

Effects of bond character and atomic size on valence dipole moments

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We are developing a new bonding model, the Valence Multipole Model, to explain a very broad range of structural behavior, and to be portable into a molecular mechanics (MM) format. Molecular geometries are described in terms of a multipole expansion of the bond valence incident to each atom. MM models based on such a description require ideal values of the multipole terms in different chemical contexts, as well as energy cost functions for deviations. Therefore, we are attempting to develop methods to predict ideal values for the multipole terms, such as the valence dipole moment (also called the vectorial bond-valence sum).

Bickmore et al. [1] showed that the valence dipole moment depends largely on the valence of the strongest bonds incident to an atom when stereoactive lone-pairs exist on the central atom. Here we keep bond valence constant, and explore the effects of bond character and atomic size, through a series of molecular geometries involving two single bonds incident to O, S, and Se atoms.

We obtained experimental and calculated (Gaussian 09, B3LYP/Def2-TZVP) geometries of these molecules, and have shown that the valence dipole moment can be predicted via the fraction ionic character of the bonds and the van der Waals radii of the atoms bonded to the central atom. We are also developing associated mathematical models.

These results should allow us to obtain initial estimates for ideal valence dipole moments, as well as model forms for describing how the ideal values should change with the chemical context. This should make possible powerful, reactive MM force fields.

[1] Bickmore *et al.* (2013) *Am. Min.* **98**, 340-349.