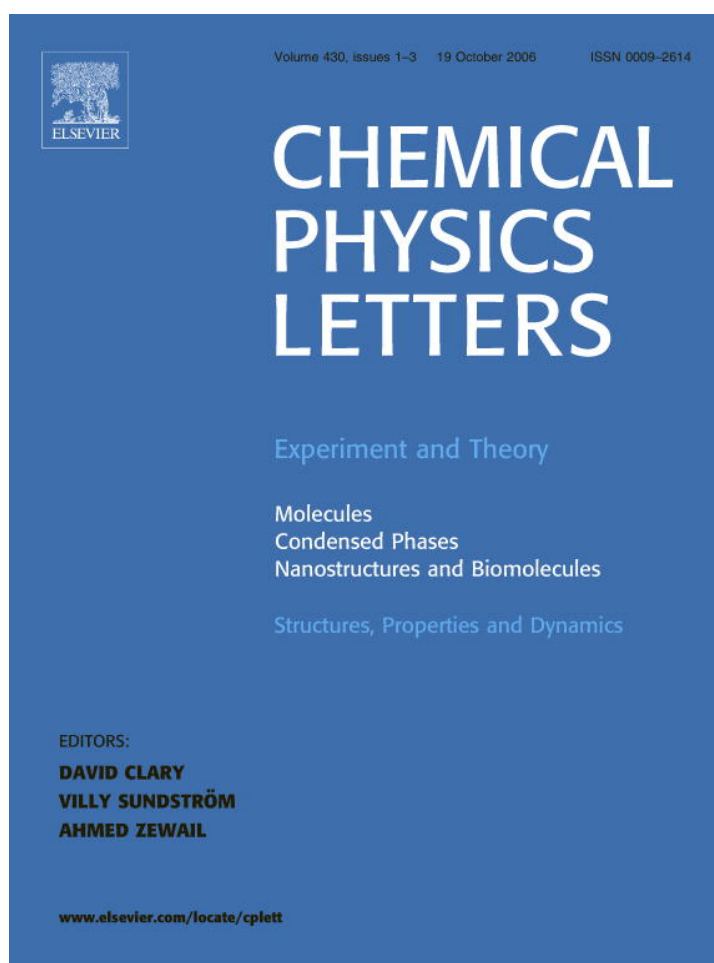


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## *Ab initio* energy partitioning at the correlated level

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Dedicated to Professor Gernot Frenking on the occasion of his 60th birthday

### Abstract

The Mayer energy partitioning is extended to the case of a general *ab initio* wavefunction. The key idea is to expand the two-electron energy in terms of the density matrix elements  $D_{\mu\nu}$ , density cumulants  $\lambda_{\mu\nu\rho\sigma}$  and two-electron integrals  $[\mu\nu|\rho\sigma]$  and to partition the cumulants into *one-atom* and *two-atom* components. The numerical results are shown at the CI-D level and are compared to those of the Hartree–Fock energy partitioning.

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### 1. Introduction

The strength of the chemical bond plays an extraordinary role in chemistry. Usually, it is measured by the bond dissociation energy, since it can be both determined experimentally and calculated using quantum-chemical techniques. However, the calculation of the dissociation energy is usually done by evaluating the energy difference  $E(\text{AB}) - E(\text{A}) - E(\text{B})$ , which requires that the molecule AB be separated into two well-defined fragments A and B. This separability is often possible, but it is not applicable to the bonds that form a part of a ring system or to weak intramolecular interactions, such as intramolecular hydrogen or agostic bonds. Hence, the question about the strength of such an intramolecular interaction must be addressed by other means. Some information about the bond strength is provided by Bader's atoms-in-molecules theory [1], by the natural bond orbital (NBO) analysis [2], and by various bond order schemes [3–7]. Albeit very useful, these approaches do not yield a direct energetic measure of bond strength and usually fail to deliver any meaningful information for weak interactions. Note that there is a number of energy partitioning methods [8,9],

which turned out to be extremely useful, but they also require that the molecule be properly divided into fragments.

Obviously, an interaction energy between two given atoms in a polyatomic molecule is not an observable property. The most sound approach to the diatomic interaction energy is to *decompose* the total energy of the molecule (within a given quantum-chemical method) into a sum of one-, two-, and possibly many-atom contributions, but even this can be done in multiple ways. Such a partitioning is rather simple for semi-empirical methods [10], but no longer trivial for *ab initio* methods due to the presence of four-center two-electron integrals in the total energy expression.

There are a number of such schemes employing partitioning of energy in the three-dimensional physical space of the molecule. They take advantage either of the Bader partitioning into atomic basins [11–15] or of 'fuzzy atoms' [13,16]. However, the present work focuses on the partitioning in the Hilbert-space of atomic orbitals. In this case, various terms of the total energy expression are attributed to one- or two-atom components according to some rules. Some requirements should be imposed on an energy partitioning method from the practical viewpoint to ensure its applicability to chemical problems. Preferably, the resulting two-atom energies should: (a) lie on the 'chemical

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scale', that is, be comparable in value with typical dissociation energies for bonding interactions; (b) follow the common trends known for dissociation energies, e.g., increase in a series of related compounds with increasing bond multiplicity; (c) provide clearly different values for bonding and non-bonding interactions. It should be noted, however, that the point (a) does not imply that the aim of such methods is to reproduce the dissociation energy. Note that Hilbert-space partitioning will become ill-defined in the limit of the infinite basis set, but this is not a problem in practice.

Of course, the energy partitioning will be different for each quantum-chemical method. In the case of the Hartree–Fock method, an efficient energy partitioning technique referred to as 'chemical energy component analysis' [17,18] was proposed by Mayer and co-workers, who made use of the one-atom projection operators. Later, Mayer was able to find a simpler and eventually more efficient partitioning scheme [19] by assigning various terms of the total Hartree–Fock energy expression to different atoms. Note that Mayer's method is very similar, though not identical, to a partitioning suggested earlier by Ichikawa and Yoshida [20]. It is also distantly related to Kollmar's early scheme [21]. Another Hartree–Fock energy partitioning was proposed by Nakai and Kikuchi [22].

When the electron correlation is taken into account, different partitioning techniques must be developed. Recently, we proposed [23] a partitioning of the total energy within the density functional theory. Our approach is based on Mayer's scheme, except that the exchange–correlation energy is treated differently. In the decisive step, the exchange–correlation energy density per electron  $\epsilon_{xc}$  is expanded into a linear combination of atom-centered basis functions.

In the present Letter, we introduce a technique for the total energy partitioning for an arbitrary correlated *ab initio* method, also based on Mayer's partitioning [19]. In order to pave the way for the general *ab initio* energy partitioning, we wish first to present an alternative derivation of Mayer's Hartree–Fock energy partitioning, emphasizing the role of the *one-atom* and *two-atom density matrices* we introduced in paper [23].

## 2. Hartree–Fock energy partitioning

First, let us consider the total Hartree–Fock energy expression in terms of atomic spin-orbitals.<sup>1</sup>

$$E^{\text{HF}} = \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} + \sum_{\mu\nu} D_{\mu\nu} [v|\hat{T}|\mu] - \sum_A \sum_{\mu\nu} D_{\mu\nu} \left[ v \left| \frac{Z_A}{r_A} \right| \mu \right] + \frac{1}{2} \sum_{\mu\nu} \sum_{\rho\sigma} (D_{\mu\nu} D_{\rho\sigma} - D_{\mu\sigma} D_{\rho\nu}) [\mu\nu|\rho\sigma]$$

<sup>1</sup> The [11|22] convention for two-electron integrals and second-order density matrix elements is used throughout the Letter.

where  $D_{\mu\nu}$  is an element of the charge–density bond order matrix in a real spin-orbital basis calculated from the MO coefficients  $C_{\mu i}$ :

$$D_{\mu\nu}^{\text{HF}} = \sum_i^{\text{occ.}} C_{\mu i} C_{\nu i} \quad (1)$$

A *one-atom density matrix* function  $\rho^A(\mathbf{x}|\mathbf{x}')$  and a *one-atom density*  $\rho^A(\mathbf{x})$  are defined as follows [23,24]:

$$\rho^A(\mathbf{x}|\mathbf{x}') = \sum_{\mu \in A} \sum_v^{\text{all}} D_{\mu\nu} \chi_\nu(\mathbf{x}) \chi_\mu(\mathbf{x}') \quad (2)$$

$$\rho^A(\mathbf{x}) = \rho^A(\mathbf{x}|\mathbf{x}) = \sum_{\mu \in A} \sum_v^{\text{all}} D_{\mu\nu} \chi_\nu(\mathbf{x}) \chi_\mu(\mathbf{x})$$

such that the one-atom contributions sum to the total density:  $\rho(\mathbf{x}) = \sum_A \rho^A(\mathbf{x})$ . This definition is consistent with the Mulliken population analysis, as the one-atom density  $\rho^A$  yields the Mulliken atomic population when integrated over the entire space. Note that these definitions are remotely related to an early work by Ruedenberg [25].

Using the above definitions for  $\rho^A(\mathbf{x})$  and  $\rho^A(\mathbf{x}|\mathbf{x}')$ , the Hartree–Fock energy expression can be easily rewritten as follows:

$$E^{\text{HF}} = \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} + \sum_{AB} \sum_{\mu \in A} \sum_{\nu \in B} D_{\mu\nu} [v|\hat{T}|\mu] - \sum_{AB} \int \frac{Z_B}{r_B} \rho^A(\mathbf{x}) d\mathbf{x} + \frac{1}{2} \sum_{AB} \int \int \frac{\rho^A(\mathbf{x}) \rho^B(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x} d\mathbf{x}' - \frac{1}{2} \sum_{AB} \int \int \frac{\rho^A(\mathbf{x}|\mathbf{x}') \rho^B(\mathbf{x}'|\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x} d\mathbf{x}' \quad (3)$$

where  $\mathbf{x}$  stands for the spatial  $\mathbf{r}$  and spin  $\omega$  coordinates of electron.

The two last terms in Eq. (3) that represent the two-electron interaction are expressed by means of one-atom density and density matrix. They have a clear physical meaning of interaction of electrons of atom A with those of atom B. Analogously, the third term in Eq. (3) describes the attraction of the electrons of atom A to the nucleus B. All these terms are assigned to the two-atom energy  $E^{AB}$ , when  $A \neq B$ , and to the one-atom energy  $E^A$ , when  $A = B$ . Obviously, the nuclear repulsion  $Z_A Z_B / R_{AB}$  is assigned to  $E^{AB}$ . Following Mayer [19], the product  $D_{\mu\nu} [v|\hat{T}|\mu]$  in the second term in Eq. (3) – the kinetic energy – enters the two-atom energy  $E^{AB}$  if  $\mu \in A$  and  $\nu \in B$ , or the one-atom energy  $E^A$  if the basis functions  $\mu$  and  $\nu$  belong to the same atom A. This is done because the kinetic energy operator  $\hat{T} = -(1/2)\nabla^2$  does not have a pronounced atomic character.

Upon inserting the definitions from Eq. (2) into Eq. (3), one obtains formulae that coincide exactly with those for the Mayer partitioning [19]. Thus, the two-atom energy  $E_{AB}$  is given by:

$$\begin{aligned}
E_{AB}^{\text{HF}} &= \frac{Z_A Z_B}{R_{AB}} + 2 \sum_{\mu \in A} \sum_{\nu \in B} D_{\mu\nu} [v|\hat{T}|\mu] - \int \frac{Z_B}{r_B} \rho^A(\mathbf{x}) d\mathbf{x} \\
&\quad - \int \frac{Z_A}{r_A} \rho^B(\mathbf{x}) d\mathbf{x} + \int \int \frac{\rho^A(\mathbf{x}) \rho^B(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x} d\mathbf{x}' \\
&\quad - \int \int \frac{\rho^A(\mathbf{x}, \mathbf{x}') \rho^B(\mathbf{x}', \mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x} d\mathbf{x}' \\
&= \frac{Z_A Z_B}{R_{AB}} + 2 \sum_{\mu \in A} \sum_{\nu \in B} D_{\mu\nu} [v|\hat{T}|\mu] - \sum_{\mu \in A} \sum_{\nu}^{\text{all}} D_{\mu\nu} \left[ v \left| \frac{Z_B}{r_B} \right| \mu \right] \\
&\quad - \sum_{\mu \in B} \sum_{\nu}^{\text{all}} D_{\mu\nu} \left[ v \left| \frac{Z_A}{r_A} \right| \mu \right] + \sum_{\mu \in A} \sum_{\rho \in B} \sum_{\nu, \sigma}^{\text{all}} D_{\mu\nu} D_{\rho\sigma} [\mu\nu|\rho\sigma] \\
&\quad - \sum_{\mu \in A} \sum_{\rho \in B} \sum_{\nu, \sigma}^{\text{all}} D_{\mu\sigma} D_{\rho\nu} [\mu\nu|\rho\sigma] \quad (4)
\end{aligned}$$

First, this brief derivation demonstrates that the Mayer partitioning is consistent with the Mulliken population analysis and Mayer's bond orders. Second, it makes evident that the two-electron part of Mayer's two-atom energy  $E^{\text{AB}}$  can be represented as interaction of the densities (or the density matrices) of atoms A and B.

### 3. *Ab initio* correlated energy partitioning

In order to devise an energy partitioning in the case of a given correlated *ab initio* method, one needs first to express the total energy  $E^{\text{tot}}$  in terms of one- and two-electron integrals. Generally, the expression for  $E^{\text{tot}}$  is given by

$$\begin{aligned}
E^{\text{tot}} &= \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} + \sum_{\mu\nu} D_{\mu\nu} [v|\hat{T}|\mu] \\
&\quad - \sum_A \sum_{\mu\nu} D_{\mu\nu} \left[ v \left| \frac{Z_A}{r_A} \right| \mu \right] + \sum_{\mu\nu\rho\sigma} \Gamma_{\mu\nu\rho\sigma} [\mu\nu|\rho\sigma] \quad (5)
\end{aligned}$$

or, analogously, in the basis of molecular spin-orbitals:

$$\begin{aligned}
E^{\text{tot}} &= \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} + \sum_{ij} D_{ij} [i|\hat{T}|j] - \sum_A \sum_{ij} D_{ij} \left[ i \left| \frac{Z_A}{r_A} \right| j \right] \\
&\quad + \sum_{ijkl} \Gamma_{ijkl} [ij|kl] \quad (6)
\end{aligned}$$

where  $D_{\mu\nu}$ ,  $\Gamma_{\mu\nu\rho\sigma}$ ,  $D_{ij}$ ,  $\Gamma_{ijkl}$  are the elements of first- and second-order density matrix in the AO and MO basis, respectively. Note that  $D_{\mu\nu}$  in Eq. (5) is no longer given by Eq. (1), but rather must be determined from the respective correlated wavefunction. In the special case of the Hartree–Fock wavefunction, Eq. (5) reduces to Eq. (3), as  $\Gamma$  can be expressed through  $D$ :

$$\Gamma_{\mu\nu\rho\sigma}^{\text{HF}} = \frac{1}{2} (D_{\mu\nu} D_{\rho\sigma} - D_{\mu\sigma} D_{\rho\nu}) \quad (7)$$

In the general case,  $\Gamma$  can be expressed through  $D$  with the help of density cumulants  $\lambda_{\mu\nu\rho\sigma}$  [26]:

$$\Gamma_{\mu\nu\rho\sigma} = \frac{1}{2} (D_{\mu\nu} D_{\rho\sigma} - D_{\mu\sigma} D_{\rho\nu}) + \lambda_{\mu\nu\rho\sigma}$$

Note that there is an alternative way to express the total energy as a sum of the Hartree–Fock and correlation energies using the Nesbet theorem [27]. That approach was used by Ayala and Scuseria [28] to establish their decomposition of the correlation energy.

In general, a correlated wavefunction  $\Psi$  is represented as a linear combination of the ground state determinant  $\Phi_0$  and excited determinants  $\Phi_I$ :

$$\begin{aligned}
\Psi &= C_0 \Phi_0 + \sum_I C_I \Phi_I \\
&\equiv C_0 \Phi_0 + \sum_a^{\text{occ}} \sum_r^{\text{virt}} C_a^r \Phi_a^r + \sum_{a < b}^{\text{occ}} \sum_{r < s}^{\text{virt}} C_{ab}^{rs} \Phi_{ab}^{rs} + \dots \quad (8)
\end{aligned}$$

In the case of a CI wavefunction, the total energy is given by the expectation value  $\langle \Psi | \hat{H} | \Psi \rangle$ . In order to derive an appropriate partitioning technique for the CI energy, it should be consistent with Mayer's Hartree–Fock partitioning. That is, if we effectively switch off the electron correlation by setting  $C_0 = 1$  and  $C_I = 0$ , we should recover Mayer's one- and two-atom energy components. This requirement is in addition to the 'common-sense' conditions (a)–(c) set forth before.

The first-order density matrix elements  $D_{ij}$  and the second-order density matrix elements  $\Gamma_{ijkl}$  can be evaluated from the CI coefficients in the MO basis using the conventional Condon–Slater rules for the first and second-order density operators, respectively. The explicit working formulae for constructing the matrix elements of  $D$  and  $\Gamma$  for different cases were provided by McWeeny [29]. The matrices  $D$  and  $\Gamma$  can be transformed to the AO basis using the conventional formulae:

$$\begin{aligned}
D_{\mu\nu} &= \sum_{ij} C_{\mu i} C_{\nu j} D_{ij} \\
\Gamma_{\mu\nu\rho\sigma} &= \sum_{ijkl} C_{\mu i} C_{\nu j} C_{\rho k} C_{\sigma l} \Gamma_{ijkl}
\end{aligned}$$

Now we are in a position to derive the partitioning of the total correlated energy. It is advantageous to separate the 'Hartree–Fock-like' part of the energy and re-write the energy expression (5) using the density cumulants:

$$\begin{aligned}
E^{\text{tot}} &= \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} + \sum_{\mu\nu} D_{\mu\nu} [v|\hat{T}|\mu] - \sum_A \sum_{\mu\nu} D_{\mu\nu} \left[ v \left| \frac{Z_A}{r_A} \right| \mu \right] \\
&\quad + \frac{1}{2} \sum_{\mu\nu\rho\sigma} (D_{\mu\nu} D_{\rho\sigma} - D_{\mu\sigma} D_{\rho\nu}) [\mu\nu|\rho\sigma] \\
&\quad + \sum_{\mu\nu\rho\sigma} \lambda_{\mu\nu\rho\sigma} [\mu\nu|\rho\sigma]
\end{aligned}$$

This expression emphasizes the freedom of choice we have when partitioning the cumulant term of the energy, as the Mayer partitioning of the 'Hartree–Fock-like' part will not be affected. The intuitively easiest way to do such a partitioning would be to treat  $\lambda_{\mu\nu\rho\sigma}$  similarly to how it has been done for the two-electron part in the Hartree–Fock case. That is, the cumulant part could be then divided into one- and two-atom components as follows:

$$\begin{aligned} \sum_{\mu\nu\rho\sigma} \lambda_{\mu\nu\rho\sigma} [\mu\nu|\rho\sigma] &= \sum_A \sum_B \sum_{\mu \in A} \sum_{\rho \in B} \sum_{\nu, \sigma}^{\text{all}} \lambda_{\mu\nu\rho\sigma} [\mu\nu|\rho\sigma] \\ &= \sum_A \left( \sum_{\mu \in A} \sum_{\rho \in A} \sum_{\nu, \sigma}^{\text{all}} \lambda_{\mu\nu\rho\sigma} [\mu\nu|\rho\sigma] \right) \\ &\quad + \sum_{A>B} \left( 2 \sum_{\mu \in A} \sum_{\rho \in B} \sum_{\nu, \sigma}^{\text{all}} \lambda_{\mu\nu\rho\sigma} [\mu\nu|\rho\sigma] \right) \end{aligned}$$

However, a number of test calculations showed that this partitioning places too much negative correlation energy into one-atom components, thus leading to unphysically positive correlation contributions to two-atom energies. The reason for this behavior is that the cumulant contributions  $\lambda_{\mu\nu\rho\sigma}[\mu\nu|\rho\sigma]$  can be rather large in value and be of different sign. Thus, an unfortunate partitioning of the cumulant part can lead to rather large one- and two-atom components of different sign. Note that an earlier attempt to introduce a partitioning based on the entire  $\Gamma$  lead to rather unphysical two-atom energies [30]. Similarly large positive correlation contributions to the two-atom components were observed by Blanco et al. [15] in the context of their AIM-based partitioning. A solution to this problem can be found if we re-arrange the cumulant term such that the summation runs over  $\mu \in A$  and  $\nu \in B$ , with  $\mu$  and  $\nu$  being indices of the same electron:

$$\begin{aligned} \sum_{\mu\nu\rho\sigma} \lambda_{\mu\nu\rho\sigma} [\mu\nu|\rho\sigma] &= \sum_A \sum_B \sum_{\mu \in A} \sum_{\nu \in B} \sum_{\rho, \sigma}^{\text{all}} \lambda_{\mu\nu\rho\sigma} [\mu\nu|\rho\sigma] \\ &= \sum_A \left( \sum_{\mu \in A} \sum_{\nu \in A} \sum_{\rho, \sigma}^{\text{all}} \lambda_{\mu\nu\rho\sigma} [\mu\nu|\rho\sigma] \right) \\ &\quad + \sum_{A>B} \left( 2 \sum_{\mu \in A} \sum_{\nu \in B} \sum_{\rho, \sigma}^{\text{all}} \lambda_{\mu\nu\rho\sigma} [\mu\nu|\rho\sigma] \right) \end{aligned} \quad (9)$$

We refer to the partitioning obtained using Eq. (9) as Model 1. Another option, which we will label Model 2, is to calculate the two-atom term in the same manner as in Mayer's original partitioning, i.e., using the first-order density matrix only.

To summarize the presentation of the correlated energy partitioning scheme, we give the working formulae for the two-atom energy contributions:

Model 1:

$$\begin{aligned} E^{\text{AB}}(M1) &= \frac{Z_A Z_B}{R_{\text{AB}}} + 2 \sum_{\mu \in A} \sum_{\nu \in B} D_{\mu\nu} [v|\hat{T}|\mu] \\ &\quad - \sum_{\mu \in A} \sum_{\nu}^{\text{all}} D_{\mu\nu} \left[ v \left| \frac{Z_B}{r_B} \right| \mu \right] - \sum_{\mu \in B} \sum_{\nu}^{\text{all}} D_{\mu\nu} \left[ v \left| \frac{Z_A}{r_A} \right| \mu \right] \\ &\quad + \sum_{\mu \in A} \sum_{\rho \in B} \sum_{\nu, \sigma}^{\text{all}} (D_{\mu\nu} D_{\rho\sigma} - D_{\mu\sigma} D_{\rho\nu}) [\mu\nu|\rho\sigma] \\ &\quad + 2 \sum_{\mu \in A} \sum_{\nu \in B} \sum_{\rho, \sigma}^{\text{all}} \lambda_{\mu\nu\rho\sigma} [\mu\nu|\rho\sigma] \end{aligned} \quad (10)$$

Model 2:

$$\begin{aligned} E^{\text{AB}}(M2) &= \frac{Z_A Z_B}{R_{\text{AB}}} + 2 \sum_{\mu \in A} \sum_{\nu \in B} D_{\mu\nu} [v|\hat{T}|\mu] \\ &\quad - \sum_{\mu \in A} \sum_{\nu}^{\text{all}} D_{\mu\nu} \left[ v \left| \frac{Z_B}{r_B} \right| \mu \right] \\ &\quad - \sum_{\mu \in B} \sum_{\nu}^{\text{all}} D_{\mu\nu} \left[ v \left| \frac{Z_A}{r_A} \right| \mu \right] \\ &\quad + \sum_{\mu \in A} \sum_{\rho \in B} \sum_{\nu, \sigma}^{\text{all}} (D_{\mu\nu} D_{\rho\sigma} - D_{\mu\sigma} D_{\rho\nu}) [\mu\nu|\rho\sigma] \end{aligned} \quad (11)$$

Both Model 1 and Model 2 are compatible with Mayer's partitioning for the Hartree–Fock case. Of course, Model 2 does not provide a complete description of the correlation effects, but it is the easiest to implement, at least insofar as only two-atom energies are needed, since only the first-order density matrix is required.

#### 4. Results and discussion

Using formulae (10) and (11), we calculated two-atom energy components for a series of covalent molecules  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , HF, HCl,  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{H}_2\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{CO}_2$ , HCN,  $\text{Li}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$ , *cis* and *trans* diimide  $\text{N}_2\text{H}_2$ , as well as for the water dimer  $(\text{H}_2\text{O})_2$  and for the ionic systems LiH and LiF.

The Hartree–Fock geometry optimization and the evaluation of molecular orbitals needed for our calculations were performed using the GAUSSIAN 03 package [31] with the standard 6-31G\*\* basis set with Cartesian polarization functions. In order to calculate the first- and second-order density matrices, we implemented the Configuration Interaction with double excitations (CI-D) within the frozen-core approximation into our own program. The CI-D method was chosen because it is the easiest to implement for the purpose of obtaining the density matrices. It is expected that other correlation methods will yield similar results. In order to test the correctness of our program, the total CI-D energies obtained were compared to the values calculated by GAUSSIAN 03. The results of the calculations are reported in Table 1. For the sake of comparison, we also report the values calculated according to Mayer's formulae using the Hartree–Fock first-order density matrix (Eq. (1)).

One generalization deducible from these results is that all the two-atom energies obtained are 'on the chemical scale' (see condition (a)). There are clear differences between the bonding and non-bonding interactions (condition (c)), with the former exhibiting negative (attractive) values about dozens or hundreds  $\text{kcal mol}^{-1}$ , while the latter have much smaller values, typically within  $10 \text{ kcal mol}^{-1}$  (negative or positive).

The comparison of the two-atom energies between the methods (Model 1 and Model 2 versus Hartree–Fock)

Table 1  
Two-atom energies (in kcal mol<sup>-1</sup>) at CI-D and Hartree–Fock level for a number of molecules calculated at the RHF/6-31G\*\* optimized geometries using various schemes (Model 1 and Model 2, see text)

Molecule/bond	Model 1	Model 2	Hartree–Fock
<b>C<sub>2</sub>H<sub>6</sub></b>			
C–C	-115.0	-118.2	-119.0
C–H	-111.3	-105.0	-108.0
C...H	5.1	4.1	4.4
H...H <sup>gem</sup>	9.3	8.4	8.6
H...H <sup>vic gauch</sup>	-0.6	-0.6	-0.6
<b>C<sub>2</sub>H<sub>4</sub></b>			
C–C	-159.1	-167.4	-166.8
C–H	-114.2	-108.1	-111.4
C...H	7.1	5.7	6.1
H...H <sup>gem</sup>	11.3	10.7	11.0
H...H <sup>vic</sup>	3.8	3.9	3.9
<b>C<sub>2</sub>H<sub>2</sub></b>			
C–C	-295.1	-313.8	-304.6
C–H	-103.1	-95.2	-98.4
C...H	-11.4	-12.2	-11.9
H...H	3.6	3.6	3.5
<b>HF</b>	-99.8	-96.2	-101.5
<b>HCl</b>	-95.1	-95.3	-100.2
<b>F<sub>2</sub></b>	-83.5	-89.9	-103.0
<b>Cl<sub>2</sub></b>	-79.3	-86.1	-92.6
<b>H<sub>2</sub>CO</b>			
C=O	-131.8	-138.9	-149.3
C–H	-109.0	-104.4	-107.7
H...H	17.7	16.6	17.1
<b>H<sub>2</sub>O</b>			
O–H	-122.3	-117.8	-122.5
H...H	27.7	27.5	27.8
<b>(H<sub>2</sub>O)<sub>2</sub></b>			
O–H <sup>a</sup>	-126.4	-121.8	-125.6
	-125.1	-120.7	-124.4
O–H <sup>b</sup>	-128.9	-126.4	-129.8
O...H <sup>b</sup>	-52.6	-52.8	-53.8
<b>CH<sub>3</sub>OH</b>			
C–O	-119.8	-125.8	-131.6
C–H	-107.4	-101.3	-104.6
O–H	-124.8	-120.3	-124.2
<b>H<sub>2</sub>O<sub>2</sub></b>			
O–O	-99.8	-106.5	-114.9
O–H	-99.1	-95.1	-98.7
H...H	16.6	16.7	16.8
<b>CO<sub>2</sub></b>			
C=O	-155.5	-167.1	-175.9
O...O	27.3	26.8	29.1
<b>HCN</b>			
H–C	-99.3	-93.4	-96.2
C–N	-149.6	-161.4	-171.4
<b>NH<sub>3</sub></b>			
N–H	-131.8	-127.0	-131.3
H...H	20.2	19.8	20.0
<b>N<sub>2</sub>H<sub>4</sub></b>			
N–N	-106.0	-114.7	-118.8
N–H	-120.9	-116.2	-119.7
H...H <sup>gem</sup>	21.5	21.2	21.4
H...H <sup>vic gauch</sup>	12.0	12.4	12.4

<b>N<sub>2</sub>H<sub>2 cis</sub></b>			
N=N	-133.7	-147.0	-153.2
N–H	-96.5	-93.1	-96.7
H...H	17.3	16.9	17.2

<b>N<sub>2</sub>H<sub>2 trans</sub></b>			
N=N	-144.5	-156.3	-162.1
N–H	-100.4	-96.1	-99.6
H...H	5.6	5.5	5.4
<b>Li<sub>2</sub></b>	-53.0	-43.1	-54.8
<b>LiF</b>	-139.2	-145.6	-151.8
<b>LiH</b>	-86.0	-88.0	-91.6

The Hartree–Fock column gives the values calculated by means of Mayer's original partitioning formula (4) using the Hartree–Fock density matrix.

<sup>a</sup> Terminal (non-hydrogen bonding) hydrogen.

<sup>b</sup> hydrogen bonding hydrogen.

shows that all three models provide rather similar results. The two-atom energies for X–H bonds are mostly very close between the methods, while those for bonds between heavier atoms differ slightly more, with the general trend of Model 1 values being slightly lower than the Model 2 and Hartree–Fock results. For the non-bonding interactions, including the hydrogen bond in the water dimer, only marginal differences are found between all three methods.

The water dimer exhibits the two-atom O...H energy for the hydrogen bond of about 53 kcal mol<sup>-1</sup> calculated by all three methods, which is intermediate between typical covalent and non-bonding interactions. Note that this value is not directly comparable to the (H<sub>2</sub>O)<sub>2</sub> → 2H<sub>2</sub>O dissociation energy, as the latter includes other diatomic interactions as well as the one-atom components.

Finally, examples of a predominantly ionic character – lithium fluoride and lithium hydride – demonstrate attractive two-atom energies, which are rather consistent between the models.

## 5. Conclusions

The present work provides a generalization of Mayer's Hartree–Fock energy partitioning for the case of an arbitrary correlated wavefunction. First, an analysis of Mayer's original partitioning is given in terms of one-atom density matrices. Then, analogous partitioning of the correlated energy (referred to as Model 1) is presented using the density cumulants. In general, test shows that the correlated energy partitioning is reliable, as it satisfies the 'common-sense' conditions imposed on the partitioning schemes of such kind. The influence of the electron correlation on the results is moderate. The method is applicable to any wavefunction, provided that the first- and second-order density matrices are available. Contrary to the Ayala–Scuseria scheme [28], it is also applicable, in principle, for excited-state wavefunctions. The tests indicate that Mayer's simple Hartree–Fock-based formula (11) using the correlated first-order density matrix (Model 2) also provides meaningful results.

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