

# A new approach to the ionic model

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## Abstract

Predicting crystal structures using the ionic model has traditionally involved two-body potentials expressed in terms of interatomic distances, but such potentials fail to properly describe electronic anisotropies and the interactions between bonds. A recent paper by Wander and Bickmore (2016) shows that both of these effects can be included if the energy is expressed in terms of a multipole expansion of the bond-valence field incident on each atom.

## Text

Quantum mechanical modelling of crystal structures is limited by the extensive calculations involved, as well as by the prior need to know how the atoms are arranged. As a result the ionic model is often preferred for predicting crystal structures. Its classical two-body potential is simpler, making it feasible to model dynamic processes or to start the modelling with a random array of atoms, but the two-body potential ignores the important interaction between the bonds by requiring fixed targets for the bond lengths. Bond valences provide an alternative development of the ionic model. The electrostatic flux that links neighboring atoms is identified with the traditional chemical bond. Each bond is characterized by a flux, also known as its bond valence, that is closely correlated with its length, but the flux theory allows the use of a different set of classical electrostatic theorems. It cannot provide the energy of the crystal, but it complements energy-based models by providing the initial atomic positions required by the

23 Schrödinger equation, and the interaction between neighboring bonds that is missing from the  
24 two-body potential model (Brown, 2014).

25         The flux theory shows that for inorganic compounds the ionic model correctly describes  
26 both ionic and covalent interactions (Brown 2014). Each atom is represented by a point charge  
27 equal to its valence, and this generates a spherically symmetric distribution of the flux, leading to  
28 a symmetric arrangement of the bonds around most atoms. However, around some atoms, for  
29 example those with stereoactive lone pairs, this symmetry is broken. An article in this issue by  
30 Wander and Bickmore (2016) suggests that where this symmetry is broken, the distribution of  
31 flux around an atom can be expanded in a series of spherical harmonics. The monopole term  
32 describes the total flux incident on the atom, the dipole term describes the non-centrosymmetric  
33 distortions, and the quadrupole term describes the centrosymmetric distortion observed in the  
34 environments of Cu(II) and Mn(III). Wander and Bickmore show how the size of these  
35 multipoles can be determined using bond valence vectors calculated from the observed lengths  
36 and directions of the bonds.

37         Their proposal can be developed in a number of different ways. For example anisotropy  
38 can be introduced into modelling by assigning values to the multipoles that seamlessly modify  
39 the flux field of the monopole, but Wander and Bickmore use the multipole expansion in a  
40 different way to construct a classical force field with which to calculate the energy. Instead of  
41 expressing this field in terms of the bond lengths, it is expressed in terms of the bond fluxes  
42 (bond valences), allowing it to incorporate the electrostatic theorems that describe the behavior  
43 of chemical bonds. The most powerful of these theorems is Gauss' law, also known as the  
44 valence sum rule: *the total flux passing through a closed surface is equal to the enclosed charge.*

45 This rule describes the interaction between the bonds and replaces the fixed bond-length targets  
46 of the traditional two-body potential. Similarly, the target dipole moment for a stereoactive lone  
47 pair can be calculated on the fly from the valence of the strongest bond formed by the lone-pair  
48 atom, as pointed out by the authors in an earlier paper (Bickmore *et al.* 2013).

49 The proof of concept described by Wander and Bickmore (2016) shows that by fitting the  
50 multipole parameters to a calibration set of aluminosilicate mineral structures, they were able to  
51 reproduce the energies of a second independent set of minerals to within 5 Kcal/mole per atom.  
52 As they point out, much work still needs to be done to extend their approach to structures  
53 containing a more varied group of elements having more significant dipole and quadrupole  
54 moments, but their paper shows how it is possible to combine the best features of two different  
55 but complementary models.

## 56 **References**

57 Bickmore, B.R., Wander, M.F.C., Edwards, J., Maurer, J., Shepherd, K., Meyer, E.,  
58 Johansen, WJ., Frank, R.A., Andros, C., and Davis, M. (2013) Electronic structure effects in the  
59 vectorial-bond-valence model. *American Mineralogist*. 98, 340–349.

60 Brown I.D. (2014). Bond valence theory. pp. 11–58 in ‘Bond Valences’ Brown I.D., and  
61 Poeppeleier, K.R. Eds *Structures and Bonding* 158, Springer, Dordrecht, Heidelberg, New  
62 York, London.

63 Wander M.F.C. and Bickmore, B.R. (2016), A preliminary valence-multipole force field:  
64 Al-Si-H-O system. *American Mineralogist* XXXX