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► **To cite this version:**

J. Contreras-García, Carlos Cardenas. On understanding the chemical origin of band gaps. *Journal of Molecular Modeling*, 2017, 23 (9), pp.271. 10.1007/s00894-017-3434-5 . hal-01613136

HAL Id: hal-01613136

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Submitted on 9 Oct 2017

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On understanding the chemical origin of band gaps

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Abstract

Conceptual DFT and Quantum Chemical Topology provide two different approaches based on the electron density to grasp chemical concepts. We present a model merging both approaches, in order to obtain physical properties from chemically meaningful fragments (bonds, lone pairs) in the solid. One way to do so is to use an energetic model that includes chemical quantities explicitly, so that the properties provided by conceptual DFT are directly related to the inherent organization of electrons within the regions provided by topological analysis. An example of such energy model is the Bond Charge Model (BCM) by Parr and collaborators. Bonds within an ELF-BCM coupled approach present very stable chemical features, with a bond length of ca. 1Å and $2\bar{e}$. Whereas the $2\bar{e}$ corroborate classical views of chemical bonding, the fact that bonds always expand along 1Å introduces the concept of geometrical transferability and enables to estimate crystalline cell parameters.

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Moreover, combining these results with conceptual DFT enables deriving a model for the band gap where the chemical hardness of a solid is given by the bond properties, charge, length and a Madelung factor, where the latter plays the major role. In short, the fundamental gap of zinc-blende solids can be understood as given by a $2\bar{e}$ bond particle asymmetrically located on a 1\AA length box and electrostatically interacting with other bonds and with a core matrix. This description is able to provide semi-quantitative insight into the band gap of zinc-blende semiconductors and insulators on equal footing, as well as a relationship between band gap and compressibility.

In other words: merging these different approaches to bonding enables to connect measurable macroscopic behavior with microscopic electronic structure properties and to obtain microscopic insight into the chemical origin of band gaps, whose prediction is still nowadays a difficult task.

1. Theoretical framework(s)

It is well known that the electron density is of paramount importance to fully understand the ground-state properties of many-electron systems. As remarked by Yang et al:¹ “Interactions between electrons determine the structure and properties of matter from molecules to solids. To describe interacting electrons, the extremely simple 3D electron density can be used as the basic variable within density functional theory^{2,3} negating the need in many cases for the massively complex many-dimensional wave function.” The electron density prominence derives from the Hohenberg-Kohn theorems,⁴ which prove the existence of a functional relation between the electron distribution and the observables of non-degenerate electronic systems on their ground-state. Moreover, Density Functional Theory (DFT) is not only an alternative way to describe the electronic structure of matter but it also provides a convenient framework to construct formal definitions of chemical concepts. This branch of DFT is known as conceptual DFT or chemical DFT (c-DFT).^{3,5-11} The formal definitions of these concepts have also permitted to demonstrate ideas basic to chemistry such as Pearson’s Hard-Soft Acids-Bases (HSAB) rule.¹² Chemical hardness,

η , and electronegativity, χ , have been two concepts developed over time for the rationalization of reactivity and chemical bonding on empirical grounds. It was one of the great successes of c-DFT to provide a rigorous definition for both of them as the response of the energy of the system, E , to the change in the number of electrons, N , at fixed external potential, v (for example due to the nuclear configuration):¹³

$$\chi = - \left(\frac{\partial E}{\partial N} \right)_v \quad (1)$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_v \quad (2)$$

These derivatives imply that the system is open to particles. If the system is not open, the energy is a piecewise function of N with straight lines between integers and discontinuity of the derivatives at integer N . If the system is open, E vs. N is a smooth function. The shape of E vs. N reflects the details of the interaction of the system with the *chemical environment*. Numerous models have been proposed in the literature,^{14–18} but the simplest interpolation of E vs N is the parabola, which provides operational definitions of the χ and η :^{13,19}

$$\chi = \frac{I+A}{2} \quad (3)$$

$$\eta = I - A \quad (4)$$

where I is the vertical ionization potential and A is the vertical electron affinity.

Note that for solids, $I - A$ is nothing but the fundamental gap,

$$\eta = E_{gap} \quad (5)$$

and $-\chi = -\frac{I+A}{2}$ falls exactly at the midpoint of the band gap, i.e., the Fermi level,

$$\chi = -E_f \quad (6)$$

Clearly, chemical DFT enables to link responses of the energy with chemical information. However, chemical information should also be encoded in the electron density and other 3D fields related to it. Indeed, many theories have been developed to understand electronic structure in real space based on the mathematical framework of topology (leading to what is known as Quantum Chemical Topology). The most prominent approaches are the Quantum Theory of Atoms In Molecules (QTAIM)^{20,21} theory and the Electron Localization Function (ELF).²²⁻²⁴ By means of the topological analysis of the three-dimensional electron density and the definition of surfaces of zero electronic flux, QTAIM divides direct space into discrete atomic basins, which provide self-consistent atomic properties such as charges and volumes, as well as a topological inter-atomic bond path motif, which is assigned to the molecular structure. The character of the bond can be extracted from various characteristics calculated at the bond critical point, such as the bond ellipticity²⁵ or metallicity.²⁶⁻²⁸ The Laplacian of the density is used as an indicator of local charge concentration,²⁹ which yields also information about bonding in real space. Currently, QTAIM is being used by both theoreticians and experimentalists in fields ranging from solid state physics and X-ray crystallography to drug design and biochemistry.³⁰

The Electron Localization Function (ELF) constitutes a very useful tool for understanding Lewis pairs in real space. ELF is based on the same-spin pair probability density, thus generating basins of localized electron pairs.²² Alternatively, ELF can also be understood as an excess of kinetic energy density induced by the Pauli principle.²³ In localized systems, the ELF value approaches 1 in regions of space where electron pairing occurs (atomic shells, bonds and lone pairs), and 0 in the limit between those surfaces, where there is a high probability of finding electrons from different localized pairs. As the system becomes more delocalized (e.g. bond formation³¹ or in metals^{32,33}), both the values at the maxima and inter-basin approach 0.5 (the value for the homogeneous electron gas).

All these topological partitions have been widely generalized to develop the so-called Quantum Chemical Topology framework, which includes the different scalar fields,³⁴⁻³⁹ and which has been successfully employed for the analysis of chemical bond in molecules and solid state as well as to

provide further understanding of chemical reactivity.⁴⁰⁻⁴³

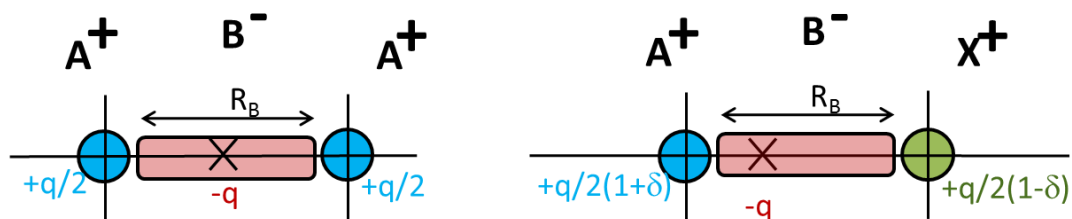


Figure 1: Bond charge model for homonuclear (left) and heteronuclear (right) molecules, A_2 and AX , respectively. The meaning of the main parameters that are needed in each case is shown in the figures: q and R_B for homonuclear molecules and q , δ and R_B do for heteronuclear ones; B label stands for the bond.

Whereas c-DFT dwells on chemical responses from the electron density, topology connects the electron density and related fields with chemical regions (bonds, lone pairs) in real space. An interesting approach would then be to combine both approaches, topology and conceptual DFT, in order to obtain chemically meaningful properties from chemically meaningful fragments (bonds, lone pairs) in the solid. One way to do so is to use a potential energy surface, PES, that includes chemical quantities explicitly, so that the properties provided by conceptual DFT (Eqs. 1 & 2) are directly related to the inherent organization of electrons within the regions provided by topological analysis.

According to this parabolic approach, the energy of the system close to equilibrium can be assumed as given by a second order expansion. Parr and collaborators used this approach providing a physical meaning (kinetic and potential energy) to each term in what is known as the Bond Charge Model (BCM).⁴⁴ The physical basis of the model starts from the simplest case, a homonuclear diatomic molecule (A_2), modeled as a three body system: two punctual core charges and a bond, which is a negative charge moving freely between them. In order to keep electrical neutrality, these charges correspond to $+q/2$ and $-q$ for the cores and the bond, respectively. The bonding charge is represented as a $-q$ charge particle in a box of length $R_B = \nu R$, where R is the interatomic distance. Close to the equilibrium, the energy of the system can be assumed as given by a second order

expansion, where terms can be associated a physical meaning:

$$E(q, R) = E_0 + E_1 + E_2 = 2E_A - \frac{Cq^2}{R} + \frac{D'q}{R_B^2}, \quad (7)$$

E_0 is the core internal energy, which should not be mistaken with the energy of the free atoms, but the energy of the atoms in the molecule once they have donated $q/2$ electrons to the bonding region ($E_0 = 2E_A$ in the homonuclear case). E_1 can be associated with the coulombic interactions (core-core, core-bond) and E_2 with the bond charge kinetic energy. Following this interpretation, the constants are given by :⁴⁴

$$C = \frac{7}{4}, \quad D' = \frac{\hbar^2 \pi^2}{2m}, \quad (8)$$

and the parameters q and ν are found empirically for each molecule. Note that these fittings have lead to values of $\nu > 1$, i.e. to bond lengths longer than the interatomic distance (e.g. $\nu = 2.3$ for H_2 ⁴⁴).

When heteronuclear molecules are considered (see Figure 1b), two extra parameters need to be fitted:

1. the deviation of the bonding charge from the center of the bond length. The asymmetry is taken into account with the r_1/r_2 parameter, the ratio of the distances from the centre of the bond charge to each of the cores
2. the contribution of each atom to the bond charge. This is taken into account with the δ parameter, so that cores will hold a charge of $+q/2(1 + \delta)$ and $+q/2(1 - \delta)$, respectively.

Coupling conceptual DFT concepts to this energetic model has lead to the development of hardness and electronegativity in molecules within the QTAIM approximation,^{45,46} showing for example that protonation increases electronegativity of a group while deprotonation decreases it.⁴⁷

Note that the main idea behind the BCM model is that the space, \mathbb{R}^3 , can be split in core and bonding regions. In the case of diatomic molecules “chemical intuition” is enough to assign these

regions because the bonding region must be a fraction of the space between both atoms.⁴⁸ However, in more complex systems, such as solids or molecules with a non traditional bonding pattern, assignation of bonding regions based only in geometrical parameters could be unsatisfactory. In those cases bonding regions should be those where Lewis pairs are localized. Then, the core and bond (valence) basins of ELF provide well-defined core and bonding regions, respectively, for the BCM model. This was done in a first article by the authors,⁴⁹ where q_B was associated with the bond charge resulting from integration of the electron density over the valence basins of ELF, and R_B to the length of the bond basin along the bonding direction. Please note that within this combined ELF-BCM approach, bond charges and lengths adopt chemically intuitive values ($q \simeq 2 e$, $R_B < R$). This model was used to understand the evolution of energy with the unit cell size, V , and thus provide a microscopic understanding of the compressibility of solids. Moreover, explanations for the low compressibility of superhard materials were given, unifying the origin of the low compressibility of diamond and BN, whose chemical bond is extremely different (from homopolar to very polarized).

Band-gap prediction is critical for applications in condensed matter and nanotechnology. As an example, the band gap of solids, specially of semiconductors, encloses great potentiality if tuned in the correct direction in the design of solar cells. However, its accurate prediction from quantum chemistry methods is still difficult nowadays. Insight into the nature of the band gap and its relationship with the chemistry of the system is thus crucial. Hence, ELF-BCM will be coupled in this contribution to conceptual DFT to provide insight into the chemical hardness, i.e. the band gap, of solids along the zinc-blende series, where insulators and semiconductors coexist and share a common crystallographic description.

After introducing the theoretical and computational framework (Sections 1&2), we will present the BCM model for solids in Section 3.1. We will then couple it to ELF quantities in Section 3.2. We will show that bonds within an ELF-BCM coupled approach present very stable chemical features, making them transferable along the series. These bonding properties will then be used in Section 3.3 to disentangle the microscopic factors determining the band gap of zinc-blende solids

in real space. We will show that the chemical hardness of a solid is given by the bond properties, R_B , q_B and M , where M plays the major role. We will put all these results together in Section 4 in order to provide semi-quantitative insight into the band gap of semiconductors and insulators on equal footing as well as the relationship of their band gaps with their compressibility. The article ends with a summary and the main conclusions.

2. Computational details

In order to obtain ELF parameters, we have carried out DFT calculations on zinc-blende-type structures ranging from covalent to polar-covalent (IV, III-V and II-VI families) in order to ensure the existence of a basin associated with the bond while covering a big range of band gaps. As noted in Ref. 49, the application of this model to metals is conceptually weak due to the common appearance of several bonding basins. We have used the ELK code⁵⁰ with a high plane-wave cut-off to ensure convergence: $K_{max}R_{MT}=9$, where K_{max} is the maximum size of the reciprocal lattice vectors and R_{MT} holds for the smallest muffin-tin radius. In order to avoid discontinuities in the electron density due to the muffin-tin, spherical harmonics within each atomic sphere were expanded up to angular quantum number $l_{max}=14$. Perdew-Wang⁵¹ and Perdew-Burke-Ernzerhof⁵² exchange-correlation functionals were used. We have used 8x8x8 Monkhorst-Pack grids and a $1 \times 10^{-5} E_h$ as convergence criterion threshold.

Due to the difficulties found to describe band gaps with DFT, specially in semiconductors, we have used experimental band gaps as reference. Thus, our calculations were done with the room temperature experimental lattice parameters.⁵³

We have used the CRITIC code developed by some of the authors to obtain the ELF topology.^{54,55} CRITIC is able not only to find ELF maxima and saddle points but it can also construct basins and integrate properties.

The ELF-BCM Madelung factors, M , have been calculated with the Environ code.⁵⁶ Ewald sums have been verified with an in-house script to calculate the electrostatic energy of a periodic

crystal composed of point-like charges and converged to 10^{-15} (a.u.).⁵⁷

3. BCM, ELF and conceptual DFT

Band gaps in solids are usually understood in reciprocal space. However, a quick look at series of solids soon reveals periodic trends (see for example Figure 4). Thus, a relationship should exist between band gap and Lewis pairing in real space. In order to obtain insight into the microscopic nature of the band gap in terms of chemical quantities, we will use the bond charge model, which was extended by Martin⁶⁰ to describe the energy of covalent crystals. For simplicity, we consider a zinc-blende-type solid, AX , with a formula unit AXB_4 accounting for the four-fold coordination of the two elements in the unit cell, where B represents the bond entity. This series has been chosen due to its high symmetry, which will provide greater insight into the effects of periodicity, as well as due to its versatile E_{gap} , ranging from those of insulators to semiconductor materials.

3.1. BCM

In an expansion of the BCM model to solids, the energy of a AXB_4 unit will be given by:

$$E = E_A + E_X + 4E_B \quad (9)$$

where E_A and E_X are constants related to the internal core energy. The bond energy, E_B , is given by:⁴⁹

$$E_B = \frac{4D'q_B}{R_B^2} - \frac{Mq_B^2}{R_B}, \quad (10)$$

where M is an average Madelung factor (also called for brevity Madelung factor) for a solid with charges $2q_B(1 + \delta)$ and $2q_B(1 - \delta)$ at A and X atomic sites, respectively as well as a $-q_B$ charge at each bond position. Note the use of “factor” instead of “constant” to avoid confusion with the common “Madelung constant” concept which only applies to atoms.

At equilibrium Eq. 10 reduces to:

$$E_B = -\frac{4D'q_B}{R_B^2} = -\frac{Mq_B^2}{2R_B}, \quad (11)$$

3.2. BCM+ELF

We can couple the bond energy from Eq. 10 to ELF quantities in order to obtain BCM parameters (R_B , q_B , δ and r_1/r_2) from first principles.⁴⁹ This also allows calculating the Madelung factor, M . Table 1 collects the parameters for our set of zinc-blende solids. R_B is calculated from the 1D ELF profile in between A and X. Charge values (q_B and δ) are extracted from the ELF charges. We have assumed that cores remain untouched, so that $q_{val} = Z_A + Z_X$, where Z is the atomic number and q_c the core charge. For our AXB₄ compounds and given the ability of ELF to recover “chemical values”, this yields $q_B = q_{val}/4 \simeq 2$. Core values for the elements up to the 4th row involved in the solids under this study have been extracted from the ELF integrations gathered in Ref. 61. Beyond the 4th row, calculations were performed for the atoms with the TopMod program.⁴⁹ The value of δ comes naturally from this definition. From Section 3.1, the valency, q_{val}^i , of each atom type is related to δ as follows:

$$q_{val}^A = 4\frac{q_B}{2}(1 - \delta) \quad (12)$$

$$q_{val}^B = 4\frac{q_B}{2}(1 + \delta) \quad (13)$$

with X being more electronegative than A (see Figure 1 and Section 3.1). Hence δ can be directly obtained from the valency and the bond charge:

$$\delta = 1 - \frac{q_{val}^A}{2q_B} = \frac{q_{val}^B}{2q_B} - 1 \quad (14)$$

Since it only depends on the bond charge (ca. 2 electrons) and the valency, values within the same family are very close. This can be seen for example in the SiC entry of Table 1. Both C and Si have

the same $q_{val} = 3.9$,⁶¹ yielding the same q_B and the same δ (see Ref. 49). Finally, the position of the bond charge is taken from the maximum of ELF along the bonding direction. It should be noted that for a proper description of the electrostatic interactions, the center of charge would be the best definition. However, since ELF values are being used for the bond size, we have kept the ELF value for coherence. Moreover, we have checked the location of both points for a trial polar bond. The deviation of the of ELF attractor of the C-N bond in formamine from the center of charge was found to be 0.07 a.u., that is ca 2.5% of the bond distance.

Table 1: q_B and R_B parameters of ELF-BCM for a broad group of diamond-type and zinc-blende-type solids from the IV, III-V and IIb-VI groups.⁴⁹ M and E_B stand for the ELF-BCM Madelung factor and the bonding energy of the crystal, respectively. Bulk moduli at zero pressure, B_0 , were taken from Ref.⁵⁸ and band gaps from Ref.⁵⁹ Lengths are in Å, charges in electrons, E_B in atomic units, B_0 is GPa and E_{gap} in eV.

AX	R_B	q_B	M	E_B	B_0	E_{gap}
Group IV						
C	0.938	1.950	10.856	-11.644	442	5.2
Si	1.132	1.950	8.577	-7.623	98	1.12
Ge	1.003	2.100	7.414	-8.625	77.2	0.66
SiC	0.985	1.950	9.356	-9.556	211	2.86
Group III-V						
BN	0.936	1.975	11.006	-12.136	397	5.0
BP	1.050	2.000	9.662	-9.739	166	4.2
BAs	1.023	2.050	8.711	-9.468	144	3.0
BSb	0.999	1.988	8.554	-8.954	108	2.6
AlP	1.122	1.975	8.925	-8.206	86	3.1
AlAs	1.080	2.025	8.028	-8.068	77	2.16
AlSb	1.093	1.963	7.304	-6.810	58	1.52
GaAs	0.992	2.100	7.662	-9.008	75	1.35
GaSb	0.986	2.038	6.764	-7.538	57	0.71
InP	1.012	1.970	8.494	-8.615	71	1.25
InAs	0.958	2.020	7.268	-8.187	60	0.35
Group IIb-VI						
ZnS	1.001	2.025	10.130	-10.976	77	3.6
ZnSe	0.970	2.075	8.631	-10.134	62	2.6
ZnTe	0.971	2.038	7.415	-8.389	51	2.2
CdS	0.976	1.975	10.016	-10.512	62	2.5
CdSe	0.938	2.025	8.591	-9.697	53	1.7

It can be seen that trends arise for each family (highlighted in colors in Figure 3): group

IV, group III-V and group IIb-VI compounds. The heads of the groups have the smallest R_B and the biggest ELF-BCM Madelung factors (see Figure 2). However, both q_B and R_B changes are negligible in comparison with the changes in the Madelung factor, M (see Figure 2). Indeed, within this framework, q_B remains very close to the Lewis expectation, ca. $2\bar{e}$, and R_B is found to lay very close to 1\AA in all cases. It should be noted that this value approximately corresponds to twice the Bohr radius (i.e. “Bohr’s diameter”).

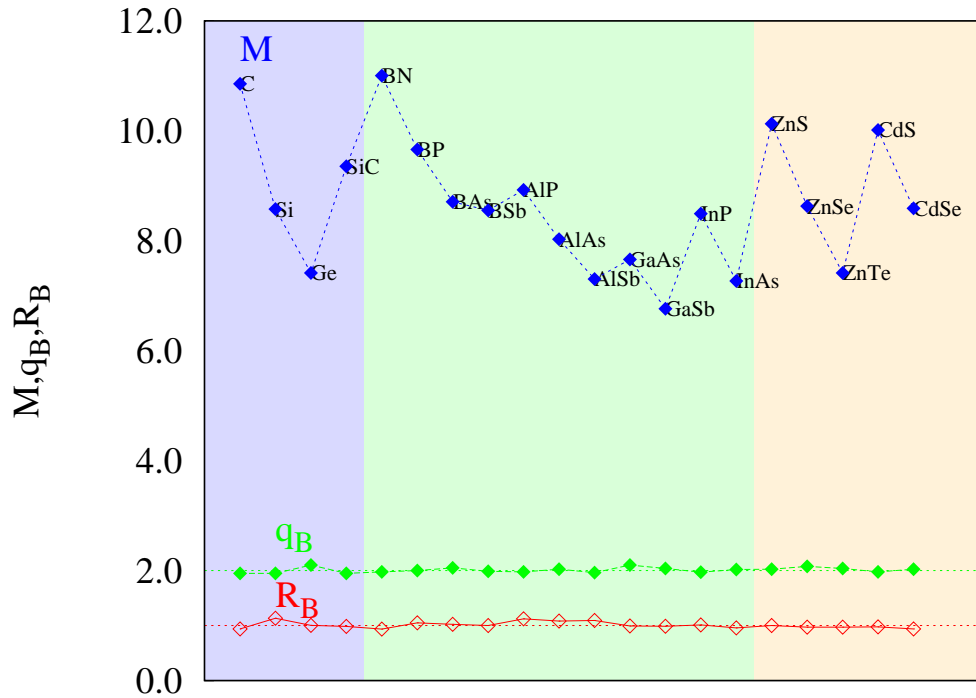


Figure 2: Evolution of ELF-BCM parameters along the zinc-blende series. Background colors have been used to highlight the three families: IV (purple), V-III (green) and IIb-VI (light orange). Lengths are in \AA , charges in electrons.

This means that the size of the bond along the interbonding direction does not depend on the lattice parameter of the crystal (which spreads over a range of ca. $3.5\text{-}6.1\text{\AA}$), neither on the two atoms involved in the bond. This transferability makes the use of ELF parameters within the BCM energy model very attractive. It also enables an estimation of cell parameters as a sum of

core+bonding contributions. In our zinc-blende solids:

$$a \simeq \frac{4}{\sqrt{3}} (r_A + r_X + R_B) \quad (15)$$

Taking ELF core radii from Ref. 61 and $R_B = 1\text{\AA}$, cell parameters can be estimated. Figure 3 shows the evolution of experimental cell parameters in our zinc-blende solids, along with the values predicted by Eq. 15. The relative (and absolute) values follow the experimental trends along the series, with two important trends appearing related to the softness of ions. Equations 1&2 can also be used in atoms to retrieve the classical concept of atomic hardness (as well as that of polarizability). Moreover, in agreement with Pearson’s approach, it has been found to be related to atomic radii, so that bigger atoms are softer and more polarizable.^{62–65} These concepts are very important to understand the deviations in Figure 3. Whereas compounds with a hard cation yield an underestimation, Eq. 15 overestimates the cell parameter in compounds with a soft cation. This is due to two contributions: the R_B estimation and the model itself. R_B tends to be slightly bigger than 1\AA in boron and aluminum compounds, and slightly smaller than 1\AA for the softer ions. However, this cannot be the only source of deviation. A look at Table 1 reveals that R_B values smaller and greater than one appear in both regions of Figure 3. We have identified the other source of deviation as due to our “shared electron model”. Softer and more polarized (i.e. bigger) atoms give greater deviations when combined together. This could be due to the greater delocalization (exchange) in between bonding basins that is overlooked in the model. Work in in process to improve the model in this direction. Hence, fulfillment of Eq. 15 can be understood as a first test to our model, which works well for the homonuclear family IV and for the III-V one with at least one hard atom.

3.3. BCM+ELF+c-DFT

If electrons were to be added or removed from the system, they would arrive or leave the bonding regions, respectively. This is, the core electrons do not take place in electron-number-changing process. Therefore, according to Eq. 2, the chemical hardness of the solid will be the chemical

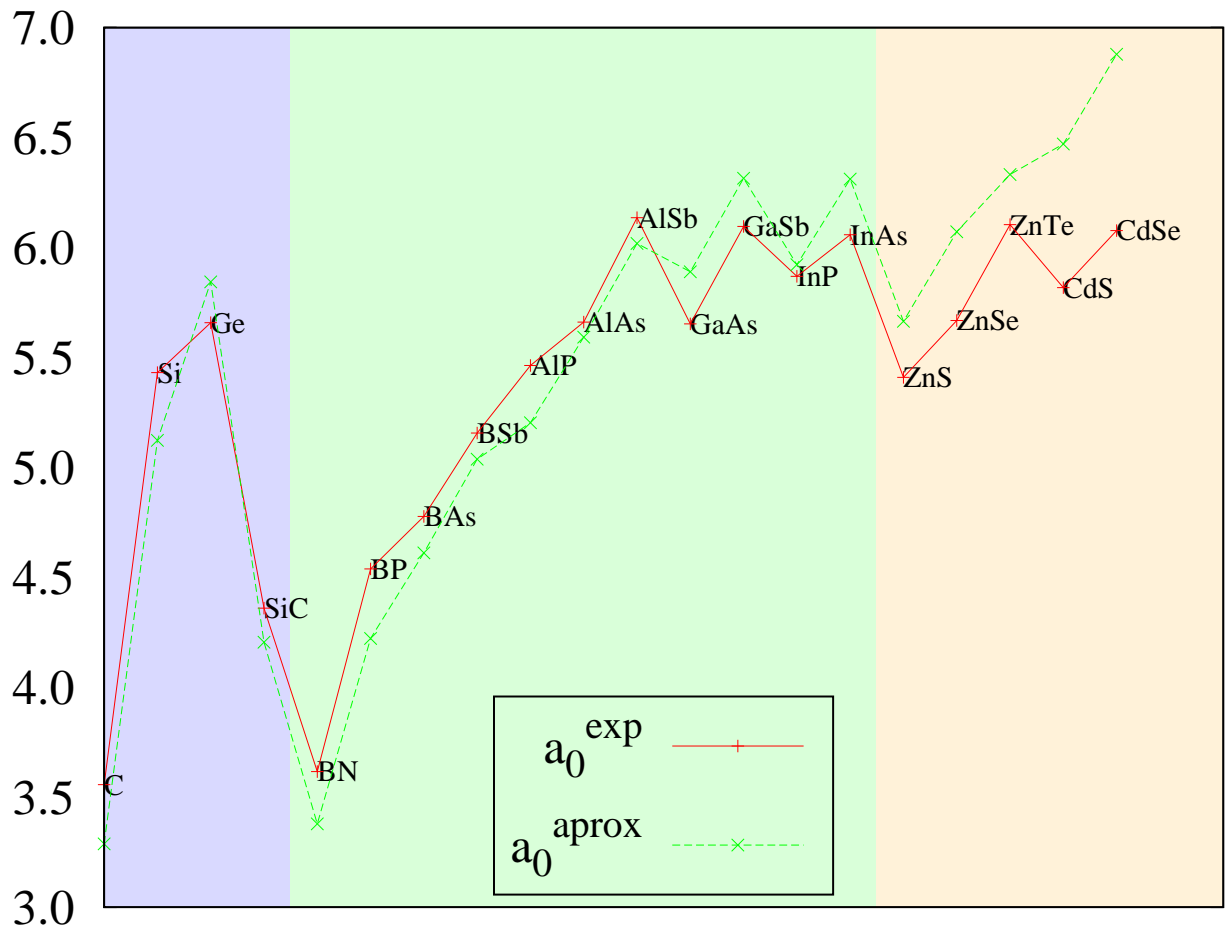


Figure 3: Evolution of experimental and estimated (Eq. 15) cell parameters (in \AA). Families are highlighted by a color code (purple for group IV, green for group III-V and light orange for group II-VIb).

hardness of the bonding regions, which is found by differentiating Eq. 10 twice with respect to q_B . This establishes a direct link between the band gap, the Madelung factor and the size of the bond basins. In other words, merging these approaches enables to recover old concepts, such as the involvement of valence electrons in the band gap, and semi-quantitatively relate their properties (charge, position of the ELF maximum) with the band gap:

$$E_{gap} = \frac{M}{R_B} \quad (16)$$

Band gaps calculated with Eq. 16 along with experimental ones are depicted in Figure 4. Although the model is too simple to predict absolute values, it is able to explain the trends in band gaps within each family. Note that the fact of considering a non equilibrium position would only shift the prediction by a factor of two, so that both approaches lead to the same conclusions. Although the model is too simple to predict absolute values, it is able to explain the trends in band gaps within each family. The band gap is bigger for the head of each family, where M is bigger and R_B smaller (see Figure 2). Band gaps also decrease for a given family (A or X fixed) as the other atom becomes softer, e.g. $BP > AIP > InP$, but also $BN > BP > BAs > BSb$.

It can be seen in Figure 3 that problems arise for soft atoms. In our band gap model this leads to the wrong trend in the CdS-ZnS couple. In addition of polarizability being problematic for the shared-electron model, metals are also less accurately described in this model. Bonding regions in metallic systems are more delocalized, so that the approximation of the bond energy is probably insufficient.

As noted above, the global chemical hardness parameter and the size of the free atom are inversely related. However, in our periodic systems, R_B is nearly constant, so that M becomes the determining factor in Eq. 16. Figure 5 has been constructed for compounds up to the 4th row (see Section 2). As can be seen, the Madelung factor becomes a good indicator of the band gap.

Hence, it would be interesting to understand the origin of M . In our chemical definition of zincblende solids, lattices are not invariant structures. Following Glasser's definition, our Madelung

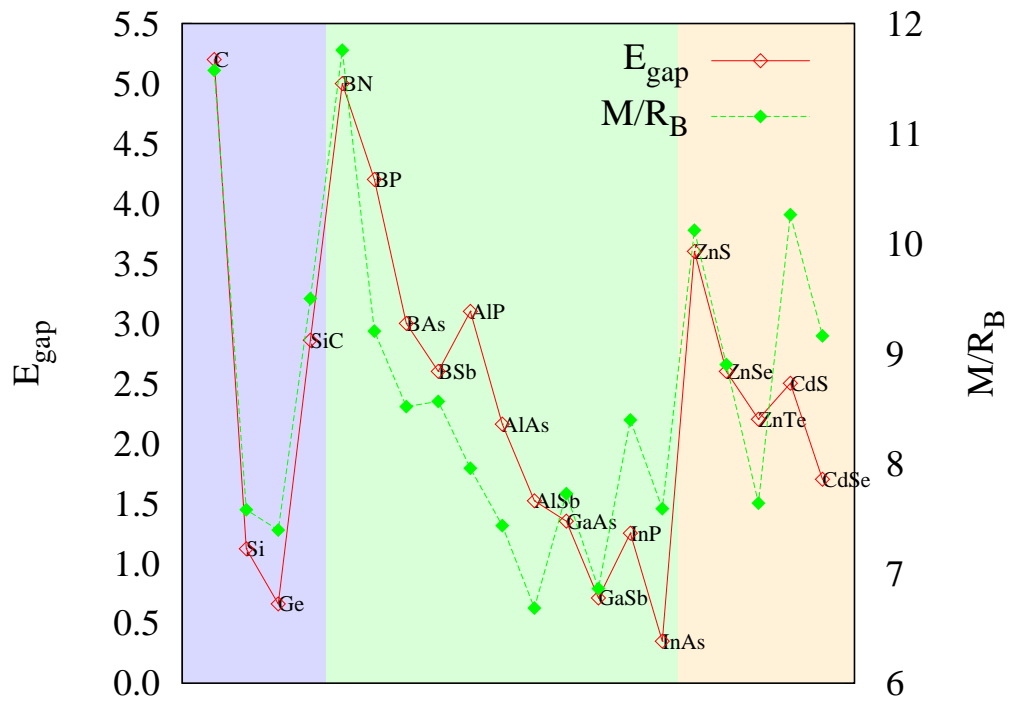


Figure 4: Band gap (in eV) for IV (purple), III-V (green) and II-VI (light orange) compounds from experimental data and from Eq. 16.

factor is given by:⁶⁶

$$M = -\frac{1}{2Z} \left[\sum_i^{neq} \left(\frac{q_i}{q_B} \right) C_i Z_i \right]. \quad (17)$$

where Z is the multiplicity of the formula unit, and the i -index runs over all non-equivalent (neq) entities in the unit cell, with Z_i being their corresponding multiplicities.

C_i is the Madelung factor for each of the non-equivalent entities:

$$C_i = -V_i^M \frac{R_B}{q_B}, \quad (18)$$

where V_i^M is the Madelung potential at the position of the i -th non-equivalent entity. Hence, C_i and M depend on a reference charge, q_B and distance, R_B .

For our AXB_4 structures, there are two contributions, C_A and C_X , which are position invariable, and one which is not, C_B . Whereas A and X are in fixed Wyckoff positions, C_B , depends on the position of the bond along the A - X axis. From the symmetry and stoichiometry of the zinc-blende-type solids, M can be simplified as

$$M = 2C_B - (1 + \delta)C_A - (1 - \delta)C_X, \quad (19)$$

which yields different values for each of the crystals studied.

The C_i contributions to M are collected in Figure 5. Whereas C_A reveals the different families, C_X reveals the internal organization within each family. The bond contribution, C_B provides a compensated picture intra and interfamilial. This is represented separately in Figure 6. The Bond Madelung factor, C_B , is found to correlate fairly well with band gap evolution, playing the major role determining the macroscopic band gap. In other words, we can understand the band gap, defined in reciprocal space, as coming from the electrostatic interaction of the bond charge with its environment (other bonds and cores).

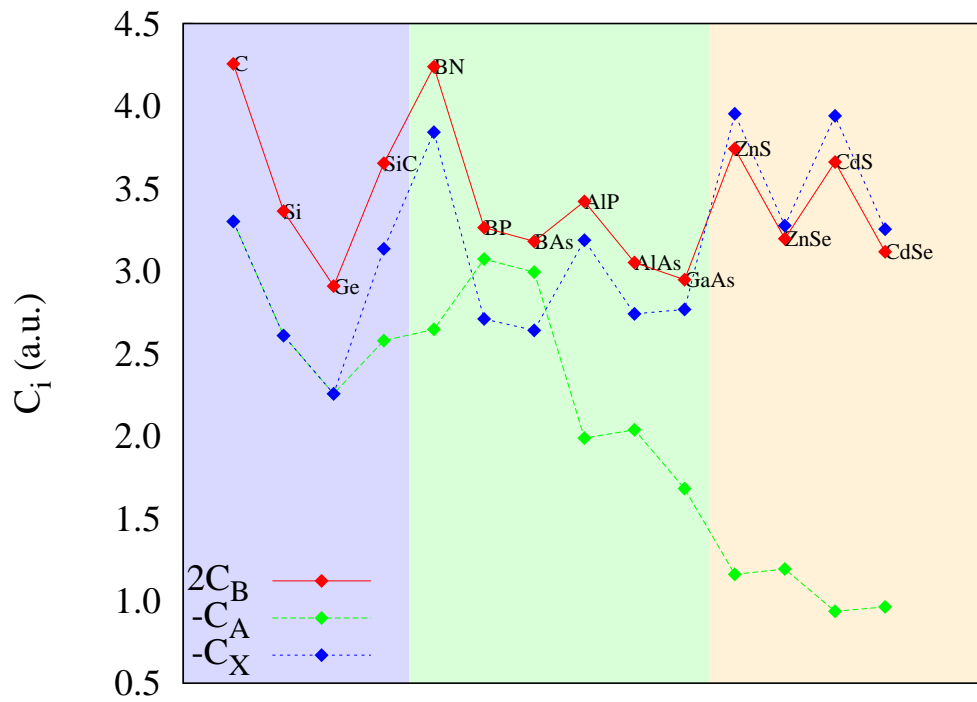


Figure 5: Ionic Madelung factors for IV (purple), III-V (green) and II-VI (light orange) compounds.

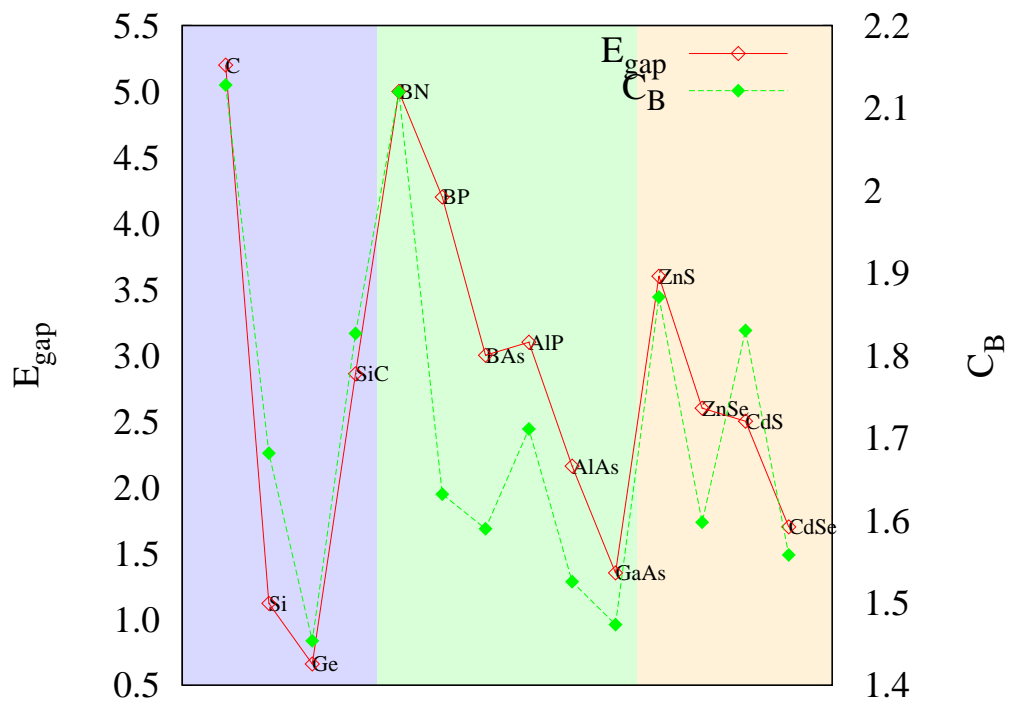


Figure 6: Experimental band gap (in eV) for IV (purple), III-V (green) and II-VI (light orange) compounds and comparison with their Bond Madelung factor, C_B .

4. “Chemical and physical hardness”

Summarizing the results from Sections 3.1-3.3, the fundamental band gap of zinc-blende solids can be understood as that of 2 electron particles asymmetrically located on a 1\AA length and electrostatically interacting among them and with a core matrix. Thus, two geometrical parameters control the trends: the cell parameter and the displacement of ELF maximum (i.e. r_1/r_2) within the bonding basin. Whereas the first factor can be estimated (we have seen in Figure 3 it is related to core radii and the estimated 1\AA bond length), we have not found an easy connection for estimating the second one (approximating the behavior to that of the homonuclear case, Wyckoff position 16e, has shown to be insufficient). However, this geometrical description of the band gap makes a direct connection with the cell volume, so that it is possible to relate it with the solid compressibility. Within the BCM model, the bulk modulus, B_0 , can be expressed as:⁴⁹

$$B_0 = \frac{2M}{9R_B} \frac{q_B^2}{V}, \quad (20)$$

giving the following relationship between the band gap and the bulk modulus:

$$B_0 = \frac{2}{9} \frac{E_{gap} q_B^2}{V}. \quad (21)$$

This expression is intimately related to the one derived by Yang,⁶⁷ where the hardness of a solid is inversely proportional to its compressibility (recall that the compressibility, κ is the inverse of the bulk modulus). This relationship is represented in Figure 7 for our set of solids, where the intrinsic relationship between chemical hardness and resistance to hydrostatic compression is apparent. Compressibility depends mainly on the chemical hardness and the volume. It has been shown within the ELF approach that volume and compressibility are related to the chemical nature of the Lewis entity in agreement with VSEPR principles:⁶⁸

$$V_{LP} > V_{MB} > V_{SB} > V_{core} \quad (22)$$

$$\kappa_{LP} > \kappa_{MB} > \kappa_{SB} > \kappa_{core}, \quad (23)$$

where LP, MB and SB stand for lone pair, multiple bond and single bond, respectively. Taking into account that within the topological approach volumes are additive, $V = \sum V_i$, it can be shown that the compressibility can be expressed as $\kappa = \sum x_i \kappa_i$, where κ_i refers to each Lewis' entity compressibility and $x_i = \frac{V_i}{V}$ to its cell occupation.⁶⁹ Hence, softer and bigger bonds are the ones that determine the compressibility of the system. Extremely localized solids, such as diamond, yield very high bulk modulus and big band gaps, whereas more delocalized bonds, like those of semiconductors, are softer and give smaller band gaps and greater compressibilities. These two quantities being interrelated by Eq. 21.

This also highlights one of the most important take-home messages of common compounds in main-group chemistry: localized orbitals and delocalized planewaves are two electronic organizations of great stability that give rise to very stable and detectable chemical patterns where “everything correlates with everything”.⁷⁰ Hence, the properties of their bonds determine many of their macroscopic properties in an interrelated manner.

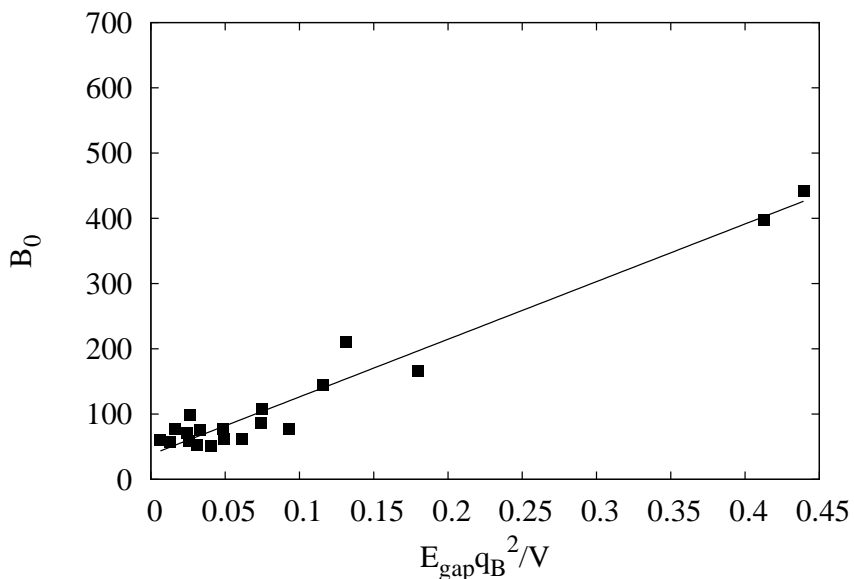


Figure 7: Relationship between the bulk modulus and the band gap in the zinc-blende series according to Eq. 21.

5. Summary and conclusions

Band gaps are error-prone quantities within quantum chemistry, but which show an important periodic behavior. Moreover, calculations of these properties do not provide a direct link with the composition, which hampers inverse design. An important issue for example for solar cells. From the chemical point of view, the link between band gap and molecular orbitals has been known for a long time (e.g. the gap in diamond corresponds to a bonding-antibonding gap, whereas in rock salt it corresponds to a charge transfer gap). This contribution intends to provide a working theoretical approach to formalize the link in real space: the relationship between the chemical bond and the band gap of solids. Making use of the Bond Charge Model, we have merged the topological description of solids in real space with the conceptual DFT description of their band gap in reciprocal space in order to understand its microscopic origin.

We have found that bonds within an ELF-BCM coupled approach present very stable chemical features, with a bond length of ca. 1\AA and $2\bar{e}$. Whereas $2\bar{e}$ charges are in agreement with classical views of chemical bonding (which was not the case of the original BCM charges), the constant bond lengths introduce the concept of geometrical transferability and enable estimating cell parameters.

Using this approach to analyze band gaps we have found that the hardness of a solid is given by the bond properties, R_B , q_B and M , where M plays the major role. Moreover, band gap trends can be explained in terms of the Madelung factor associated with the bond.

Hence, the fundamental band gap of zinc-blende solids can be understood as that of 2 electron particles asymmetrically located on a 1\AA length and electrostatically interacting among them and with a core matrix. This description is able to provide semi-quantitative insight into the band gap of zinc-blende solids (from semiconductors to insulators) on equal footing as well as the relationship with compressibility. As far as applications to metals is concerned, due to the appearance of numerous bonding basins, the coupling of ELF and c-DFT becomes more difficult.

Acknowledgments

CC acknowledges support by the Fondo Nacional de Investigaciones Científicas y Tecnológicas (FONDECYT, Chile) under grant #1140313, Financiamiento Basal para Centros Científicos y Tecnológicos de Excelencia-FB0807, and project RC-130006 CILIS, granted by the fondo de Innovación para la competitividad Del Ministerio de Economía, Fomento y Turismo, Chile,

References

- (1) A. J. Cohen, P. Mori-Sánchez, and W. Yang. *Science* (2002) 321,792
- (2) W. Kohn, L. J. Sham, *Phys. Rev.* (1965) 140, A1133.
- (3) R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989
- (4) P. C. Hohenberg, W. Kohn, *Phys. Rev.* (1964) 136, B864
- (5) H. Chermette, *Coord. Chem. Rev.* (1998) 180, 699
- (6) P. Fuentealba, C. Cardenas, *Chem. Model.* (2015) 11, 151
- (7) S.-B. Liu, *Acta Physico-Chimica Sinica* (2009) 25, 590
- (8) J. Gazquez, *J. Mex Soc.* (2008) 52, 3
- (9) P. K. Chattaraj, U. Sarkar, D. R. Roy, *Chem. Rev.* (2006) 106, 2065
- (10) P. W. Ayers, J. S. M. Anderson, L. J. Bartolotti, *Int. J. Quantum Chem.* (2005) 101, 520
- (11) P. Geerlings, F. de Proft, W. Langenaeker, *Chem. Rev.* (2003) 103, 1793
- (12) R. G. Pearson. *Proc. Nati. Acad. Sci. USA* (1986) 83, 8440
- (13) R. G. Parr, R. G. Pearson, *JACS* (1983) 105,7512

- (14) P. W. Ayers, *Faraday Discussions* (2007) 135, 161
- (15) P. Fuentealba, C. Cardenas, *J. Molec. Model.* (2013), 19, 2849
- (16) S. Noorizadeh, E. Shakerzadeh, *J. Phys. Chem. A* (2008) 112, 3486
- (17) S. Noorizadeh, H. Parsa, *J. Phys. Chem. A* (2013) 117, 939
- (18) F. Heidar-Zadeh, M. Richer, S. Fias, R. A. Miranda-Quintana, M. Chan, M. Franco-Pérez, C. González-Espinoza, E. Cristina, T. D. Kim, C. Lanssens, Caitlin and A. H. G. Patel and others, *Chem. Phys. Lett.* (2016) 660, 307
- (19) R. G. Parr, R. A. Donnelly, M. Levy, W. E. Palke, *J. Chem. Phys.* (1978) 68, 3801
- (20) R. F. W. Bader, *Atoms in Molecules, A Quantum Theory*. Oxford: Clarendon, 1990
- (21) R. F. W. Bader, In *The Encyclopedia of Computational Chemistry*; P. Schleyer, N. L. Alinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. III Schaefer, P. R. Schreiner, Eds.; Wiley: Chichester, U.K., 1998
- (22) A. D. Becke, K. Edgecombe, *J. Chem. Phys.* (1990) 92, 5397
- (23) A. Savin, O. Jepsen, J. Flad, L. Andersen, H. Preuss, *Angew. Chem. Int. Ed. Engl.* (1992) 31, 187
- (24) B. Silvi, A. Savin, *Nature* (1994) 371, 683
- (25) R. F. W. Bader, T. Slee, D. Cremer, E. Kraka, *J. Am. Chem. Soc.* (1983) 105, 5061
- (26) S. Jenkins, *J. Phys.: Condens. Matter* (2002) 14, 10251
- (27) S. Jenkins, P. W. Ayers, S. R. Kirk, P. Mori-Sánchez, A. Martín Pendás, *Chem. Phys. Lett.* (2009) 471, 174
- (28) N. Seriani *J. Phys.: Condens. Matter* (2010) 22, 255502

- (29) R. F. W. Bader, P. MacDougall, C. Lau, *J. Am. Chem. Soc.* (1984) 106, 1594
- (30) C. F. Matta and R. J. Boyd, Eds. *The Quantum Theory of Atoms in Molecules. From Solid State to DNA and Drug Design*; Wiley-VCH: Weinheim, 2007.
- (31) J. Contreras-García, J. M. Recio, *Theor. Chem. Acc.* (2011) 128, 411
- (32) M. Marques, M. Santoro, C. L. Guillaume, F. Gorelli, J. Contreras-García, R. Howie, A. F. Goncharov, E. Gregoryanz, *Phys. Rev. B* (2011) 83, 184106
- (33) M. Marques, G.J. Ackland, L.F. Lundegaard, J. Contreras-García, M.I. McMahon, *Phys. Rev. Lett.* (2009) 103, 115501
- (34) P.L.A. Popelier, *Quantum Chemical Topology: on bonds and potentials*, in: D.J. Wales (Ed.) *Structure and bonding: Intermolecular forces and clusters I*, Springer, Heidelberg, 2005
- (35) P.L.A. Popelier, E.A.G. Bremond, *Int. J. Quantum Chem.* (2009) 109, 2542
- (36) F. Cortés-Guzmán, R. F. W. Bader, *Coord. Chem. Rev.* (2005) 249, 633
- (37) G. Merino, A. Vela, T. Heine, *Chem. Rev.* (2005) 105, 3812
- (38) P. L. A. Popelier, P. J. Smith, *Specialist Periodical Reports Chemical Modelling: Applications and Theory*; A. Hinchliffe, Ed.; The Royal Society of Chemistry: Cambridge, 2002; p 391
- (39) P. L. A. Popelier, F. M. Aicken, S. E. O'Brien, *Specialist Periodical Reports Chemical Modelling: Applications and Theory*; A. Hinchliffe, Ed.; The Royal Society of Chemistry: Cambridge, 2000; p 143
- (40) S. Berski, J. Andrés, B. Silvi, L.R. Domingo, *J. Phys. Chem. A* (2006) 110, 13939
- (41) J. Poater, M. Duran, M. Sola, B. Silvi, *Chem. Rev.* (2005) 105, 3911
- (42) J. Berges, I. Fourre, J. Pilmé, J. Kozelka, *Inorg. Chem.* (2013) 52, 1217
- (43) B. Silvi, *J. Phys. Chem. A* (2003) 107, 3081

- (44) R. F. Borkman, R. G. Parr, J. Chem. Phys. (1968) 48, 1116
- (45) R. J. Boyd, K. E. Edgecombe, J. Am. Chem. Soc. (1988) 110, 4182
- (46) L. Komorowski, S. L. Boyd, R. J. Boyd, J. Phys. Chem. (1996) 100, 3448
- (47) R. J. Boyd, S. L. Boyd, J. Am. Chem. Soc. (1992) 114, 1652
- (48) T. Berlin, J. Chem. Phys. (1951) 19, 208
- (49) J. Contreras-García, M. Marques, J.M. Menendez, J.M. Recio, Int. J. Mol. Sci. (2015) 16, 8151
- (50) <http://elk.sourceforge.net/>
- (51) J. P. Perdew, Y. Wang, Phys. Rev. B (1992) 45, 13244
- (52) J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. (1996), 77, 3865
- (53) D W Palmer, www.semiconductors.co.uk, 2008.03.
- (54) J. Contreras-García, A. Martín Pendás, B. Silvi, J. M. Recio, J. Phys. Chem. Solids (2008), 69, 2204
- (55) J. Contreras-García, B. Silvi, A. Martín Pendás, J. M. Recio, J. Chem. Theory Comput. (2009), 5, 164
- (56) Available upon request at the Oviedo Quantum Chemistry Group (<http://azufre.quimica.uniovi.es/qcg-home.html>)
- (57) <http://azufre.quimica.uniovi.es/software.html>
- (58) M. L. Cohen, Phys. Rev. B (1985) 32, 7988
- (59) P. Manca, J. Phys. Chem. Solids (1961) 20, 268
- (60) R. M. Martin, Chem. Phys. Lett. (1968) 2, 268

- (61) M. Kohout, A. Savin, *Int. J. Quant. Chem.* (1996) 60, 875
- (62) J. L. Gasquez, E. Ortiz, *J. Chem. Phys.* (1984) 81, 2741
- (63) C. Cardenas, P. W. Ayers, F. de Proft, D. J. Tozer, P. Geerlings, *Phys. Chem. Chem. Phys.* (2011) 13, 2285
- (64) C. Cardenas, *Chem. Phys. Lett.* (2011) 513, 127
- (65) C. Cardenas, W. Tiznado, P. W. Ayers, P. Fuentealba, *J. Phys. Chem. A* (2011) 115, 2325
- (66) L. Glasser, *Inorg. Chem.* (2012) 51, 2420
- (67) W. Yang, R. Parr, *Physics and Chemistry of Minerals* (1987) 15, 191
- (68) J. Contreras-Garcia, P. Mori-Sánchez, B. Silvi, J. M. Recio, *J. Chem. Theor. Comp.* (2009) 5, 2108
- (69) A. Martín Pendás, A. Costales, M. A. Blanco, J. M. Recio, and V. Luaña, *Phys. Rev. B* (2000) 62, 13970
- (70) Patricio Fuentealba at Solvay Workshop “Conceptual Quantum Chemistry: Present Aspects and Challenges for the Future” (Brussels, Belgium, 2016)