Bond energy and bonding geometry around anions with lone pairs

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Most simple models of chemical bonding describe a limited range of behaviour. The valence shell electron pair repulsion (VSEPR) model, for example, predicts the bonding geometry incident to atoms with lone electron pairs [1]. However, it is only valid for covalent bonds. The polar covalence model [2] predicts many bond energies well, but does not address bonding geometry. The bond-valence model [3] addresses only bond lengths.

We are creating a new bonding model, the Valence Multipole Model, for predicting full structures. Here, bond valence is treated as a vector quantity, and a multipole expansion of the bond valence incident to each atom is used to describe the geometry. Within this context, we are examining both bonding geometries and bond energies.

Using a large number of experimental and calculated structures and bond energies, for systems in which two single bonds are incident to O, S, and Se atoms, we have shown that bond energies and bonding geometries (as described by valence dipole moments) are highly related. The connection can be readily explained by combining concepts from all three aforementioned bonding models, including the lone-pair bond-weakening effect described in Sanderson's polar covalence model.

[1] Gillespie & Hargittai (1991) *The VSEPR Model of Molecular Geometry*, Boston, Allyn and Bacon. [2] Sanderson (1983) *Polar Covalence*, New York, Academic Press. [3] Brown (2002) *The Chemical Bond in Inorganic Chemistry: The Bond-Valence Model*, New York, OUP.