................ 15
Table 1. Simulation of the progressive distortion of a regular octahedron and its effect of the weighted average distance $^*d_{ij \rightarrow r}$ and effective coordination number $^*ECoN_{ij \rightarrow r}$.

<table>
<thead>
<tr>
<th></th>
<th>Regular octahedron: Figure 1(a)</th>
<th>Distortion 1: Figure 1(b)</th>
<th>Distortion 2: Figure 1(c)</th>
<th>Distortion 3: Figure 1(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{ij \rightarrow rs}$</td>
<td>$\frac{d_{ij \rightarrow rs}}{d_{ij \rightarrow rs}}$</td>
<td>$\frac{d_{ij \rightarrow rs}}{d_{ij \rightarrow rs}}$</td>
<td>$\frac{d_{ij \rightarrow rs}}{d_{ij \rightarrow rs}}$</td>
<td>$\frac{d_{ij \rightarrow rs}}{d_{ij \rightarrow rs}}$</td>
</tr>
<tr>
<td>$d_{ij \rightarrow rs1}$</td>
<td>2.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.940</td>
</tr>
<tr>
<td>$d_{ij \rightarrow rs2}$</td>
<td>2.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.970</td>
</tr>
<tr>
<td>$d_{ij \rightarrow rs3}$</td>
<td>2.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.990</td>
</tr>
<tr>
<td>$d_{ij \rightarrow rs4}$</td>
<td>2.000</td>
<td>1.000</td>
<td>1.000</td>
<td>2.000</td>
</tr>
<tr>
<td>$d_{ij \rightarrow rs5}$</td>
<td>2.000</td>
<td>1.000</td>
<td>1.000</td>
<td>2.040</td>
</tr>
<tr>
<td>$d_{ij \rightarrow rs6}$</td>
<td>2.000</td>
<td>1.000</td>
<td>1.000</td>
<td>2.060</td>
</tr>
</tbody>
</table>

$^*d_{ij \rightarrow r}$ | 2.000 | 1.000 | 1.000 | 1.995 | 6.00 | 5.91 | 1.918 | 5.69 | 1.912 |

$^*ECoN_{ij \rightarrow r}$ | 2.000 | 1.000 | 1.000 | 1.995 | 6.00 | 5.91 | 1.918 | 5.69 | 1.912 |

Table 2. Calculation of ECoN and the parameters contributing to it for the structure of KNaTiO$_3$ (structural data from Werthmann and Hoppe, 1985). $h$ is the multiplicity of the Wyckoff position.

<table>
<thead>
<tr>
<th>PC</th>
<th>$h$</th>
<th>V</th>
<th>$h$</th>
<th>$d_{ij \rightarrow rs}$</th>
<th>FIR</th>
<th>$^*MEFIR$</th>
<th>$^*d_{ij \rightarrow r}$</th>
<th>$^*w$</th>
<th>$^*ECoN_{ij \rightarrow r}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti1</td>
<td>4</td>
<td>O1</td>
<td>4</td>
<td>1.7570</td>
<td>0.556</td>
<td>0.596</td>
<td>1.887</td>
<td>1.416</td>
<td>4.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2×1.9098</td>
<td>0.604</td>
<td>0.770</td>
<td>0.927</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td></td>
<td></td>
<td>2×2.0034</td>
<td>0.634</td>
<td></td>
<td>0.887</td>
<td>0.667</td>
<td>0.770</td>
</tr>
<tr>
<td>K1</td>
<td>4</td>
<td>O1</td>
<td>4</td>
<td>2×2.7924</td>
<td>1.662</td>
<td>1.760</td>
<td>2.959</td>
<td>1.341</td>
<td>8.04</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td></td>
<td>2×2.9093</td>
<td>1.732</td>
<td></td>
<td>2.959</td>
<td>1.341</td>
<td>8.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2×3.0757</td>
<td>1.831</td>
<td>0.770</td>
<td>0.770</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td></td>
<td></td>
<td>2×3.1244</td>
<td>1.860</td>
<td>0.770</td>
<td>0.770</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td></td>
<td></td>
<td>2×3.6514</td>
<td>2.174</td>
<td></td>
<td>0.679</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td></td>
<td></td>
<td>2×3.6514</td>
<td>2.174</td>
<td></td>
<td>0.079</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Calculation of ECoN and the parameters contributing to it for the structure of $\alpha'$-Ba$_2$TiO$_4$ (structural data from Guenter and Jameson, 1984).

<table>
<thead>
<tr>
<th>PC</th>
<th>V</th>
<th>$d_{ij \rightarrow rs}$</th>
<th>FIR</th>
<th>$^w$MEFIR</th>
<th>$^w$d$_{ij \rightarrow r}$</th>
<th>$^w w$</th>
<th>$^w$ECoN$_{(ij \rightarrow r)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba1</td>
<td>O3</td>
<td>2.5393</td>
<td>1.401</td>
<td>1.509</td>
<td>2.736</td>
<td>1.434</td>
<td>5.54</td>
</tr>
<tr>
<td></td>
<td>O12</td>
<td>2.7154</td>
<td>1.498</td>
<td></td>
<td></td>
<td></td>
<td>1.045</td>
</tr>
<tr>
<td></td>
<td>O10</td>
<td>2.7240</td>
<td>1.503</td>
<td></td>
<td></td>
<td></td>
<td>1.026</td>
</tr>
<tr>
<td></td>
<td>O9</td>
<td>2.7587</td>
<td>1.522</td>
<td></td>
<td></td>
<td></td>
<td>0.950</td>
</tr>
<tr>
<td></td>
<td>O8</td>
<td>2.9594</td>
<td>1.633</td>
<td></td>
<td></td>
<td></td>
<td>0.548</td>
</tr>
<tr>
<td></td>
<td>O5</td>
<td>3.0263</td>
<td>1.670</td>
<td></td>
<td></td>
<td></td>
<td>0.435</td>
</tr>
<tr>
<td></td>
<td>O12</td>
<td>3.3986</td>
<td>1.876</td>
<td></td>
<td></td>
<td></td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>O9</td>
<td>3.4941</td>
<td>1.928</td>
<td></td>
<td></td>
<td></td>
<td>0.035</td>
</tr>
<tr>
<td>Ba2</td>
<td>O7</td>
<td>2.5718</td>
<td>1.419</td>
<td>1.564</td>
<td>2.837</td>
<td>1.561</td>
<td>6.16</td>
</tr>
<tr>
<td></td>
<td>O8</td>
<td>2.7522</td>
<td>1.519</td>
<td></td>
<td></td>
<td></td>
<td>1.181</td>
</tr>
<tr>
<td></td>
<td>O5</td>
<td>2.7872</td>
<td>1.538</td>
<td></td>
<td></td>
<td></td>
<td>1.106</td>
</tr>
<tr>
<td></td>
<td>O12</td>
<td>3.0013</td>
<td>1.656</td>
<td></td>
<td></td>
<td></td>
<td>0.669</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>3.0071</td>
<td>1.659</td>
<td></td>
<td></td>
<td></td>
<td>0.659</td>
</tr>
<tr>
<td></td>
<td>O10</td>
<td>3.1208</td>
<td>1.722</td>
<td></td>
<td></td>
<td></td>
<td>0.462</td>
</tr>
<tr>
<td></td>
<td>O1</td>
<td>3.3184</td>
<td>1.831</td>
<td></td>
<td></td>
<td></td>
<td>0.210</td>
</tr>
<tr>
<td></td>
<td>O8</td>
<td>3.3600</td>
<td>1.854</td>
<td></td>
<td></td>
<td></td>
<td>0.172</td>
</tr>
<tr>
<td></td>
<td>O6</td>
<td>3.4019</td>
<td>1.877</td>
<td></td>
<td></td>
<td></td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba3</td>
<td>4</td>
<td>O11</td>
<td>4</td>
<td>2.5389</td>
<td>1.401</td>
<td>1.563</td>
<td>2.836</td>
</tr>
<tr>
<td>O6</td>
<td>4</td>
<td></td>
<td></td>
<td>2.7956</td>
<td>1.543</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td></td>
<td></td>
<td>2.8319</td>
<td>1.563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>4</td>
<td></td>
<td></td>
<td>2.9213</td>
<td>1.612</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>4</td>
<td></td>
<td></td>
<td>2.9579</td>
<td>1.632</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>4</td>
<td></td>
<td></td>
<td>3.1532</td>
<td>1.740</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td></td>
<td></td>
<td>3.3056</td>
<td>1.824</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td></td>
<td></td>
<td>3.3578</td>
<td>1.853</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td></td>
<td></td>
<td>3.4173</td>
<td>1.886</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O5</td>
<td>4</td>
<td></td>
<td></td>
<td>3.6230</td>
<td>1.999</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba4</td>
<td>4</td>
<td>O10</td>
<td>4</td>
<td>2.6305</td>
<td>1.452</td>
<td>1.529</td>
<td>2.772</td>
</tr>
<tr>
<td>O9</td>
<td>4</td>
<td></td>
<td></td>
<td>2.7123</td>
<td>1.497</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td></td>
<td></td>
<td>2.7473</td>
<td>1.516</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O11</td>
<td>4</td>
<td></td>
<td></td>
<td>2.7772</td>
<td>1.533</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td></td>
<td></td>
<td>2.7878</td>
<td>1.538</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O8</td>
<td>4</td>
<td></td>
<td></td>
<td>2.8327</td>
<td>1.563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O12</td>
<td>4</td>
<td></td>
<td></td>
<td>2.9010</td>
<td>1.601</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td></td>
<td></td>
<td>3.1039</td>
<td>1.713</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba5</td>
<td>4</td>
<td>O2</td>
<td>4</td>
<td>2.6350</td>
<td>1.454</td>
<td>1.523</td>
<td>2.760</td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td></td>
<td></td>
<td>2.6857</td>
<td>1.482</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O6</td>
<td>4</td>
<td></td>
<td></td>
<td>2.7063</td>
<td>1.493</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O7</td>
<td>4</td>
<td></td>
<td></td>
<td>2.7870</td>
<td>1.538</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>4</td>
<td></td>
<td></td>
<td>2.7995</td>
<td>1.545</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O7</td>
<td>4</td>
<td></td>
<td></td>
<td>2.8391</td>
<td>1.567</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>O8</td>
<td>4</td>
<td>2.8751</td>
<td>1.587</td>
<td></td>
<td></td>
<td>0.757</td>
<td></td>
</tr>
<tr>
<td>O5</td>
<td>4</td>
<td>2.9076</td>
<td>1.605</td>
<td></td>
<td></td>
<td>0.693</td>
<td></td>
</tr>
<tr>
<td>Ba6</td>
<td>O6</td>
<td>4</td>
<td>2.6684</td>
<td>1.473</td>
<td>1.530</td>
<td>2.774</td>
<td>1.230</td>
</tr>
<tr>
<td>O9</td>
<td>4</td>
<td>2.6762</td>
<td>1.477</td>
<td></td>
<td></td>
<td>1.213</td>
<td></td>
</tr>
<tr>
<td>O5</td>
<td>4</td>
<td>2.6841</td>
<td>1.481</td>
<td></td>
<td></td>
<td>1.196</td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td>2.7682</td>
<td>1.528</td>
<td></td>
<td></td>
<td>1.012</td>
<td></td>
</tr>
<tr>
<td>O12</td>
<td>O4</td>
<td>4</td>
<td>2.8298</td>
<td>1.562</td>
<td></td>
<td></td>
<td>0.880</td>
</tr>
<tr>
<td>O4</td>
<td>4</td>
<td>2.9132</td>
<td>1.608</td>
<td></td>
<td></td>
<td>0.710</td>
<td></td>
</tr>
<tr>
<td>O10</td>
<td>O11</td>
<td>4</td>
<td>2.9146</td>
<td>1.608</td>
<td></td>
<td></td>
<td>0.707</td>
</tr>
<tr>
<td>O11</td>
<td>O14</td>
<td>4</td>
<td>3.0045</td>
<td>1.658</td>
<td></td>
<td></td>
<td>0.540</td>
</tr>
<tr>
<td>Ti1</td>
<td>O1</td>
<td>4</td>
<td>1.7884</td>
<td>0.566</td>
<td>0.570</td>
<td>1.802</td>
<td>1.045</td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td>1.7895</td>
<td>0.566</td>
<td></td>
<td></td>
<td>1.042</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td>1.8152</td>
<td>0.574</td>
<td></td>
<td></td>
<td>0.956</td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>4</td>
<td>1.8173</td>
<td>0.575</td>
<td></td>
<td></td>
<td>0.949</td>
<td></td>
</tr>
<tr>
<td>Ti2</td>
<td>O7</td>
<td>4</td>
<td>1.7994</td>
<td>0.569</td>
<td>0.575</td>
<td>1.818</td>
<td>1.062</td>
</tr>
<tr>
<td>O6</td>
<td>4</td>
<td>1.8183</td>
<td>0.575</td>
<td></td>
<td></td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>O5</td>
<td>4</td>
<td>1.8212</td>
<td>0.576</td>
<td></td>
<td></td>
<td>0.990</td>
<td></td>
</tr>
<tr>
<td>O8</td>
<td>4</td>
<td>1.8360</td>
<td>0.581</td>
<td></td>
<td></td>
<td>0.941</td>
<td></td>
</tr>
<tr>
<td>Ti3</td>
<td>O11</td>
<td>4</td>
<td>1.7970</td>
<td>0.569</td>
<td>0.575</td>
<td>1.819</td>
<td>1.073</td>
</tr>
<tr>
<td>O10</td>
<td>4</td>
<td>1.8251</td>
<td>0.577</td>
<td></td>
<td></td>
<td>0.979</td>
<td></td>
</tr>
<tr>
<td>O9</td>
<td>4</td>
<td>1.8252</td>
<td>0.577</td>
<td></td>
<td></td>
<td>0.979</td>
<td></td>
</tr>
<tr>
<td>O12</td>
<td>O12</td>
<td>4</td>
<td>1.8307</td>
<td>0.579</td>
<td></td>
<td></td>
<td>0.961</td>
</tr>
</tbody>
</table>
Table 4. Charge Distribution (CHARDI) and Bond Valence Sum (BVS) for the structure of KTiNO$_3$. CHARDI computed with CHARDI2015 (Nespolo and Guillot, 2016); BVS computed with Kdist (Knizek, 2017).

<table>
<thead>
<tr>
<th></th>
<th>CHARDI</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>4.01</td>
<td>3.92</td>
</tr>
<tr>
<td>K</td>
<td>0.99</td>
<td>0.83</td>
</tr>
<tr>
<td>Na</td>
<td>1.01</td>
<td>1.09</td>
</tr>
<tr>
<td>O1</td>
<td>-2.06</td>
<td>-1.95</td>
</tr>
<tr>
<td>O2</td>
<td>-1.97</td>
<td>-1.94</td>
</tr>
</tbody>
</table>

Table 5. Charge Distribution (CHARDI) and Bond Valence Sum (BVS) for the structure of $\alpha'$-Ba$_2$TiO$_4$. CHARDI computed with CHARDI2015 (Nespolo and Guillot, 2016); BVS computed with Kdist (Knizek, 2017).

<table>
<thead>
<tr>
<th></th>
<th>CHARDI</th>
<th>BVS</th>
<th></th>
<th>CHARDI</th>
<th>BVS</th>
<th></th>
<th>CHARDI</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba1</td>
<td>2.01</td>
<td>1.78</td>
<td>O1</td>
<td>-2.04</td>
<td>-2.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba2</td>
<td>1.99</td>
<td>1.56</td>
<td>O2</td>
<td>-1.91</td>
<td>-1.93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba3</td>
<td>1.99</td>
<td>1.59</td>
<td>O3</td>
<td>-1.93</td>
<td>-1.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba4</td>
<td>2.01</td>
<td>2.04</td>
<td>O4</td>
<td>-2.01</td>
<td>-1.86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba5</td>
<td>2.00</td>
<td>2.17</td>
<td>O5</td>
<td>-2.02</td>
<td>-1.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba6</td>
<td>2.00</td>
<td>2.05</td>
<td>O6</td>
<td>-2.01</td>
<td>-1.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti1</td>
<td>4.05</td>
<td>4.14</td>
<td>O7</td>
<td>-2.03</td>
<td>-2.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti2</td>
<td>3.96</td>
<td>3.98</td>
<td>O8</td>
<td>-2.01</td>
<td>-1.87</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti3</td>
<td>3.99</td>
<td>3.97</td>
<td>O9</td>
<td>-1.96</td>
<td>-1.95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O10</td>
<td>-2.04</td>
<td>-1.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O11</td>
<td>-2.00</td>
<td>-1.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O12</td>
<td>-2.01</td>
<td>-1.88</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>