The use of cation-cation and anion-anion bonds to augment the bond-valence model

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ABSTRACT

The bond-valence model has, for several decades, been widely used for creating quantitative structure-activity relationships (QSARs), crystal structure modeling, and verification of proposed structures. Certain limitations of the model, such as the neglect of interactions between cations and between anions, have prevented it from being more broadly applied. In this work, we use cation-cation and anion-anion bonds to augment the existing bonding model in the systems H-Al-Si-O and K-Al-Si-O. The bond valence-length curves for these interactions employ the same mathematical form as ionic bonds, but make only a small contribution to the overall bonding in ionic materials. In the systems examined here, oxygen-oxygen interactions were much more important than those between cations for producing accurate bond-valence sums. Both anion-anion and cation-cation bonding could prove important, however, for our ultimate goal of producing valence-based force fields for use in molecular dynamics simulations. Rolling these interactions into the bond-valence framework would produce behavior similar to hard-sphere repulsive or van der Waals terms, but would more flexibly account for the complete bonding environment. The overall improvement in valence sums was robust, was maintained outside the calibration set, and was invariant to elemental substitution. We conclude that this minor alteration of the bond-valence approach will significantly improve bond-valence models in conjunction with other recent extensions of the approach.

Keywords: Crystal structure, bond valence, ligand, silicate, aluminosilicate

INTRODUCTION

F. Albert Cotton once quipped that:

[T]heories of chemical bonding—neglecting not a few which are entirely valueless—fall into one of two categories: those which are too good to be true and those which are too true to be good. “True” in this context is intended to mean “having physical validity” and “good” to mean “providing useful results, especially quantitative ones, with a relatively small amount of computational effort.” The proper, rigorous wave equation for any molecular situation represents a theory of that situation which is too true to be good (Cotton 1964).

Five decades later, this observation is still apropos. Computational resources and quantum mechanical methods have developed considerably since 1964, but not enough to obviate the need for simpler models of atomic interaction, such as some of the popular bonding models (Gillespie and Popelier 2001) and molecular mechanics force fields (Rappé and Casewit 1997), which are computationally less expensive and promote fluent thinking about molecular structure and reactivity (Brown, T.L. 2003). In all cases, these simpler models represent atoms and molecules in somewhat physically unrealistic ways, but their associated mathematical descriptions tend to mimic certain aspects of real systems, at least when empirically calibrated. This allows for qualitative, or even quantitative, predictions about certain phenomena, but not others. It is generally the case that, at some point, attempts to make such models more physically realistic end up complicating their mathematical descriptions to the point that they become unusable for most practical purposes. Therefore, attempts to make “good” models more “true” should not be undertaken lightly.

The bond-valence model (BVM) is certainly one that is too good to be true. Over the past several decades, the BVM has been applied to a large number of ionic and polar-covalent systems, successfully rationalizing and predicting energetically favorable combinations of bond lengths about individual atoms (Brown 1977, 1981, 2002, 2009). In fact, it is a standard tool for screening proposed crystal structures, and has been employed in both structure prediction (Brown 2002) and the creation of quantitative structure-activity relationships (QSARs) (Hiemstra et al. 1989, 1996; Hiemstra and Van Riemsdijk 1996; Bickmore et al. 2004, 2006a, 2006b). The application of the BVM has been limited, however, because at least in its quantitative form, it is concerned solely with bond lengths, and not with the complete spatial distribution of ligands. One factor affecting this spatial distribution is necessarily ligand-ligand interactions, but the BVM has traditionally been developed within a generally ionic framework, in which bonds only exist between cations and anions. If ligand-ligand interactions are treated at all within a typical BVM-based structural model, it is usually by the introduction of simple repulsive potentials (Brown 2002) or arguments based...