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Bond orders and valences in the SCF theory: a comment

I. Mayer

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525
Budapest, P.O. Box 17, Hungary

The calculation of bond order and valence indices for *ab initio* and semiempirical wave functions is discussed by emphasizing their relations to the exchange part of the second order density matrix. Comments are also given on a recent work of Gopinathan and Jug, as well as propositions made to avoid ambiguity in the nomenclature.

Key words: Bond orders in *ab initio* theory—valences in *ab initio* theory—bond orders in semiempirical theory—valences in semiempirical theory—free valence index—Wiberg index

1. Introduction

In a recent couple of papers [1a, b] Gopinathan and Jug have discussed the valence index of an atom in a molecule, as it was defined in 1973 by Armstrong et al. [2] and, independently, by Borisova and Semenov [3]. (The basic idea traces back to Wiberg's classical paper [4].) The valence index discussed by these authors [1-3] is defined for the SCF wave functions, assuming the basis set being orthonormal, as is the case in the CNDO-type semiempirical theories; the generalization for *ab initio* (or EHT) wave functions has been recently given in [5-7]. (Another way of generalization [8, 9] which is based on Löwdin-orthogonalization of the basis with a subsequent use of the formulae valid for the orthonormal basis, has been shown to be less adequate [10].)

No doubt, Gopinathan and Jug [1] present some interesting details concerning the connection of valence indices with the "natural bond orbitals", as well as the results for some individual molecules may also be of interest. However, there are disputable points concerning Wiberg's bond indices, and especially, the simultaneous occurrence of the papers of Gopinathan and Jug [1] and of ours [5-7] can introduce a harmful confusion in the concepts and nomenclature concerning valence indices, especially for open-shell systems. In fact, Gopinathan and Jug consider (see p. 500 in [1]) that the odd electron in a free radical does not contribute to the valence of the atom on which it is situated. This means, for instance, that they assume the carbon atom in the methyl radical to be (approximately) three-valent; at the same time in Refs. [2, 5-7] it is assumed to have a valence of (about) four; as shown in [5-7], one may say that three of them are actually used in the bonds and one is free. (The latter approach is obviously much closer to the chemical intuition.) Accordingly, for open-shell systems indices of both total and free valences were introduced in [5-7]. Gopinathan and Jug [1] also use the term "free valence index" with the same notation as ours; however, they attribute a completely different meaning to it, not related to the unpaired electrons but expressing the deviation of the actual valence index from some idealized (reference) integer value. Accordingly, the "free valences" of Gopinathan and Jug [1] are also defined for closed-shell systems, in contrast to ours [5-7].

We feel rather uncomfortable about the same term "free valence" being attributed to completely different parameters. It may be of interest to note that Armstrong et al. [2] have already mentioned both these quantities (within the framework of the CNDO method) as possible measures of reactivity, but without attributing any specific name to either of them.

Here we propose to use the term "free valence index" only for the difference between the total valence of an atom (as defined in accord with [2, 5-7]) and the sum of the bond orders formed by it, because this quantity can be expressed [7] (also see below) *via* the spin-density, i.e. reveals an intimate connection with the existence of some unsaturated valence in a free radical due to its unpaired spin. At the same time, one may also attribute a specific term to the quantity discussed by Gopinathan and Jug [1]; one can propose e.g. "excess valence" or "valence defect", maybe both, depending on the sign of the difference between the actual and nominal (reference) valence values.

The aim of the present note is partly to comment on some points in Ref. [1], but mainly to discuss in some detail the basic formulae [2-7] for bond orders and valences, by the use of which these parameters can actually be calculated from the SCF wave functions. These quantities can provide useful information of direct chemical character concerning the systems studied. The formulae will be given for both general (non-orthogonal; *ab initio*, EHT) and orthonormal (CNDO etc.) basis sets. The presentation will be based on the relationships we obtained most recently between the bond order and valence indices from one hand and the second order density matrix from the other.

2. The bond order and valence indices

We shall first introduce the spinless LCAO "density matrix" $\boldsymbol{P}$ and spin-density matrix $\boldsymbol{P}^s$, defined as

$$\begin{aligned} \boldsymbol{P} &= \boldsymbol{P}^\alpha + \boldsymbol{P}^\beta; \\ \boldsymbol{P}^s &= \boldsymbol{P}^\alpha - \boldsymbol{P}^\beta, \end{aligned} \tag{1}$$

with

$$P^{\sigma} = \sum_{i=1}^{n_\sigma} c_i^{\sigma} c_i^{\sigma\dagger}, \tag{2}$$

where c_i^σ is the column-vector of the i-th MO of spin $\sigma(\sigma = \alpha$ or $\beta)$ of the single determinant wave function, † denotes the adjoint and n_σ is the number of electrons with spin σ. Open-shell systems are treated at the UHF level, while for closed-shell systems doubly filled (RHF) orbitals are used, i.e. $c_i^\alpha = c_i^\beta = c_i$; $P^\alpha = P^\beta$, so $P = 2\sum_i^{\text{occ.}} c_i c_i^\dagger$ and $P^s = 0$.

Now, it is known [11] that the specific property of the single determinant wave functions is that the second order density matrix ρ_2 can be expressed in terms of the first order one ρ_1:

$$\rho_2(1,2;1',2') = \rho_1(1;1')\rho_1(2;2') - \rho_1(2;1')\rho_1(1;2'). \tag{3}$$

The first term in the right-hand-side of (3) is related to the Coulombic, the second to the exchange part of the electron-electron repulsion energy.

The exchange part of the second order density matrix is normalized (cf. [11]) as

$$N = \int\int \rho_1(2;1)\rho_1(1;2)\, d\tau_1\, d\tau_2 \tag{4}$$

N being the number of electrons, and the integrations include summations over spins. Substituting the LCAO expression of the first order density matrix ρ_1 into (4) we obtain this normalization after some algebra in the form

$$\begin{aligned} N = {} & \tfrac{1}{2}\sum_{A} \sum_{\mu,\nu\in A} [(PS)_{\mu\nu}(PS)_{\nu\mu} + (P^sS)_{\mu\nu}(P^sS)_{\nu\mu}] \\ & + \sum_{A<B} \sum_{\mu\in A} \sum_{\nu\in B} [(PS)_{\mu\nu}(PS)_{\nu\mu} + (P^sS)_{\mu\nu}(P^sS)_{\nu\mu}]. \end{aligned} \tag{5}$$

Here S is the overlap matrix of the basis and the notations like $\mu \in A$ mean that the summations should be extended to all the basis orbitals centered on the given atom. The equality in (5) can be proven also based on the identity given in [7]: $(PS)^2 = 2PS - (P^sS)^2$.

The bond order between atoms A and B is defined[1] as the diatomic contribution to the right-hand-side of (5):

$$B_{AB} = \sum_{\mu\in A} \sum_{\nu\in B} [(PS)_{\mu\nu}(PS)_{\nu\mu} + (P^sS)_{\mu\nu}(P^sS)_{\nu\mu}]. \tag{6}$$

If the basis is orthonormalized, then matrix S is the unity matrix, and the bond order index (6) becomes identical to Wiberg's bond index [4] proposed originally in the framework of the CNDO theory; admitting also open-shell systems it can be written as

$$W_{AB} = \sum_{\mu\in A} \sum_{\nu\in B} (|P_{\mu\nu}|^2 + |P^s_{\mu\nu}|^2). \tag{7}$$

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[1] Following an idea in [8], we have introduced a minor improvement in the definition of bond orders and free valences for the open-shell case, as compared with [5, 6]

As noted in [5], both the bond order index B_{AB} in the *ab initio* case and the Wiberg index in the CNDO one are closely related to the exchange part of the interaction between the atoms in question; in particular, the comparison with the CNDO energy partitioning scheme in [12] shows that $E_{AB}^{exch} = -\frac{1}{2}\gamma_{AB} W_{AB}$, where E_{AB}^{exch} is the diatomic exchange energy component and γ_{AB} is the diatomic Coulomb integral [cf. also Eq. (30) in Ref. 13].

It is repeatedly stated in Ref. [1] that Wiberg's bond indices are related to the case of a non-orthogonal basis (see, in particular, pp. 499 and 523). This is, however, not the case, as Wiberg [4] defined in the framework of the CNDO theory. The mistake in [1] is often recurring, and perhaps is connected with the specific handling of the overlap integrals in the CNDO method: at first one calculates explicitly the overlaps between the basis orbitals, but only for being used to parametrize the off-diagonal core matrix elements, and then the overlap integrals are omitted from any further consideration. Accordingly, the overlap matrix does not enter the normalization of the orbitals or the SCF equations [14]. (The assumption $S_{\mu\nu} = \delta_{\mu\nu}$ is the only one consistent with the ZDO approximation for the integrals.)

The Wiberg index W_{AB} is always positive; this is usually, but not necessarily, also the case for the general bond order index B_{AB}. (Very small negative values have already been encountered [6].) The positiveness of the Wiberg index led to a mistake in [1] (it is also often recurring) that the Wiberg index would be "incapable of describing antibonding situation", being the measure of "total extent of electron pairing between the two given atoms" and would not, therefore, "a measure of the difference: number of bonding [electron] pairs minus that of antibonding pairs" (see p. 523 in [1]). But this is usually not the case, because the difference between the number of bonding and antibonding orbitals is automatically accounted for when matrix $\boldsymbol{P}$ is formed from the orbital coefficients. So, it was proven by Borisova and Semenov [3] that the Wiberg index of homonuclear diatomics is just

$$W_{AB} = \tfrac{1}{2}(n_b - n_a) \tag{8}$$

where n_b and n_a are the number of occupied bonding and antibonding molecular spin-orbitals, respectively. Here we do not wish to repeat the derivation given in [3]; one can ascertain the correctness of this conclusion by recalling, e.g. that for systems like H_2, N_2, F_2 and He_2 the Wiberg indices are 1, 3, 1 and 0, respectively, in full agreement with the classical chemical notion of bond orders in these molecules[2] (also see [13]).

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[2] Borisova and Semenov [3] derived Eq. (8) first in the form

$$W_{AB} = \tfrac{1}{2}[n_b + n_a - 2\min(n_b, n_a)]. \tag{8a}$$

Because, for ground state systems, $n_b \geq n_a$, this equation reduces to (8). An interesting exception is C_2 [15]; one can prove that for this molecule one of the conditions under which Borisova and Semenov performed their derivation is not fulfilled

In light of the above discussion I do not see a need for the introduction of the new ("projected") bond index proposed in [1], especially because no definite physical meaning can be attributed to it.

Although the presence of the overlap integrals makes the derivations more complicated, exactly the same conclusions hold for the general bond order indices B_{AB} defined in Eq. (6), in the case of homonuclear diatomics treated at the minimal basis *ab initio* (or EHT) level [5-7], as were discussed above for the Wiberg indices. So the bond orders quoted for H_2, N_2 etc. are again obtained. In particular, the bond order between two He atoms is zero. However, the *Mulliken's overlap population*, as it is easy to see, is *negative* in this case. This fact, perhaps, may be considered as an expression of the repulsive character of the interaction. One can, therefore, agree with the following reformulation of the statement quoted above: neither the bond order indices B_{AB} in the general case, nor the Wiberg indices W_{AB} in the case of an orthonormal basis set, can appropriately distinguish between the non-bonding (neutral) and antibonding (repulsive) situations occurring *for chemically non-bonded atoms.*

For molecules more complicated than the homonuclear diatomics, the bond orders B_{AB} (or W_{AB} if the basis is orthonormalized) are influenced also by the factors like bond polarity and delocalization effects. Nonetheless, for pairs of chemically bonded atoms, they are usually close to the "classical" values of bond orders, and even the small variations may reflect well the changes in the bond strengths in series of related molecules.[3]

Concerning valences, one can observe that the terms in both sides of Eq. (5) giving the normalization of the exchange part of the second order density matrix can be grouped according to the individual atoms to yield

$$Q_{A}^{e} = \frac{1}{2}\left\{ \sum_{\mu,\nu\in A} (\boldsymbol{PS})_{\mu\nu}(\boldsymbol{PS})_{\nu\mu} + \sum_{B(B\neq A)} \sum_{\mu\in A} \sum_{\nu\in B} [(\boldsymbol{PS})_{\mu\nu}(\boldsymbol{PS})_{\nu\mu} + (\boldsymbol{P}^{s}\boldsymbol{S})_{\mu\nu}(\boldsymbol{P}^{s}\boldsymbol{S})_{\nu\mu}] + \sum_{\mu,\nu\in A} (\boldsymbol{P}^{s}\boldsymbol{S})_{\mu\nu}(\boldsymbol{P}^{s}\boldsymbol{S})_{\nu\mu} \right\} \tag{9}$$

where $Q_{A}^{e} = \sum_{\mu\in A} (\boldsymbol{PS})_{\mu\mu}$ is the electron population on atom A. ($\sum_{A} Q_{A}^{e} = N$.)

By using Eq. (6) and introducing the appropriate notations V_A and F_A, Eq. (9) can be transformed to

$$V_A = \sum_{B(B\neq A)} B_{AB} + F_A \tag{10}$$

where

$$V_A = 2 \sum_{\mu\in A} (\boldsymbol{PS})_{\mu\mu} - \sum_{\mu,\nu\in A} (\boldsymbol{PS})_{\mu\nu}(\boldsymbol{PS})_{\nu\mu} \tag{11}$$

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[3] It was also possible to define [16] "partial Wiberg indices" as different (*sp-sp*, *sp-d* and *d-d*) components of a Wiberg index, by performing the summation in Eq. (7) only for the orbitals of the given type. These parameters were found to be useful for clarifying the role of *d*-orbitals in forming the individual bonds of a given molecule. Their generalization to the *ab initio* case seems also straightforward

is the total valence of atom A and

$$F_A = \sum_{\mu,\nu\in A} (\boldsymbol{P}^s\boldsymbol{S})_{\mu\nu}(\boldsymbol{P}^s\boldsymbol{S})_{\nu\mu} \tag{12}$$

is its free valence.

If the basis is orthonormal, one has instead of (11) and (12)

$$V_A(\mathrm{ort}) = 2\sum_{\mu\in A} P_{\mu\mu} - \sum_{\mu,\nu\in A} |P_{\mu\nu}|^2 \tag{13}$$

and

$$F_A(\mathrm{ort}) = \sum_{\mu,\nu\in A} |P^s_{\mu\nu}|^2 \tag{14}$$

while Eq. (10) does not change.

Obviously, the free valence index vanishes for closed-shell systems ($\boldsymbol{P}^s = \boldsymbol{0}$), so in their case the valence of the atom is equal to the sum of its bond orders:

$$V_A = \sum_{B(B\neq A)} B_{AB} \quad \text{(closed shells)} \tag{15}$$

and

$$V_A(\mathrm{ort}) = \sum_{B(B\neq A)} W_{AB} \quad \text{(closed shells)} \tag{16}$$

for the case of general (non-orthogonal) and orthonormal basis sets, respectively. It is to be noted that the free valence index F_A was originally defined [5] directly as the difference of the total valence of the atom and the sum of its bond orders; this type of definition also seems to be generalizable beyond the SCF level [17].

Following Wiberg [4], the physical meaning of these formulae can be summarized as follows. The quantity $b_\mu = 2q^e_\mu - (q^e_\mu)^2$, q^e_μ being the electron population of the μ-th basis orbital χ_μ, is a measure of the extent to which orbital χ_μ participates in the bonding: on one hand b_μ has a maximum of 1 for an orbital occupied by one electron (as is the case if the orbital enters a pure covalent bond) and is 0 for both an empty and a doubly filled (e.g. lone pair) orbital having no role in bonding. On the other hand, Wiberg [4] proved that for closed-shell systems and orthonormal basis sets b_μ is the sum of all the partial bond orders $|P_{\mu\nu}|^2$ formed by the given orbital:

$$b_\mu = \sum_{\nu(\nu\neq\mu)} |P_{\mu\nu}|^2. \tag{17}$$

By summing the quantity b_μ for all the orbitals of the atom A but subtracting the intra-atomic partial bond orders having no chemical significance, one arrives [2, 3] at the definition Eq. (13):

$$V_A(\mathrm{ort}) = \sum_{\mu\in A} b_\mu - \sum_{\substack{\mu,\nu\in A\\(\mu\neq\nu)}} |P_{\mu\nu}|^2. \tag{18}$$

Now, Eq. (11) can be considered as a generalization of this approach for the case of an overlapping basis [5]. (See [10] for a detailed discussion of some problems connected with such type of generalization.)

We shall note that the quantity $\sum_i n_i^2 c_{ia}^2 - q_a^2$ used in Ref. [1] is exactly the same as our b_μ for the closed-shell RHF wave functions, but it is not applicable in the UHF case. As we have already noted, this quantity is defined [1] in such a manner that for the single determinant open-shell RHF description of a free radical (the occupation numbers n_i equal 2 for all the molecular orbitals, except one having $n_i = 1$) the valence contribution of an odd electron fully localized on a single atomic orbital is zero. Our assumption that such an unpaired electron gives a contribution equal to unity to both the total and the free valence of the atom corresponds much better to the chemical picture. In the framework of the treatment of Ref. [1] there is no analogue for the free valence index, as it is defined above in accord with [5-7]. We shall emphasize once again that the quantity Gopinathan and Jug [1] call "free valence" (for which we have proposed above the term "excess valence" or "valence defect") is the difference $V_A^r - V_A$, V_A^r being the "reference" value for the atoms of given type, and has nothing in common with our F_A.

An important property of the bond order and valence indices is their rotational and hybridizational invariance; in particular, if the basis is orthonormalized (e.g. CNDO) and one turns to McWeeny's natural hybrid orbitals diagonalizing the intra-atomic block of the matrix $\boldsymbol{P}$ (i.e. $P_{\mu'\nu'} = q_{\mu'}^e \delta_{\mu'\nu'}$ for $\mu', \nu' \in A$), then one has

$$V_A(\text{ort}) = \sum_{\mu' \in A} b_{\mu'} = \sum_{\mu' \in A} [2q_{\mu'}^e - (q_{\mu'}^e)^2]. \tag{19}$$

This was first shown by Borisova and Semenov [3] and discussed also by Gopinathan and Jug [1].

Finally, we shall mention the following problem: all the different but equivalent formulae given for valences in Ref. [1] are valid only for orthonormal basis sets. As a consequence, the valences of the nitrogen and carbon atoms in the N_2 and C_2 molecules, respectively, quoted in Table 1 on p. 514 of Ref. [1] for the case of double and triple zeta *ab initio* bases, cannot be correct if were calculated by using either of them[4]. This conclusion is also confirmed by the comparison with the much more reasonable valence values for the 4-31G basis, which is double zeta type in the valence shell, as were obtained in [5] by using the formula Eq. (11) correctly taking into account the overlap effects.

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