

# COMMENTS

## Comment on “Analysis on Solvated Molecules with a New Energy Partitioning Scheme for Intra- and Intermolecular Interactions”

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### Introduction

In the recent paper,<sup>1</sup> Sato and Sakaki proposed a “new energy partitioning scheme” in which the Hartree–Fock energy of a molecule is decomposed into atomic and diatomic components. This scheme is identical with that of Ichikawa and Yoshida<sup>2</sup> and that of mine<sup>3</sup> except for the exchange energy component, which is the “the exact arithmetic average” of the expressions given in these two papers. However, the formula of Ichikawa and Yoshida<sup>2</sup> and therefore that of Sato and Sakaki<sup>1</sup> are not symmetric with respect to the two electrons (two density matrices), and mine is.<sup>4</sup>

Obviously, the exchange energy of a molecular system is a single number that may be decomposed into components in an infinite number of different ways. In such a situation, one has to require the approach be consistent with other known tools of analyzing the results of quantum chemical calculations and reduce in this manner the degree of arbitrariness present in the decomposition. In an ideal case, one can conclude that there is a unique decomposition, which is preferred from a theoretical point of view, irrespective of whether or not we are pleased with the numerical values obtained. For that reason, we have recently considered<sup>6</sup> the exchange energy component as to exclude definitions that do not behave properly if applied to the limiting case of the CNDO-type semiempirical theories. In that limit, one has the relationship<sup>7</sup>

$$E_{AB}^x = -\frac{1}{2} \gamma_{AB} W_{AB} \quad (1)$$

where  $\gamma_{AB}$  is the two-center electron–electron repulsion integral and  $W_{AB}$  is the diatomic Wiberg index<sup>8</sup> giving the bond order (multiplicity) in the framework of the semiempirical theories using orthogonal basis orbitals. For the RHF case, one has

$$W_{AB} = \sum_{\mu \in A} \sum_{\nu \in A} |D_{\mu\nu}|^2 \quad (2)$$

It may be noted that for large distances  $\gamma_{AB}$  behaves as  $1/R_{AB}$ ; thus, the exchange energy component has the asymptotic expansion

$$E_{AB}^x \sim -\frac{W_{AB}}{2R_{AB}} \quad (3)$$

which is the obvious counterpart of the asymptotic behavior of

the Coulomb energy:

$$E_{AB}^{\text{Coulomb}} = \gamma_{AB} Q_A Q_B \sim -\frac{Q_A Q_B}{R_{AB}} \quad (4)$$

where  $Q_A$  and  $Q_B$  are the atomic electron populations.

However, it appears that all three exchange energy components mentioned above<sup>1–3</sup> behave properly in the CNDO limit; thus, one needs a more refined analysis to decide which of them is preferable. To do that, we shall return to the analysis performed two decades ago<sup>9,10</sup> concerning the connection between the bond order index<sup>11</sup> (the generalization of the Wiberg index) and the exchange part of the second-order density matrix, sometimes also called the “Fermi hole”.

For our purpose, it is sufficient to consider the exchange density<sup>12</sup> (diagonal part of the exchange part of the spinless second-order density matrix) defined in terms of the occupied RHF molecular orbitals  $\varphi_i(\vec{r})$  as

$$\varrho^x(\vec{r}, \vec{r}') = 2 \sum_{ij}^{\text{occ}} \varphi_i^*(\vec{r}) \varphi_j^*(\vec{r}') \varphi_j(\vec{r}) \varphi_i(\vec{r}') \quad (5)$$

(We have omitted the overall negative sign.) By introducing the linear combination of atomic orbitals (LCAO) expansion ( $\varphi_i = \sum_{\mu} c_{\mu}^i \chi_{\mu}$ ) of the molecular orbitals and the usual density matrix  $\mathbf{D}$  with the elements  $D_{\mu\nu} = 2 \sum_i^{\text{occ}} c_{\mu}^i c_{\nu}^{i*}$ , one gets

$$\varrho^x(\vec{r}, \vec{r}') = \frac{1}{2} \sum_{\mu, \nu, \rho, \tau} D_{\mu\nu} D_{\rho\tau} \chi_{\mu}^*(\vec{r}) \chi_{\nu}^*(\vec{r}') \chi_{\rho}(\vec{r}) \chi_{\tau}(\vec{r}') \quad (6)$$

Integrating over both coordinates, we have the normalization of the exchange density as

$$\int \int \varrho^x(\vec{r}, \vec{r}') d\mathbf{v} d\mathbf{v}' = \frac{1}{2} \sum_{\mu, \nu, \rho, \tau} D_{\mu\nu} S_{\mu\rho} D_{\rho\nu} S_{\nu\tau} = \frac{1}{2} \sum_{\rho, \tau} (\mathbf{DS})_{\tau\rho} (\mathbf{DS})_{\rho\tau} = N_e \quad (7)$$

where  $N_e$  is the number of electrons and  $\mathbf{S}$  is the overlap matrix with the elements  $S_{\mu\nu} = \int \chi_{\mu}^*(\vec{r}) \chi_{\nu}(\vec{r}) d\mathbf{v}$ .

One can decompose the integral in eq 7 of the exchange density between the atoms and pairs of atoms according to the indices  $\rho$  and  $\tau$ . We get the diatomic contribution corresponding to the pair of atoms A and B if orbital  $\chi_{\rho}$  is centered on atom A and orbital  $\chi_{\tau}$  on atom B or vice versa. Summing these two cases, we get the bond order<sup>11</sup> between atoms A and B:

$$B_{AB} = \sum_{\rho \in A} \sum_{\tau \in B} (\mathbf{DS})_{\tau\rho} (\mathbf{DS})_{\rho\tau} \quad (8)$$

This is the direct generalization of the Wiberg index (eq 2) because, as known,<sup>13</sup> the proper LCAO representation of the first-order density matrix in the case of overlapping basis sets is not matrix  $\mathbf{D}$  but matrix  $\mathbf{DS}$ ; it has the correct idempotency property  $(\mathbf{DS})^2 = 2\mathbf{DS}$ . According to these considerations (also

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see refs 9 and 10), the bond order gives the diatomic contribution to the total exchange density (Fermi hole).

The fact that the diatomic contribution to the integral of the exchange density is given by the right-hand side of eq 8 indicates that the part of the exchange density itself that is to be assigned to the given pair of atoms is given by the integrands there:

$$Q_{(AB)}^x(\vec{r}, \vec{r}') = \frac{1}{2} \sum_{\rho \in A} \sum_{\tau \in B} \sum_{\mu, \nu} D_{\tau\mu} D_{\rho\nu} \chi_{\mu}^*(\vec{r}) \chi_{\nu}^*(\vec{r}') \chi_{\rho}(\vec{r}) \chi_{\tau}(\vec{r}') \quad (9)$$

$$+ \frac{1}{2} \sum_{\rho \in B} \sum_{\tau \in A} \sum_{\mu, \nu} D_{\tau\mu} D_{\rho\nu} \chi_{\mu}^*(\vec{r}) \chi_{\nu}^*(\vec{r}') \chi_{\rho}(\vec{r}) \chi_{\tau}(\vec{r}') \quad (10)$$

The diatomic exchange energy component that corresponds to this diatomic exchange density is

$$E_{AB}^x = -\frac{1}{2} \iint \frac{1}{|\vec{r} - \vec{r}'|} Q_{(AB)}^x(\vec{r}, \vec{r}') d\mathbf{v} d\mathbf{v}' = -\frac{1}{2} \sum_{\rho \in A} \sum_{\tau \in B} \sum_{\mu, \nu} D_{\tau\mu} D_{\rho\nu} [\mu\nu|\rho\tau] \quad (11)$$

where we have combined the two terms by interchanging some summation indices as well as the variables of integration. Here and further on, we use the [12|12] convention for the two-electron integrals:

$$[\mu\nu|\rho\tau] = \iint \chi_{\mu}^*(\vec{r}_1) \chi_{\nu}^*(\vec{r}_2) \frac{1}{r_{12}} \chi_{\rho}(\vec{r}_1) \chi_{\tau}(\vec{r}_2) d\mathbf{v}_1 d\mathbf{v}_2 \quad (12)$$

The result obtained indicates that there is no room for using different definitions of the diatomic exchange energy component if one wishes to be consistent with the generally accepted definition of the bond order index, measuring the diatomic contribution to the normalization of the exchange density. The definition used by Ichikawa and Yoshida<sup>2</sup> would be in the present notations (assuming real orbitals and coefficients)

$$-\frac{1}{2} \sum_{\rho \in A} \sum_{\tau \in B} \sum_{\mu, \nu} D_{\tau\rho} D_{\nu\mu} [\mu\nu|\rho\tau] \quad (13)$$

which cannot be put in correspondence with the definition of the bond order (eq 8),<sup>14</sup> and the “arithmetic average” of the two definitions<sup>1</sup> cannot be either; thus, neither of them is acceptable. (If the diatomic exchange density should integrate to  $B_{AB}$ , then it cannot contain a density matrix element one subscript of which is restricted to atom A and another to atom B.)

It is worth checking that it is my definition (eq 11) that is able to recover an asymptotic expression analogous to eq 3. To do this, at first we observe that in all the three papers<sup>1–3</sup> the Coulomb component of the diatomic energy is

$$E_{AB}^{\text{Coulomb}} = \sum_{\rho \in A} \sum_{\tau \in B} \sum_{\mu, \nu} D_{\rho\mu} D_{\tau\nu} [\mu\nu|\rho\tau] \quad (14)$$

One introduces the asymptotic expression valid for large  $R_{AB}$

$$[\mu\nu|\rho\tau] \sim \frac{S_{\mu\rho} S_{\nu\tau}}{R_{AB}} \quad (15)$$

substituting what one gets into the expression that could be expected

$$E_{AB}^{\text{Coulomb}} \sim \frac{1}{R_{AB}} \sum_{\rho \in A} \sum_{\tau \in B} \sum_{\mu, \nu} D_{\rho\mu} S_{\mu\rho} D_{\tau\nu} S_{\nu\tau} = \frac{Q_A Q_B}{R_{AB}} \quad (16)$$

where  $Q_A = \sum_{\rho \in A} (\mathbf{DS})_{\rho\rho}$  is Mulliken’s gross atomic population of atom A.

Similarly, substituting the asymptotic expression (eq 15) into eq 11 of the exchange energy component, one gets

$$E_{AB}^x \sim -\frac{1}{2} \frac{1}{R_{AB}} \sum_{\rho \in A} \sum_{\tau \in B} \sum_{\mu, \nu} D_{\tau\mu} S_{\mu\rho} D_{\rho\nu} S_{\nu\tau} = -\frac{B_{AB}}{2R_{AB}} \quad (17)$$

in full analogy to eq 3. At the same time, no such expression can be obtained for the choice made in either refs 1 or 2.

In previous papers,<sup>3,15</sup> I have obtained eq 11 by means independent of those considered here. At the same time, the above analysis indicates that eq 11 is an expression of diatomic exchange energy component that is compatible with the accepted formula of the diatomic bond order index. I think, therefore, that we should stick to this definition.

Finally, it may be of meaning to have another look at the origin of this controversy. The authors of ref 1 “adapted the spirit of the philosophy of Mulliken population analysis” (as I did too), but they did not take into account the following mathematical nuance. In the Mulliken population analysis, one “halves” the overlap density

$$Q_{(AB)}(\vec{r}) = \sum_{\mu \in A} \sum_{\nu \in B} [D_{\mu\nu} \chi_{\nu}^*(\vec{r}) \chi_{\mu}(\vec{r}) + D_{\nu\mu} \chi_{\mu}^*(\vec{r}) \chi_{\nu}(\vec{r})] \quad (18)$$

between the atoms A and B in question. However, in order to obtain the correct expressions of the Mulliken’s gross atomic populations  $Q_A = \sum_{\mu \in A} (\mathbf{DS})_{\mu\mu}$  and  $Q_B = \sum_{\nu \in A} (\mathbf{DS})_{\nu\nu}$  (which follow from the fact the finite basis representation of the first-order density matrix is<sup>13</sup> matrix  $\mathbf{DS}$ ), one should not assign  $1/2 Q_{AB}(\vec{r})$  to both atoms, but the terms containing  $D_{\mu\nu} \chi_{\nu}^*(\vec{r}) \chi_{\mu}(\vec{r})$  should be assigned to atom A and those with  $D_{\nu\mu} \chi_{\mu}^*(\vec{r}) \chi_{\nu}(\vec{r})$  to atom B.<sup>17</sup> That means that one should always perform the systematization of the terms according to the orbitals entering to the “kets” of every overlap, one- or two-electron integral in which the given overlap density enters. Following this rule, one gets consistent sets of formulas for population analysis, bond orders, and energy components in a straightforward manner, and the energy decomposition becomes essentially unique. My formulas pass such a consistency test, and those in ref 1 correspond to the use of  $1/2 Q_{AB}(\vec{r})$  above and would, therefore, mean abandoning the generally accepted expression of bond order indices and even that of Mulliken populations.

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## References and Notes

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- (2) Ichikawa, H.; Yoshida, A. *Int. J. Quantum Chem.* **1999**, *71*, 35.
- (3) Mayer, I. *Chem. Phys. Lett.* **2003**, *382*, 265.
- (4) The decomposition of the exchange energy by Ichikawa and Yoshida<sup>2</sup> in fact follows the early scheme of Kollmar<sup>5</sup> who attempted (with little success) to decompose the *ab initio* energy, first calculating the overall Fock matrix and then decomposing only the expression  $E = 1/2 \text{Tr}[(\mathbf{h} + \mathbf{F})\mathbf{D}]$  into atomic and diatomic components according to the density matrix indices involved. (Ichikawa and Yoshida<sup>2</sup> proceed in this way with the exchange energy  $E^x = -1/2 \text{Tr}(\mathbf{KD})$ , where  $-\mathbf{K}$  is the exchange part of the Fockian.)

- (5) Kollmar, H. *Theor. Chim. Acta* **1978**, 50, 235.
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- (14) The exchange density corresponding to the formula of Ichikawa and Yoshida<sup>2</sup> integrates to  $\sum_{\rho \in A} \sum_{\tau \in A} D_{\rho\tau}(\text{SDS})_{\tau\rho}$ , instead of  $B_{AB}$ . (It would

be rather artificial to define a new “bond order index” containing this non-symmetric quantity; such a definition would be also much less chemical than the original one, as it could not, for instance, recover the integer values for first row diatomics (e.g., 3 for  $\text{N}_2$ ) if a minimal basis set is used, as does<sup>16</sup>  $B_{AB}$ .)

(15) Mayer, I. *Phys. Chem. Chem. Phys.* **2006**, 8, 4630.

(16) Mayer, I. *J. Comput. Chem.* **2007**, 28, 204.

(17) Although it is immaterial if real orbitals are used, this distinction is required from a strict theoretical standpoint. It may be worth noting here that the authors of ref 1 also admit the possibility of using complex orbitals in the definition of the two-electron integrals, but further on, they use an energy formula that is only valid for real ones.