Valence multipole force fields

MATTHEW C. F. WANDER* AND BARRY R. BICKMORE

Dept. of Geological Sciences, Brigham Young University, Provo, UT 84602, USA. (*correspondence: mcfwander@gmail.com)

We have expanded the bond-valence model to address full molecular geometries and predict full structures, rather than just bond lengths, along with reasonable expectation values for the energy. The key to this is a particular choice of the energy decomposition, i.e., what part of the energy results from which aspects of the structure. This decomposition is based on the valence multipole model. It separates the energy into isometric or total bonding, vector or bonding asymmetry, and quadrupole or ellipsoidal deformations. Further, we equate bond valence and bond order, a critical issue for many chemists, via Johnson's force constant model for bonding.

Some advantages of this type of energy decomposition are as follows. 1) All of the structural descriptors are based on the overall bonding environment of the atoms, rather than individual bond lengths, angles, etc. 2) And yet, these multi-body terms are relatively computationally inexpensive, because they are calculated by combining pair-wise terms (i.e., the individual bond valences). 3) As long as we can predict how the values of the structural descriptors will change with the chemical context, such force fields are capable of addressing chemical reactions in which coordination number changes, in a mathematically simple manner.

Our prototype force field is for the Al-Si-H-O system, and has been tested against numerous molecular and crystal structures, including different coordination numbers for the atoms, where thermodynamic information could also be obtained. Provided bond valence sums are satisfied to within 20% of the ideal for all atoms, this model can provide accuracies of ~5 kJ/mol per unique atom, comparable to most quantum mechanical calculations. This holds true equally well for both small gas-phase molecules and solid-state systems like crystals, corresponding to a free energy range of ~6000 kJ/mol.

This formulation is specifically designed for interfacial systems, given the advantages of reactive bonding and the ability to handle any coordination environment, as well as coordination number changes.