

Cite this: DOI: 10.1039/xxxxxxxxxx

## Real space bond orders are energetic descriptors<sup>†</sup>

A. Martín Pendás\*, E. Francisco

Received Date

Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

Orbital invariant position space techniques are used to show a theoretical link between the conventional concept of bond order and the energetics of chemical interactions. Taking profit of the parallelism between the covalent and ionic interaction energies in the interacting quantum atoms (IQA) approach, a real space ionic bond order is defined. Expanding the covalent and ionic interaction energies as a multipolar series we show that the zero-th order terms in the expansion, those dominating the total interaction, are nothing but distance-scaled bond orders. A chemically intuitive picture emerges in which bonding is brought about by the Coulomb attraction of permanently transferred electrons, that give rise to ionic terms, and of shared pairs that count half to this electrostatics, which provide the covalent contributions. A set of representative molecules are examined to explore how the zero-th order approximation works. We show that, as expected, it improves with interatomic distance.

### 1 Introduction

Ever since the introduction of the electron pair by Lewis<sup>1</sup> in 1916 and the first successful description of the hydrogen molecule by Heitler and London with the new quantum mechanics,<sup>2</sup> the chemical bond concept has been a continuous spring of fascination. One of the sustained sources of controversy in this terrain is related to difficulties in reconciling the electron-counting and the energetic sides of bonding. The former leads to the formal concept of bond order (BO) as the number of shared electron pairs participating in a bond; the latter, to any of the many available definitions of bond energy.<sup>3</sup> The recognition of the different propensity of atoms to retain the electrons of the Lewis pair by Pauling<sup>4</sup> gave rise to the notion of electronegativity and to the heteropolar bond. From this on, literally dozens of covalent as well as ionic bond orders have been introduced, and bond energy-bond order relations (BEBO) proposed.<sup>5</sup> **For instance, one of the first attempts to connect bond orders with energetics can be traced back to the early studies of Hückel theory.** Today, the state of affairs has not yet sedimented, as it can be grasped from the completely messed up definition of bond order found in the IUPAC's gold book: "The electron population in the region between atoms A and B of a molecular entity at the expense of electron density in the immediate vicinity of the individual atomic centers".

Bond orders as well as bond energies suffer from two main definition difficulties: the tenacious obstacle of isolating atoms,

bonds or any other molecular fragment within molecules, and the non-invariance of orbital-based descriptors to changes in either the theoretical level or the methodological paradigm (molecular orbital theory, valence bond techniques, etc). This lies at the root of the multiplicity of definitions which we have referred to.

Real space techniques known as *Quantum Chemical Topology* (QCT)<sup>6</sup> solve the two problems above at once. By using descriptors invariant under general orbital transformations (i.e. based on position space reduced density matrices) they provide: (i) a consistent exhaustive partition of space into atomic regions, through the quantum theory of atoms in molecules (QTAIM);<sup>7</sup> (ii) methodology-independent objects; (iii) an exact energetic decomposition into atomic energies and pairwise additive interaction terms via the interacting quantum atoms (IQA) approach.<sup>8,9</sup>

Covalent BOs in QCT were already defined in 1974 by Bader and Stephens.<sup>10</sup> These authors showed with clever arguments that a measure of the number of electrons shared between two atoms in a molecule could be obtained from the loss of interatomic electron pairs upon bond formation. They called this index the delocalization index, DI, since it vanishes when electrons are fully localized. DIs have been fruitfully used in the last two decades, providing a wealth of chemically appealing information.<sup>11–13</sup> After the introduction of IQA,<sup>8</sup> it is also known that the covalent energy associated to a given interatomic interaction may be described through the so-called interatomic exchange-correlation energy,  $E_{xc}$ . It has been recently shown<sup>14,15</sup> that  $E_{xc}$  can be expanded as a multipolar series, so that the leading term is directly related to the DI. **This relationship has also been investigated by Badri and Foroutan-Nejad.<sup>16</sup>** In this way, a direct, physically sound covalent BEBO relation appears. **It has also been**

Departamento de Química Física y Analítica, Universidad de Oviedo, Oviedo, Spain.  
E-mail: ampendas@uniovi.es

<sup>†</sup> Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

shown that, within the context of Hückel's Theory, DIs have close-form expressions that can be related to the topological resonance energy per  $\pi$  electron.<sup>17,18</sup>

Notice that delocalization indices, as well as all IQA energetic quantities such as the covalent exchange-correlation energies may in principle be determined experimentally. QTAIM basins are routinely obtained from high resolution X-ray diffraction<sup>19</sup> experiments, and DIs or IQA energies depend on reduced density matrices which are expectation values of Dirac operators. The quantum crystallography program,<sup>20</sup> promises to provide us with a combined theoretical/experimental framework leading to all these quantities in a near future.

We show in this paper that much as with the well-known covalent DI, a similar ionic BO can be defined by following an equivalent path to that leading to the covalent BEBO/QCT relation. This means that a full bond order-bond energy landscape exists after all. QCT/IQA bond orders are nothing but approximate electron counting energy measures of the ionic and covalent contributions to a given chemical interaction. They are transformed into energetic components by the same type of interatomic distance scaling laws, thus providing a homogeneous link between covalent/ionic energies and covalent/ionic classical BO descriptors. The rigorous expressions unveiled here show how finally bond orders can be transformed into energetic quantities.

In the following section, we summarize the steps necessary to establish the covalent and full bond-energy-bond-order (BEBO) relations within the QCT/IQA methodology. Then, their connection to the concept of electron distribution functions in real space are discussed (Section 3). Finally, we examine how the derived BEBO relations actually work for a set of over 800 prototypical interactions (Section 4) and give the more relevant conclusions (Section 5).

## 2 Bond-Energy-Bond-Order Relation in the QCT/IQA Methodology

The IQA<sup>8</sup> method provides an exact energetic decomposition of the energy of a molecular system into chemically meaningful components without sacrificing a deeply rooted physical background. It starts from a QTAIM decomposition of space into quantum atomic regions  $A_i$ ,  $R^3 = \cup_i A_i$ . Any union of these domains can be considered also a proper quantum system, so the analysis can be performed hierarchically, starting with atoms that interact, continuing with interacting functional groups, and ending with monomers or molecules that feel their mutual presence.

The energy in IQA<sup>8</sup> is written as a sum of atomic (or fragment) self-energies ( $E_{self}^A$ ), the intra-domain expectation value of the Hamiltonian in region  $A$ , and interatomic (or inter-fragment) interaction energies ( $E_{int}^{AB}$ ),

$$E = \sum_A E_{self}^A + \sum_{A>B} E_{int}^{AB}. \quad (1)$$

$E_{self}^A$  contains the kinetic energy, electron-electron repulsion and electron-nucleus attraction, as well as the internuclear repulsion among the electrons and the nuclei lying in  $A$ . In the absence of other atoms (or groups), the self-energy coincides with the total

energy, and is minimum. As a group starts feeling the interaction of others,  $E_{self}^A$  changes, rising except when large charge transfers appear. The  $E_{int}^{AB}$  terms sum up the nuclei-nuclei ( $E_{nn}^{AB}$ ), electron-nuclei ( $E_{en}^{AB}$ ), nuclei-electron ( $E_{ne}^{AB}$ ), and electron-electron ( $E_{ee}^{AB}$ ), interactions of particles in fragment  $A$  with those of particles in fragment  $B$ ,

$$E_{int}^{AB} = E_{nn}^{AB} + E_{en}^{AB} + E_{ne}^{AB} + E_{ee}^{AB}. \quad (2)$$

In the following we will be only interested in these interaction terms, which lie at the root of chemical bonding. To compute all except the  $E_{ee}^{AB}$  contribution we only need the electron density,  $\rho(\mathbf{r})$ . Unfortunately, the latter depends on the pair density,  $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ , measuring the density of pairs of electrons at points  $\mathbf{r}_1$  and  $\mathbf{r}_2$ :

$$E_{ee}^{AB} = \int_A d\mathbf{r}_1 \int_B d\mathbf{r}_2 \frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \quad (3)$$

Writing  $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$  as the sum of its classical ( $cl$ ) and exchange-correlation ( $xc$ ) parts,  $\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)$ ,  $E_{ee}^{AB}$  can in turn be split as  $E_{ee}^{AB} = E_{ee,cl}^{AB} + E_{xc}^{AB}$ . Moreover, in the Born-Oppenheimer approximation we can also define a classical nuclear density,  $\rho_n(\mathbf{r}) = \sum_\alpha Z_\alpha \delta(\mathbf{r} - \mathbf{R}_\alpha)$ , where  $\alpha$  runs over the nuclei and  $Z$  denotes the nuclear charge, and a total charge density,  $\rho_t(\mathbf{r}) = \rho_n(\mathbf{r}) - \rho(\mathbf{r})$ . Adding together all terms in  $E_{int}^{AB}$  depending on  $\rho_t$ , i.e. all but  $E_{xc}^{AB}$ , we can separate  $E_{int}^{AB}$  into electrostatic or classical ( $E_{cl}^{AB} = E_{nn}^{AB} + E_{en}^{AB} + E_{ne}^{AB} + E_{ee,cl}^{AB}$ ) and exchange-correlation ( $E_{xc}^{AB}$ ) terms,  $E_{int}^{AB} = E_{cl}^{AB} + E_{xc}^{AB}$ . It is now well-known that  $E_{cl}^{AB}$  measures the ionic component of a chemical interaction, i.e. that due to true charge transfer that leads to net charges over the  $A, B$  groups, while  $E_{xc}^{AB}$  describes its covalent contribution.<sup>8,9</sup> Both the classical and exchange-correlation interaction energies between two atoms (or fragments) admit a common algebraic description:

$$E_{cl \text{ or } xc}^{AB} = \int_A d\mathbf{r}_1 \int_B d\mathbf{r}_2 \frac{\tau_{cl \text{ or } xc}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}, \quad (4)$$

$$\tau_{cl}(\mathbf{r}_1, \mathbf{r}_2) = \rho_t(\mathbf{r}_1)\rho_t(\mathbf{r}_2),$$

$$\tau_{xc}(\mathbf{r}_1, \mathbf{r}_2) = -\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2).$$

We have recently shown that total interaction energies  $E_{int}^{AB}$  behave as intrinsic bond energies,<sup>21</sup> and can be used to solve several longstanding problems in the appropriate definition of these important quantities.  $E_{int}$ 's fulfill all the requisites to be used as rigorous energetic descriptors of bond strength. For instance, the great difficulties found when trying to reconcile bond dissociation energies with the bond energy concept<sup>22</sup> are easily overcome when the bond energy between fragments  $A, B$  are measured from their in-the-molecule energy reference. This leads to an immediate identification of these in-the-molecule bond energies (in situ bond energies) with  $E_{int}^{AB}$ .

Covalent bond orders in QCT, accounting for interatomic electron pair loss, are defined from the exchange correlation density by<sup>10</sup>

$$DI(A, B) = \delta^{AB} = 2 \int_A d\mathbf{r}_1 \int_B d\mathbf{r}_2 \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2). \quad (5)$$

It may be shown<sup>23</sup> that delocalization indices measure the inter-

atomic electron population fluctuations, being integer numbers (i.e. 1,2, etc) for ideal single, double and, in general, multiple bonds, and that electron correlation tends to decrease their values. They naïvely count delocalized electrons, exactly as in electron counting BOs. A look at Eq. 4 (used with  $\tau_{xc}$ ) and Eq. 5 reveals a clear relationship between  $E_{xc}^{AB}$  and  $\delta^{AB}$ . In the case of a long-range (lr)  $A-B$  interaction, and using the polar representation of the inter-fragment distance vector  $\mathbf{R}_{AB}$  such that  $\mathbf{R}_{AB} = (R_{AB}, \hat{R}_{AB})$ , a multipolar expansion<sup>15</sup> may be used to demonstrate that

$$\left(E_{xc}^{AB}\right)_{lr} = \sum_{l_1 m_1} \sum_{l_2 m_2} C_{l_1 m_1 l_2 m_2}(\hat{R}_{AB}) \frac{\delta_{l_1 m_1 l_2 m_2}^{AB}}{R_{AB}^{l_1+l_2+1}}, \quad (6)$$

where  $C_{l_1 m_1 l_2 m_2}$  are structural coefficients and  $\delta_{l_1 m_1 l_2 m_2}^{AB}$  are generalized exchange-correlation multipoles.<sup>15</sup> The monopole-monopole ( $l_1 = m_1 = l_2 = m_2 = 0$ ) term dominates at large distances, and is characterized by  $C_{0000} = 1$  and  $\delta_{0000}^{AB} = -\delta^{AB}/2$ , so that to zero-th order,

$$E_{xc}^{AB} \approx (E_{xc}^{AB})_{lr} \approx -\frac{\delta^{AB}}{2R_{AB}}. \quad (7)$$

Expansion 6 reproduces very well even 1,2 interactions if cut at the quadrupolar level ( $l_1 + l_2 = 2$ ). In a more approximate but vibrant chemical way, Eq. 7 shows that covalent energies are dominated by the covalent BO, i.e. by  $\delta^{AB}$ . Notice that, at constant interatomic distance, this approximation to the covalent energy is strictly proportional to the bond order, as intuition dictates. Deviations, of course, appear if more terms in the expansion are retained.<sup>15</sup> Eqs. 6 and 7 are rigorous theoretical results that use no hand-waving arguments. As far as the conditions for convergence of the multipolar approximation are fulfilled, they are exact.

The shrewd reader will have noticed that these arguments are immediately generalizable to the electrostatic or ionic part of an interaction. To do that, we simply take Eq. 4 (used with  $\tau_{cl}$ ) and repeat the reasoning with the  $cl$  part. An ionic BO is thus to be defined as

$$IO(A,B) = t^{AB} = -\int_A d\mathbf{r}_1 \int_B d\mathbf{r}_2 \rho_t(\mathbf{r}_1) \rho_t(\mathbf{r}_2) = -Q^A Q^B \quad (8)$$

As it can be seen from the last equality, this ionic bond order has sign, being equal to minus the product of the net atomic charges ( $Q$ ) of the  $A, B$  atoms (or fragments). Positive/negative values of  $t^{AB}$  signal stabilizing/destabilizing ionic contributions, and for ideal ionic charge transfers IO also runs over the integers. A single ionic bond would be close to that existing in LiF, for instance. Caution is to be taken not to confuse the purely *charge transfer* IO here introduced and valence-bond or Pauling's covalent-ionic resonance.

Of course, a parallel set of expressions equivalent to Eq. 6 and Eq. 7 can be written down. The  $C$  coefficients in Eq. 6 are exactly transported into the multipolar expansion of  $(E_{cl}^{AB})_{lr}$ , but now the standard electrostatic multipole moments  $Q_{lm}$  are used instead of

the generalized exchange-correlation multipoles  $\delta_{l_1 m_1 l_2 m_2}^{AB}$ :

$$\left(E_{cl}^{AB}\right)_{lr} = \sum_{l_1 m_1} \sum_{l_2 m_2} C_{l_1 m_1 l_2 m_2}(\hat{R}_{AB}) \frac{Q_{l_1 m_1}^A Q_{l_2 m_2}^B}{R_{AB}^{l_1+l_2+1}}, \quad (9)$$

with

$$Q_{lm}^\Omega = \left(\frac{4\pi}{2l+1}\right)^{\frac{1}{2}} \int_\Omega d\mathbf{r} r^l S_{lm}(\hat{r}) \rho_t(\mathbf{r}). \quad (10)$$

The  $Q_{lm}^\Omega$  multipolar moments reconstruct exactly the molecular electric multipoles, and have found their way into the construction of accurate force fields.<sup>24</sup>

To zero-th order ( $l_1 = m_1 = l_2 = m_2 = 0$ ),  $Q_{00}^\Omega = Q^\Omega$ , and

$$E_{cl}^{AB} \approx (E_{cl}^{AB})_{lr} \approx \frac{Q^A Q^B}{R_{AB}} = -\frac{t^{AB}}{R_{AB}}, \quad (11)$$

so that the ionic term is approximated by the point charge interaction of atomic net charges placed at the nuclear positions. As before, and as far as convergence is assured, Eqs. 9 and 11 are again analytical results.

Overall, an appealing  $R_{AB}^{-1}$  dependence of the total intrinsic strength of a given interatomic interaction is obtained and, to zero-th order,

$$E_{int}^{AB} = E_{cl}^{AB} + E_{xc}^{AB} \approx -\frac{1}{R_{AB}} \left( t^{AB} + \frac{\delta^{AB}}{2} \right) = -\frac{\varepsilon^{AB}}{R_{AB}}, \quad (12)$$

with

$$\varepsilon^{AB} = t^{AB} + \delta^{AB}/2 \quad (13)$$

being an effective electron count BO.

Covalent and ionic bond orders get then an energetic fingerprint, and are defined on the same footing, using strictly equivalent formulations. We think that this sets a firm theoretical foundation to BEBO relations with terms that hold a very intuitive chemical meaning.

### 3 Connection to Electron Population Distribution Functions

The approximate Coulombic dependence of both the ionic and covalent terms appeals to the (quantum mechanical) electrostatic nature of particle interactions. It is the total effective electron transfer that counts electrostatically speaking. This can be illustrated by a two-center ( $A, B$ ) two-electron system. We have three possible coarse-grained spatial arrangements of electrons. Either two electrons in  $A$  and none in  $B$ , this with probability  $p(2,0)$ , one in  $A$  and one in  $B$  (probability  $p(1,1)$ ), or none in  $A$  and two in  $B$  (probability  $p(0,2)$ ). A full generalization of these ideas through electron distribution functions (EDFs) exists.<sup>25-27</sup> Taking into account that  $\delta^{AB} = -2\text{cov}(n_A, n_B)$ , where  $\text{cov}(n_A, n_B)$  is the covariance of the electron population distribution,

$$\text{cov}(n_A, n_B) = \langle n_A n_B \rangle - \langle n_A \rangle \langle n_B \rangle, \quad (14)$$

$Q^A = 1 - \langle n_A \rangle$  and  $Q^B = 1 - \langle n_B \rangle$ , it is straightforward to show that

$$\varepsilon^{AB} = 1 - \langle n_A n_B \rangle = 1 - p(1,1) = p(2,0) + p(0,2). \quad (15)$$

In other words, to zero-th order a bond's energy may be modeled as the electrostatic attraction between the effective charges transferred from  $A$  to  $B$  (or viceversa). In this count, an ionically (completely) transferred electron adds as one full unit charge, leading to  $|Q^A| = |Q^B| = 1$ , while a covalent pair is made up of two delocalized electrons with a 1/2 probability of being found together in either center (i.e. an ionic snapshot) and a 1/2 probability of being found separated. Any of the charge-separated distributions adds  $|Q^A Q^B| = 1$  to the electrostatic count. Summarizing, in  $-1/R_{AB}$  units, a full ionic bond adds one to the intrinsic bond energy, an ideal covalent half this number. Notice that  $\epsilon^{AB} \in [0, 1]$  for this 2c-2e model. A fully ionic  $\epsilon = 1$  situation corresponds to  $t^{AB} = 1$ ,  $\delta^{AB} = 0$ , while the contrary is true for an  $\epsilon = 1/2$  symmetric covalent bond, with  $\delta^{AB} = 1$ ,  $t^{AB} = 0$ . This corresponds to the standard wisdom opposing covalency and ionicity. For a 2e system engaged in 2c bonding, a constant  $\epsilon^{AB}$  may be achieved by increasing continuously  $\delta^{AB}$  while decreasing  $t^{AB}$  appropriately (or viceversa) within given limits (since a constant  $p(1, 1)$  constrains the maximum value of  $p(2, 0)$  or  $p(0, 2)$  in Eq. 15).

These ideas may be easily put in layman's terms: to a first approximation, the interaction energy in a 2e-2c bond is due to the electrostatic attraction of the net charges located at each center. For a pure ionic link, the  $Q_A = +1$ ,  $Q_B = -1$  snapshot (exchange  $A$  and  $B$  if necessary to fit the actual polarity) is found 100% the time, while for a pure covalent link that figure is reduced to 50%.

The expansion here presented establishes a rigorous link between bond orders and bond strengths. Since it is based on a multipole expansion, its numerical performance improves as distance increases. We should not expect anything but a broad agreement for strong 1,2 interactions, where the expansion needs not even converge, but it should become increasingly accurate in intermolecular cases, where it may become a simple estimator of the interaction intensity given that the computation of atomic charges and delocalization indices in QCT is inexpensive relative to that of the classical or exchange-correlation energies. Notwithstanding, we stress that several multipolar terms (i.e. dispersion) may become energetically dominant at large distances. These are obviously not covered at all by the zero-th order terms, and are not considered in this work.

## 4 Illustrative results

Let us examine how well the reported correlations work in actual systems. A practical note is due here. Strictly speaking, standard density functional theory (DFT) lacks a proper second order density matrix, thus IQA cannot be applied to it directly. However, a number of techniques have been devised to approximately overcome this barrier.<sup>28,29</sup> Since it is our aim here to provide exact results, only wavefunctions methods will be reported. This means using Hartree-Fock at the single-determinant level and complete active space (CAS), any brand of configuration interaction (CI) or several couple-cluster (CC) levels in the case that we want to include electron correlation. Anyway, IQA/DFT decompositions are perfectly suited to the present formalism if the approximations used to reconstruct the pair density are correctly used.

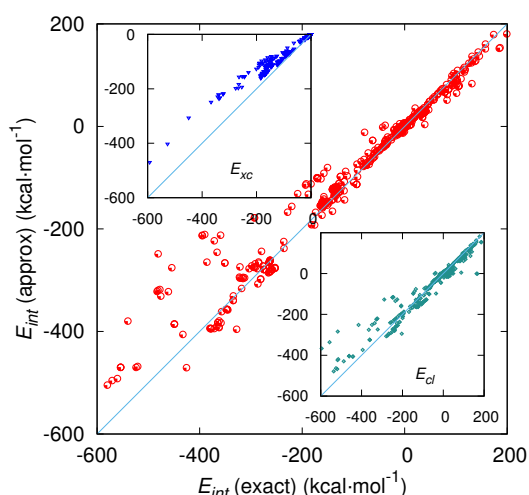
We begin with the first and second row homo-diatomics. We have used the same computational conditions as in one of our

Molecule	$R_{AB}$	$\delta^{AB}$	$E_{xc}^{AB}$	$E_{xc}^{AB*}$	$E_{cl}^{AB}$	$E_{int}^{AB}$
H <sub>2</sub>	1.400	0.851	-150.4	-190.7	26.4	-124.0
He <sub>2</sub>	5.433	0.005	-0.6	-0.3	0.0	-0.6
Li <sub>2</sub>	5.053	0.835	-62.0	-51.8	0.8	-61.2
Be <sub>2</sub>	4.768	0.589	-59.4	-38.8	2.5	-56.9
B <sub>2</sub>	3.025	1.368	-197.8	-141.9	29.8	-168.0
C <sub>2</sub>	2.370	1.805	-331.7	-239.0	87.4	-244.3
N <sub>2</sub>	2.090	1.952	-433.1	-293.0	137.4	-295.7
O <sub>2</sub>	2.304	1.541	-311.0	-209.9	86.2	-224.8
F <sub>2</sub>	2.644	0.925	-166.4	-109.8	33.1	-133.3
Ne <sub>2</sub>	5.155	0.034	-3.2	-2.1	0.0	-3.2

**Table 1** Exact and zero-th order (with asterisk) classical, exchange-correlation, and total interaction energies for first and second row diatomics at their theoretical equilibrium distances. Since  $Q^A = Q^B = 0$ ,  $E_{cl}^{AB*} = 0$ , so that  $E_{int}^{AB*} = E_{xc}^{AB*}$ . Delocalization indices and distances in a.u., energies in kcal·mol<sup>-1</sup>. See the text for a description of the computational details.

previous works.<sup>30</sup> GAMESS TZV(2d,p) basis sets have been used except for Be<sub>2</sub> and F<sub>2</sub> where the cc-pVTZ basis was chosen. All our data are from full valence CAS calculations except in H<sub>2</sub> and He<sub>2</sub>, where full-CI is reported. The electronic structure was obtained with the GAMESS code,<sup>31</sup> and the IQA calculations with PROMOLDEN.<sup>32</sup> Strongly bonded homonuclear diatomics are the worst scenario for our model, with short interatomic distances and no permanent charge transfer. In these conditions, the multipolar approximation ceases to be valid, since the real space regions overlap in the multipolar sense.<sup>15</sup> This means that even the full multipolar expansion of  $E_{xc}^{AB}$  does not converge to the exact value. The same occurs with the electrostatic energy. Moreover, since the net charge of each atomic domain vanishes by symmetry, this leads to a vanishing zero-th order estimation of the electrostatic energy. The total electrostatic energy between two neutral non-interpenetrating densities is necessarily positive, and the repulsion between the isolated atomic densities will be indeed large if the distance is sufficiently short. This repulsion is dominated by the dipolar repulsion of the QAIM atomic densities, and is adequately modeled if first and further multipolar orders are retained, but is fully absent in the zero-th order approximation.

Table 1 summarizes our data. It can be readily seen that as  $R_{AB}$  decreases (and bonds strengthen) the zero-th order approximation loses predictability. This is rather notorious in N<sub>2</sub>, where the electrostatic interaction between the mirror densities of the two N atoms is clearly repulsive and not at all negligible,  $E_{cl}^{NN} = 137$  kcal·mol<sup>-1</sup>. Since the zero-th order value is non-zero, i.e. since covalency is the only stabilizing interaction in homodiatomics,  $E_{xc}$  is semi-quantitatively approximated by the DI alone, Eq. 7. Errors increase with decreasing distance, as the multipolar approximation deteriorates. For instance the zero-th order  $E_{xc}$  is as large as 32% off in dinitrogen. Improved accuracies are found for the  $E_{int}$ 's through some error cancelation. It is indeed striking that such simple relations as those proposed here may reasonably predict the intrinsic bond energies of some of the strongest bonds in chemistry. The worst scenario situation improves if we increase  $Z$ , since interatomic distances increase and atomic multipoles decrease. For instance,  $E_{cl}^{AB}$  decreases to 39.6 and 32.1 kcal/mol



**Fig. 1** Comparison of the zero-th order covalent ( $E_{xc}$ ), ionic ( $E_{cl}$ ), and total interaction energies ( $E_{int}$ ) with their exactly computed values for a set of over 800 different interactions covering several bonding and distance regimes. Details of the systems can be found in the text and the supplementary information. Energies in  $\text{kcal}\cdot\text{mol}^{-1}$ .

Molecule	Molecule
$\text{H}_2\text{O}\cdots\text{H}_2\text{O}$	$\text{CH}_2\text{FOH}$
$\text{H}_2\text{O}\cdots\text{NH}_3$	$\text{CH}_3\text{CF}_3$
$\text{FHF}^-$	$\text{CH}_3\text{BeH}$
$\text{HF}\cdots\text{H}_2\text{O}$	$\text{CH}_3\text{BH}_2$
$\text{HF}\cdots\text{HF}$	$\text{CH}_3\text{CH}_2\text{F}$
$\text{HF}\cdots\text{N}_2$	$\text{CH}_3\text{CH}_2\text{Li}$
$\text{HF}\cdots\text{NH}_3$	$\text{CH}_3\text{CLi}_3$
$\text{NH}_3\cdots\text{H}_2\text{O}$	$\text{CH}_3\text{NH}_2$
$\text{NH}_3\cdots\text{NH}_3$	$\text{CH}_3\text{OH}$
$\text{BH}_3\text{NH}_3$ (staggered)	$\text{C}_6\text{H}_6$ (benzene)
$\text{BH}_3\text{NH}_3$ (eclipsed)	$\text{C}_2\text{H}_6$ (ethane)
$\text{N}_5^+$	$\text{C}_3\text{H}_8$ (propane)
$\text{Li}_9\text{H}_9$	$\text{C}_4\text{H}_{10}$ (butane)
$\text{CH}_2\text{CF}_2$ (cis)	$\text{C}_5\text{H}_{12}$ (pentane)
$\text{CH}_2\text{CF}_2$ (trans)	$\text{C}_6\text{H}_5\text{OH}\cdots\text{C}_6\text{H}_5\text{OH}$

**Table 2** Molecules computed in this work at the RHF//6-311G(d,p) level.

for  $\text{P}_2$  and  $\text{As}_2$ , respectively, in CAS//aug-cc-pVTZ calculations. Chemically, this implies that the interaction energy is much better represented by  $E_{xc}^{AB}$ , which is still large,  $-280$  and  $-239$   $\text{kcal/mol}$ , respectively.

As distances increase and we enter into the non-bonded or intermolecular regimes the practical usefulness of our approach improves. To show how the zero-th order energies approach the exact ones at large distances we have computed the zero-th order ionic, covalent, and total interaction energies for a relatively heterogeneous set of molecules, both at the single determinant, non-correlated level, as well as including electron correlation at the CCSD(T) level. Since the expressions reported do not depend on the theoretical level, we can plot all the results together. We have thus obtained the necessary IQA energetic parameters at the optimized geometry and using a RHF//6-311G(d,p) level, for all different pairs ( $\sim 400$ ) of the dataset collected in Table 2

Molecule	Geometry	Molecule	Geometry
HNC	NIST	$\text{HF}\cdots\text{N}_2$	optimized
FCN	NIST	$\text{H}_2\text{CO}\cdots\text{H}_2\text{CO}$	optimized
$\text{HF}\cdots\text{CO}$	optimized	HCOOH	NIST
$\text{HCN}\cdots\text{HF}$	KB49	$\text{HF}\cdots\text{H}_2\text{O}$	optimized
$\text{CH}_4$	NIST	$\text{HF}\cdots\text{F}_2$	optimized
$\text{H}_2\text{CF}^+$	optimized	$\text{NH}_3\cdots\text{F}_2$	optimized
HCN	NIST	$\text{CH}_3\text{F}\cdots\text{CH}_3\text{F}$	KB49
$\text{C}_2\text{H}_4$	NIST	$\text{NH}_3\cdots\text{NH}_3$	S22
$\text{HF}\cdots\text{HF}$	KB49	$\text{H}_2\text{CO}$	NIST
$\text{H}_2\text{O}$	optimized	$\text{HF}\cdots\text{ClF}$	optimized
$\text{CH}_4\cdots\text{HF}$	KB49	$\text{NH}_3$	NIST
$\text{CH}_4\cdots\text{CH}_4$	S22	$\text{BH}_3$	NIST
$\text{H}_2\text{O}\cdots\text{H}_2\text{O}$	optimized	$\text{CH}_3\text{OH}$	NIST
$\text{OC}\cdots\text{BH}_3$	optimized	$\text{C}_2\text{H}_2$	NIST
$\text{CH}_4\cdots\text{NH}_3$	KB49	$\text{NO}\cdots\text{NO}$	NIST

**Table 3** Molecules studied in work at the CCSD(T)/aug-cc-pVDZ level. See the text for details. Geometries have been taken from the NIST, KB49 or S22 data bases<sup>33–36</sup>, or optimized with GAMESS-US<sup>31</sup>.

to sketch the reliability at the non-correlated level. Similarly, another set of around 400 interactions has been computed at the CCSD(T)/aug-cc-pVDZ level for the dataset collected in Table 3, that includes several hydrogen bonded dimers, simple triatomics like HNC or FCN, small molecules like water, formaldehyde, ammonia, methanol, ethylene, acetylene, methane, etc. In this case, geometries have been taken from the NIST, KB49 or S22 data bases<sup>33–36</sup>, or optimized at the CCSD/aug-cc-pVDZ level with GAMESS-US<sup>31</sup>. Density matrices were obtained with the pySCF suite<sup>37</sup>. IQA calculations were performed with promolden.<sup>32</sup> The complete set of systems, including geometries, details of the calculations, and all the specific energetic parameters of these  $\sim 800$  interactions can be found in the supporting information.

Figure 1 shows that the zero-th order approximation performs rather well, worsening considerably for strong interactions. This is the expected result, since strong interactions usually imply small interatomic distances (so the conditions of convergence of the multipolar approximation easily break down) and large density distortions, accompanied by non-negligible further order multipole moments beyond the zero-th order terms. The zero-th order approximated covalent term is systematically underestimated with respect to the exact value, as the top inset reveals. We have previously shown that the match improves considerably if dipole and quadrupole terms are added.<sup>15</sup> Notice that  $E_{xc}^{AB}$  is consistently stabilizing. This is not the case for  $E_{cl}^{AB}$  which shows destabilizing (interaction between cations) as well as stabilizing (interaction between oppositely charged moieties) regions. It is rather clear that the agreement is better in the positive window, this being related to the more compact (with smaller further order multipoles) densities of cations with respect to anions. If an interaction energy tolerance between the exact and the approximate results is pre-selected, Fig. 1 can be used to isolate an energy window in which the tolerance level is met. This may be used to predict intrinsic bond energies to a given accuracy from inexpensive calculations.

## 5 Conclusions

The orbital invariant interacting quantum atoms (IQA) method of *Quantum Chemical Topology* has been used to show the deep theoretical link existing between the traditional bond order concept and the intrinsic energetics of chemical bonds. This is easily uncovered in real space theories of the chemical bond. We have shown how the already known relation between the covalent energy of an interaction,  $E_{xc}$ , and the covalent bond order, as measured by  $\delta$ , may be exactly translated to the ionic part of the interaction by defining a parallel ionic bond order  $\iota$  that turns out to be the signed product of net atomic charges. If only monopole-monopole terms are retained in a multipolar expansion of both terms, the intrinsic bond interaction energy  $E_{int}$  turns out to be inversely proportional to the interatomic distance. This allows for an appealing interpretation of the leading bond energetic contributions as coming from the Coulomb attraction of permanently transferred electrons, giving rise to ionic terms, and of shared pairs that count half to this electrostatics and bring about the covalent contributions. The performance of this model improves with distance, and due to its simplicity may find real world applications for estimating intermolecular interactions.

## Acknowledgements

We thank the spanish MINECO/FEDER, grant CTQ2015-65790-P, and the FICYT, grant GRUPIN14-049

## References

- 1 G. N. Lewis, *J. Am. Chem. Soc.*, 1916, **38**, 762–786.
- 2 W. Heitler and F. London, *Z. Physik*, 1927, **44**, 455–472.
- 3 M. Kaupp, D. Danovich and S. Shaik, *Coordination Chemistry Reviews*, 2017, **344**, 355–362.
- 4 L. Pauling, *Proc. Natl. Acad. Sci. U.S.A.*, 1928, **14**, 359–362.
- 5 H. S. Johnston and C. Parr, *Journal of the American Chemical Society*, 1963, **85**, 2544–2551.
- 6 P. L. A. Popelier and E. A. Brèmond, *Int. J. Quant. Chem.*, 2009, **109**, 2542–2553.
- 7 R. F. W. Bader, *Atoms in Molecules*, Oxford University Press, Oxford, 1990.
- 8 M. A. Blanco, A. Martín Pendás and E. Francisco, *J. Chem. Theory Comput.*, 2005, **1**, 1096–1109.
- 9 E. Francisco, A. Martín Pendás and M. A. Blanco, *J. Chem. Theory Comput.*, 2006, **2**, 90–102.
- 10 R. F. W. Bader and M. E. Stephens, *Chem. Phys. Lett.*, 1974, **26**, 445–449.
- 11 A. Gallo-Bueno, E. Francisco and A. Martín Pendás, *Phys. Chem. Chem. Phys.*, 2016, **18**, 11772–11780.
- 12 A. Gallo-Bueno, M. Kohout and A. Martín Pendás, *J. Chem. Theory Comput.*, 2016, **12**, 3053–3062.
- 13 A. Martín Pendás, J. M. Guevara-Vela, D. Menéndez-Crespo, A. Costales and E. Francisco, *Phys. Chem. Chem. Phys.*, 2017, **19**, 1790–1797.
- 14 M. Rafat and P. L. A. Popelier, *The Quantum Theory of Atoms in Molecules*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2007, pp. 121–140.
- 15 E. Francisco, D. Menéndez-Crespo, A. Costales and A. Martín Pendás, *J. Comput. Chem.*, 2017, **38**, 816–829.
- 16 Z. Badri and C. Foroutan-Nejad, *Phys. Chem. Chem. Phys.*, 2016, **18**, 11693–11699.
- 17 J. Cioslowski, E. Matito and M. Sòla, *J. Phys. Chem.*, 2007, **111**, 6521–6525.
- 18 E. Matito, F. Feixas and M. Sòla, *J. Mol. Struct.*, 2007, **811**, 2–11.
- 19 *Modern Charge-density Analysis*, ed. C. Gatti and P. Macchi, Springer, Dordrecht., 2012.
- 20 S. Grabowsky, A. Genoni and H.-B. Bürgi, *Chem. Sci.*, 2017, **8**, 4159–4176.
- 21 D. Menéndez-Crespo, A. Costales, E. Francisco and A. Martín Pendás, *Chem. Eur. J.* 10.1002/chem.201800979.
- 22 D. Cremer, A. Wu, A. Larsson and E. Kraka, *Journal of Molecular Modeling*, 2000, **6**, 396–412.
- 23 E. Francisco, A. Martín Pendás, M. García-Revilla and R. Álvarez Boto, *Comput. Theor. Chem.*, 2013, **1003**, 71–78.
- 24 F. Zielinski, P. I. Maxwell, T. L. Fletcher, S. J. Davie, N. Di Pasquale, S. Cardamone, M. J. L. Mills and P. L. A. Popelier, *Sci. Rep.*, 2017, **7**, 12817–12835.
- 25 A. Martín Pendás, E. Francisco and M. A. Blanco, *J. Phys. Chem. A*, 2007, **111**, 1084–1090.
- 26 E. Francisco, A. Martín Pendás and M. A. Blanco, *J. Chem. Phys.*, 2007, **126**, 094102–1–094102–13.
- 27 A. Martín Pendás, E. Francisco and M. A. Blanco, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1087–1092.
- 28 P. Maxwell, A. Martín Pendás and P. L. A. Popelier, *Phys. Chem. Chem. Phys.*, 2016, **18**, 20986–21000.
- 29 E. Francisco, J. L. Casals-Sainz, T. Rocha-Rinza and A. Martín Pendás, *Theor. Chem. Acc.*, 2016, **135**, 170.
- 30 A. Martín Pendás, E. Francisco and M. A. Blanco, *The Journal of Physical Chemistry A*, 2006, **110**, 12864–12869.
- 31 M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347–1363.
- 32 A. Martín Pendás and E. Francisco, *Promolden: A QTAIM/IQA code (Available from the authors upon request by writing to ampendas@uniovi.es)*.
- 33 *WebBook, NIST Standard Reference Database Number 69*, National Institute of Standards and Technology, Gaithersburg MD, 20899, 2017.
- 34 P. Jurečka, J. Šponer, J. Černý and P. Hobza, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1985–1993.
- 35 M. S. Marshall, L. A. Burns and C. D. Sherrill, *J. Chem. Phys.*, 2011, **135**, 194102–1–194102–10.
- 36 F. O. Kannemann and A. D. Becke, *J. Chem. Theory Comput.*, 2010, **6**, 1081–1088.
- 37 Q. Sun, T. C. Berkelbach, N. S. Blunt, G. H. Booth, S. Guo, Z. Li, J. Liu, J. McClain, S. Sharma, S. Wouters and G. K.-L. Chan, *The Python-based Simulations of Chemistry Framework (PySCF)*, <http://arxiv.org/abs/1701.08223>, 2017.

Real space bond orders are energetic descriptors

