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The valence quadrupole moment

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Abstract

The bond-valence model has recently been expanded to include a directional component, the vectorial bond-valence sum, which is useful for characterizing non-centrosymmetric distortions involving lone-pair and second-order Jahn-Teller effects. Here we show that the bond-valence sum and vectorial bond-valence sum are equivalent to monopole and dipole terms in a multipole expansion of the bond valence incident to an atom. We then extend the multipole expansion to include a quadrupole term, which describes the ellipsoidal deviation from spherical symmetry of the bonding environment, and is useful for characterizing centrosymmetric distortions, such as those caused by first-order Jahn-Teller effects. These distortions follow characteristic patterns in valence space, which depend upon factors that include the *d*-orbital configuration and size of the transition metal involved. This extended approach, called the Valence Multipole Model, should prove useful for modeling molecular and crystal structures, including those associated with spin transitions.

Keywords: Bond valence, vectorial bond-valence model, valence multipole model, bond angle, molecular mechanics, Jahn-Teller effect, crystal field effects