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Covalent bond indices and ionicities from similarity measures

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Abstract

This work proposes the use of the mathematical concepts of similarity and distance in metric spaces to relate the covalency and ionicity indices of chemical bondings. Numerical results arising from the Bray–Curtis and divergence measures are reported and discussed in selected molecules. The procedure opens new possibilities to define and to relate complementary quantities.

1. Introduction

Most of the chemical indices used to describe electronic structures of atoms and molecules are not *sensu strictu* observables from a quantum mechanical point of view. This is the case when dealing with concepts such as *covalency* (described by bond indices whose physical meaning is the electron population or shared electrons involved in bondings between atoms), *unshared populations* (electrons not involved in bondings, i.e., core and lone pair electrons), *ionicity*, *valence*, *free valence* (which accounts for the unpaired electrons), etc. The main task to properly define any feasible parameter describing any of these mentioned concepts is to clarify its physical meaning and then to find a suitable quantitative formulation tool [1,2].

The techniques of particle population analysis evaluate electron populations associated with atomic regions and shared electron populations in bonding regions. These methods draw out the required information by means of the *first-order reduced density matrix* (1-RDM) [3]. Similarly, the hole population analyses provide hole populations using the *first-order hole reduced density matrix* (1-HRDM), related with the concepts of free valence or effectively unpaired populations [4]. As is well-known, these techniques are classified according to the nature of the used space, Hilbert space [5–8] or physical space [9,10]. These procedures permit one to evaluate the electronic magnitudes in several ways, applying different approaches to describe the same concepts. Therefore, the definitions of the electronic parameters are not unique. This is, for instance, the case of bond indices [11,12] and free valences of atoms within the molecular framework, where different manners to relate electron populations with their counterpart hole populations lead to various definitions of the effectively unpaired electron density matrix [4,13,14].

In a previous work [15] we have shown the relationship between two different approaches to define the effectively unpaired electron density matrix or u matrix. Using the mathematical concepts of *similarity* and *distance* in metric spaces, we have achieved to relate both definitions of this quantity pointing out that each of them arises from different measures of a space. In this work we deal with ionicities and covalent bond indices. We use again the interrelated mathematical concepts of *distance* and *similarity* measures in metric spaces to show that different possibilities to define these mathematical tools provide different definitions for the chemical parameters, leading to different numerical values. This treatment also allows us to show the complementary character of these parameters in a rigorous way. To perform this task we describe the molecular systems in terms of the *domain-restricted first-order reduced density*

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matrices [16,17] arising from the decomposition of the 1-RDM according to the isopycnic localization model [17]. This procedure, which has been widely tested, has the advantage of performing only one set of localized orbitals in which all domain-restricted matrices are diagonal [18,19]. Therefore, bond indices and ionicities may be defined within the same basis set for all domains.

The article is organized as follows. In Section 2, we briefly introduce the theoretical framework of the domain-restricted 1-RDMs as well as the concepts of similarity and distance measures and their relationships according to the metrics used. Section 3 is devoted to establish the definitions for bond index and ionicity arising from the *Bray–Curtis* and *divergence* metrics. Section 4 describes the computational details and the discussion of the numerical results obtained in selected molecular systems, to assess the capability of those definitions. Finally, in Section 5 we collect the concluding remarks.

2. Theoretical background

Let us begin by introducing the decomposition of the spin-free first-order reduced density matrix corresponding to an N-electron system, according to the isopycnic localization model [17]. As is well-known any linear transformation which leaves the first-order reduced density matrix unchanged is called isopycnic [20]. This is the framework in which our theoretical and numerical developments will be carried out. We will express that first-order reduced density matrix, $\Gamma(x,x')$, in terms of its orthonormal natural orbitals, $\psi_i(x)$, and their corresponding occupation numbers, n_i [3]

$$\Gamma(x,x') = \sum_i n_i \psi_i^*(x)\psi_i(x'), \tag{1}$$

where x, x' stand for the space coordinates. Under an isopycnic linear transformation [20] given by $\phi_i(x) = \sum_j C_{ij}\psi_j(x)$, the first-order reduced density matrix remains invariant, ($C_{ij} = U_{ij}\ (n_j/v_i)^{1/2}$ and U_{ij} and v_i are the matrix elements of a unitary matrix and the occupation numbers of the functions ϕ_i, respectively), that is

$$\Gamma(x,x') = \sum_i v_i \phi_i^*(x)\phi_i(x') \tag{2}$$

fulfilling $v_i = \sum_j n_j U_{ij}^* U_{ij}$ and $0 \leqslant v_i \leqslant 2$. This isopycnic transformation is accomplished by finding a set of coefficients $\underline{C}$ which maximize the localization index [18,21] $L = \sum_i \sum_{klmn} v_i^2 C_{ik}^* C_{il} C_{im}^* C_{in} \sum_\Omega \langle\psi_k|\psi_l\rangle_\Omega \langle\psi_m|\psi_n\rangle_\Omega$, where $\langle\psi_k|\psi_l\rangle_\Omega$ and $\langle\psi_m|\psi_n\rangle_\Omega$ stand for the overlap integrals over the Bader atomic domains Ω [9]. Although the localized orbitals ϕ_i resulting from this procedure are in general nonorthonormal, they are associated with chemical concepts (appropriate localization in space, high transferability, etc.) [18,21] so that they can be regarded as the theoretical counterparts of the classical chemical pictures such as bonds, non-bonding electron pairs, core orbitals, valences and so forth.

The isopycnic localization model [17] for partitioning the first-order reduced density matrix into *domain-restricted first-order reduced density matrices* $\Gamma_\Omega(x,x')$ is expressed by

$$\Gamma(x,x') = \sum_\Omega \Gamma_\Omega(x,x') = \sum_\Omega \sum_i v_i(\Omega)\phi_i^*(x)\phi_i(x'), \tag{3}$$

where $v_i(\Omega) = v_i\langle\phi_i|\phi_i\rangle_\Omega$ stands for the occupation numbers for each Γ_Ω and the integrals $\langle\phi_i|\phi_i\rangle_\Omega$ are again defined over the Bader domains Ω, satisfying the relationships $0 \leqslant \langle\phi_i|\phi_i\rangle_\Omega \leqslant 1$ and $\sum_\Omega \langle\phi_i \mid \phi_i\rangle_\Omega = 1$.

We have shown [22] that the domain-restricted first-order reduced density matrices $\Gamma_\Omega(x,x')$ constitute first-order reduced density matrices associated with the domains Ω. All these matrices diagonalize in identical basis set $\{\phi_i\}$ and possess similar features to those of the ordinary reduced density matrices: each matrix is Hermitian and its trace, given by $N_\Omega = \sum_i v_i(\Omega)$, is the Bader charge (the number of electrons within the domain Ω). Moreover, the occupation numbers $v_i(\Omega)$ of the nonorthogonal localized orbitals ϕ_i fulfill $0 \leqslant v_i(\Omega) \leqslant 2$.

As will be shown in next section, an analysis of the domain-restricted reduced density matrices may be carried out by means of the mathematical concepts of *distance* [23] and *similarity* measures [24,25]. The *distance* measure, d, between two n-dimensional elements $\mathbf{x}$ and $\mathbf{y}$ in a metric space M is defined as a real valued function fulfilling the following properties [15,24,25]:

$$\begin{aligned} &\mathrm{d}(\mathbf{x},\mathbf{y}) \geqslant 0; \quad \mathrm{d}(\mathbf{x},\mathbf{y}) = 0 \iff \mathbf{x} = \mathbf{y}, \\ &\mathrm{d}(\mathbf{x},\mathbf{y}) = \mathrm{d}(\mathbf{y},\mathbf{x}) \quad \text{(symmetry)}, \\ &\mathrm{d}(\mathbf{x},\mathbf{z}) \leqslant \mathrm{d}(\mathbf{x},\mathbf{y}) + \mathrm{d}(\mathbf{y},\mathbf{z}) \quad \text{(triangle inequality)}. \end{aligned} \tag{4}$$

Particular examples [24,25] of distance measure d in different metric spaces M are those of Bray–Curtis (BC)

$$\mathrm{d}^{BC}(\mathbf{x},\mathbf{y}) = \frac{\sum_{i=1}^n |x_i - y_i|}{\sum_{i=1}^n |x_i + y_i|} \tag{5}$$

and divergence (D)

$$\mathrm{d}^{\mathrm{D}}(\mathbf{x},\mathbf{y}) = \frac{\sum_{i=1}^n (x_i - y_i)^2}{\sum_{i=1}^n (x_i + y_i)^2}, \tag{6}$$

where $\{x_i\}$ and $\{y_i\}$ stand for the components of the $\mathbf{x}$ and $\mathbf{y}$ elements, respectively.

The concept of *similarity*, s, is complementary to the idea of distance. Its value is given by a real valued function s fulfilling the properties

$$\begin{aligned} &0 \leqslant s(\mathbf{x},\mathbf{y}) \leqslant 1, \\ &s(\mathbf{x},\mathbf{x}) = 1, \\ &s(\mathbf{x},\mathbf{y}) = s(\mathbf{y},\mathbf{x}), \end{aligned} \tag{7}$$

that quantifies the number of matches between some features of two objects (quantitative or qualitative), whereas the distance measures the ‘difference’ between them. The use of similarities instead of distances requires to consider some specific functional relationships between s and d. In this work we will use $s = 1 - d$ due to the physical nature of the quantities involved [24,25]. Note that in this framework the distance function is bounded to unity, i.e., it is normalized [24,25].

3. Ionicity and covalent bond indices from different similarity measures

3.1. Bray–Curtis metric

As it has been mentioned above, the definition of a quantity is a consequence of the chosen metric. Let us first present an ionicity definition expressed as [16,26]

$$\imath_{\mathrm{AB}}(i) = \left|\frac{v_i(\mathrm{A}) - v_i(\mathrm{B})}{v_i(\mathrm{A}) + v_i(\mathrm{B})}\right|, \tag{8}$$

where v_i(A) and v_i(B) stand for the occupation numbers of the ith isopycnic localized natural orbital corresponding to the *domain-restricted first-order reduced density matrices* associated with the domains A and B, respectively. At this stage it may be noted that Eq. (8) can be regarded as a partial distance d_i between v_i(A) and v_i(B) occupation numbers within the Bray–Curtis metric (cf. Eq. (5)). Thus, the proposed specific functional relationship provides the corresponding *similarity* s_i given by $s_i = 1 - d_i$. This allows us to define the quantity

$$p_{\mathrm{AB}}(i) = 1 - \left|\frac{v_i(\mathrm{A}) - v_i(\mathrm{B})}{v_i(\mathrm{A}) + v_i(\mathrm{B})}\right| = 1 - \imath_{\mathrm{AB}}(i) \tag{9}$$

which may be physically interpreted as a covalent bond index because it is complementary of the ionicity. A purely covalent nature requires $p_{\mathrm{AB}}(i) = 1$, which means that both occupation numbers are equal $v_i(\mathrm{A}) = v_i(\mathrm{B})$. In the case that one of the occupation numbers is zero (i.e., $v_i(\mathrm{A}) = 0$ or $v_i(\mathrm{B}) = 0$), $p_{\mathrm{AB}}(i) = 0$ and the bonding contribution of this orbital is totally ionic. Intermediate cases reveal the ionic fraction of the bonding. As Eqs. (8) and (9) express partial distances d_i and similarities s_i respectively, it can be concluded that covalent bond indices $p_{AB}(i)$ are partial similarities between particle populations of given orbitals corresponding to different atomic domains. Thus the total ionicity of a bonding or simply the bond ionicity between two domains may be defined as a weighted average of the partial ionicities as

$$\begin{aligned}\Xi_{\mathrm{AB}} &= \sum_i \left|\frac{v_i(\mathrm{A}) + v_i(\mathrm{B})}{2}\right| \cdot \imath_{\mathrm{AB}}(i) \\ &= \sum_i \left|\frac{v_i(\mathrm{A}) - v_i(\mathrm{B})}{2}\right|,\end{aligned} \tag{10}$$

where the weight is given by the mean population of each orbital in both domains A and B, i.e., $\frac{v_i(\mathrm{A})+v_i(\mathrm{B})}{2}$. Thus, this average takes into account the importance of the contribution of each orbital involved in the summation throughout its corresponding mean population. Hence, using the same rule for the bond index it follows that

$$\begin{aligned}P_{\mathrm{AB}} &= \sum_i \left|\frac{v_i(\mathrm{A}) + v_i(\mathrm{B})}{2}\right| \cdot p_{\mathrm{AB}}(i) \\ &= \sum_i \left(\left|\frac{v_i(\mathrm{A}) + v_i(\mathrm{B})}{2}\right| - \left|\frac{v_i(\mathrm{A}) - v_i(\mathrm{B})}{2}\right|\right).\end{aligned} \tag{11}$$

Therefore Eqs. (10) and (11) express total ionicity and covalent bond index from Bray–Curtis similarity measure.

3.2. Divergence metric

Let us now consider identical complementary quantities than in the previous subsection but using a different measure. The ionic and covalent fractions associated with the ith orbital arising from the divergence metric are given by

$$\imath_{\mathrm{AB}}(i) = \left(\frac{v_i(\mathrm{A}) - v_i(\mathrm{B})}{v_i(\mathrm{A}) + v_i(\mathrm{B})}\right)^2 \tag{12}$$

and

$$p_{\mathrm{AB}}(i) = 1 - \left(\frac{v_i(\mathrm{A}) - v_i(\mathrm{B})}{v_i(\mathrm{A}) + v_i(\mathrm{B})}\right)^2, \tag{13}$$

respectively. Hence, Eq. (12) defines a partial distance while Eq. (13) expresses the corresponding partial similarity. Using the square of the mean population $\left(\frac{v_i(\mathrm{A})+v_i(\mathrm{B})}{2}\right)^2$ to weight each orbital contribution one obtains

$$\begin{aligned}\Xi_{\mathrm{AB}} &= \sum_i \left(\frac{v_i(\mathrm{A}) + v_i(\mathrm{B})}{2}\right)^2 \cdot \imath_{\mathrm{AB}}(i) \\ &= \sum_i \left(\frac{v_i(\mathrm{A}) - v_i(\mathrm{B})}{2}\right)^2\end{aligned} \tag{14}$$

and

$$\begin{aligned}P_{\mathrm{AB}} &= \sum_i \left(\frac{v_i(\mathrm{A}) + v_i(\mathrm{B})}{2}\right)^2 \cdot p_{\mathrm{AB}}(i) \\ &= \sum_i \left[\left(\frac{v_i(\mathrm{A}) + v_i(\mathrm{B})}{2}\right)^2 - \left(\frac{v_i(\mathrm{A}) - v_i(\mathrm{B})}{2}\right)^2\right] \\ &= \sum_i v_i(\mathrm{A})v_i(\mathrm{B}).\end{aligned} \tag{15}$$

Eqs. (14) and (15) represent the total ionicity and the covalent bond index in the divergence metric, respectively. Note that Eq. (15) coincides with Cioslowski et al. definition for the covalent bond order within the framework of the isopycnic localization procedure reported in Ref. [26]. Therefore the functional relationship between the partial distances and similarities $d_i = 1 - s_i$ chosen for introducing the covalency and ionicity definitions seems to be a suitable indicator for describing such chemical quantities of complementary character.

To finish this section it is important to underline that Eqs. (8) and (15) were early proposed as partial ionicities and total covalent bond order definitions respectively in Ref. [26]. These definitions, as it is clear now from our derivations, were not considered within a measure framework and thus do not lie within the same metric space. Consequently there is not a complementary relationship between them. Eqs. (9)–(11), which are derived for the first time in the present work, lie within the same metric space and correspond to definitions of partial bond orders or covalent orbital contributions, total ionic and total covalent bond orders, respectively induced by the BC measure. Similar considerations are valid for Eqs. (12)–(14) regarding they are related to Eq. (15) in the divergence measure. Hence, an appropriate evaluation of the ionic character of a determined bonding and its complementary covalent character requires to express both quantities in the same metric space in order to get an appropriate comparison of results. Thus, Eqs. (8) and (9) must be used jointly (Bray–Curtis metric) or alternatively Eqs. (12) and (13) (divergence metric), as $\iota_{AB}(i)$ can be interpreted as the Bray–Curtis or divergence distance between $v_i(A)$ and $v_i(B)$ occupation numbers, $p_{AB}(i)$ can be interpreted as the similarity between these populations. These arguments do not invalidate the definitions previously reported by other authors [21,26,27] but they provide a rigorous scheme for interpretation of results. Comparative analyses of several index definitions have been reported in Refs. [28,29].

4. Computational details and discussion

The definition of partial ionicity $\iota_{AB}(i)$ is a linear function of the difference of electronic occupations of the involved orbitals within the Bray–Curtis measure (cf. Eq. (8)) whereas it is quadratic within the divergence metric (cf. Eq. (12)). Then, both definitions will provide close numerical values when these differences nearly vanish or when they take their maximum values. These situations correspond to $v_i(A) \approx v_i(B)$ and to $v_i(A) \approx 2$ and $v_i(B) \approx 0$ ($v_i(A) \approx 0$ and $v_i(B) \approx 2$). The first case stands for *purely covalent* orbital contributions. The second one means *purely ionic* contributions.

In order to analyze the results arising from the covalency and ionicity definitions reported in the previous section, we have chosen a set of selected systems which covers different types of bonding. The calculations for these systems were carried out using the GAUSSIAN 03 package [30], which generated both the first-order reduced density matrix elements and the overlap matrices $\langle\psi_i|\psi_j\rangle_\Omega$. In a subsequent step, these matrices were subjected to the proposed formalisms using our own computational code which are available upon request. The reported results were obtained at configuration interaction (CI) level of approximation using single and double excitations (CISD). The employed basis sets have been 6-31G** except for the acetylene molecule which has been calculated with the 6-31G basis set to

Table 1

Calculated fragment electronic populations, $v_i(\Omega)$, type and degeneracies of the isopycnic natural orbitals, ionicities of bonds (as a percentage) of Bray–Curtis (BC) and divergence (D) type, $\iota^{BC}_{AB,}(i)$, $\iota^{D}_{AB}(i)$ and covalent bond indices of Bray–Curtis (BC) and divergence (D) type, P^{BC}_{AB}, P^{D}_{AB} for second-row hydrides in the CISD treatment using the 6-31G** basis set

System	Fragment (Ω)	N_Ω	v_i (Ω)	Assignment	Degeneracy	$\iota^{BC}_{AB}(i)$	$\iota^{D}_{AB}(i)$	Bond	P^{BC}_{AB}	P^{D}_{AB}
BeH_2	Be	2.277	1.991	$1s_{Be}$	1			Be–H	0.174	0.261
			0.138	σ_{BeH}	2	85.8	73.6			
	H	1.862	1.804	σ_{BeH}	1	85.8	73.6	H–H	0.057	0.088
BH_3	B	2.946	1.997	$1s_{B}$	1			B–H	0.410	0.512
			0.307	σ_{BH}	3	67.4	45.4			
	H	1.685	1.576	σ_{BH}	1	67.4	45.4	H–H	0.133	0.136
CH_4	C	5.845	2.000	$1s_{C}$	1			C–H	1.016	0.970
			0.947	σ_{CH}	4	1.1	0.0			
	H	1.039	0.967	σ_{CH}	1	1.1	0.0	H–H	0.080	0.038
NH_3	N	8.010	2.000	$1s_{N}$	1			N–H	0.663	0.875
			1.929	Lone pair	1					
			1.339	σ_{NH}	3	37.7	14.2			
	H	0.663	0.606	σ_{NH}	1	37.7	14.2	H–H	0.054	0.015
H_2O	O	9.148	2.000	$1s_{O}$	1			O–H	0.430	0.655
			1.974	σ-lone pair	1					
			1.953	π-lone pair	1					
			1.573	σ_{OH}	2	60.4	36.4			
	H	0.426	0.389	σ_{OH}	1	60.4	36.4	H–H	0.032	0.006
HF	F	9.711	2.000	$1s_{F}$	1			F–H	0.290	0.479
			1.988	σ-lone pair	1					
			1.975	π-lone pair	2					
			1.706	σ_{FH}	1	73.0	53.3			
	H	0.289	0.289	σ_{FH}	1	73.0	53.3			

avoid the occurrence of the non-nuclear attractor which appears with the former set [17,31,32]. For all systems, the geometries were optimized within this approximation.

Tables 1 and 2 report numerical results which allow us to discuss the general features stated above. The two definitions for partial ionicity (see Eqs. (8) and (12)) and covalency (see Eqs. (11) and (15)) can provide different values for these quantities according to the used metrics, which can have effects on the characterization of the bonding nature. Table 1 gathers the results corresponding to the hydrides of the second-row elements in order to study the different bondings H–X (X = Be, B, C, N, O, F) according to the electronegativity of the elements of that series.

Let us illustrate how to read the partial quantities from this Table before giving a detailed discussion of the reported values. Consider for instance, the σ_{BeH} bond in the BeH_2 system; the electronic populations v_i for this bonding orbital are 0.138 and 1.804 for Be and H domains, respectively; therefore in the BC metric, application of Eq. (8) for the partial ionicity gives $\frac{|1.804 - 0.138|}{|1.804 + 0.138|} = 0.858$ and expressed as a percentage $\iota^{BC}_{\sigma_{BH}} = 85.8$ which is the value given in the table. The other quantities are obtained straight from the formulas indicated above. As can be seen in that Table, the greatest quantitative difference between both metric definition results appears in the ionicity contributions to the bonds in NH_3 and H_2O systems. In the first system the $\iota^{BC}(\sigma_{NH})$ index is more than two times greater than that of the divergence metric, $\iota^{D}(\sigma_{NH})$. However, for the H_2O molecule the difference between both metric-dependent ionicity contributions ($\iota^{BC}(\sigma_{OH})$ and $\iota^{D}(\sigma_{OH})$) is lower than for the NH_3 one. The covalent bond indices do not show important differences for both molecules although they are greater than for the other systems reported in this Table. The ionicity from both measures decreases outstandingly from the BeH bond towards the CH bond, then to grow also in a valuable way up to the FH bond. As expected, the minimum of ionicity (or the maximum of covalency) appears in the system CH_4 for the CH bond, in good agreement with the well-known covalent nature of this bond. Then, all the values of ionicity

Table 2
Calculated fragment electronic populations, $v_i(\Omega)$, type and degeneracies of the isopycnic natural orbitals, ionicities of bonds (as a percentage) of Bray–Curtis (BC) and divergence (D) type, $\iota^{BC}_{AB}(i), \iota^{D}_{AB}(i)$ and covalent bond indices of Bray–Curtis (BC) and divergence (D) type, P^{BC}_{AB}, P^{D}_{AB} for diatomic molecules and hydrocarbons in the CISD treatment using the 6-31G** basis set

System	Ω	N_Ω	$v_i(\Omega)$	Assignment	Degeneracy	$\iota^{BC}_{AB}(i)$	$\iota^{D}_{AB}(i)$	Bond	P^{BC}_{AB}	P^{D}_{AB}
N_2	N	7.000	2.000	$1s_N$	1			N–N	3.022	2.913
			1.966	σ-lone pair	1					
			0.989	$\sigma_{NN'}$	1	0.0	0.0			
			0.974	$\pi_{NN'}$	2	0.0	0.0			
CO	C	4.738	1.996	$1s_C$	1			C–O	0.953	1.558
			1.856	σ-lone pair	1					
			0.224	σ_{CO}	1	77.4	59.8			
			0.288	π_{CO}	2	70.5	49.7			
	O	9.262	2.000	$1s_O$	1					
			1.983	σ-lone pair	1					
			1.754	σ_{CO}	1	77.4	59.8			
			1.666	π_{CO}	2	70.5	49.7			
F_2	F	9.000	2.000	$1s_F$	1			F–F	1.135	1.180
			1.978	σ-lone pair	1					
			1.956	π-lone pair	2					
			0.964	$\sigma_{FF'}$	1	0.0	0.0			
C_2H_6 (D_{3h})	C	5.838	2.000	$1s_C$	1			C–C′	1.067	0.985
$H_3C–C'H'_3$			0.936	$\sigma_{CC'}$	1			C–H	1.003	0.963
			0.930	σ_{CH}	3	2.6	0.1			
	H	1.054	0.979	σ_{CH}	1	2.6	0.1	H–H	0.082	0.040
C_2H_4	C	5.953	2.000	$1s_C$	1			C–C	2.005	1.857
$H_2C–C'H'_2$			0.981	σ_{CH}	2	1.6	0.0	C–H	1.022	0.984
			0.965	$\sigma_{CC'}$	1					
			0.917	$\pi_{CC'}$	1					
	H	1.024	0.951	σ_{CH}	1	1.6	0.0	H–H	0.077	0.031
C_2H_2*	C	6.137	2.000	$1s_C$	1			C–C	2.959	2.785
HC–C′H′			1.175	σ_{CH}	1	19.2	3.7	C–H	0.857	0.986
			0.972	$\sigma_{CC'}$	1					
			0.955	$\pi_{CC'}$	2					
	H	0.863	0.797	σ_{CH}	1	19.2	3.7	H–H	0.053	0.001

* Calculated in the 6-31G basis set.

are consistent with the electronegativity of the elements which compose the bonds. The covalent bond index values follow a similar pattern to that of the ionicity one. They are very similar in both metrics in the series of systems BeH_2 to CH_4. From there, the difference between the values from both metrics begins to be notable, which again fit with the difference of electronegativities of the elements forming the bond as may be observed from numerical values of the electron populations N_Ω for each domain in the table.

Table 2 refers to systems more complex than the previous one. It contains results corresponding to homonuclear and heteronuclear diatomic molecules and organic systems which are paradigmatic examples of single, double and triple bonds. Although the atoms N and F possess a very different electronegativity, the ionicities in the molecules N_2 and F_2 are identically zero due to symmetry reasons and their covalent bond indices (covalency) are similar for both metrics. The last three compounds in this Table are of organic nature. C_2H_6 shows a low partial ionicity contribution at the CH bond and a zero one at the CC bond in both metrics. The covalent bond indices are close to one for both bonds in both metrics, revealing a single bond. C_2H_4 also shows a low ionicity at its CH bond in both metrics (zero at the divergence one). The covalent bond indices fit well with this picture but different values arise from Bray–Curtis and divergence metrics for the CC bond (2.005 and 1.857, respectively). The first of these results predicts a double bond while the second one predicts a slight but appreciable departure from this kind of bonding which may be interpreted in terms of the diradical character of this bond [33]. The CC covalent bond indices in C_2H_2 system are consistent with a triple bond. However, its σ_{CH} bonds possess an appreciably different covalent bond index in both metrics (close to one in the divergence metric and lower in the Bray–Curtis one). This result is in agreement with the high ionicity of this bond in the BC metric. These two last systems seem to be better described by the divergence metric.

The CO molecule constitutes a particular case. As can be observed in Table 2, this system presents three orbitals forming the CO bond, that is, an orbital σ_{CO} and two π_{CO} degenerate ones, all of them with strong ionic character. The most striking result is the low covalency found, since the BC metric predicts an effective single bond whereas the divergence one provides the value 1.6, although it is commonly admitted that this linkage is triple (bond multiplicity) according to the presence of the three orbitals above mentioned [34,35]. However, this kind of discrepancy is only apparent and occurs in compounds having high ionicity bonds as the CO molecule. In these situations the bond order must be assessed taking into account also the influence of the ionicity. As a consequence of the interrelation between covalency and ionicity, the restricted summations over the bonding orbitals in Eqs. (10) and (11) (for the BC measure) or in Eqs. (14) and (15) (for the divergence one) express jointly the number of electron pairs involved in the bonding although these electron pairs are unequally shared by both atoms in this kind of systems. Hence, as it has been mentioned above, the covalent bond index definition can be extended to an ionic bond index and the sum of both covalent and ionic electron populations associated with the orbitals which constitute a bonding turn out to be representative of the bond order. Thus, the bond multiplicity that would be expected from Lewis' structure (3 in the case of the CO molecule) is reached jointly by both contributions.

5. Concluding remarks

In this work, we have shown that the use of different similarity measures allows us to relate two different procedures to define covalency and ionicity indices. This result opens the possibility of using any arbitrary measure to explore other ways to understand and formulate a determined quantity. We highlight that a definition for any quantity may be expressed in terms of a similarity which implies the use of a determined measure. This method provides a rigourous mathematical support to properly describe complementary quantities. As a direct consequence of this analysis we indicate the necessity of considering covalent and ionic electron population contributions to recover Lewis bond multiplicities.

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