Covalent bond orders revisited: the open-shell case

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This article states the concept of covalent bond order for open-shell systems from the invariance properties of the first- and second-order reduced density matrices for all the components of a multiplet state. A general bond order definition is formulated in the framework of the electronic population analyses in the Hilbert space of atomic orbitals.

1. Introduction

The concept of covalent bond order (or bond index) has had paramount importance in the understanding of chemical bonding. The description of chemical bonding as an electron pairing phenomenon entails the formulation of the bond order, which shows a determined electron population in some molecular regions. As most of the physical and chemical quantities describing molecular electronic distributions, the bond order is not an expectation value of a quantum mechanical operator and, consequently, it cannot be uniquely defined. However, any definition of bond order, to be acceptable, should fulfil the physical features of the molecular systems and the chemical intuition. Such a concept has been widely developed for closed-shell systems and much less for open-shell cases.[1–9] Perhaps the most popular definition of bond order between two nuclei A and B, BO_{AB} (the two-center electronic population shared out among these nuclei) for an open-shell system has been reported by Mayer[4–6] and extensively applied by other authors.[10] Nevertheless, such open-shell bond order definition has not been derived for correlated state functions, nor does it fit the physical requirements of uniqueness for the spin multiplet components in absence of a magnetic field, as may be expected for any physical quantity. In this work we attempt to derive a general expression for the bond order in the Hilbert space partitioning scheme avoiding this shortcoming, *i.e.* following the above mentioned physical requirement to be an acceptable definition, also beyond the independent particle models. To perform this task we will follow the method used in ref. 11 employing the second-order reduced density[12–16] and their relationships with the spin density.[17]

The organization of this article is as follows. The second section is devoted to the theoretical derivation of the covalent bond order from the reduced density matrix structure and its invariance properties for the spin components of a given multiplet. The third section reports the computational details and the numerical results found for some selected molecular systems in ground and excited states. A discussion of our results and their comparison with those arising from Mayer's

definition is also reported in that section showing that our proposal removes the ambiguity of the different bond orders for different spin components of a multiplet. Finally, the last section points out the remarks and conclusions of this work.

2. Theoretical

The matrix elements of the second-order reduced density matrix, ^2D (2-RDM), corresponding to an N-electron system in an $i,j,k,l,\ldots$ orthogonal spin orbital basis set is

$$^2D_{kl}^{ij} = \frac{1}{2}{}^1D_k^i{}^1D_l^j - \frac{1}{2}{}^1D_l^i{}^1D_k^j + \frac{1}{2}\Delta_{kl}^{ij} \qquad (1)$$

where $^1D_k^i$ and Δ_{kl}^{ij} are the matrix elements of the first-order reduced density matrix (1-RDM) and the cumulant of the 2-RDM, respectively.[11–15] The terms in the r.h.s. of eqn (1) stand for the Coulomb, exchange and cumulant terms, respectively. Spin variable integration of eqn (1) leads to the spin-free 2-RDM which reads

$$^2\mathbb{D}_{kl}^{ij} = \frac{1}{2}{}^1\mathbb{D}_k^i{}^1\mathbb{D}_l^j - \frac{1}{4}{}^1\mathbb{D}_l^i{}^1\mathbb{D}_k^j - \frac{1}{4}{}^1\mathbb{D}^{(s)i}{}_l{}^1\mathbb{D}^{(s)j}{}_k + \frac{1}{2}\Gamma_{kl}^{ij} \quad (2)$$

where $^2\mathbb{D}_{kl}$, $^1\mathbb{D}_k^i = {}^1\mathbb{D}^{\alpha i}{}_k + {}^1\mathbb{D}^{\beta i}{}_k$, $^1\mathbb{D}^{(s)i}{}_k = {}^1\mathbb{D}^{\alpha i}{}_k - {}^1\mathbb{D}^{\beta i}{}_k$ and Γ_{kl}^{ij} stand for the matrix elements of the spin-free 2-RDM, 1-RDM, spin density matrix and those of the 2-RDM cumulant matrix, respectively, in the $i,j,k,l,\ldots$ orthogonal orbital basis set. $^1\mathbb{D}^{\alpha}$ and $^1\mathbb{D}^{\beta}$ are the spin up and spin down density matrices, respectively. The exchange term (second term in the r.h.s. of eqn (1)) becomes split into a particle–particle exchange term and an explicit spin density exchange contribution (third term in the r.h.s. of eqn (2)), thus segregating the many-body effects and the *irreducible* spin contributions of the cumulant in the last term of eqn (2). The invariance properties of the density matrices play a key role in establishing and interpreting the bond order definitions rigorously. These properties are expressed by the relations[17,18]

$$^2\mathbb{D}_{jl}^{ik}(S,S_z) = {}^2\mathbb{D}_{jl}^{ik}(S,S); \quad {}^1\mathbb{D}_j^i(S,S_z) = {}^1\mathbb{D}_j^i(S,S) \qquad (3)$$

for all S_z, *i.e.*, $^1\mathbb{D}$ and $^2\mathbb{D}$ are independent of the spin projection and are only a function of the total spin S ($S_z = S$, maximum projection), while it is not true neither for $^1\mathbb{D}^{(s)}$ nor for Γ, *i.e.*, the terms $^2\mathbb{D}_{kl}^{ij}$, $\frac{1}{2}{}^1\mathbb{D}_l^i{}^1\mathbb{D}_j^k$ and $\frac{1}{4}{}^1\mathbb{D}_l^i{}^1\mathbb{D}_j^k$ are independent of the S_z component of the multiplet state as well as the sum $\frac{1}{4}{}^1\mathbb{D}^{(s)i}{}_l{}^1\mathbb{D}^{(s)k}{}_j + \frac{1}{2}\Gamma_{kl}^{ij}$ whereas the terms $\frac{1}{4}{}^1\mathbb{D}^{(s)i}{}_l{}^1\mathbb{D}^{(s)k}{}_j$ and $\frac{1}{2}\Gamma_{kl}^{ij}$ are, individually, S_z-dependent. It may be noted that all the results in this article are symmetric under the inversion of S_z

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projections, *i.e.*, the results are symmetric for the same module of S_z despite the sign of the projection, hence we will only make use of the positive projections.

After transforming the spin-free $^2\mathbb{D}$ matrix into an atomic orbital (AO) basis set defined by the atomic functions $\{\mu,\nu,\ldots\}$ centered in each atom it reads,[19]

$$^2\mathbb{P}_{\sigma\lambda}^{\mu\nu} = \frac{1}{2}\,{}^1\mathbb{P}_{\sigma}^{\mu}{}^1\mathbb{P}_{\lambda}^{\nu} - \frac{1}{4}\,{}^1\mathbb{P}_{\lambda}^{\mu}{}^1\mathbb{P}_{\sigma}^{\nu} - \frac{1}{4}\,{}^1\mathbb{P}_{\lambda}^{(s)\mu}\,{}^1\mathbb{P}_{\sigma}^{(s)\nu} + \frac{1}{2}\Gamma_{\sigma\lambda}^{\mu\nu} \quad (4)$$

where the terms in eqn (4) and their invariance properties correspond to those of eqn (3) expressed as $^2\mathbb{P}_{\sigma\lambda}^{\mu\nu}(S,S_z) = {}^2\mathbb{P}_{\sigma\lambda}^{\mu\nu}(S,S)$ and $^1\mathbb{P}_{\sigma}^{\mu}(S,S_z) = {}^1\mathbb{P}_{\sigma}^{\mu}(S,S)$. Within this scenario, the partitioning of the normalized difference, *i.e.*, the number of particles conservation[11,20] may be expressed by

$$\sum_{\mu\nu}({}^1\mathbb{P}\mathbb{S})_{\mu}^{\mu}({}^1\mathbb{P}\mathbb{S})_{\nu}^{\nu} - 2\sum_{\mu\nu\sigma\lambda}\mathbb{S}_{\mu}^{\sigma}\,{}^2\mathbb{P}_{\sigma\lambda}^{\mu\nu}\mathbb{S}_{\nu}^{\lambda} = \frac{1}{2}\sum_{\mu\nu}({}^1\mathbb{P}\mathbb{S})_{\mu}^{\nu}({}^1\mathbb{P}\mathbb{S})_{\nu}^{\mu}$$

$$+ \frac{1}{2}\sum_{\mu\nu}({}^1\mathbb{P}^{(s)}\mathbb{S})_{\mu}^{\nu}({}^1\mathbb{P}^{(s)}\mathbb{S})_{\nu}^{\mu} - \sum_{\mu\nu\sigma\lambda}\mathbb{S}_{\mu}^{\sigma}\Gamma_{\sigma\lambda}^{\mu\nu}\mathbb{S}_{\nu}^{\lambda} = N$$

$$(5)$$

where N is the number of electrons in the system and $\mathbb{S}$ stands for the overlap matrix in the *AO* basis set. The bond order BO_{AB} is defined as a two-center term in the one- and two-center terms partitioning of eqn (5).

Eqn (5) and the above discussed invariance relations permit to equate

$$\left[({}^1\mathbb{P}^{(s)}\mathbb{S})_{\mu}^{\nu}({}^1\mathbb{P}^{(s)}\mathbb{S})_{\nu}^{\mu} - 2\sum_{\lambda\gamma}\mathbb{S}_{\mu}^{\lambda}\Gamma_{\lambda\gamma}^{\mu\nu}\mathbb{S}_{\nu}^{\gamma}\right]_{\forall S_z}$$

$$= \left[({}^1\mathbb{P}^{(s)}\mathbb{S})_{\mu}^{\nu}({}^1\mathbb{P}^{(s)}\mathbb{S})_{\nu}^{\mu} - 2\sum_{\lambda\gamma}\mathbb{S}_{\mu}^{\lambda}\Gamma_{\lambda\gamma}^{\mu\nu}\mathbb{S}_{\nu}^{\gamma}\right]_{S_z=S} \quad (6)$$

where the subscript $S_z = S$ indicates that the r.h.s. of eqn (6) must be evaluated at the maximum projection while the l.h.s. at any arbitrary $S_z \neq S$. It has been shown that the many-body cumulant term Γ is strictly of non-pairing nature in the case of closed-shell systems[11,21,22] and no spin terms are present in such a case. Hence, considering that the *irreducible* spin effects only appear in open-shell cases for $S_z \neq S$, as well as the invariance expressed by eqn (6), it may be concluded that it is convenient to use the r.h.s. of this equation to define the bond orders, because the pairing and non-pairing character of terms is well defined at this side of the invariant quantity (6). Consequently, from these physical considerations the bond order BO_{AB} is defined from eqn (5) by the exchange terms (the terms with pairing character) in this equation evaluated in the highest spin projection state $S_z = S$. Therefore, the bond order becomes expressed by

$$BO_{AB} = \sum_{\nu\varepsilon A}\sum_{\mu\varepsilon B}({}^1\mathbb{P}\mathbb{S})_{\mu}^{\nu}({}^1\mathbb{P}\mathbb{S})_{\nu}^{\mu}$$

$$+ \sum_{\nu\varepsilon A}\sum_{\mu\varepsilon B}[{}^1\mathbb{P}^{(s)}(S,S)\mathbb{S}]_{\mu}^{\nu}[{}^1\mathbb{P}(s)(S,S)\mathbb{S}]_{\nu}^{\mu}$$

$$(7)$$

where the spin density matrix has been explicitly written as evaluated in the maximum projection of the spin number of the system. Eqn (7) coincides with the form of Mayer's bond

order definition[5]

$$BO_{AB}^M = \sum_{\nu\varepsilon A}\sum_{\mu\varepsilon B}[({}^1\mathbb{P}\mathbb{S})_{\mu}^{\nu}({}^1\mathbb{P}\mathbb{S})_{\nu}^{\mu}$$

$$(8)$$

$$+ ({}^1\mathbb{P}^{(s)}(S,S_z)\mathbb{S})_{\mu}^{\nu}({}^1\mathbb{P}^{(s)}(S,S_z)\mathbb{S})_{\nu}^{\mu}]$$

but differs in two fundamental concepts: on the one hand eqn (7) definition is supported by rigorous arguments and has not ambiguity when applied to open-shell systems, contrarily to Mayer's definition, hence, *the unique bond order as physically expected is that evaluated at the spin density* $^1\mathbb{P}^{(s)}$ *corresponding to the maximum projection* $S_z = S$, while Mayer's formula (*cf.* ref. 6 in which it has been established that it may be applied "to the wavefunction in question") yields different bond orders for different spin projections because, as it is a function of the spin density, it is obvious that this quantity depends on each one of the $2S + 1$ projections S_z of the total spin S of the N-electron system. On the other hand, eqn (7) *is valid for both independent and correlated particle models of the state functions* because it has been derived from a general 2-RDM, while Mayer's formula has been calculated for one determinant state function and then postulated to be valid beyond the Hartree–Fock level.[5]

3. Results and discussion

Table 1 shows the results of covalent bond orders for the systems O_2, CH_2 and linear HBBH in their triplet ground state and for the C_2 molecule in a triplet excited state. The aim is to describe the bond orders calculated in these systems according to our bond order definition presenting, for the sake of comparison, the different Mayer's bond orders arising from each one of the $2S + 1$ projections of the total spin S of the N-electron system. The numerical calculations were performed at the equilibrium geometries[23–25] at the restricted open-shell Hartree–Fock (ROHF) reference state in the single and double excitation configuration interaction approximation (CISD), with the 6-31G basis sets. The spin-free first- and second-order reduced density matrices were obtained with the PSI3[26] package. The spin density matrices were calculated, in the molecular basis set, by the modified formula reported in ref. 27 and 28

$$^1\mathbb{D}^{(s)i}_{\,j} = \frac{S_z}{S(S+1)}\left\{\frac{(N+2)}{2}\,{}^1\mathbb{D}_{j}^{i} - 2\sum_{k}({}^2\mathbb{D}_{jk}^{ik} + {}^2\mathbb{D}_{kj}^{ik})\right\} \quad (9)$$

and then transformed into the AO basis set. The table reports Mayer's total bond orders BO_{AB}^M and their corresponding spin contributions $BO_{AB}^{M(s)}$ (the second term in the r.h.s. of eqn (8)). The results show that these spin contributions are very different for each one of the spin projections in the systems O_2, C_2 and linear HBBH, while they remain almost identical for all spin projections in the CH_2 one. It can be observed that the greater differences appear for pure covalent bonds X–X (X = O, C, B), while the bonds X–H (X = C, B) only exhibit slight changes for the different multiplet states. The BO_{AB} values from eqn (7) coincide with the counterpart BO_{AB}^M ones for $S_z = S$, as has been commented above. These values provide the

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Table 1 Mayer's bond orders (BO_{AB}^M) calculated for multiplet states of open-shell systems using the 6-31G basis sets at ROHF-CISD approximation

System	State	S	S_z	Bond	$BO_{AB}^{M\,a}$	$BO_{AB}^{M(s)b}$
O_2	$^3\Sigma_g^-$	1	0	OO	1.069	0.000
			± 1		1.474	0.405
CH_2	$^3B_1$	1	0	CH	0.893	0.000
			± 1		0.897	0.004
C_2	$^3\Sigma_g^+$	1	0	CC	1.104	0.000
			± 1		1.553	0.449
HBBH (linear)	$^3\Sigma_g^-$	1	0	BB	1.620	0.000
			± 1		2.087	0.467
			0	BH	0.884	0.000
			± 1		0.881	−0.002
			0	B$\cdots$H	0.042	0.000
			± 1		0.043	0.001

[a] Total bond order (eqn (8)). [b] Spin contribution to the total bond order (second term in the r.h.s. of eqn (8)).

best agreement with the bond multiplicities expected for these systems,[24,25] thus confirming our theoretical proposal.

4. Concluding remarks

In the present work we have dealt with the covalent bond order concept as an indicator of the covalent contribution of the electron cloud to the bonds in a molecular system.[8] According to theoretical arguments, we have proposed a bond order definition in the framework of the population analysis in the Hilbert space, which is physically acceptable for open-shell systems because it is identical for all degenerate multiplet components in absence of magnetic fields. This definition is valid for both independent particle and correlated state functions. Moreover, we have performed numerical calculations providing chemically meaningful results, which confirm our theoretical predictions. It is worthy to remark that this definition of bond order for the open-shell case may also be performed within partitioning models of the physical space (3D), such as Atoms in Molecules (AIM)[29] or "fuzzy" atoms,[30] among others. Works in this line are being carried out in our laboratories and will be published elsewhere.

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