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REVISION 2

TITLE: The valence quadrupole moment

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## Abstract

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The bond-valence model has recently been expanded to include a directional component,

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the vectorial bond-valence sum, which is useful for characterizing non-centrosymmetric

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distortions involving lone-pair and second-order Jahn-Teller effects. Here we show that the

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bond-valence sum and vectorial bond-valence sum are equivalent to monopole and dipole terms

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in a multipole expansion of the bond valence incident to an atom. We then extend the multipole

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expansion to include a quadrupole term, which describes the ellipsoidal deviation from spherical

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symmetry of the bonding environment, and is useful for characterizing centrosymmetric

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distortions, such as those caused by first-order Jahn-Teller effects. These distortions follow

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characteristic patterns in valence space, which depend upon factors that include the *d*-orbital

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configuration and size of the transition metal involved. This extended approach, called the

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Valence Multipole Model, should prove useful for modeling molecular and crystal structures,

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including those associated with spin transitions.

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**Keyword:** Bond valence, vectorial bond-valence model, valence multipole model, bond angle,

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molecular mechanics, Jahn-Teller effect, crystal field effects

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## Introduction

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Molecular modeling has become increasingly important for exploring the physical and chemical properties of materials, including both known minerals and minerals hypothesized to exist in the mantle (Cygan, 2001; Stixrude, 2001). Quantum mechanics (QM) provides a powerful theoretical framework for understanding structure-property and structure-reactivity relationships, but direct application of the theory is often too computationally expensive for the large numbers of atoms and the longer simulation times frequently needed to simulate geochemically significant materials and processes. Therefore, classically derived methods like molecular mechanics (MM) are often used to reduce computational expense.

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MM methods treat systems of atoms as “balls on springs,” where bond lengths and bond angles between particular atom types are given an ideal value, and simple energy cost functions are assigned for deviations from those ideal values. This approach to partitioning the potential energy surface is fraught with difficulties. One pervasive problem is that no single ideal value for bond lengths and bond angles exists (Rappé and Casewit, 1997; Hinchliffe, 2003), so MM methods tend to predict structures with unrealistically high symmetry (Comba et al., 2009). Furthermore, ideal bond lengths and angles depend strongly on coordination number (Rappé and Casewit, 1997; Hinchliffe, 2003; Comba et al., 2009). MM force fields often address this by treating two atoms of the same element with different coordination numbers, as fundamentally different atom types; but this solution precludes simulating chemical reactions involving coordination number changes. Furthermore, bond lengths and angles can also be strongly coupled (Rappé and Casewit, 1997; Hinchliffe, 2003; Comba et al., 2009). MM force fields sometimes include higher-order terms to correct for such multi-body effects, but this complicates the potential energy model, multiplying the number of adjustable parameters and requiring the

66 computation to keep track of more complicated spatial relationships than the traditional atom-  
67 pair distances and bond angles (Hinchliffe, 2003; Cramer, 2004).

68 It would be useful, therefore, to develop mathematically simpler methods for mimicking  
69 multi-body effects in force fields. The bond-valence model (BVM) is an obvious choice to  
70 address at least part of this problem, and in fact, bond-valence terms have been included in a few  
71 MM force fields and related molecular-scale models (Lufaso and Woodward, 2001; Adams and  
72 Swenson, 2002; Grinberg et al., 2002; Cooper et al., 2003; Adams et al., 2004; Grinberg et al.,  
73 2004; Shin et al., 2005; Adams and Rao, 2009; Liu et al., 2013a; Liu et al., 2013b; Takenaka et  
74 al., 2013; Adams and Rao, 2014). The BVM (see Theory section below) posits that bond lengths  
75 can be converted into “bond valence” units using a simple, empirically calibrated equation, and  
76 that the valence of all bonds incident to an atom should ideally sum to exactly cancel out the  
77 atomic valence (i.e., oxidation number) of that atom. (Essentially, the BVM is a method for  
78 relating bond length to bond order.) This rule, called the “valence-sum rule,” is usually obeyed  
79 quite closely in real crystal structures, and anomalous structures are almost always unstable  
80 (Brown, 2002). This instability suggests there is an energy penalty for deviation from this ideal.  
81 An energy cost function based on deviation from the valence-sum rule, however, would be  
82 different than typical pair-wise or multi-body terms in MM force fields, because it would be a  
83 multi-body term that takes into account the total bonding environment of an atom, but does so  
84 simply by summing pair-wise terms (bond valences.)

85 The BVM is not a panacea, though, because its quantitative aspect (the valence-sum rule)  
86 deals only with bond lengths, and has nothing to do with the spatial arrangement of bonds. Part  
87 of this problem has recently been addressed via the “vectorial bond-valence model” (VBVM),  
88 which may provide a way to predict favorable bond angle configurations. Again, this is based on

89 the multi-body summations of pair-wise terms. Harvey et al. (2006) showed that if we treat each  
90 bond as a vector in the direction from the cation to the anion centers and magnitude equal to the  
91 bond valence, even distorted coordination polyhedra about group 12 cations tend to result in  
92 vector sums close to zero. Bickmore et al. (2013) used a database of 178 simple oxide structures  
93 to demonstrate that this is a general result for all atoms *not* subject to noncentrosymmetric  
94 distortions, caused by electronic structure effects such as lone-pair and second-order Jahn-Teller  
95 (SOJT) effects. They also showed that non-zero, vectorial bond-valence sums caused by such  
96 noncentrosymmetric distortions vary systematically as a function of the strongest bond valence  
97 incident to the atom, and finally that outliers with respect to these trends tend to be metastable  
98 under ambient conditions.

99         The VBVM, as presently formulated, is not complete, however. It is not sensitive to  
100 centrosymmetric distortions, such as those caused by first-order Jahn-Teller (FOJT) effects,  
101 because these require no change to the vectorial bond-valence sums. Including FOJT effects in a  
102 molecular mechanics framework is quite difficult (Comba et al., 2009), so a mathematically  
103 simple method to address this across a broad range of conditions would be quite helpful.

104         In this contribution, therefore, we introduce a further expansion of the BVM to address  
105 both noncentrosymmetric and centrosymmetric distortions by introducing a new valence-based  
106 structural descriptor called the “valence quadrupole moment.” This quantity describes how  
107 spherically symmetrical the distribution of bond valences is about an atom, and is highly  
108 predictable on the basis of the magnitudes of the incident bond valences.

109         We call this expanded model the Valence Multipole Model (VMM). With the VMM, a  
110 mathematically simple, multi-body approach to predicting the effects of bonded interactions on  
111 coordination geometries in a very large number of compounds may be within reach.

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## Theory

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119 The Bond-Valence Model (BVM)

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$$S_i + V_i = 0 \text{ v.u.} \quad (1)$$

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The VMM encompasses the VBVM, which encompasses the BVM. Every stage in this gradual expansion has involved showing how bond valence can be used to describe and predict more aspects of molecular structures. In this section, we briefly describe the theory behind these models, including our new valence quadrupole moment term.

The BVM was developed to rationalize physically reasonable structures in systems where the bonds are between cation-anion pairs. In a quantitative sense, however, the model has primarily been useful for predicting plausible combinations of cation-anion bond lengths in such systems (Brown 2002). A plausible combination of bond lengths incident to ion  $i$  is one in which the valence-sum rule (Eqn. 1) is obeyed, i.e., the sum of bond valences between ion  $i$  and its bonded atoms  $j$  ( $S_i = \sum_j s_{ij}$ ) exactly negates the atomic valence of ion  $i$  ( $V_i$ ).

The atomic valence of an ion is equivalent to its oxidation number, and represents the number of valence electron states available for polar bonding. The valence of a bond is taken to be negative when incident to a cation and positive when incident to an anion, and bond valence is measured in valence units (v.u.) There are ways to address fully covalent bonds in the BVM (O'Keeffe and Brese, 1992; Wander et al., 2015a), but we neglect these here.

When applied only to polar bonds (c.f. Wander et al., 2015a), bond valence is sometimes equated with the electric flux between atomic centers, in which case Eqn. 1 is simply a reformulation of Gauss's Law, which must always be exactly fulfilled (Preiser et al., 1999;

135 Brown, 2002; 2014). In practice, however, one estimates bond valence by means of empirical  
136 correlations between bond length and valence, derived by assuming Eqn. 1 and applying a  
137 mathematical model such as Eqn. 2 to the bond lengths in a calibration set of experimentally  
138 derived, stable crystal structures (c.f. Wander et al., 2015b). Here,  $R$  is the bond length between  
139 ion  $i$  and a counter-ion  $j$ , whereas  $R_o$  and  $B$  are empirically derived parameters specific to a given  
140 cation-anion pair.

$$141 \quad |s_{ij}| = e^{((R_o - R)/B)} \quad (2)$$

142 The assumption that bond valence is predictable solely on the basis of bond length may  
143 not be exactly true, on the one hand, and therefore bond-valence sums calculated via such  
144 estimates may not strictly follow the valence-sum rule. On the other hand, Eqn. 2 does appear to  
145 be useful for expressing ideal values of bond valence for a given bond length, and apparent  
146 deviations from the valence-sum rule carry some energy cost (Lufaso and Woodward, 2001;  
147 Brown, 2002; Adams et al., 2004; Adams and Rao, 2009; Brown, 2009; Perez-Mato et al., 2009;  
148 Bickmore et al., 2013; Adams and Rao, 2014; Bickmore, 2014).

149 Although the BVM is mathematically and conceptually simple, it is powerful in that it is  
150 usually quantitatively accurate, and its predictions concern combinations of bond lengths, rather  
151 than single bonds.

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### 153 The Vectorial Bond-Valence Model (VBVM)

154 The valence-sum rule predicts acceptable combinations of bond lengths about a central  
155 ion, but does not address bond directionality. The VBVM addresses directionality by treating  
156 bonds as vectors ( $\vec{s}_{ij}$ ) with direction from cation center to anion center and magnitude equal to  
157 the bond valence. The valence vectors representing bonds incident to a given ion are summed

158  $(\vec{S}_i = \sum_j \vec{s}_{ij})$ , and the norm (i.e., magnitude) of the vectorial bond-valence sum ( $\|\vec{S}_i\|$ ) is taken  
159 as a single-parameter descriptor of the lopsidedness of the bonding distribution.

160  $\|\vec{S}_i\|$  turns out to be fairly predictable. Harvey et al. (2006), for instance, showed that  
161  $\|\vec{S}_i\| \approx 0$  v.u. for the Group 12 cations they examined, even when the coordination polyhedra  
162 were significantly distorted. But what of ions for which electronic structure effects (e.g., lone-  
163 pair and second-order Jahn-Teller effects) dictate that the coordination sphere should ideally be  
164 noncentrosymmetrically distorted? Bickmore et al. (2013) showed that while such distortions  
165 result in  $\|\vec{S}_i\| \neq 0$ , they are still predictable as a function of the valence of the strongest bond ( $s_1$ )  
166 incident to the central ion in the suite of 178 simple oxides studied. Trends for ions of the same  
167 type, but different oxidation states, tend to differ, but collapse into a single trend when  $\|\vec{S}_i\|$  is  
168 plotted vs. the “minimum coordination number” ( $N_{min} = V_i/s_1$ ). They also showed that the  
169 trends discovered are completely consistent with the predictions of the valence shell electron pair  
170 repulsion (VSEPR) model (Gillespie and Hargittai, 1991; Müller, 2007).

171 We once again have a simple, yet predictable, multi-body structural descriptor ( $\|\vec{S}_i\|$ )  
172 based on summation of pair-wise terms. This multi-body term does not dictate any particular  
173 bond length or angle, but especially when combined with the valence-sum rule (Eqn. 1), does put  
174 stringent constraints on acceptable combinations of bond lengths and bond angles about each ion  
175 in a structure.

176 Another important point brought out by this work is that bond valence is an effective  
177 means of transforming bond lengths between disparate ion pairs into a common currency that (at  
178 least when normalized to the atomic valence of a central ion) implies consistent effects on  
179 bonding geometry. This should prove important for structural modeling, because it will make it  
180 easier to incorporate new atom types into force fields.



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## 182 Centrosymmetric Distortions and the Ligand Field Theory

183 While  $\|\vec{S}_i\|$  is useful for quantifying the lopsidedness of the distribution of bond valence  
184 about an ion due to noncentrosymmetric distortions of the coordination sphere, it is incapable of  
185 putting constraints on centrosymmetric distortions such as are commonly associated with  
186 unevenly filled *d*-subshells in transition metals. Here we employ ligand field theory (LFT) to  
187 qualitatively describe the origin and nature of these distortions (e.g., Burns, 1993; Müller, 2007).

188 Just as the VSEPR model explains the spatial distribution of bonds about main group  
189 elements in terms of repulsion between bonding and lone electron pairs, LFT explains the spatial  
190 distribution of bonds about transition metals in terms of mutual repulsion between bonding  
191 electron pairs and nonbonding valence electrons, which are generally in *d*-subshells of transition  
192 metals. The five orbitals in a *d*-subshell have lobes of electron probability density oriented in  
193 various directions, and when populated evenly are spherically symmetrical. Thus, bonding  
194 electron pairs will have no preferred direction, and will spread out as symmetrically as possible.  
195 When the *d*-orbitals are populated unevenly, however, the bonding orbitals tend to be repelled  
196 more from the more populated *d*-orbitals, raising the energy levels of the *d*-orbitals oriented  
197 closest to the bonding orbitals and lowering the energy levels of the others. The result is that  
198 certain coordination numbers are favored more than they otherwise would be, given the cation-  
199 anion radius ratio, and certain distortions of the coordination polyhedron may also be favored.

200 Some of the favored distortion types are due to the first-order Jahn-Teller (FOJT) effect,  
201 which results in centrosymmetric distortions of the first coordination sphere. In fact, all *d*-orbital  
202 configurations except  $d^0$ ,  $d^5$  (high-spin), and  $d^{10}$  are expected to produce such distortions, but  
203 with some configurations the effect is so small as to be negligible, while in others the effect is

204 quite strong. Ligand octahedra, for instance, tend to elongate parallel to  $d_{z^2}$ , while the bonds  
205 parallel to  $d_{x^2-y^2}$  contract, or (rarely) vice versa. This effect is especially strong for  $d^4$  (high-  
206 spin),  $d^7$  (low-spin), and  $d^9$  configurations. Ligand tetrahedra about  $d^4$  (high-spin),  $d^8$ , and  $d^9$   
207 transition metals tend to flatten toward a square planar configuration to allow the bonded  
208 electron pairs to avoid preferentially filled  $t_{2g}$  orbitals, or in the case of  $d^8$ , to avoid all but  
209  $d_{x^2-y^2}$ . To a lesser degree, the ligands about  $d_3$  and  $d_8$  transition metals might distort in a  
210 scissoring motion toward an elongated tetrahedral configuration to avoid preferentially filled  $e_g$   
211 orbitals (Müller, 2007).

212 In all these cases, the distortion is centrosymmetric and total bond valence is conserved,  
213 so neither  $S_i$  nor  $\|\vec{S}_i\|$  changes. The spherical symmetry of the coordination spheres does  
214 change, however.

215

## 216 The Valence Quadrupole Moment

217 Ellipsoidal deviation from spherical symmetry can be quantified in terms of a quadrupole  
218 moment, which is the third (second-order) term of a multipole expansion, a mathematical series  
219 used to approximate an arbitrary function that depends on angles. It is used primarily to describe  
220 distributions in three-(or higher)-dimensional space. A multipole expansion includes a monopole  
221 moment (a scalar, or zeroth-order tensor), a dipole moment (a 3x1 vector, or first-order tensor), a  
222 quadrupole moment (a 3x3 matrix, or second-order tensor), and higher-order terms such as an  
223 octupole moment, etc. Frequently, a multipole expansion is truncated after the first few terms,  
224 because it will still usefully approximate the complete function for a local environment.

225 Truncated multipole expansions are commonly used as simplified descriptions of the spatial

226 distribution of electric charge in electric fields and the distribution of mass in gravitational fields  
227 (e.g., Pijpers, 1998; Hinchcliffe, 2003; Bambi, 2011).

228 To generate a multipole expansion, one performs a Taylor series expansion around a  
229 function that is assumed to obey the Laplace Equation (Jackson, 1998), e.g., electrostatic and  
230 gravitational fields. For instance, consider an arbitrary distribution of  $N$  point charges  $q_i$  with  
231 position vectors  $\vec{r}_i$ . The electric potential ( $\Phi$ ) at position  $\vec{R}$  outside the distribution can be  
232 calculated using Eqns. 3-6, where  $\epsilon_0$  is the permittivity of a vacuum,  $\alpha$  and  $\beta$  are the Cartesian  
233 unit vectors:  $x$ ,  $y$ , and  $z$ , and  $R$  or  $r_i$  represents the distance from the origin to position  $\vec{R}$  or  $\vec{r}_i$ ,  
234 respectively.  $\delta_{\alpha\beta}$  is the Kronecker delta, which is one in the case that direction  $\alpha$  equals direction  
235  $\beta$ , but otherwise zero.

$$236 \quad 4\pi\epsilon_0\Phi = \left[\frac{q_{tot}}{R}\right] + \left[\frac{1}{R^3}\sum_{\alpha=x,y,z}P_{\alpha}R_{\alpha}\right] + \left[\frac{1}{6R^5}\sum_{\alpha=x,y,z}\sum_{\beta=x,y,z}Q_{\alpha\beta}(3R_{\alpha}R_{\beta} - \delta_{\alpha\beta}R^2)\right] + \dots \quad (3)$$

$$237 \quad q_{tot} = \sum_i^N q_i \quad (4)$$

$$238 \quad P_{\alpha} = \sum_i^N q_i r_{i\alpha} \quad (5)$$

$$239 \quad Q_{\alpha\beta} = \sum_i^N q_i (3r_{i\alpha}r_{i\beta} - \delta_{\alpha\beta}\|\vec{r}_i\|^2) \quad (6)$$

240 In Eqn. 3, the first bracketed term is the electric monopole, the second is the dipole, and  
241 the third is the quadrupole. The monopole represents the overall charge within a certain volume,  
242 the dipole represents the linear distribution of the charges about a central location, and the  
243 quadrupole represents their spherical distribution (Hinchcliffe, 2003). If we want to describe the  
244 distribution of bond valence about a central atom, we might instead perform a multipole  
245 expansion on the bond-valence vectors ( $\vec{s}_{ij}$ ), with the central atom at the origin of this “valence  
246 space.” In this case, the bond valence sum ( $S_i$ ) is the monopole moment, the vectorial bond  
247 valence sum ( $\vec{S}_i$ ) is the dipole moment, and we define the valence quadrupole moment ( $\Theta_i$ ) as  
248 follows.

249 We find it most useful to define the valence quadrupole moment about central atom  $i$   
 250 ( $\Theta_i$ ) in terms of bond-valence vectors ( $\vec{s}_{ij}$ ) normalized to the valence sum ( $S_i$ ). Eqn. 7  
 251 describes these “fractional” bond-valence vectors ( $\vec{p}_{ij}$ ), and Eqns. 8-9 describe  $\Theta_i$ . Here  $N$  is the  
 252 number of bonds  $j$  incident to the central atom, and  $p_{ij\alpha}$  or  $p_{ij\beta}$  represents the magnitude of  $\vec{p}_{ij}$   
 253 projected onto one of the Cartesian directions, where  $\alpha, \beta = x, y, z$ . (E.g.,  $\vec{p}_{ijx} = \vec{x} \cdot \vec{p}_{ij}$ , where  
 254  $\vec{x}$  is the unit vector in the  $x$  direction.) The  $\Theta_i$  values calculated using fractional bond-valence  
 255 vectors ( $\vec{p}_{ij}$ ), instead of normal bond-valence vectors ( $\vec{s}_{ij}$ ), thus depend only upon the shape of  
 256 the bond-valence distribution, and not on the atomic valence of the central atom, or its over- or  
 257 under-bondedness.

$$258 \quad \vec{p}_{ij} = \begin{bmatrix} p_{ijx} \\ p_{ijy} \\ p_{ijz} \end{bmatrix} = \vec{s}_{ij} / S_i \quad (7)$$

259

$$260 \quad \Theta_i = \frac{1}{2} \left[ \sum_{j=1}^N \sum_{\alpha=x,y,z} \sum_{\beta=x,y,z} \left( 3p_{ij\alpha}p_{ij\beta} - \delta_{\alpha\beta} \|\vec{p}_{ij}\|^2 \right) \right] \quad (8)$$

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$$262 \quad \Theta_i = \frac{1}{2} \begin{pmatrix} \sum_{j=1}^N \left( 3(p_{ijx})^2 - \|\vec{p}_{ij}\|^2 \right) & 3 \sum_{j=1}^N p_{ijx}p_{ijy} & 3 \sum_{j=1}^N p_{ijx}p_{ijz} \\ 3 \sum_{j=1}^N p_{ijy}p_{ijx} & \sum_{j=1}^N \left( 3(p_{ijy})^2 - \|\vec{p}_{ij}\|^2 \right) & 3 \sum_{j=1}^N p_{ijy}p_{ijz} \\ 3 \sum_{j=1}^N p_{ijz}p_{ijx} & 3 \sum_{j=1}^N p_{ijz}p_{ijy} & \sum_{j=1}^N \left( 3(p_{ijz})^2 - \|\vec{p}_{ij}\|^2 \right) \end{pmatrix} \quad (9)$$

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265 The valence quadrupole moment has zero trace, by definition, and can be thought of as  
 266 describing an ellipsoid encompassing the bond-valence distribution. If one is only interested in  
 267 the shape, rather than the orientation, of such an ellipsoid, one may remove extraneous

268 information by rotating the coordinate system to diagonalize the matrix, leaving only three non-  
269 zero terms.

270 One may further condense the information in the quadrupole moment matrix down to a  
271 single term by taking the Frobenius norm ( $\|\Theta_i\|$ ) with Eqn. 10, where  $\theta_{mn}$  represents the nine  
272 elements of  $\Theta_i$  in rows  $m$  and columns  $n$ . The Frobenius norm does not depend on the rotation  
273 of the axes (Horn and Johnson, 2012; Golub, 2013).

274

$$275 \quad \|\Theta_i\| = \sqrt{\sum_{m=1}^3 \sum_{n=1}^3 |\theta_{mn}|^2} \quad (10)$$

276

277  $\|\Theta_i\|$  is a scalar representing the spherical distortion of the bonding about an atom, with a  
278 value of zero for spherically symmetrical distributions, and higher values representing  
279 distributions distorted away from spherically symmetrical. For reference, Figure 1 shows several  
280 common configurations of a central ion and surrounding ligands, along with their corresponding  
281 values of  $\|\Theta_i\|$ . In all of these examples, the magnitudes of the fractional bond valences between  
282 a central atom and its ligands sum to 1.

283

284

## Methods

285 Our purpose, in this study, is to test the hypothesis that  $\|\Theta_i\|$  is predictable largely on the  
286 basis of the magnitudes of the incident bond valences, especially in cases where centrosymmetric  
287 distortions of coordination polyhedra play a role (e.g., in transition metals). Therefore, we  
288 analyzed the coordination environments of 2995 unique atoms  $i$  in 471 oxide structures to obtain  
289  $\|\Theta_i\|$  values. The  $\|\Theta_i\|$  values were, in turn, compared with the fractional bond valences  
290 ( $p_{ij} = s_{ij}/S_i$ ) of bonds incident to atom  $i$ .

291

292 Structures

293       Crystal structures were acquired from three online databases: the Crystallography Open  
294 Database (<http://www.crystallography.net>), the American Mineralogist Crystal Structure  
295 Database (Downs and Hall-Wallace 2003), and the Inorganic Crystal Structure Database  
296 (<http://icsd.fiz-karlsruhe.de>). Structures were chosen for analysis if they were published after  
297 1960, all cations had unambiguous oxidation states, SoftBV valence parameters (see below)  
298 could be obtained for the cation-oxygen pairs, and deviation from ideal valence sums was <15%.  
299 Structures were excluded from the study if strong, fully metallic or covalent bonds were present.

300

301 Analysis

302       We analyzed the crystal structures using a MATLAB™ program designed to read  
303 crystallographic information files, and compute interatomic distances, bond valences, bond-  
304 valence vectors and valence quadrupole moments. The program is available from B.R. Bickmore  
305 upon request.

306       We used the SoftBV parameters derived by Adams and coworkers (Adams 2001; Adams  
307 and Swenson 2002; Adams et al. 2004; Adams and Rao 2009) to account for the effects of  
308 polarizability. Because of the way they are derived, each set of SoftBV parameters is associated  
309 with a cutoff distance that is long enough to account for very weak, secondary interactions.

310

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## Results

312       In the oxide structures analyzed,  $\|\Theta_i\|$  appears to be predictable based on the valences of  
313 the strongest bonds incident to the atoms. Figure 2 shows each atom in the database, color-coded

314 to indicate  $O^{2-}$ , “normal” cations not expected to exhibit distortions due to electronic structure  
315 effects, and cations subject to lone pair, FOJT, or SOJT effects.  $\|\Theta_i\|$  is plotted vs. both  $p_1$  and  
316 the second-strongest fractional bond valence ( $p_2$ ). The trends for all these ions are broadly  
317 similar, approximately falling on a curved, triangular surface. The trends for different types of  
318 ions are different enough that they cannot be accurately predicted on the basis of the same  
319 equations, but Fig. 2 shows that normalizing the bond valences to the atomic valences moves  
320 these trends into rough coincidence, and whatever differences are left can be ascribed to other  
321 aspects of the electronic structure. These include bond character and atomic size, but as noted  
322 above, we will address these effects in a forthcoming study.

323 In the remainder of this section, we will specifically discuss the behavior of  $O^{2-}$  and the  
324 transition metals subject to FOJT Effects. The discussion of  $O^{2-}$  behavior is meant to illustrate  
325 the rough trend expected for all atoms (Fig. 2), but in most cases we find that  $\|\Theta_o\|$ , does not add  
326 much information to the monopole and dipole, because non-centrosymmetric distortions  
327 dominate the coordination geometry of low coordination number anions subject to lone-pair  
328 effects. The coordination geometry of cations subject to SOJT effects is also non-  
329 centrosymmetric. Therefore, the most important application of  $\|\Theta_o\|$ , will be the to characterize  
330 centrosymmetric FOJT distortions.

331

332 Oxygen

333 Figure 3 recreates Figure 2, but limits its scope to  $O^{2-}$ . Here,  $\|\Theta_o\|$  tends to be near zero  
334 when fractional bond strengths for the strongest two bonds are both  $\leq 0.25$  indicating  
335 coordination numbers  $\geq 4$ .

336 For higher coordination numbers, the distortion pathways can be understood by reference  
337 to Figure 4, in which certain theoretical pathways are outlined around the edges of the triangular  
338 surface. To generate these theoretical pathways, we began with a molecular fragment in which  
339  $p_1 = p_2 = p_3 = p_4 = 0.25$ , in a perfect tetrahedral configuration ( $\|\Theta_O\| = 0$ ). During distortion of  
340 the fragment, we enforced the valence sum rule (Eqn. 1), and constrained  $\|\vec{S}_O\|$  to follow the  
341 relationship shown in Eqn. 11, which Bickmore et al. (2013) demonstrated for  $O^{2-}$  with  $p_1 > 0.5$ .  
342 Furthermore, maximum symmetry was maintained, while still obeying the previous two criteria.

$$343 \quad \|\vec{S}_O\| = \frac{4}{3}p_1 - \frac{1}{3} \quad (11)$$

344 On the trend marked by the blue line, we first kept  $s_1 = s_2 = s_3$  and gradually moved one  
345 of the bonded atoms away, adjusting the location of the other three to comply with the criteria  
346 listed above. The continuation of the blue line was generated by gradually removing the second  
347 and then the third bonded atoms, until only one remained ( $p_1 = 1$ ,  $\|\vec{S}_O\| = 2$  v.u.) The red line  
348 was generated by simultaneously removing two bonded atoms. The path marked by the magenta  
349 line corresponds to simultaneously removing three bonded neighbors, finally meeting the blue  
350 line at the corner corresponding to a 1-coordinated  $O^{2-}$ . The data points in between these trends  
351 represent those with less symmetrical bond distributions.

352 We found that  $\|\Theta_O\|$  could be well described as a function of  $p_1$  and  $p_2$  in cases where  $p_3$   
353  $< 0.25$ , as in Eqn. 12. However, for  $p_3 \geq 0.25$ , the model shown in Eqn. 13 improved the fit.



$$\begin{aligned} \|\Theta_i\| = & 0.06324 - 0.1792(p_1) - 0.6837(p_2) + 1.371(p_1)^2 + 0.5719(p_1)(p_2) \\ & + 1.596(p_1)^2 \qquad \qquad \qquad (p_3 < 0.25) \qquad \qquad (12) \end{aligned}$$

$$\begin{aligned} \|\Theta_i\| = & 0.06324 - 0.1792(p_1) - 0.6837(p_2) + 1.371(p_1)^2 + 0.5719(p_1)(p_2) + 1.596(p_1)^2 \\ & + 0.140(p_3) \qquad \qquad \qquad (p_3 \geq 0.25) \qquad \qquad (13) \end{aligned}$$

354 Figure 5 shows the predicted vs. observed values of  $\|\Theta_o\|$ . While there are clear trends  
355 in the data, considerable scatter remains, especially among the data points around  $p_1 = p_2$ . This  
356 appears to be related partially to steric effects, but also largely to the effects of bond character  
357 (covalent or ionic) and atomic size. These effects will be quantified in a forthcoming study.

358

#### 359 Transition Metals

360 Transition metals with unevenly distributed  $d$ -electrons are subject to the First-Order  
361 Jahn-Teller (FOJT) effect, which induces centrosymmetric distortions for coordination numbers  
362 4-6. The precise distortion pathways preferred by the different transition metal ions depend on  
363 factors such as  $d$ -orbital occupancy and ion size, but we can make the following generalizations.  
364 First, transition metals not subject to Jahn-Teller effects (including FOJT and SOJT) tend to  
365 adopt  $\|\Theta_i\| \approx 0$  in the range  $0.16 < p_1 < 0.25$  ( $N_{min} = 4-6$ ). Those that are subject to FOJT  
366 effects tend to have increasing  $\|\Theta_i\|$  values as  $p_1$  goes from  $\sim 0.16$  to  $\sim 0.25$ , with those subject to  
367 the strongest distortions approaching a square-planar configuration ( $\|\Theta_i\| \approx 0.15$ ) at  $p_1 \approx 0.25$   
368 (see Figure 1g).

369 Figures 6-11 illustrate these trends for ions of different transition metal elements: Co, Cr,  
370 Cu, Fe, Mn, and Ni, respectively. (Here,  $\|\Theta_i\|$  is plotted vs.  $p_1$ , rather than both  $p_1$  and  $p_2$ ,  
371 because we found that including  $p_2$  added no information for centrosymmetrical distortions.)  
372 These figures clearly show that different ions of the same element, having different  $d$ -orbital

373 configurations, exhibit distinctly different distortion pathways. For example,  $\text{Fe}^{3+}$  is not  
374 expected to exhibit FOJT distortion, because it has a high-spin  $d^5$  configuration at low pressures.  
375 Indeed,  $\|\Theta_{\text{Fe}^{3+}}\|$  (Figure 9) clusters around zero for  $0.16 < p_I < 0.25$ , whereas  $\|\Theta_{\text{Fe}^{2+}}\|$   
376 increases from  $\sim 0$  to  $\sim 0.06$ - $0.15$  over this interval, indicating that it prefers flattened tetrahedral  
377 or square-planar configurations when 4-coordinated. Similar trends can be seen by comparing  
378  $\text{Mn}^{2+}$  ( $d^5$ ) to  $\text{Mn}^{3+}$  ( $d^4$ ) and  $\text{Mn}^{4+}$  ( $d^3$ ) (Figure 10).  $\text{Mn}^{2+}$  does not show any trend over  $0.16 < p_I$   
379  $< 0.25$ ,  $\text{Mn}^{4+}$  shows a weak trend, and  $\text{Mn}^{3+}$  shows a strong trend, as would be expected given  
380 their  $d$ -orbital configurations.

381 Obviously, there is quite a bit of scatter about the trends we have highlighted, but this is  
382 to be expected in disparate crystal structures, where various other factors influence the  
383 configurations. However, the usefulness of  $\|\Theta_i\|$  for modeling structures can be illustrated by  
384 pressure series in which a transition metal undergoes a spin transition. Lavina et al. (2010), for  
385 instance, tracked changes in the crystal structure of siderite ( $\text{FeCO}_3$ ) from 0-56 GPa using X-Ray  
386 diffraction, and Farfan et al. (2012) characterized the  $\text{Fe}^{2+}$  spin transition that occurs at  $\sim 46$  GPa  
387 using *in situ* Raman spectroscopy. Abrupt structural and spectroscopic changes occurred at the  
388 spin transition, above which the trends exhibited some hysteresis. Figure 12 shows  $\|\Theta_{\text{Fe}^{2+}}\|$   
389 plotted vs. pressure for this series. The changes in  $\|\Theta_{\text{Fe}^{2+}}\|$  with pressure are small, but  
390 relatively smooth until the spin transition at  $\sim 46$  GPa, where there is a distinct shift in slope.  
391 Above this pressure, the hysteresis is also observed. While a number of common structural  
392 descriptors also exhibit abrupt shifts at the spin transition, it is important to note that the reason  
393 for the shift is related to the electronic structure of the  $\text{Fe}^{2+}$ , and  $\|\Theta_{\text{Fe}^{2+}}\|$  is a convenient single-  
394 parameter summary of the octahedral distortion about that atom. This seems likely to be useful

395 for constraining the behavior of model structures in ways that mimic the real quantum  
396 mechanical causes.

397

398

### **Implications**

399 When combined with our previous work (Bickmore et al., 2013), this work shows that  
400 multipole expansions of the bond valence incident to atoms, including monopole (bond-valence  
401 sum), dipole (vectorial bond-valence sum), and quadrupole terms, are capable of describing the  
402 total bonding environment of atoms, even if the coordination sphere is subject to distortions due  
403 to several common electronic structure effects, in a predictable manner. If we combine  
404 predictions of ideal values for the valence multipole terms with energy cost functions for  
405 deviation from those ideals, it should be possible to incorporate the VMM into a molecular  
406 mechanics type of framework, as has already been partially done (Grinberg et al., 2002; Cooper  
407 et al., 2003; Grinberg et al., 2004; Shin et al., 2005; Shin et al., 2007; Shin et al., 2008; Grinberg  
408 et al., 2009; Liu et al., 2013a; Liu et al., 2013b; Takenaka et al., 2013). If so, it would be  
409 possible to model electronic structure effects very simply that have so far proven very difficult  
410 for non-quantum mechanical models.

411

### **Acknowledgements**

412 We gratefully acknowledge the National Science Foundation (EAR-1227215 and EAR-  
413 1424682) and the Brigham Young University College of Physical and Mathematical Sciences  
414 undergraduate mentoring program for funding this project. We also thank Prof. I. D. Brown and  
415 Prof. Frank Hawthorne for providing helpful reviews of the initial manuscript.

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513 Figure Captions

514

515 Figure 1. The norm of the valence quadrupole moment ( $\|\Theta_i\|$ ) describes the ellipsoidal deviation  
516 from spherical symmetry of the coordination shell about a specified atom.  $\|\Theta_i\|$  about a central  
517 atom are shown for a variety of coordination polyhedra, with fractional bond valence of the first  
518 two strongest bonds of the system  $p_1$  and  $p_2$ . These sample configurations are used as reference  
519 points for some of the subsequent figures.

520

521 Figure 2.  $\|\Theta_i\|$  for all atoms in the database is plotted vs. the fractional bond valence of the two  
522 strongest bonds. This shows that using fractional bond valence puts the quadrupole moments for  
523 all types of atoms roughly in coincidence, regardless of oxidation state. Any differences,  
524 therefore, can be attributed to various electronic structure effects.

525

526 Figure 3.  $\|\Theta_O\|$  for all oxygen atoms in the database is plotted vs. the fractional bond valence of  
527 their two strongest incident bonds. The pattern is a curved, triangular surface at  $p_1 \geq p_2 \geq 0.25$ ,  
528 and clusters around 0 for  $p_2 \leq p_1 \leq 0.25$ .

529

530 Figure 4. (a)  $\|\Theta_O\|$  plotted vs.  $p_1$  and  $p_2$ . (b) The sample configurations shown in Fig. 1. Also  
531 shown are predicted deformation pathways from a tetrahedral coordination polyhedron. We  
532 assume that the valence sum rule is always obeyed, and the valence dipole moment for O  
533 behaves as described in Bickmore et al. (2013). The magenta line begins with a tetrahedron  
534 ( $\|\Theta_O\| = 0$ ,  $p_1 = p_2 = 0.25$ ), and evolves as three atoms are gradually stretched, leaving a  
535 structure with a single bond ( $\|\Theta_O\| = 1.22$ ,  $p_1 = 1$ ,  $p_2 = 0$ ). The blue line begins with a

536 tetrahedron ( $\|\Theta_o\| = 0$ ,  $p_1 = p_2 = 0.25$ ), and then evolves as individual bonds are stretched and  
537 removed, one at a time, until three bonds ( $\|\Theta_o\| = 0.16$ ,  $p_1 = p_2 = p_3 = 0.333$ ), then two bonds  
538 ( $\|\Theta_o\| = 0.52$ ,  $p_1 = p_2 = 0.5$ ), and finally one bond ( $\|\Theta_o\| = 1.22$  v.u.,  $p_1 = 1$ ,  $p_2 = 0$ ) remains.  
539 The red line begins with a tetrahedron ( $\|\Theta_o\| = 0$ ,  $p_1 = p_2 = 0.25$ ), and then evolves as two  
540 bonds are stretched simultaneously, leaving two bonds ( $\|\Theta_o\| = 0.52$ ,  $p_1 = p_2 = 0.5$ ).

541

542 Figure 5. The predicted  $\|\Theta_o\|$  (Eqns. 12-13) vs. actual  $\|\Theta_o\|$ .

543

544 Figure 6.  $\|\Theta_i\|$  vs.  $p_1$  for chromium ions with atomic valences of +2, +3, +4, +5, and +6. The  
545 sample configurations from Fig. 1 are plotted, as well.

546

547 Figure 7.  $\|\Theta_i\|$  vs.  $p_1$  for manganese ions with atomic valences of +2, +3, and +4. The sample  
548 configurations from Fig. 1 are plotted, as well.

549

550 Figure 8.  $\|\Theta_i\|$  vs.  $p_1$  for iron ions with atomic valences of +2 and +3. The sample  
551 configurations from Fig. 1 are plotted, as well.

552

553 Figure 9.  $\|\Theta_i\|$  vs.  $p_1$  for cobalt ions with atomic valences of +2 and +3. The sample  
554 configurations from Fig. 1 are plotted, as well.

555

556 Figure 10.  $\|\Theta_i\|$  vs.  $p_1$  for nickel ions with atomic valences of +2, and +3. The sample  
557 configurations from Fig. 1 are plotted, as well.

558

559 Figure 11.  $\|\Theta_i\|$  vs.  $p_I$  for copper ions with +2 atomic valences. The sample configurations  
560 from Fig. 1 are plotted, as well.

561

562 Figure 12.  $\|\Theta_{Fe^{2+}}\|$  vs. pressure for the siderite ( $FeCO_3$ ) structure. Note that the change in  
563  $\|\Theta_{Fe^{2+}}\|$  with pressure is relatively smooth until  $\sim 46$  GPa, at which point a spin transition occurs  
564 and a distinct shift in the trend occurs. Above this pressure, hysteresis is also observed.

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