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

Keywords: Bond Valence Model; Ionic Model; Electrostatic Flux

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.

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MS43 O2

Chemical bond in inorganic structures: the quantum view Mauro Prencipe *Department of Mineralogical and Petrological Sciences, University of Torino, Italy.*
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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.

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MS43 O3

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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Keywords : computation, iodate, structure

The crystal engineering of efficient materials for quadratic nonlinear optics (NLO) led us to develop the coordination

chemistry of metallic iodates. In addition to the acentric crystal structure, the molecular or ionic arrangement of the crystal has to contain a periodic system of polarizable free electrons in order to obtain highest non linear susceptibilities. So, the IO_3^- iodate anion with the lone pair of electrons on iodine is an appropriate building block as proposed by Bergman [1]. The coordination of this asymmetrical ligand to cations favours the formation of acentric inorganic crystals. Furthermore, these metallic iodates present high non linear coefficients and high optical damage thresholds on powders and are particularly interesting for infrared applications as they possess a large domain of transparency from visible to the beginning of the far-infrared (12 □m) [2-5]. The environment of I(V) in iodate groups is formed by three strong bonds (mean bond length: 1.80 Å) corresponding to an AX_3E conformation. In addition, the environment of iodine is generally filled up by three weak bonds (mean bond lengths in the range 2.45 Å to 3.00 Å) arranged around the lone pair direction. This leads to an octahedron in which the iodine atom is displaced off centre along the ternary axis [6]. In the I_2O_5 iodic anhydride structure we observe intermediate I-O bond lengths (1.94-1.96 Å) and short I…O interactions (2.22 Å) which give a five coordination number of iodine. The discovery of new oxo-iodine (V) anions as IO_4^{3-} and $I_3O_8^-$ brings some questions. Indeed, some interatomic distances between oxygen and iodine from different anions are in the same range as bond lengths. Thus what is the maximal I-O bond length that we have to consider to define a chemical entity? Bond or interaction that is the question.

In order to answer this question, theoretical calculations using the gas-phase geometries for theses species are optimized with several basis sets and computational methods. The optimized geometries are compared with the experimental structures. The bonding in iodates has been investigated from the natural bond orbital and electron localization function analyses.

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MS43 O4

Charge Distribution (CD) of anion-centred structures

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Keywords: Anion-centred structures; Charge Distribution; Ionic radius

The charge distribution (CD) method [1] gives a description of the connectivity of crystal structures based on a Madelung scheme. The applicability of the method does not depend on the nature of the chemical bonds in the structure, provided that this does not contain polycations or polyanions (groups containing cation-cation or anion-anion bonds). The method computes the Effective Coordination Number (ECoN) on the basis of the experimental geometry of each coordination polyhedra and distributes the result among all the chemical bonds in which are involved atoms of the given polyhedron. The formal oxidation number (charge) is used as weight of this distribution that, after summing up around each atom, should be obtained back. Discrepancies around the corner atoms (**V**-atoms) suggest a certain degree of over- or under-bonding, whereas discrepancies around the **P**olyhedra-**C**entring-Atoms question the structure validity or the applicability of the method. In the computation, no empirical parameter is used, apart from an exponent that is constant and simply determines the decrease rate of the bond strength with the bond length: this is a fundamental difference with respect to other empirical methods like. e.g., the bond-valence method.

In the Madelung scheme, crystal structures are commonly described as packing more or less compact of electronegative atoms (the "anions") with the electropositive atoms (the "cations") occupying the empty sites formed by the packing. A smaller, but not negligible, number of structures have been reported, where the role of the two types of atoms seems be inverted, or at least interchangeable. Recent studies have drawn more attention on this alternative description. We have generalized the software developed for the CD calculation to treat both cases, and now the same structure can be easily analysed in terms of CD both as "cation-centred (CC)" and "anion-centred (AC)". A number of structure previously considered doubtful or significantly over-under-bonded appear correct and well balanced when the AC description is adopted. Apart from cases where the numerical effect of very distorted CC polyhedra vs. more regular AC polyhedra seems to explain the difference, the AC description seems in general more reasonable when the structure contains large cations. In fact, often the relative sizes of the atoms seem to be a key factor, an aspect which determines the (not necessarily close) packing of the structure. In this respect, the effective atomic size needs to be evaluated carefully taking into account the previous critics to the concept of ionic radii [2]. Finally, a comparison of the results in both models (CC and AC) is recommended before making a conclusion about the validity and the bonding balance of the structure.

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MS43 O5

What we can learn from interatomic distances - Some case studies using the bond valence method.

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Keywords: bond length/bond strength, chalcogenides, mixed valence

The bond valence method [1, 2] relating a bond length to its bond valence by the formula:

$$v_{ij}=\exp[(R0_{ij}-d_{ij})/b_{ij}],$$

$R0_{ij}$, b_{ij} being individual parameters for a pair of bonded atoms, and d_{ij} the actual bond distance, is very useful for the analysis of interatomic distances in general. In this paper some special applications and experiences will be presented.

In complex anions the charge of a ligand can be estimated as the difference between its chemical valence and its