The Valence multipole model: An expanded chemical bonding model

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Simple chemical bonding models, such as Lewis dot structures, the Valence Shell Electron Pair Repulsion (VSEPR) model, Pauling's Rules, Ligand Field Theory, and the bond-valence model (BVM), have played an important role in chemistry. They not only allow us to think more fluently about chemical systems, but can sometimes also provide quantitatively accurate predictions. These simple models, however, are typically useful only for a limited range of bond types, or for particular aspects of a structure (bond lengths vs. bond angles, etc.)

We are developing an expanded chemical bonding model that is capable of subsuming many previous models, and is suitable for adoption into a molecular mechanics framework for atomistic simulations. The Valence Multipole Model (VMM) is an expansion of the BVM in which structures are described in terms of multipole expansions of the bond valence incident to each atom. The monopole is the bond-valence sum, the dipole is the vector sum of the bond valences, and the quadrupole describes the spherical symmetry of the bond distribution. These descriptors are capable of describing full structures, but they depend on the complete bonding environment of each atom, rather than any particular bond length or angle. The dipole and quadrupole terms can successfully describe non-centrosymmetric or centrosymmetric distortions of a coordination sphere, respectively, and are largely predictable on the basis of bond valences, electronegativities, and expected electronic structure effects (e.g., lone pairs and Jahn-Teller distortions). The bond-valence calculations have also been modified to account for anion-anion and cation-cation bonding, and to be applicable over a wider range of bond lengths. Using information about, for instance, the vibrational properties and dissociation energies of relevant bonds, we can also build energy cost functions to create a more complete model.

Beyond its transferability to a molecular mechanics framework, the VMM is a fairly simple framework for understanding most types of chemical bonding, and it can be used to easily rationalize many crystal-chemical trends.