MS43 O1

The Basis of the Bond Valence Model, its Strengths and Weaknesses I.David Brown *Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada.* E-mail: idbrown@mcmaster.ca

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The bond valence model [1] is an exact representation of the ionic model. It gives a good empirical description of all types of polar bond, regardless of ionicity or covalency. Unlike Atoms in Molecules (AIM) [2] where the property of an atom depends on its context, the atoms in the ionic model are invariant soft charged spheres bound together in a crystal by electrostatic forces. Each cation is linked (bonded) to its neighbouring anions by electrostatic flux (lines of field) that sum around each atom to the atomic charge. The magnitude of the flux is known as the bond valence. The structure of a solid can thus be represented by a network in which the nodes (atoms) are linked by bonds. However, just as the atoms of the bond valence model are not the same as the atoms in AIM, so the bonds in this model are not the same as the bond paths in AIM. Atomic charges in the ionic model may be assigned any value provided that the charge on a given atomic species is always the same, that the cations are positive, the anions negative, and the whole array is electroneutral. However, it is conventional for the charges to be chosen equal to the number of valence electrons used in bonding as this results in the bond valence being the same as the number of electron pairs associated with the bond. To prevent the array of charges from collapsing to a point it is necessary to introduce a repulsive force between the atoms, conveniently represented by an inverse exponential with two empirically fitted parameters, relating the bond valence to the bond length. The bond network can be represented by a graph making the model conceptually and computationally simple.

Bond valences can be predicted by ensuring the sum of bond valences around any loop in the graph is zero. It is thus possible to predict the ideal bond lengths in any compound from the bond graph without knowledge of the 3-dimensional structure; indeed in high symmetry cases the 3-dimensional structure can be predicted directly from

the bond graph. The valence sum rule allows the localized bonding of the bond valence model to reproduce the long-range effects of the ionic model, and the separation of the chemical and spatial aspects of the model make it possible to identify structures that are destabilized by internal strains.

[1] Brown I.D., The Chemical Bond in Inorganic Chemistry: The Bond Valence Model. Oxford University Press, 2002.
[2] Bader R.W.F., Atoms in Molecules: A Quantum Theory. Clarendon Press, Oxford, 1990.

MS43 O2

Chemical bond in inorganic structures: the quantum view Mauro Prencipe *Department of Mineralogical and Petrological Sciences, University of Torino, Italy.* Email: mauro.prencipe@unito.it

Keywords: Quantum mechanics; Chemical bonding theory; Hellmann-Feynman theorem

Since more than one century it is known that atoms are made up by nuclei and electrons, and a proper and physically consistent description of their interactions, in molecules and crystals, must be done within the quantum-mechanical framework, being classical models contradicted, at a very fundamental level, by experimental facts. However, the computational difficulties connected to the resolution of the Schrödinger equation for systems containing more than one electron, hindered for decades the application of the quantum formalism to crystals and, at variance with the approach generally followed in molecular physics, empirical models based on classical mechanics were largely developed to describe atomic interactions. On the other hand, in molecular physics much of the attention was focused on the most effective techniques to get, at a reasonable computational cost, the best approximations to the exact wave function from the Schrödinger equation; the view of the *real* physics underlying atomic interactions was partially lost, and a terminology was introduced which, in some cases, attached a *reality* to *unphysical* quantities that are, instead, deeply connected to the approximations implied in the methods employed to solve the quantum problem; this is for instance the case of the *exchange force* which does not exist, though it is often invoked to *explain* the strength of covalent bonds. Some of such fictitious *quantum* forces are, at times, introduced in essentially classical descriptions of interactions to account for the stability of given arrangement of atoms; the equilibrium nuclear configuration is often viewed as due to the balance of *long range* attractive classical electrostatic forces, and repulsive *short range* forces, the latter being considered of quantum origin (improperly termed as *Pauli* or *Fermi* forces). It is to be noted that quantum-mechanics does not invent any new force in addiction to those classically known; quantum-mechanics is just a framework developed to take in due account the interference of an observer on the observed object; no new mysterious forces of quantum-mechanical origin should be used to describe the dynamics of a molecular or crystalline system. In the last decade, the significant improvement of the performance of computational resources allowed for the calculation, at the quantum level, of accurate electron densities even for relatively complex structures and, by making use of the Hellmann-Feynman theorem, within the framework of the Bader's theory [1] which extends quantum-mechanics to open systems, a physically consistent description of the forces on nuclei can be obtained. With particular reference to simple ionic systems a fully quantum-mechanical view of interactions will be discussed, without the introduction of any of the fictitious forces quoted above.

[1] Bader R.W.F., Clarendon Press, Oxford, 1990;
[2] Prencipe M., Nestola F., *Phys. Chem. Minerals*, 2007, 34, 37.

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Bond strengths, a crucial question for the chemist. Insight on the oxoanions containing iodine(V). Isabelle Gautier-Luneau,[a] Yan Suffren,[a] Delphine Phanon,[a] Hélène Jamet,[b] *[a]Institut Néel, CNRS, Grenoble; [b]DCM, Université Joseph Fourier, Grenoble, France.*
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The crystal engineering of efficient materials for quadratic nonlinear optics (NLO) led us to develop the coordination