A preliminary valence-multipole potential energy model: Al-Si-H-O system

MATTHEW C.F. WANDER1,* AND BARRY R. BICKMORE1

1Department of Geological Sciences, Brigham Young University, Provo, Utah 84602, U.S.A.

ABSTRACT

Here we test the concept that a potential energy model (force field) based on an expansion of the bond-valence model can use molecular geometry to make a reasonable prediction of the thermodynamic energy. The backbone of the model is a non-standard choice of structural descriptors for the energy decomposition, which relates the energy to particular aspects of the structure. Most force fields use a many-body decomposition to describe structures (with two-, three-, and possibly four-body terms, etc.), whereas ours employs a multipole expansion of the bond valence incident to each atom. This valence multipole model separates the energy associated with each atom into terms related to total bonding (valence monopole), bonding asymmetry (valence dipole), and ellipsoidal deformation (valence quadrupole). All of these are inherently multi-body terms that are calculated by combining two-body terms (bond valences). Provided bond valence sums are satisfied to within 0.2 v.u. of the ideal for all atoms, this model can provide accuracies of ~5 kJ/mol per unique atom in the Al-Si-H-O system, at least for the equilibrium structures tested here, comparable to most quantum mechanical calculations. More development is needed to produce a fully functional force field suitable for molecular dynamics simulations, but this work shows that the development of such a force field is likely to be feasible.

Keywords: Bond valence, multipole expansion, molecular mechanics, molecular modeling

INTRODUCTION

Molecular modeling has become increasingly popular in geochemistry and mineralogy, as knowledge of molecular-scale mechanisms and structures has become progressively more important. Quantum mechanical (QM) models are the gold standard for molecular modeling, but can be prohibitively computationally expensive, especially for the larger systems of atoms sometimes needed to adequately represent natural materials and processes. Molecular mechanics (MM) potential energy models, or “force fields,” are common, less computationally intensive alternatives, but are subject to several difficulties that have often limited their scope and effectiveness.

We suggest that some of these problems can be addressed by restructuring the basic architecture of an MM force field. In this contribution, we report on the construction, optimization, and initial testing of a potential energy model (intended to be a precursor to a fully reactive force field) for the Al-Si-H-O system, designed around the valence multipole model (VMM) (Bickmore et al. 2013; Shepherd et al. 2016), which is an extension of the bond-valence model (BVM) (Brown 2002, 2009, 2014). To our knowledge, this is the first example of a potential energy model constructed completely from a bond-valence model of chemistry rather than by using the BVM to augment existing architectures. Early indications are that such models are capable of excellent accuracy, with limited computational expense, at least with respect to estimating thermodynamic energies of equilibrium structures. Considering how often bond valence has been used in quantitative structure-activity relationships (Hiemstra et al. 1989, 1996; Sverjensky 1994, 2005; Hiemstra and Van Riemsdijk 1996; Sverjensky and Sahai 1996; Sahai and Sverjensky 1997b, 1997a; Sverjensky et al. 1997; Lufaso and Woodward 2001; Sahai 2002; Bickmore et al. 2004, 2006a, 2006b; Etxebarria et al. 2005; Perez-Mato et al. 2009; Bickmore 2014), this is a significant development in itself.

theory

To introduce this new approach, we discuss the standard architecture of MM force fields, give a basic explanation of the VMM, and show how a potential energy model based on the VMM would differ from the standard architecture, while allowing for broader applicability and greater accuracy, at a reasonable computational cost.

Standard MM force fields

MM force fields mimic interactions between atoms and molecules by treating them essentially as “balls on springs” (Hinchliffe 2003). That is, the geometry of a system of atoms is defined in terms of a set of structural descriptors (e.g., interatomic distances and bond angles), ideal values are specified for the descriptors (e.g., preferred bond lengths and angles), and energy cost functions are applied to deviations from the ideal values. The simplest and most often used of these energy cost functions is Hooke’s Law for springs (Eq. 1), in which the spring length is the structural descriptor of interest. Here, $u$ is the potential energy, $k$ is a constant, $x_0$ is the ideal value of the structural descriptor of interest, and $x$ is the actual value.

$$ u = \frac{1}{2} k (x - x_0)^2 $$

(1)

Each of these energy terms includes one or more parameters that can be adjusted to fit the overall model to some set of data, including crystal or molecular structures, thermodynamic data, or...