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Bond Orders and Their Relationships with Cumulant and Unpaired Electron Densities

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This paper reports the relationships among different covalent bond-order concepts, second-order cumulant densities, and atomic populations of effectively unpaired electrons. This framework leads to the derivation of suitable formulas to perform population analyses at correlated level in Mulliken and topological versions. Numerical determinations in some molecules confirm the usefulness of these proposals for describing chemical bondings.

1. Introduction

The concept of bond order has played an important role in the understanding of molecular structures, as well as in studies of mechanisms of chemical reactions in which the breaking and formation of chemical bondings is usually described on the basis of this term. Unfortunately, the quantum theory does not provide a rigorous definition of this concept because it is not itself an observable quantity. An early definition of covalent bond order was reported by Wiberg[1] some decades ago on the basis of results arising from semiempirical wave functions. Since then a great effort has been dedicated by many authors to establish an appropriate definition of this concept from ab initio calculation results.[2−13] Two definitions of covalent bond order have mainly been proposed. One of them is based on the exchange term derived from the second-order reduced density matrix;[2,3] a second definition arises from the fluctuation or covariance of the electron population of two centers.[14−16] Both definitions are coincident in the closed-shell Hartree−Fock picture but lead to different results when correlated wave functions are used.[10,11,13]

The study of the properties of the cumulant of the second-order reduced density matrix has recently aroused a considerable interest.[17−21] This tool allows one to relate, in an exact way, the elements of the correlated second-order reduced density matrix with products of elements of the first-order reduced density matrix. Similarly, the effectively unpaired electron density, although proposed some time ago,[22,23] has more recently been revealed to be a suitable method to describe the extent of the radical and diradical character in molecules and transition states.[24,25] The effectively unpaired electron density matrix represents the spatial distribution of odd electrons in open-shell molecules, but it also accounts for the partial split of electron pairs that appear even in closed-shell systems when the electronic correlation is taken into account.[22−26] We have lately established the connection among the cumulant densities, the density of the effectively unpaired electrons, and population analyses.[27] On the basis of this connection, the first aim of this report is the implementation of these tools, cumulant of the second-order reduced density matrix and density of effectively unpaired electrons, to describe bond orders. The approach provides to establish a rigorous relation between both above-mentioned definitions of bond order. We have carried out this study as in the Mulliken scheme of population analysis, in which the electronic charge is partitioned in a Hilbert space spanned by the basis functions, as in the topological version, in which the partitioning is performed over the physical space. As a consequence of our treatment, the usual classification of the N electrons of a system as core and nonbonding electrons, electron shared between two nuclei, and free-valence electrons is obtained in a natural way, providing useful tools for computational purposes.

The paper is organized as follows. The second section reports the basic theory, which allows one to establish appropriate relationships between different population indices. The third section describes some calculations of population analyses based on the correlated first-order reduced density matrix. The obtained results confirm the interest of the proposed equations.

2. Theoretical Treatment

Let us consider a set of orthonormal orbitals $\{i, j, k, l, ...\}$ and the corresponding set of spin−orbitals $\{i^\alpha, j^\alpha, ..., i^\beta, j^\beta, ...\}$. The spin-free first-order and second-order reduced density matrices are defined, respectively, as

$$ {}^1D^i_j = \langle \mathscr{L} | \sum_\sigma c^\dagger_i\sigma c_j\sigma | \mathscr{L} \rangle \tag{1}$$

$$ {}^2D^{ik}_{jl} = \frac{1}{2}\langle \mathscr{L} | \sum_\sigma \sum_{\sigma'} c^\dagger_i\sigma c^\dagger_k\sigma' c_l\sigma' c_j\sigma | \mathscr{L} \rangle \tag{2}$$

where $c^\dagger_i\sigma$, $c_j\sigma$, etc. are the usual creation and annihilation fermion operators and σ and σ' are the spin coordinates (α or β). $|\mathscr{L}\rangle$ is the N-electron state of the system. Note that the trace of the matrix ${}^2D$ is $\binom{N}{2}$. Hence, according to the values of the traces of the matrices ${}^1D$ and ${}^2D$, it is possible to write

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$$N = \sum_i \sum_k [{}^1D^{i}_{i}{}^1D^{k}_{k} - 2\,{}^2D^{ik}_{ik}] \tag{3}$$

Obviously, if the basis set is nonorthogonal, eq 3 must be substituted by $N = \sum_{i,k}[({}^1PS)^i_i\ ({}^1PS)^k_k - 2(S^2PS)^{ik}_{ik}]$, where ${}^1P$, ${}^2P$, and S are the usual charge density, pair density, and overlap matrices, respectively. Two treatments can be carried out in eq 3, as is described in the two following subsections.

2.1. Mulliken Treatment. A Mulliken-type partitioning can be obtained from eq 3 if we write

$$N = \sum_A \Delta_A + \sum_{A<B} \Delta_{AB} \tag{4}$$

where

$$\Delta_A = \sum_i^A \sum_k^A ({}^1D^{i}_{i}{}^1D^{k}_{k} - 2\,{}^2D^{ik}_{ik}) \tag{5}$$

$$\Delta_{AB} = 2\sum_i^A \sum_k^B ({}^1D^{i}_{i}{}^1D^{k}_{k} - 2\,{}^2D^{ik}_{ik}) \qquad (A < B) \tag{6}$$

and A, B, etc. stand for different nuclei of the system.

The diatomic terms Δ_{AB} constitute a definition of *bond order* between two nuclei A and B, at any level of theory, according to eq 6. It turns out to be equivalent to the definition of bond order in terms of covariance (correlation of fluctuations) of the charge operators $\hat{q}_A$ and $\hat{q}_B$, that is, $\Delta_{AB} = -2\langle(\hat{q}_A - \langle\hat{q}_A\rangle)(\hat{q}_B - \langle\hat{q}_B\rangle)\rangle$, where, as is well-known, $\hat{q}_A = \sum_\sigma \sum_i^A \sigma c_i^\dagger \sigma c_i \sigma$ and similarly for $\hat{q}_B$.[9]

We propose to express, in eq 3, the matrix elements ${}^2D^{ik}_{ik}$ through the cumulant of the second-order reduced density matrix, the matrix elements of which will be denoted as (Λ^{ik}_{jl})[20,21,27] so that

$${}^2D^{ik}_{ik} = \frac{1}{2}{}^1D^{i}_{i}{}^1D^{k}_{k} - \frac{1}{4}{}^1D^{i}_{k}{}^1D^{k}_{i} + \frac{1}{2}\Lambda^{ik}_{ik} \tag{7}$$

Another tool that we wish to introduce in eq 3 is the effectively unpaired electron matrix the elements of which are defined as[22,23]

$$u^i_j = 2\,{}^1D^i_j - \sum_k {}^1D^{i}_{k}{}^1D^{k}_{j} \tag{8}$$

As has recently been shown, the u matrix is related with the Λ matrix through the tensorial contraction[27]

$$u^i_j = -2\sum_k \Lambda^{ik}_{jk} \tag{9}$$

so eq 3 can finally be written as

$$N = \frac{1}{2}\sum_i [\sum_k {}^1D^{i}_{k}{}^1D^{k}_{i} - u^i_i] + \sum_i u^i_i \tag{10}$$

The second term of the right-hand side (rhs) in eq 10, $\sum_i u^i_i$, represents the number of unpaired electrons of the system;[22−27] consequently, the first term, $\frac{1}{2}\sum_i[\sum_k {}^1D^i_k {}^1D^k_i - u^i_i]$, must account for the paired ones.

If we perform a Mulliken-type partitioning in eq 10 into terms involving one or two centers, we can write

$$N = \sum_A p_A + \sum_{A<B} I_{AB} + \sum_A u_A \tag{11}$$

where

$$p_A = \frac{1}{2}[\sum_i^A \sum_k^A {}^1D^{i}_{k}{}^1D^{k}_{i} - \sum_i^A u^i_i] \tag{12}$$

$$I_{AB} = \sum_i^A \sum_k^B {}^1D^{i}_{k}{}^1D^{k}_{i} \tag{13}$$

and

$$u_A = \sum_i^A u^i_i \tag{14}$$

Because the monatomic terms u_A expressed by eq 14 stand for the effectively unpaired electrons on the nucleus A,[25,27] the other monatomic terms p_A in eq 11 must be related to the effectively paired electrons on this nucleus. These one-electron matrices have been obtained from contractions (sums over all of the functions of the basis set) of two-electron quantities, which contain Coulomb and exchange correlations.[13] Hence, the u and p matrices also contain information about both types of correlations in open-shell systems as in closed-shell ones (when they are described by correlated wave functions). The expression of the diatomic terms I_{AB} of eq 11 according to eq 13 constitutes the *exchange* definition of bond order.[2,3,11] This definition of bond order depends on the square of the first-order reduced density matrix elements, and consequently, it does not distinguish between net bonding and net antibonding, as has recently been pointed out.[28−30]

Equations 6, 7, and 13 lead to establishment of the rigorous mathematical relationship between the two definitions of bond order

$$\Delta_{AB} = I_{AB} - 2\sum_i^A \sum_i^B \Lambda^{ik}_{ik} \tag{15}$$

In the case of a closed-shell determinant, all of the elements Λ^{ik}_{ik} are zero,[20] so both expressions of bond order are identical. Obviously, neither of these definitions of bond order correspond to the Huckel concept of bond order although they are related to the square of this quantity.[30]

2.2. Topological Treatment. Within this approach, let us consider, in eq 3, the partitioning of the whole real space according to the Bader's atomic regions, Ω_A.[31] Taking into account that this partitioning holds $\Omega = \cup_A \Omega_A$ and $\Omega_A \cap \Omega_B = \emptyset$ ($\forall$ A, B; $A \neq B$), eq 3 can be written in the form

$$N = \sum_{\Omega_A}\sum_{\Omega_B}\sum_{i,j,k,l} [{}^1D^{i}_{j}{}^1D^{k}_{l} - 2\,{}^2D^{ik}_{jl}]S_{ij}(\Omega_A)S_{kl}(\Omega_B) \tag{16}$$

where $S_{ij}(\Omega_A)$, $S_{kl}(\Omega_B)$, etc. are the elements of the overlap matrices calculated over the regions Ω_A, Ω_B, etc.

In eq 16, the following partitioning can be performed

$$N = \sum_{\Omega_A} \Delta_{\Omega_A} + \sum_{\Omega_A<\Omega_B} \Delta_{\Omega_A\Omega_B} \tag{17}$$

where

$$\Delta_{\Omega_A} = \sum_{i,j,k,l} ({}^1D^{i}_{j}{}^1D^{k}_{l} - 2\,{}^2D^{ik}_{jl})S_{ij}(\Omega_A)S_{kl}(\Omega_A) \tag{18}$$

$$\Delta_{\Omega_A\Omega_B} = 2\sum_{i,j,k\,l} ({}^1D^{i1}_jD^k_l - 2\,{}^2D^{ik}_{jl})S_{ij}(\Omega_A)S_{kl}(\Omega_B) \qquad (\Omega_A < \Omega_B) \quad (19)$$

The expression of $\Delta_{\Omega_A\Omega_B}$ in eq 19 constitutes the topological version of the fluctuation-type definition of bond order between the regions Ω_A and Ω_B at correlated level.[10]

The substitution of eqs 7 and 9 in expression 16 leads to

$$N = \frac{1}{2}[\sum_{\Omega_A}\sum_{\Omega_B}\sum_{i,j,k,l} {}^1D^{i1}_lD^k_jS_{ij}(\Omega_A)S_{kl}(\Omega_B) - \sum_{\Omega_A}\sum_{i,j}u^i_jS_{ij}(\Omega_A)] + \sum_{\Omega_A}\sum_{i,j}u^i_jS_{ij}(\Omega_A) \quad (20)$$

or, alternatively,

$$N = \sum_{\Omega_A}p_{\Omega_A} + \sum_{\Omega_A<\Omega_B} I_{\Omega_A\Omega_B} + \sum_{\Omega_A} u_{\Omega_A} \quad (21)$$

where

$$p_{\Omega_A} = \frac{1}{2}[\sum_{i,j,k,l} {}^1D^{i1}_lD^k_jS_{ij}(\Omega_A)S_{kl}(\Omega_B) - \sum_{i,j}u^i_jS_{ij}(\Omega_A)] \quad (22)$$

$$I_{\Omega_A\Omega_B} = \sum_{i,j,k,l} {}^1D^{i1}_lD^k_jS_{ij}(\Omega_A)S_{kl}(\Omega_B) \quad (23)$$

and

$$u_{\Omega_A} = \sum_{i,j}u^i_jS_{ij}(\Omega_A) \quad (24)$$

Equations 22, 23, and 24 are the counterparts of eqs 12, 13, and 14, respectively, in the topological version. Likewise, the topological fluctuation-type bond order and the topological exchange-type bond order are related by the expression

$$\Delta_{\Omega_A\Omega_B} = I_{\Omega_A\Omega_B} - 2\sum_{i,j,k,l}\Lambda^{ik}_{jl}S_{ij}(\Omega_A)S_{kl}(\Omega_B) \quad (25)$$

In the next section, some calculations in selected molecules are described to evaluate the usefulness of the partitioning proposed in eqs 11 and 21.

3. Results and Discussion

Numerical determinations have been carried out to test the above methodology for localizing paired and unpaired electrons, as well as for describing chemical bondings using exchange-type bond order indices at correlated level. All of the calculations reported in this section were performed using a modified Gaussian 94[32] program, which generated the first-order reduced density matrices, as well as the overlap integrals $S_{ij}(\Omega_A)$ that appear in eqs 22−24. In a second step, these matrices were subjected to population analysis by our own computational implementation. The employed basis sets have been 6-31G** with d polarization functions on the heavy atoms and p functions on the hydrogen ones for the compounds described in Tables 1 and 2. The results reported in Table 3 have been obtained with the simpler basis set 6-31G. All of the geometries were optimized for these basis sets within configuration interaction (CI) wave functions with single and double excitations (SDCI). The Mulliken-type calculations have been carried out in the atomic basis sets. Because these basis sets are nonorthogonal, the matrix elements ${}^1D^i_j$ have systematically been replaced by $({}^1PS)^i_j$, where ${}^1P$ and S are the usual charge density and overlap matrices, respectively.

TABLE 1: Calculated Values of Populations p_A, p_C, u_A, and u_C and Bond Orders I_{AB}, and I_{AC} (Mulliken-type) and Populations p_{Ω_A}, p_{Ω_C}, u_{Ω_A}, and u_{Ω_C} and Bond Orders $I_{\Omega_A\Omega_B}$, and $I_{\Omega_A\Omega_C}$ (Topological) in Diatomic Molecules in the SDCI Approximation for A, B = H, N, O, or F

	H_2	N_2	O_2	F_2	CO
p_A	0.464	5.364	6.800	8.248	6.774
p_C					4.400
u_A	0.060	0.346	0.377	0.322	0.331
u_C					0.303
I_{AB}	0.946	2.569	1.642	0.856	
I_{AC}					2.202
p_{Ω_A}	0.463	5.243	6.601	8.118	8.088
p_{Ω_C}					3.725
u_{Ω_A}	0.060	0.346	0.377	0.322	0.398
u_{Ω_C}					0.237
$I_{\Omega_A\Omega_B}$	0.955	2.822	2.045	1.119	
$I_{\Omega_A\Omega_C}$					1.552

TABLE 2: Calculated Values of Populations p_A, p_H, u_A, and u_H and Bond Orders I_{AH} (Mulliken-type) and Populations p_{Ω_A}, p_{Ω_H}, u_{Ω_A}, and u_{Ω_H}, and Bond Orders $I_{\Omega_A\Omega_H}$ (Topological) for Second-Row Hydrides in the SDCI Approximation for A = B, C, N, O, or F

	BH_3	CH_4	NH_3	H_2O	HF
p_A	3.200	4.319	6.111	7.480	8.691
p_H	0.537	0.379	0.269	0.211	0.167
u_A	0.189	0.250	0.298	0.302	0.264
u_H	0.059	0.052	0.047	0.045	0.041
I_{AH}	0.940	0.932	0.879	0.849	0.831
p_{Ω_A}	2.111	3.738	6.412	8.172	9.191
p_{Ω_H}	1.197	0.447	0.172	0.065	0.026
u_{Ω_A}	0.074	0.219	0.309	0.325	0.281
u_{Ω_H}	0.097	0.060	0.044	0.033	0.025
$I_{\Omega_A\Omega_H}$	0.507	0.944	0.860	0.650	0.478
$I_{\Omega_H\Omega_{H'}}$	0.137				

TABLE 3: Calculated Values of Populations p_C, p_H, p_A, u_C, u_H, and u_A and Bond Orders $I_{CC'}$, I_{CH}, and I_{CA} (Mulliken-type) and Populations p_{Ω_C}, p_{Ω_H}, p_{Ω_A}, u_{Ω_C}, u_{Ω_H}, and u_{Ω_A} and Bond Orders $I_{\Omega_C\Omega_{C'}}$, $I_{\Omega_C\Omega_H}$, and $I_{\Omega_C\Omega_A}$ (topological) for Several Organic Compounds in the SDCI Approximation for A = N or F

	C_2H_6	C_2H_4	C_2H_2	HCN	CH_3F
p_C	4.395	4.185	3.995	3.939	4.096
p_H	0.372	0.369	0.264	0.255	0.368
p_A				5.541	8.818
u_C	0.197	0.262	0.309	0.305	0.195
u_H	0.040	0.039	0.034	0.035	0.039
u_A				0.321	0.211
$I_{CC'}$	0.882	1.814	3.057		
I_{CH}	0.929	0.926	0.832	0.839	0.908
I_{CA}				2.737	0.740
p_{Ω_C}	3.830	3.890	4.012	3.363	3.560
p_{Ω_H}	0.440	0.419	0.319	0.279	0.419
p_{Ω_A}				6.288	8.836
u_{Ω_C}	0.177	0.246	0.299	0.263	0.170
u_{Ω_H}	0.047	0.047	0.044	0.042	0.045
u_{Ω_A}				0.356	0.219
$I_{\Omega_C\Omega_{C'}}$	0.953	1.782	2.654		
$I_{\Omega_C\Omega_H}$	0.937	0.940	0.934	0.894	0.913
$I_{\Omega_C\Omega_A}$				2.440	0.821

Although all of the studied systems are closed-shell molecules, they have nonzero unpaired electron population values. This is due to the partial split of electron pairs, pointed out in the Introduction, which arises from the dispersal of the occupation numbers of the orbitals in the expansion on several Slater determinants, which occurs when a system is described using correlated wave functions. The results in Table 1 refer to simple diatomic molecules in the ground state (except in the oxygen case). The first conclusion that can be drawn from these results is that the monatomic populations of the paired, as well as the unpaired, electrons are similar in the Mulliken and the topological versions for the homonuclear molecules. However, in the case of the CO molecule, the value of $p_{\Omega_O} = 8.088$ is clearly higher than its counterpart $p_O = 6.774$. Hence, the stronger electronegative character of the oxygen atom is more clearly pointed out in the topological approach. The values of $u_{\Omega_C} = 0.237$ and $u_C = 0.303$ also agree with this property. This confirms again the well-known shortcomings of the Mulliken-type partitionings to describe chemical bondings in polar molecules.[12] The found values of the bond orders are close to the conventional ones; they are higher in the topological method than in the Mulliken one, except in the case of the heteronuclear molecule CO of which the lower value $I_{\Omega_O\Omega_C} = 1.552$ shows again that the electron pairs are unequally shared, which provides the previously commented high p_{Ω_O} value.

Table 2 reports the results corresponding to some hydrides of the second-row elements. The extent of the polarity of the A−H bonding is clearly reflected on the values of I_{AH} and $I_{\Omega_A\Omega_H}$. Both topological and Mulliken results show a decreasing of the sharing of electrons along the sequence A = N, O, F, represented by the decreasing of the I_{AH} and $I_{\Omega_A\Omega_H}$ values. This is due to the corresponding increasing of the electronegativity of the nucleous A, although the topological results describe a lower sharing than the Mulliken ones. The ionic character of these bondings is correspondingly reflected on the increasing of the p_A and p_{Ω_A} populations and the decreasing of the corresponding p_H and p_{Ω_H} ones. However, the values of $I_{CH} = 0.932$ and $I_{\Omega_C\Omega_H} = 0.944$ are similar in the nonpolar CH_4 molecule. The high value found for the population $p_{\Omega_H} = 1.197$ in the BH_3 molecule clearly predicts the presence of negative charge on the hydrogen atoms in this molecule, while the value $p_H = 0.537$ in the Mulliken procedure is considerably lower. The nonnegligible $I_{\Omega_H\Omega_{H'}}$ value has also been pointed out in ref 10 using a fluctuation-type topological treatment.

Table 3 describes the numerical values obtained in some organic compounds, which are considered as standard models of different bond order multiplicities (C_2H_6, C_2H_4, C_2H_2, HCN). This table also describes the molecule CH_3F as an example of a system posessing an atom with high electronegativity. These results confirm that this methodology is feasible to characterize the multiplicity of the C−C and C−N bondings and also yields reasonable values for the C−H bondings in all cases. The value $p_{\Omega_F} = 3.560$ is lower than its counterpart $p_F = 4.096$ showing a higher ionic character of the bonding C−F in the topological procedure. It is also interesting to point out the increasing of the u_C and u_{Ω_C} values in the series C_2H_6, C_2H_4, C_2H_2, which predicts a corresponding increasing of the reactivity of the carbon atom.[26,27]

In conclusion, this report has proposed a partitioning of the N electrons in a molecule according to three terms with clear physical meaning (eqs 11 and 21). One of these terms, I_{AB} or $I_{\Omega_A\Omega_B}$, is identified with the exchange-type bond order and, together with the proposed p_A and u_A or p_{Ω_A} and u_{Ω_A} monatomic indices, leads to meaningful results in the description of the molecules used as test examples. The performed numerical determinations show a better behavior of the topological version for describing polar bondings. The reported methodology only needs the first-order density matrices, which is interesting in a computational point of view because it avoids the much more expensive use of higher-order reduced density matrices. Further studies are currently being carried out in our laboratories with the cumulants of the second-order reduced density matrixes to compare fluctuation-type and exchange-type bond orders (see eqs 15 and 25), as well as their basis dependence, etc. The results will be published elsewhere.[33]

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