

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

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We reply to the comment made by Professor Mayer. In the comment, he questioned the reasonableness of the energy decomposition scheme proposed by us. However, “arbitrariness” is not avoidable because there is no way to uniquely define bond order index. In this response, we recall the many-body nature of our definition and propose another definition of bond order index to demonstrate the reliability of our decomposition scheme.

In the recent paper by Mayer,<sup>1</sup> he questioned the reasonableness of the energy decomposition scheme that we have proposed in the recent issue of this journal.<sup>2</sup> Several definitions have been proposed,<sup>2–5</sup> in which the Hartree–Fock total energy of a molecule is decomposed into atomic and diatomic components. Mayer showed in the comment paper that, although the asymptotic behavior of the Coulomb energy in the three schemes, namely, the schemes proposed by Mayer,<sup>3</sup> by Ichikawa et al.,<sup>4</sup> and by us,<sup>2</sup> are exactly the same, the exchange energy components behave properly within the framework of the CNDO limit. His point is that only his definition is acceptable when considering the overlapping basis sets, because the asymptotic expression of his definition can be related to his bond order index<sup>6</sup> between atoms A and B,  $B_{AB}^{\text{Mayer}}$ .

$$B_{AB}^{\text{Mayer}} = \sum_{\rho \in A} \sum_{\tau \in B} (\mathbf{DS})_{\tau\rho} (\mathbf{DS})_{\rho\tau} \quad (1)$$

Mayer’s discussion looks logical, but he may have misinterpreted the following two serious points: (1) Our definition of energy partitioning is not derived so as to be the “arithmetic average” of the two expressions given by Mayer and by Ichikawa. As described in the original paper, the definition is derived from the application of Mulliken-type equipartitioning to deal with many-center terms. The “arithmetic average” is just a consequence of this procedure and (2) The partitioning scheme by Mayer is logically consistent with his own bond order index,  $B_{AB}^{\text{Mayer}}$ . We appreciate the reliability of these definitions. However, as he has mentioned in the comment,<sup>1</sup> 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 a similar manner, there is no unique definition of the bond order index. In fact, various definitions have been proposed so far.<sup>7,8</sup> Obviously, there is no reason to justify only his definition of bond order index. It is the same with the partitioning energy. The important thing is that the partitioning energy components must be derived by a logically correct procedure and be consistent with physically meaningful quanti-

ties. In this case, the expression of the atomic and diatomic energy must be compatible with a formula of bond order index.

## 1. Atomic and Diatomic Energy Reflected Many-Body Nature

Here, we would like to recall the derivation of our definition on the atomic and diatomic energies of a molecule. Only the most important point, the two-electron term, is addressed. As shown in eq 8 in the original paper,<sup>2</sup> the two-electron term can be written as

$$E^{\text{ee}} = \sum_{ABCD} \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \sum_{d \in D} (ab|cd) \left\{ D_{ab} D_{cd} - \frac{1}{2} D_{ac} D_{bd} \right\} \equiv \sum_{ABCD} E_{ABCD}^{\text{ee}} \quad (2)$$

where

$$E_{ABCD}^{\text{ee}} = \sum_{a \in A} \sum_{b \in B} \sum_{c \in C} \sum_{d \in D} (ab|cd) \left\{ D_{ab} D_{cd} - \frac{1}{2} D_{ac} D_{bd} \right\} \quad (3)$$

We adopt chemists’ notation for two-electron integrals.

$$(ab|cd) = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_a^*(1) \chi_b(1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_c^*(2) \chi_d(2) \quad (4)$$

The basis set  $\chi_a$  is located at atom A and so on. The combination of electrons labeled 1 and 2, which are respectively related to the two overlapping atom pairs (AB and CD), is shown in Figure 1. The pair can be A–C, A–D, B–C, and B–D. Thus, the two-electron term  $E^{\text{ee}}$  is rewritten so as to treat all these pairs equivalently.

$$\sum_{ABCD} E_{ABCD}^{\text{ee}} = \frac{1}{4} \left\{ \sum_{AC} \sum_{BD} + \sum_{AD} \sum_{BC} + \sum_{BC} \sum_{AD} + \sum_{BD} \sum_{AC} \right\} E_{ABCD}^{\text{ee}} \quad (5)$$

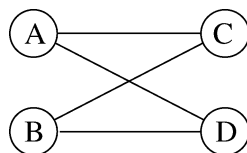
Below, we change the labels ( $A \rightarrow I, C \rightarrow J$ ) to discriminate the two atoms’ index (I and J) from other atoms.

$$E^{\text{ee}} = \frac{1}{4} \sum_{IJ} \left\{ \sum_{BD} E_{IBJD}^{\text{ee}} + \sum_{BC} E_{IB CJ}^{\text{ee}} + \sum_{AD} E_{A I D}^{\text{ee}} + \sum_{AC} E_{A I C J}^{\text{ee}} \right\} \quad (6)$$

This can be further rewritten as follows:

$$E^{\text{ee}} = \frac{1}{4} \sum_{IJ} \left[ \sum_{BD} (ib|jd) \left\{ D_{ib} D_{jd} - \frac{1}{2} D_{ij} D_{bd} \right\} + \sum_{BC} (ib|cj) \left\{ D_{ib} D_{cj} - \frac{1}{2} D_{ic} D_{bj} \right\} + \sum_{AD} (ai|jd) \left\{ D_{ai} D_{jd} - \frac{1}{2} D_{aj} D_{id} \right\} + \sum_{AC} (ai|cj) \left\{ D_{ai} D_{cj} - \frac{1}{2} D_{ac} D_{ij} \right\} \right] \quad (7)$$

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**Figure 1.** Label of electrons: the left-hand side (A and B) and the right side (C and D) are, respectively, for electrons labeled “1” and “2” and vice versa.

By unifying all the atomic labels appearing in the right-hand side, we obtain

$$E^{\text{ee}} = \frac{1}{4} \sum_{\text{IJ}} \sum_{\text{BD}} \left[ (ib|jd) \left\{ D_{ib}D_{jd} - \frac{1}{2} D_{ij}D_{bd} \right\} + (ib|dj) \left\{ D_{ib}D_{dj} - \frac{1}{2} D_{id}D_{bj} \right\} + (bi|jd) \left\{ D_{bi}D_{jd} - \frac{1}{2} D_{bj}D_{id} \right\} + (bi|dj) \left\{ D_{bi}D_{dj} - \frac{1}{2} D_{bd}D_{ij} \right\} \right] \quad (8)$$

Because all of the basis sets are real, by using the symmetry of two-electron integrals, we reach the final expression as follows:

$$E^{\text{ee}} = \sum_{\text{IJ}} \sum_{\text{BD}} \left[ (ib|jd) \left\{ D_{ib}D_{jd} - \frac{1}{2} \frac{D_{ij}D_{bd} + D_{id}D_{bj}}{2} \right\} \right] \equiv \sum_{\text{IJ}} E_{\text{IJ}}^{\text{ee}} \quad (9)$$

As is clear from these derivations, we never take the “arithmetic average” to define the atomic and diatomic energy. Partitioning of four-center contributions naturally leads to an energy expression, which is, eventually, the “arithmetic average” of two different expressions, Mayer’s definition and Ichikawa’s one. It is also noted that Mayer’s expression can be obtained if the contributions from the first and fourth terms in eq 5 are ignored.

## 2. Relation to Bond Order Index

We shall begin with the consideration of the asymptotic behavior for large  $R$ .

$$(ab|cd) \sim \frac{S_{ab}S_{cd}}{R} \quad (10)$$

As discussed in the comment by Mayer,<sup>1</sup> the first component of eq 9 becomes a simple Coulomb interaction between Mulliken’s gross atomic populations (charges):

$$E_{\text{IJ}}^{\text{Coulomb}} = \sum_{i \in \text{I}} \sum_{j \in \text{J}} \sum_{b,d} D_{ib}D_{jd}(ib|jd) \sim \frac{1}{R} \left[ \sum_{i \in \text{I}} (\mathbf{DS})_{ii} \right] \left[ \sum_{j \in \text{J}} (\mathbf{DS})_{jj} \right] \quad (11)$$

The exchange component in eq 9 becomes

$$E_{\text{IJ}}^{\text{Exchange}} = \frac{1}{4} \sum_{i \in \text{I}} \sum_{j \in \text{J}} \sum_{b,d} (D_{ij}D_{bd} + D_{id}D_{bj})(ib|jd) \sim \frac{1}{4R} \sum_{i \in \text{I}} \sum_{j \in \text{J}} [D_{ij}(\mathbf{SDS})_{ji} + (\mathbf{DS})_{ij}(\mathbf{DS})_{ji}] \quad (12)$$

Thus, eq 12 leads to another definition of bond order index, as follows:

$$B_{\text{AB}} = \frac{1}{2} \sum_{a \in \text{A}} \sum_{b \in \text{B}} [D_{ab}(\mathbf{SDS})_{ba} + (\mathbf{DS})_{ab}(\mathbf{DS})_{ba}] = \frac{1}{2} \sum_{a \in \text{A}} \sum_{b \in \text{B}} \left[ \frac{1}{2} (\mathbf{DSD})_{ab}(\mathbf{SDS})_{ba} + (\mathbf{DS})_{ab}(\mathbf{DS})_{ba} \right] \quad (13)$$

where the idempotency is used. The second term of each equation obviously corresponds to Mayer’s definition, eq 1. The first term is related to the Coulson-type expression of bond order and a one-particle density matrix in the general case.<sup>8</sup> Thus, the definition is based on more than two-body density matrices. The physical meaning of this expression must be further investigated,<sup>9</sup> but we would like to emphasize that this expression is derived from the natural treatment of the Hartree–Fock energy expression, in which an inherent many-body character is directly involved. It is well-known that eq 1 is a generalization of Wiberg’s definition based on a semiempirical method,<sup>10</sup> and the starting point of this definition is the consideration on the two-center interaction. In contrast, the foundation of our definition is the consideration on the four-center interaction, indicating that no term is neglected in our approach. It should be noted that both Mayer’s and our definitions are reduced to Wiberg’s definition in the CNDO limit.

Using these quantities, we can approximate the total energy as follows:

$$E \sim \sum_{\text{IJ}} E_{\text{IJ}}^{\text{kin}} + \sum_{\text{IJ}} \frac{(Z_{\text{I}} - Q_{\text{I}})(Z_{\text{J}} - Q_{\text{J}})}{R_{\text{IJ}}} - \sum_{\text{IJ}} \frac{B_{\text{IJ}}}{2R_{\text{IJ}}} \quad (14)$$

where  $E_{\text{IJ}}^{\text{kin}}$  is the contribution from kinetic energy and  $Q_{\text{I}}$  are the Mulliken gross atomic populations.

Table 1 summarized the numerical assessment of the newly defined bond order index, eq 13. The new definition estimates a chemical bond slightly weaker than Mayer’s expression, but both of the expressions provide very similar results.<sup>11</sup> As discussed in the previous paper,<sup>2</sup> the strength of the diatomic (two-center) interaction by Mayer’s expression is slightly stronger than the exact Hartree–Fock energy (for example, see Figure 1 in ref 2). Thus, the behaviors of the partitioned energy and the corresponding bond order index are consistent, and all these physical numbers are reliable. In our preliminary computations, the characters of the new bond order index, including basis set dependency, troubles in treatment of diffuse function, etc., are very similar to Mayer’s expression. It is also noted that Mayer’s expression essentially represents covalency of bonding,<sup>12</sup> and the contribution from ionicity is a different issue. The bond order of a triple bond is expected to be close to three but is not necessary in general. The bond order index by Mayer,  $B_{\text{AB}}^{\text{Mayer}}$ , has been used for a long time and is now recognized as the standard expression for bond order index in ab initio molecular orbital calculations. The energy expression proposed by Mayer<sup>3</sup> is consistent with  $B_{\text{AB}}^{\text{Mayer}}$ . We are confident that both of the expressions are reasonable. However, none of them is one and only.

Before closing this reply, we recall Mulliken’s original paper,<sup>13</sup> in which he mentioned as follows:

“Referring back to the simple two-center case, it is seen that the overlap term is related completely symmetrically to the two centers,... Hence, it appears necessary to assign exactly half of the overlap population, plus, of course, the appropriate net atomic population, to each center.”

What we follow is his way of thinking. The complex basis sets that Mayer mentioned seem to be indiscussible from the view point of Mulliken’s philosophy; furthermore, the treatment

**TABLE 1. Illustrative Values of Bond Order for Some Small Molecules Calculated Using STO-3G, 4-31G, and 6-31G(d,p) Basis Sets<sup>a</sup>**

| molecules       | bond | STO-3G |       | 4-31G |       | 6-31G(d,p) |       |
|-----------------|------|--------|-------|-------|-------|------------|-------|
|                 |      | eq 13  | Mayer | eq 13 | Mayer | eq 13      | Mayer |
| H <sub>2</sub>  | H–H  | 1.000  | 1.000 | 1.000 | 1.000 | 1.000      | 1.000 |
| methane         | C–H  | 0.989  | 0.991 | 0.963 | 0.963 | 0.977      | 0.978 |
| ethane          | C–H  | 0.985  | 0.984 | 0.969 | 0.961 | 0.983      | 0.977 |
|                 | C–C  | 0.996  | 1.009 | 0.885 | 0.945 | 0.927      | 0.966 |
| ethylene        | C–H  | 0.980  | 0.976 | 0.971 | 0.963 | 0.981      | 0.975 |
|                 | C–C  | 1.988  | 2.020 | 1.915 | 1.963 | 1.930      | 1.969 |
| acetylene       | C–H  | 0.985  | 0.985 | 0.846 | 0.862 | 0.876      | 0.893 |
|                 | C–C  | 2.969  | 3.000 | 3.225 | 3.276 | 3.173      | 3.190 |
| methyl radical  | C–H  | 0.975  | 0.979 | 0.946 | 0.946 | 0.963      | 0.964 |
| water           | O–H  | 0.898  | 0.964 | 0.771 | 0.796 | 0.856      | 0.884 |
| C <sub>2</sub>  | C–C  | 3.130  | 3.326 | 3.055 | 3.232 | 3.183      | 3.310 |
| N <sub>2</sub>  | N–N  | 2.778  | 3.000 | 2.356 | 2.660 | 2.599      | 2.796 |
| CO              | C–O  | 2.334  | 2.515 | 1.919 | 2.140 | 2.162      | 2.307 |
| HCN             | H–C  | 0.965  | 0.968 | 0.850 | 0.859 | 0.888      | 0.892 |
|                 | C–N  | 2.847  | 2.989 | 2.847 | 2.921 | 2.890      | 2.932 |
| CN <sup>–</sup> | C–N  | 2.698  | 2.884 | 2.593 | 2.763 | 2.736      | 2.857 |
| CN radical      | C–N  | 2.007  | 2.162 | 2.068 | 2.200 | 2.400      | 2.506 |

<sup>a</sup> All the computations were performed with the optimized geometry. This set of molecules was investigated in the first paper of  $B_{AB}^{\text{Mayer},6}$ .

of the two-body density including up to a four-center contribution is the issue we must consider. We think that what the really essential point is that our expression gives much more numerically acceptable behavior, although Mayer's expression looks more strict.

We consider both Mayer's and our expressions to be reasonable and acceptable from the view point of theoretical consideration. In this context, seeking the reduction of arbitrariness concerning this issue does not make any sense. Further self-composed discussions and investigations including theoretical background as well as numerical assessments are highly desired to understand the nature of electronic structure theory much more deeply.

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