

Charge distribution analysis of ceramic materials

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The Charge Distribution method is the latest development of the Pauling's idea of bond strength and is based on a geometrical analysis of the coordination polyhedra. Differently from other methods extending Pauling's approach, it uses only one empirical parameter independent from the experimental conditions, and can thus be applied equally well to structures at ambient and at extreme conditions. The kernel of the method consist in the calculation of the Effective Coordination Number (ECoN), a non-integer number that gives the weighted number of anions coordinating each cation, and the distribution of the formal oxidation numbers among all chemical bonds through the corresponding fractions of ECoN. The applications include: 1) structure validation; 2) analysis of the ordering pattern of elements substituting isomorphously; 3) analysis of the correlation between properties and structure, through the so-called Over-Under-Bonding effects. Examples are discussed in details.

Key words: Charge Distribution, ECoN, Structure validation.

Introduction

The understanding of the basic features of inorganic structures largely benefits of the well-known Pauling's rules [1]. Of these, the most extensively used is the second rule, or *Electrostatic Valence Principle*, which states that the sum of the electrostatic bond strengths $s(ij)$ calculated for the M-A bonds formed by the r -th anion $A(r)$ with the cations $M(ij)$ – where i identifies the atomic species and j the crystallographic type – is equal to the charge of the anion, $q(r)$:

$$-\sum_{ij}s(ij)=q(r). \quad (1)$$

The electrostatic bond strength of each bond formed by the cation $M(ij)$ with the anions $A(r)$ is defined as the ratio of the cation charge $q(ij)$ and its coordination number $N(ij)$:

$$s(ij)=q(ij)/N(ij). \quad (2)$$

Pauling's second rule is useful for structure validation: its failure can indicate either the presence of serious mistakes in the structure determination or a wrong interpretation, such as the overlooking of long but still active bonds. The rule is also used to infer the position of missing light atoms in presence of heavier

atoms in structures determined by X-ray diffraction. The typical example is that of H^+ , whose precise position cannot be determined by this technique.

Eqs. (1) and (2) implicitly assume that each cation $M(ij)$ is bonded to only one type of anion, and that the coordination polyhedron is regular or semi-regular (all the bonds have the same length). Whereas many compounds are actually mono-anionic, the second assumption, which is based upon the idea of interpreting the bond length as the sum of ionic radii, is only seldom realized. The larger the deviation of a coordination polyhedron from (semi) regular shape, the more Eq. (1) is violated.

Pauling's second rule applies to structures with non-regular polyhedra only if the dependence of the bond strength (s) from the bond length (d) is introduced. Such dependence is obtained through an empirical non-linear function:

$$s(ij \rightarrow r)=f[d(ij \rightarrow r), \mathbf{p}] \quad (3)$$

where ' $ij \rightarrow r$ ' indicates the bond between the $M(ij)$ cation and the $A(r)$ anion, and \mathbf{p} is the vector of the empirical parameters. Differently from Eq. (2), where all bonds around a cation by definition have the same strength, in Eq. (3) the dependence on the anions, through the index r , has to appear explicitly. The bond strength computed according to Eq. (3) is commonly termed *Bond Valence* (BV). Several curves have been proposed by different authors, such as:

Brown-Shannon, Brown-Wu [2, 3]:

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$$s(ij \rightarrow r) = s_0 [d(ij \rightarrow r)/R_0]^{-N} \quad (4)$$

Brown-Altarmatt [4]:

$$s(ij \rightarrow r) = s_0 \exp\{[R_0 - d(ij \rightarrow r)]/B\}. \quad (5)$$

These authors derived the empirical parameters of their curves for the most common cations M and for A = oxygen by fitting a large set of refined structures. R_0 and N or B are the fitted parameters and s_0 is a constant that is usually chosen arbitrarily to be 1.0. Empirical parameters for curves of anions other than oxygen are available in literature (e.g. [5-7]) but the main applications are for oxygenated compounds, which are widespread in the inorganic realm.

The BV method represents a clear improvement with respect to Pauling's original approach, but has some limitations, which can be summarized as follows:

1. The empirical parameters depend on the M-A pair;
2. The empirical parameters are obtained by fitting on structures determined at ambient conditions, and the curves give less reliable results the more the experimental conditions diverge from those at which the parameters were obtained;
3. The charge $Q(ij)$ of the cations $M(ij)$, and the charge $Q(r)$ of the anions $A(r)$ are calculated in a parallel way:

$$Q(r) = -\sum_{ij} s(ij \rightarrow r) \frac{h(ij)}{h(r)} \quad (6)$$

$$Q(ij) = \sum_r s(ij \rightarrow r) \quad (7)$$

and convey thus the same type of information [the ratio $h(ij)/h(r)$ of the multiplicities of the Wyckoff positions in Eq. (6) removes multiple contributions from bonds that are equivalent by symmetry. It does not enter in Eq. (7) because also equivalent bonds contribute to the coordination sphere of the (ij) -th cation].

4. The deviations of $Q(ij)$ and $Q(r)$ from the formal oxidation numbers $q(ij)$ and $q(r)$ are commonly used to discuss the presence of either physical or electronic strains in the structure, but the method has no internal criterion to confirm that the divergence actually reflects some sound structural features, instead of deriving from errors in the structure or from the method itself, which can simply be too approximate in some cases. An independent evaluation is thus necessary.

5. The empirical curves give worse results when bond distances span a wide range of lengths, as in the cases, for instance, of Na-O and Tl-O. These M-A pairs require not only specific parameters, but specific curves with three empirical parameters, instead of two [8].

Effective Coordination Number (ECoN)

The coordination number for regular or semi-regular

polyhedra is unequivocally determined. When the bonds are no longer all equal but span a limited range of lengths with a clear gap with respect to non-bonding distances, the number of anions coordinated by a cation can still be unequivocally identified, but this coordination number does not measure the relative weight of each bond. For example, six bonds forming a distorted trigonal antiprism are not equivalent to six bonds forming a regular octahedron, even when the (*unweighted*) arithmetic mean distance is identical, but the classical coordination number is 6 in both cases. When the bonds span a wide range of lengths, the determination of the coordination number itself becomes problematic, because of the difficulties of separating bonding and non-bonding contacts. The solution consists in the extension of the definition of coordination number to a real (non-integer) number that measures the relative weight of each bond. This non-integer number is termed *Effective Coordination Number*, ECoN [9, 10] and is defined in terms of a *weighted* mean distance in each coordination polyhedron. The following equations are written considering also the cases of structures with more than one species of anions, which are indicated as $A(rs)$: exactly as for i and j in case of cations, r identifies the atomic species and s refer to the crystallographic type [11, 12]. The L -th bond length between $M(ij)$ and $A(rs)$ is indicated as $d(ij \rightarrow rs)_L$, where the bond lengths are classified with increasing length, $d(ij \rightarrow rs)_1$ being the shortest. The weighted mean distance is calculated as:

$$\langle {}^1d(ij \rightarrow r) \rangle = \frac{\sum_s \sum_L d(ij \rightarrow rs)_L m(ij \rightarrow rs)_L \cdot \exp\left\{1 - \left[\frac{d(ij \rightarrow rs)_L}{d(ij \rightarrow rs)_1}\right]^6\right\}}{\sum_s \sum_L m(ij \rightarrow rs)_L \cdot \exp\left\{1 - \left[\frac{d(ij \rightarrow rs)_L}{d(ij \rightarrow rs)_1}\right]^6\right\}} \quad (8)$$

where $m(ij \rightarrow rs)_L$ is the multiplicity of the L -th bond. $\langle {}^1d(ij \rightarrow r) \rangle$ decreases with the increase of the distortion of the coordination polyhedron. The relative weight of each bond in a polyhedron is measured by the *bond weight*:

$${}^1\text{BW}(ij \rightarrow rs)_L = \exp\left\{1 - \left[\frac{d(ij \rightarrow rs)_L}{\langle {}^1d(ij \rightarrow r) \rangle}\right]^6\right\} \quad (9)$$

and ECoN is given by the sum of the bond weights:

$$\begin{aligned} {}^1\text{ECoN}(ij \rightarrow r) &= \sum_s \sum_L m(ij \rightarrow rs)_L \cdot {}^1\text{BW}(ij \rightarrow rs)_L \\ {}^1\text{ECoN}(ij) &= \sum_r {}^1\text{ECoN}(ij \rightarrow r). \end{aligned} \quad (10)$$

For polyhedra with only one species of anions ${}^1\text{ECoN}(ij \rightarrow r)$ and ${}^1\text{ECoN}(ij)$ coincide. For largely distorted coordination polyhedra, Eq. (8) has to be modified through

an iterative procedure which converges after n steps:

$$\langle {}^n d(ij \rightarrow r) \rangle = \frac{\sum_s \sum_L d(ij \rightarrow rs)_L m(ij \rightarrow rs)_L \cdot \exp \left\{ 1 - \left[\frac{d(ij \rightarrow rs)_L}{\langle {}^{n-1} d(ij \rightarrow r) \rangle} \right]^6 \right\}}{\sum_s \sum_L m(ij \rightarrow rs)_L \cdot \exp \left\{ 1 - \left[\frac{d(ij \rightarrow rs)_L}{\langle {}^{n-1} d(ij \rightarrow r) \rangle} \right]^6 \right\}} \quad (11)$$

The bond weight ${}^n \text{BW}(ij \rightarrow rs)_L$ is obtained by substituting $\langle {}^n d(ij \rightarrow rs) \rangle$ for $\langle {}^1 d(ij \rightarrow rs) \rangle$ in Eq. (9), and ${}^n \text{ECoN}(ij)$ by substituting ${}^n \text{BW}(ij \rightarrow rs)_L$ for ${}^1 \text{BW}(ij \rightarrow rs)_L$ in Eq. (10).

The effect of the deviation from the (semi)regularity in the shape of the coordination polyhedra can be seen in the example in Table 1, where a regular octahedron with six distances of 2.00 Å (a distance that could correspond, for instance, to the Mg-O bond) is progressively distorted while keeping the arithmetic mean distance at 2.00 Å (further examples can be found in [9]). From Table 1 it clearly appears that: 1) the effect of the polyhedron distortion is much more accentuated on ECoN than on the weighted mean distance; 2) at low distortions, there is practically no difference between the non-iterative calculation and the iterative one; when the distortion increases, however, the non-iterative calculation gives a shorter average bond length and tends thus to underestimate the weight of each bond, and especially of longer bonds; the iteration

Table 1. Details of ECoN calculation for four different polyhedra all with the same arithmetic mean $\langle \text{M-O} \rangle$ distance

M-O(1)	2.00	1.95	1.89	1.80
${}^1 \text{BW}[\text{M} \rightarrow \text{O}(1)]$	1.00	1.14	1.27	1.30
${}^n \text{BW}[\text{M} \rightarrow \text{O}(1)]$	1.00	1.14	1.28	1.36
M-O(2)	2.00	1.97	1.94	1.87
${}^1 \text{BW}[\text{M} \rightarrow \text{O}(2)]$	1.00	1.08	1.11	1.08
${}^n \text{BW}[\text{M} \rightarrow \text{O}(2)]$	1.00	1.08	1.13	1.13
M-O(3)	2.00	1.99	1.97	1.92
${}^1 \text{BW}[\text{M} \rightarrow \text{O}(3)]$	1.00	1.02	1.02	0.92
${}^n \text{BW}[\text{M} \rightarrow \text{O}(3)]$	1.00	1.02	1.03	0.98
M-O(4)	2.00	2.00	2.02	1.99
${}^1 \text{BW}[\text{M} \rightarrow \text{O}(4)]$	1.00	0.99	0.87	0.71
${}^n \text{BW}[\text{M} \rightarrow \text{O}(4)]$	1.00	0.99	0.88	0.76
M-O(5)	2.00	2.04	2.07	2.18
${}^1 \text{BW}[\text{M} \rightarrow \text{O}(5)]$	1.00	0.87	0.73	0.27
${}^n \text{BW}[\text{M} \rightarrow \text{O}(5)]$	1.00	0.87	0.74	0.30
M-O(6)	2.00	2.05	2.11	2.24
${}^1 \text{BW}[\text{M} \rightarrow \text{O}(6)]$	1.00	0.84	0.62	0.18
${}^n \text{BW}[\text{M} \rightarrow \text{O}(6)]$	1.00	0.84	0.63	0.20
$\langle \text{M-O} \rangle$	2.00	2.00	2.00	2.00
$\langle {}^1 d(\text{M} \rightarrow \text{O}) \rangle$	2.00	2.00	1.98	1.90
$\langle {}^n d(\text{M} \rightarrow \text{O}) \rangle$	2.00	2.00	1.98	1.91
${}^1 \text{ECoN}$	6.00	5.93	5.62	4.46
${}^n \text{ECoN}$	6.00	5.93	5.69	4.73

corrects this artifact. The classical coordination number is 6 in all cases but the weight of the longer bonds decreases rapidly and ECoN shows that in the last case the total contribution of the six oxygen atoms to the coordination of M is less than 5.

In the above equations the only empirical parameter is the exponent 6. It was chosen because it resulted in ${}^1 \text{ECoN}$ identical with the classical coordination number for simple and regular structures [9]. This exponent, and thus also Eqs. (8)–(11), does not depend either on the type of structure or on the experimental conditions.

Charge Distribution

So far, the analysis of the coordination polyhedra has been purely geometric. The next step consists in introducing the chemical specificity, and this is obtained by *distributing* the formal oxidation numbers, $q(ij)$ and $q(rs)$, among the chemical bonds as a function of the bond weights, through the contribution by the $A(rs)$ anion to ${}^n \text{ECoN}(ij \rightarrow r)$:

$$\Delta^n \text{ECoN}(ij \rightarrow rs) = \frac{\sum_L m(ij \rightarrow rs)_L {}^n \text{BW}(ij \rightarrow rs)_L}{{}^n \text{ECoN}(ij \rightarrow r)} \quad (12)$$

The fraction of $q(ij)$ that the cation $M(ij)$ shares with the anion $A(rs)$ is obtained by multiplying $\Delta^n \text{ECoN}$ by $q(ij)$:

$$\Delta q(ij \rightarrow rs) = \Delta^n \text{ECoN}(ij \rightarrow rs) q(ij) F(ij \rightarrow r), \quad (13)$$

where $F(ij \rightarrow r)$ is a scale factor: for structures with only one species of anions, $F(ij \rightarrow r) = 1$ (for details, see [12]). The computed ‘charge’ of the anions is then obtained by summing up $\Delta q(ij \rightarrow rs)$, taking however into account the ratio of the multiplicities of the respective Wyckoff positions (to avoid counting more than once the contributions from the same ion):

$$Q(rs) = - \sum_i \sum_j \Delta q(ij \rightarrow rs) \frac{h(ij)}{h(rs)} \quad (14)$$

The ‘charge’ of the cation $M(ij)$ is computed as the weighted sum of $q(rs)/Q(rs)$ for the anions $A(rs)$ bonded to $M(ij)$, where the weight is the fraction of shared $q(ij)$ defined by Eq. (13):

$$Q(ij) = \sum_r \sum_s \Delta q(ij \rightarrow rs) \frac{q(rs)}{Q(rs)} = \left[\sum_r \sum_s \Delta^n \text{ECoN}(ij \rightarrow rs) \frac{q(rs)}{Q(rs)} F(ij \rightarrow r) \right] q(ij). \quad (15)$$

A structure which is correctly solved and perfectly valence-balanced has both $q(rs)/Q(rs)$ and $q(ij)/Q(ij)$ ideally equal to 1. Structural strains affect $q(rs)/Q(rs)$, which deviates from 1: in this case we speak of *over- or under-bonding (OUB) effect*. When a real OUB effect is present, some $q(rs)/Q(rs)$ ratios deviate from 1, but all the $q(rs)/Q(rs)$ ratios corresponding to the $A(rs)$

bonded the cation $M(ij)$ enter in the calculation of $Q(ij)$ in Eq. (15), and $q(ij)/Q(ij)$ should not be affected by the OUB effect. Reasons for $q(ij)/Q(ij)$ significantly deviating from 1 can be: 1) the refined structure model is inadequate including overlooked (light) atoms and disorder; 2) wrong assignment of oxidation numbers, including the case of sites with isomorphous substitutions; 3) presence of M-M or A-A bonds, which are not accounted for by the $M(ij) \rightarrow A(rs)$ bonding pattern assumed by the CD method; 4) the coordination of one or more cations is so distorted that the polyhedral description is too approximate. When instead $q(ij)/Q(ij)$ is reasonably close to 1, $Q(rs)$, ${}^n\text{ECoN}(ij \rightarrow r)$ and, with reference to each bond, ${}^n\text{BW}(ij \rightarrow r)_L$, are suitable parameters to investigate structural changes, e.g. as a function of composition, temperature and pressure [11, 13]. The $q(ij)/Q(ij)$ ratio is thus the internal criterion to evaluate the reliability of the structure and the applicability of the method. An analogous criterion is instead not available in the BV method.

The bond valence computed through the empirical curves, Eq. (3), is interpreted as the number of electrons pairs associated with a bond [14]. Instead, the bond weight, Eq. (9), is a purely geometric quantity that depends only on the geometrical features (size, distortion, etc.) of the coordination polyhedra. The chemical specificity enters *a posteriori*, through Eq. (13). Besides, the ‘charges’ are the result of the *distribution* of the formal oxidation numbers, whereas the empirical curves compute the ‘charges’ directly from the bond distances.

Example 1: investigation of the cation distribution

The structure of $\text{LuFeZn}_4\text{O}_7$ was refined [15] during a study of the polysomatic series $\text{LuFeO}_3(\text{ZnO})_n$ (for details about polysomatic series see [16]). The structure was refined by single-crystal X-ray diffraction, but the distribution of Fe among the M sites could not be determined because of the presence of the much heavier Lu atom. Different ordering models gave practically the same agreement with the experimental data, leaving unanswered the question about the distribution of Fe.

The cation ordering can be investigated by CD analysis, because of the different $q(ij)$ (2 vs. 3) of Zn and Fe.

Table 2 gives the analysis of the geometry of the coordination polyhedra in $\text{LuFeZn}_4\text{O}_7$ in terms of ECoN and its components. Lu occupies a regular octahedron; sites X1 and X2 are undistorted and distorted trigonal bipyramids respectively, and X3 is a trigonal pyramid, very close to a tetrahedron. X2 is significantly less regular than X1, as shown by ${}^n\text{ECoN}$ (4.03 vs. 4.34) and by the very small bond weight X2-O1.

Table 3 (see [17]) gives the Charge Distribution analysis for two models: Fe disordered among the three X sites (upper half) and Fe avoiding X3 (as suggested

Table 3. Charge Distribution for $\text{LuFeZn}_4\text{O}_7$ for two different model of Fe ordering: complete disorder (upper half) and partial order in the sites X1 and X2 (lower half) (after [17])

Site	Occupation	q	CD		BV [3]	
			Q	q/Q	Q	q/Q
Lu	Lu	3.00	2.88	1.04	3.20	0.94
X1	Zn/Fe : 4/1	2.20	2.40	0.92	2.23	0.99
X2	Zn/Fe : 4/1	2.20	2.22	0.99	2.04	1.08
X3	Zn/Fe : 4/1	2.20	2.14	1.03	1.95	1.13
	σ		0.14		0.21	
O1	O	-2.00	-1.79	1.12	-1.92	1.04
O2	O	-2.00	-1.98	1.01	-1.86	1.08
O3	O	-2.00	-2.05	0.98	-1.78	1.12
O4	O	-2.00	-2.08	0.96	-2.10	0.95
	σ		0.13		0.17	
Lu	Lu	3.00	2.96	1.01	3.20	0.94
X1	Zn/Fe : 2/1	2.33	2.41	0.97	2.27	1.03
X2	Zn/Fe : 2/1	2.33	2.27	1.03	2.08	1.12
X3	Zn	2.00	2.05	0.98	1.88	1.06
	σ		0.07		0.20	
O1	O	-2.00	-1.90	1.05	-1.96	1.02
O2	O	-2.00	-2.09	0.96	-1.89	1.06
O3	O	-2.00	-1.93	1.04	-1.75	1.14
O4	O	-2.00	-2.03	0.99	-2.09	0.96
	σ		0.09		0.17	

Table 2. Analysis of the coordination polyhedra for $\text{LuFeZn}_4\text{O}_7$ (bond distances after [15]). X1~X3 indicate the three cation sites occupied by Fe and Zn (see Table 3). $h(ij)$ and $h(rs)$ are the multiplicities of the Wyckoff positions occupied by cations and anions respectively

$M(ij)$	$h(ij)$	$A(rs)$	$h(rs)$	$d(ij \rightarrow rs)$	$\langle M-O \rangle$	$\langle {}^n d(ij \rightarrow r) \rangle$	${}^n\text{BW}(ij \rightarrow rs)$	${}^n\text{ECoN}(ij)$
Lu	2	O4	4	2.207 ($\times 6$)	2.207	2.207	1.00	6.00
X1	2	O1	2	1.929 ($\times 3$)	2.033	1.979	1.16	4.34
		O2	4	2.190 ($\times 2$)			0.44	
X2	4	O2	4	1.959 ($\times 3$)	2.094	1.983	1.07	4.03
		O3	4	2.056			0.79	
		O1	2	2.535			0.03	
X3	4	O4	4	1.969	1.986	1.985	1.05	4.00
		O3	4	1.992 ($\times 3$)			0.98	

by the fact that in general Zn preferentially occupies tetrahedral sites [18]). The overall deviation of Q with respect to q is measured by the parameter

$$\sigma = \left\{ \sum_{ij} [q(ij) - Q(ij)]^2 / N - 1 \right\}^{1/2} \quad (16)$$

which reduces to the classical standard uncertainty for atoms all with the same q .

The disordered model results in $Q(ij)$ significantly deviating from $q(ij)$ for Lu and X1 and a high σ , whereas the model with only Zn in X3 gives a much better agreement for all the cationic sites and a much lower σ . The strong OUB suggested for O1 by the disordered model is unlikely and comes from the imprecision of the model itself. The partially ordered model confirms the underbonding of O1, but drastically reduces it to a much more reasonable value.

For the sake of comparison, in Table 3 the BV analysis according to the Brow-Wu [3] curve is also given. The two models are practically not differentiated, showing that the BV approach is less sensible to details like the isomorphous substitution of atoms with close atomic numbers.

Example 2: distorted polyhedra, and the vanadyl group

The structure of $K_2V_3O_8$ [19] contains three crystallographically independent cation-centered coordination polyhedra. The K-centered polyhedron, as often occurs for alkali metals, spans a wide range of bond lengths, where it is difficult to quantitatively separate bonding and non-bonding contacts. The V1-centered square pyramid is typical of the vanadyl group, with one unusually short bond and four much longer bonds. The V2-centered polyhedron is instead a distorted tetrahedron in which the shortest and the longest bonds are almost equally separated from the two central bonds, which in their turn are close to the arithmetic mean distance $\langle M-O \rangle$. Table 4 shows that for the V2-centered tetrahedron the iterative calculation converges almost immediately, resulting in $\langle {}^n d(ij \rightarrow r) \rangle$ practically identical to $\langle {}^1 d(ij \rightarrow r) \rangle$ and close to $\langle M-O \rangle$.

Instead, for the K1- and V1-centered polyhedra $\langle {}^1 d(ij \rightarrow r) \rangle$ is too short, resulting in bond weights and ECoN unrealistically low. This effect is compensated by the iterative algorithm, which gradually lengthens the average bond length until convergence. The corresponding CD analysis is given in Table 5. Without iteration, a strong OUB is reported for O3 and O4, but the lack of agreement on the cations indicates that such OUB is not realistic. The iterative calculation (CD-IT) leads instead to complete agreement on the cations, substantiating thus the figures on the anions. The OUB on O3 is confirmed, although reduced in value, whereas that on O4 almost disappears. The *underbonding* on O4 and especially on O3 is only apparently larger than the *overbonding* on O1 and O2 and comes from the different multiplicities of the Wyckoff positions occupied by the oxygen atoms.

The BV analysis indicates strong overbonding on all cations and on three of the four anions, which clearly derives from the inadequateness of the method to analyze structures with distorted coordination polyhedra like those of the present example.

Table 5. Charge Distribution for $K_2V_3O_8$ [19] without (CD) and with (CD-IT) iteration. For comparison, the results of the BV computation according to two different empirical curves are also given

Site	q	CD		CD-IT		BV [3]		BV [4]	
		Q	q/Q	Q	q/Q	Q	q/Q	Q	q/Q
K	1.00	1.00	0.99	0.99	1.01	1.29	0.92	1.25	0.80
V1	4.00	3.69	1.08	4.02	1.00	4.24	0.94	4.31	0.93
V2	5.00	5.15	0.97	5.00	1.00	5.23	0.96	5.27	0.95
σ		0.24		0.02		0.31		0.34	
O1	-2.00	-1.93	1.04	-2.04	0.98	-2.18	0.92	-2.24	0.89
O2	-2.00	-2.06	0.97	-2.03	0.98	-2.27	0.88	-2.17	0.92
O3	-2.00	-1.79	1.12	-1.82	1.10	-2.11	0.95	-2.18	0.91
O4	-2.00	-2.34	0.84	-1.93	1.04	-1.89	1.06	-1.85	1.08
σ		0.25		0.11		0.21		0.22	

Table 4. Analysis of the coordination polyhedra for $K_2V_3O_8$ [19]

$M(ij)$	$h(ij)$	$A(rs)$	$h(rs)$	$d(ij \rightarrow rs)$	$\langle M-O \rangle$	$\langle {}^1 d(ij \rightarrow r) \rangle$	${}^1 BW(ij \rightarrow rs)$	${}^1 ECoN(ij)$	$\langle {}^n d(ij \rightarrow r) \rangle$	${}^n BW(ij \rightarrow rs)$	${}^n ECoN(ij)$
K	4	O2	4	2.430	3.069	2.573	1.34	3.25	2.662	1.53	4.20
		O1	8	2.673 ($\times 2$)			0.77			0.98	
		O3	2	3.090			0.14			0.24	
		O2	4	3.191 ($\times 2$)			0.07			0.14	
		O1	8	3.298 ($\times 2$)			0.03			0.07	
		O4	2	3.422 ($\times 2$)			0.01			0.03	
V1	2	O4	2	1.582	1.872	1.674	1.34	2.26	1.761	1.61	3.38
		O1	8	1.945 ($\times 4$)			0.23			0.44	
V2	4	O2	4	1.628			1.22			1.23	
		O1	8	1.700 ($\times 2$)	1.706	1.690	0.97	3.80	1.692	0.97	3.83
		O3	2	1.794			0.65			0.66	

Table 6. Analysis of the coordination polyhedra for CaFeSi₂O₆ at two different pressures [20]

<i>p</i> (GPa)	M(<i>ij</i>)	<i>h</i> (<i>ij</i>)	A(<i>rs</i>)	<i>h</i> (<i>rs</i>)	<i>d</i> (<i>ij</i> → <i>rs</i>)	⟨M-O⟩	⟨ ¹ <i>d</i> (<i>ij</i> → <i>r</i>)⟩	¹ BW(<i>ij</i> → <i>rs</i>)	¹ ECoN(<i>ij</i>)	⟨ ⁿ <i>d</i> (<i>ij</i> → <i>r</i>)⟩	ⁿ BW(<i>ij</i> → <i>rs</i>)	ⁿ ECoN(<i>ij</i>)		
0	Ca	4	O4	8	2.334 (×2)	2.509	2.416	1.21	6.46	2.429	1.24	6.89		
			O1	8	2.352 (×2)								1.16	1.19
			O3	8	2.632 (×2)								0.51	0.54
			O3	8	2.721 (×2)								0.35	0.38
	Fe	4	O2	8	2.085 (×2)	2.128	2.125	1.11	5.95	2.125	1.11	5.95		
			O1	8	2.136 (×2)								0.97	0.97
			O1	8	2.162 (×2)								0.90	0.90
	Si	8	O2	8	1.584	1.634	1.626	1.16	3.89	1.627	1.16	3.90		
			O1	8	1.600								1.10	1.10
			O3	8	1.667								0.85	0.86
			O3	8	1.685								0.79	0.79
	9.9	Ca	4	O4	8	2.296 (×2)	2.429	2.375	1.20	7.06	2.382	1.22	7.20	
O1				8	2.306 (×2)	1.18								1.20
O3				8	2.536 (×2)	0.62								0.64
O3				8	2.577 (×2)	0.53								0.55
Fe		4	O2	8	2.036 (×2)	2.079	2.076	1.12	5.95	2.076	1.12	5.95		
			O1	8	2.094 (×2)								0.95	0.95
			O1	8	2.107 (×2)								0.91	0.91
Si		8	O2	8	1.567	1.618	1.609	1.15	3.87	1.610	1.15	3.88		
			O1	8	1.575								1.13	1.13
			O3	8	1.654								0.83	0.84
			O3	8	1.675								0.76	0.76

Example 3: structures at non-ambient conditions

Table 6 gives the geometrical analysis of the coordination polyhedra of CaFeSi₂O₆, a compound belonging to the pyroxene group [20], at zero and at 9.9 GPa. The close values of ¹ECoN and ⁿECoN, and of ⟨¹*d*(*ij*→*r*)⟩ and ⟨ⁿ*d*(*ij*→*r*)⟩ to ⟨M-O⟩ shows that all Fe- and Si-centered polyhedra have limited distortion, whereas Ca-centered polyhedron is more distorted, as usual in the compounds with the structure of pyroxenes [11].

Table 7 shows the CD and BV analysis. The CD (without iteration) and CD-IT (with iteration) calculations give practically identical results: because of the

limited distortion of the polyhedra, the iterative algorithm converges almost immediately. The results of the calculation employing the empirical curves show less good, but still reasonable, figures for the structure at 0 GPa, but completely meaningless figures for the structures at 9.9 GPa. The comparable quality of the refinement at the two pressures is confirmed by the CD calculation. The bad results of the BV calculation clearly derive by using for a high-pressure structure empirical parameters that were obtained on a set of structures at ambient conditions.

Discussion**Table 7.** Charge Distribution for CaFeSi₂O₆ [20] at two different pressures. For comparison, the results of the BV computation according to two different empirical curves are also given

Site	<i>q</i>	0 GPa								9.9 GPa							
		CD		CD-IT		BV [3]		BV [4]		CD		CD-IT		BV [3]		BV [4]	
		<i>Q</i>	<i>q/Q</i>														
Ca	2.00	2.00	1.00	2.00	1.00	1.97	1.01	1.87	1.07	2.00	1.00	2.00	1.00	2.29	0.87	2.44	0.82
Fe	2.00	1.96	1.02	1.96	1.02	2.15	0.93	2.08	0.97	1.97	1.02	1.97	1.02	2.44	0.82	2.37	0.84
Si	4.00	4.02	1.00	4.02	1.00	3.91	1.02	3.92	1.02	4.02	1.00	4.01	1.00	4.08	0.98	4.09	0.98
σ		0.03		0.03		0.13		0.08		0.03		0.03		0.38		0.41	
O1	-2.00	-2.11	0.95	-2.11	0.95	-2.06	0.97	-2.07	0.97	-2.13	0.94	-2.13	0.94	-2.27	0.88	-2.29	0.87
O2	-2.00	-1.94	1.03	-1.93	1.04	-1.84	1.09	-1.87	1.07	-1.90	1.06	-1.89	1.06	-1.97	1.02	-2.00	1.00
O3	-2.00	-1.96	1.02	-1.96	1.02	-2.06	0.97	-2.04	0.98	-1.98	1.01	-1.98	1.01	-2.20	0.91	-2.20	0.91
σ		0.10		0.10		0.13		0.11		0.12		0.12		0.24		0.25	

The CD method represents the most recent approach based on Pauling's idea of bond strength. Differently from other methods, it consists essentially of a geometrical analysis of the coordination polyhedra, whose details are used for structure validation and to investigate details that may be hardly determined in other ways, like the isomorphous substitution of atoms with close atomic numbers. When applied to compounds belonging to the same structural series or with common features, it may also reveal some definite trend as a function of composition, temperature and pressure [11, 12]. Differently from methods employing empirical curves, the CD method can analyze equally well structures determined at ambient conditions and under extreme conditions.

As shown in the examples above, the CD method applies equally well to both ionic and covalent bonds. However, the term 'charge' applied to the weighted sum of the bond weights, Eqs. (13)–(15), reflects essentially an ionic model of the chemical bond, where the computed 'charges' $Q(ij)$ and $Q(rs)$ are completely concentrated on the cations and the anions respectively. Therefore, the figures shown by $Q(ij)$ and $Q(rs)$ do not have the same meaning of, *e.g.*, the Mulliken population. The deviation from q shown by these two methods may even be in opposite directions, especially when the covalent character of the bond is relevant, simply because of the different meaning of the two analyses. The OUB effect as measured by the $Q(rs)$ is essentially a *geometrical* effect that has to be interpreted in terms of the adimensional bond weights.

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