

Electron Density Based Partitioning Scheme of Interaction Energies

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ABSTRACT: In this paper, a new partitioning of the complex interaction energy is proposed. This new partitioning is based on the decomposition of the one-electron and exchange-correlation densities into unperturbed and deformation densities. Thus, the proposed energy fragmentation can be applied at the SCF level and post-SCF levels as long as the corresponding density matrices have been evaluated previously. It provides the typical description of the complex interaction as a summation of electrostatic, exchange-repulsion, and polarization terms. However, the new method allows splitting up the exchange-repulsion into exchange and Pauli-repulsion energies. A full theoretical description of the method is presented, and some examples of its application to small complexes are discussed. A comparison with results obtained using perturbation methods is also carried out, showing that the first order terms obtained from symmetry adapted perturbation theories are perfectly reproduced with the new method. A clear bridge between qualitative deformation density plots and quantitative measures of the interaction energy components can be established within the framework of this new partitioning scheme, giving rise to a graphical and very intuitive interpretation of the complex formation.

1. INTRODUCTION

The most employed method for the calculation of intermolecular energies is the supermolecular ansatz^{1–3} in which the interaction energy is calculated as the difference in the total energies of the complex and the monomers. Because of its simplicity, this approach is widely used; in fact, any ab initio or DFT program package can provide the complex and monomer energies, the latter corrected for the unwanted basis set superposition error.^{4,5} However, the information provided by the supermolecular approach about the intermolecular interaction is very poor, as it gives only the value of the intermolecular energy and does not give any physical insight into the nature of the interaction. This drawback can be solved using a perturbational treatment of intermolecular interactions. The perturbation theory has been applied to the problem of intermolecular forces since the early days of quantum chemistry, and it continues to provide the rational framework for their understanding, modeling, and computation.^{1,2,6} Thus, perturbation methods provide an interpretation of the potential energy surfaces obtained by the supermolecular approach^{1,4} and have been the keystone in the development of ab initio intermolecular force fields.^{1,7}

According to perturbation theory, all intermolecular interactions contain four fundamental physical contributions: electrostatic, exchange-repulsion, induction, and dispersion.^{1,2,6,7} The exchange-repulsion energy includes both the intermolecular electron–electron repulsion due to the Pauli exclusion principle and the exchange energy due to the exchange effects resulting from the tunneling of the electrons between interacting systems.^{1,8} The induction and dispersion energies together constitute the polarization term.^{1,2}

The conceptually simplest perturbation approach to the intermolecular interactions is the standard application of the Rayleigh–Schrödinger perturbation (RSPT) to a dimer, the so-called polarization theory.^{1,6,8,9} This approach is very successful in describing the interaction between two molecules a long distance apart, but at short range, it fails completely. Among

the perturbation theories that solve this problem, the symmetry-adapted perturbation approach of Jeziorski et al.⁶ (SAPT) has been the most used. Its popularity is mainly due to a lower computational cost in the calculation of the perturbational terms.

On the other hand, most of the perturbational approaches are based in molecular orbital theory, and they use the Heitler–London method to construct the initial wave function of the system. However, this wave function is not variationally optimized, which causes some ambiguity in the separation of the first order terms, namely, electrostatic and repulsion energies.^{10,11} This problem can be solved using a recently proposed method based on density functional theory (DFT), where the intermediate complex electron densities are obtained variationally.¹¹ Since it is based on DFT, the calculation of the energy terms requires only the knowledge of the one-electron densities. The method also provides the charge transfer contribution to the energy. However, this term is part of the short-range induction energy¹ and has been a source of controversy, giving rise to a good deal of confusion. Ayers et al.¹¹ separate the charge transfer contribution from the induction energy on the basis of a more or less arbitrary limit of the density of each fragment of the complex. Finally, the calculation of the dispersion contribution within this approach will be strongly influenced by the development of van der Waals functionals in density functional theory.

The aim of this work is to propose a new fragmentation of the intermolecular interaction energy based on the electron density that can be of general application. The energy fragmentation is performed by means of the unperturbed monomer electron densities and the intermolecular deformation densities associated with each energy term. Therefore, the method of calculation of the energy terms is given by the level of computation of the electron densities, so that the new partitioning may be considered of general application. As expected for any new

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interaction energy partitioning, the method keeps a strong relation with other previously proposed schemes. So, it gives essentially the same first order contributions as the well-known SAPT method of Jeziorski et al.,⁶ and therefore they are directly comparable. However, the new scheme splits the short-range repulsive term into exchange and repulsion energies, giving a separate value to each of them. The second order terms are analogous to the second order SAPT contributions plus their exchange corrections, and a correspondence between them may also be expected.

If the method is considered from a practical point of view, one of its strongest points emerges: once the electron densities are obtained, the computation of all intermolecular terms takes virtually negligible time compared to the calculation of the electron densities. So the bottleneck for the calculations is the computation of the densities. Since most of quantum chemical program packages provide the electron density during the SCF or post-SCF procedures, this method will use in the most expensive step of the calculation any strategy, approach, or ansatz employed by the quantum chemical program packages to obtain the energy. This reduces significantly the computational cost, allowing the calculation of the different intermolecular energy terms in very large systems. Finally, density deformation plots associated with each intermolecular term can be obtained using this new scheme. These density plots may be a graphical and very intuitive tool to understand the nature of the different intermolecular terms and the delicate balance between them. In the next sections, we will expose the proposed method together with its application to some systems at different levels of calculation.

2. THEORETICAL DEVELOPMENTS

The total nonrelativistic energy of any molecular or atomic system can be exactly expressed in terms of the one-electron density, $\rho(\vec{r}_1)$, and the two-electron density, $\rho(\vec{r}_1, \vec{r}_2)$. Since the latter can be expressed as the sum of the product of the one-electron densities plus the exchange-correlation density, $\rho_{XC}(\vec{r}_1, \vec{r}_2)$, the expression of the energy is given by

$$E = -\frac{1}{2} \int \nabla^2 \rho(\vec{r}_1, \vec{r}_1')_{r_1'=r_1} d\vec{r}_1 + \int \hat{v}_N \rho(\vec{r}_1) d\vec{r}_1 + \frac{1}{2} \iint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \frac{\rho_{XC}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \sum_{I=1}^N \sum_{J>I}^N \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad (1)$$

where \hat{v}_N represents the electrostatic potential created by the nuclei, N the number of nuclei, and Z the nuclear charge (in atomic units). In the case of two interacting molecular or atomic systems A and B , the nuclear electrostatic potential and energy, the one-electron density, and the exchange-correlation density can be expressed in terms of their values for the noninteracting systems plus their changes along the interaction. Thus, they can be written as eqs 2–345:

$$\sum_{I=1}^N \sum_{J>I}^N \frac{Z_I Z_J}{R_{IJ}} = \sum_{I=1}^{N_A} \sum_{J>I}^{N_A} \frac{Z_I Z_J}{R_{IJ}} + \sum_{I=1}^{N_B} \sum_{J>I}^{N_B} \frac{Z_I Z_J}{R_{IJ}} + \sum_{I=1}^{N_A} \sum_{J=1}^{N_B} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad (2)$$

$$\hat{v}_N = \hat{v}_{N_A} + \hat{v}_{N_B} \quad (3)$$

$$\rho(\vec{r}_1) = \rho_A(\vec{r}_1) + \rho_B(\vec{r}_1) + \Delta\rho(\vec{r}_1) \quad (4)$$

$$\rho_{XC}(\vec{r}_1, \vec{r}_2) = \rho_{XC,A}(\vec{r}_1, \vec{r}_2) + \rho_{XC,B}(\vec{r}_1, \vec{r}_2) + \rho_{XC,AB}(\vec{r}_1, \vec{r}_2) + \Delta\rho_{XC}(\vec{r}_1, \vec{r}_2) \quad (5)$$

where $\Delta\rho$ is the one-electron deformation density. The third and fourth terms in eq 5 represent the intermolecular fraction of the exchange-correlation density before electron polarization and the changes experienced in the total exchange-correlation density due to the electron polarization, respectively.

The one-electron deformation density is in turn the result of two effects: on one hand, the effect over the monomers' one-electron densities of the Pauli exclusion principle, $\Delta\rho_{\text{Pauli}}$, which is given by the difference between the electron density obtained from the antisymmetrized product of the monomers' wave functions and the electron density obtained from the Hartree product; on the other hand, the effect over the one-electron density of the electron polarization due to the intermolecular interaction, $\Delta\rho_{\text{Pol}}$, which is given by the difference between the total and the Pauli deformation densities. Thus, eq 4 can be replaced by eq 6.

$$\rho(\vec{r}_1) = \rho_A(\vec{r}_1) + \rho_B(\vec{r}_1) + \Delta\rho_{\text{Pauli}}(\vec{r}_1) + \Delta\rho_{\text{Pol}}(\vec{r}_1) \quad (6)$$

By introducing eqs 2, 3, 5, and 6 in eq 1, the following expression is obtained for the energy of the interacting systems.

$$E = -\frac{1}{2} \int \nabla^2 \rho_A(\vec{r}_1, \vec{r}_1')_{r_1'=r_1} d\vec{r}_1 - \frac{1}{2} \int \nabla^2 \rho_B(\vec{r}_1, \vec{r}_1')_{r_1'=r_1} d\vec{r}_1 - \frac{1}{2} \int \nabla^2 \Delta\rho_{\text{Pauli}}(\vec{r}_1, \vec{r}_1')_{r_1'=r_1} d\vec{r}_1 + -\frac{1}{2} \int \nabla^2 \Delta\rho_{\text{Pol}}(\vec{r}_1, \vec{r}_1')_{r_1'=r_1} d\vec{r}_1 + \int \hat{v}_{N_A} \rho_A(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_{N_B} \rho_B(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_{N_A} \rho_B(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_{N_B} \rho_A(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_{N_A} \Delta\rho_{\text{Pauli}}(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_{N_A} \Delta\rho_{\text{Pol}}(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_{N_B} \Delta\rho_{\text{Pauli}}(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_{N_B} \Delta\rho_{\text{Pol}}(\vec{r}_1) d\vec{r}_1 + \frac{1}{2} \iint \frac{\rho_A(\vec{r}_1) \rho_A(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \frac{\rho_B(\vec{r}_1) \rho_B(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \iint \frac{\rho_A(\vec{r}_1) \rho_B(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \frac{\Delta\rho_{\text{Pauli}}(\vec{r}_1) \Delta\rho_{\text{Pauli}}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \frac{\Delta\rho_{\text{Pol}}(\vec{r}_1) \Delta\rho_{\text{Pol}}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \iint \frac{\Delta\rho_{\text{Pauli}}(\vec{r}_1) \Delta\rho_{\text{Pol}}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2$$

$$\begin{aligned}
& + \iint \frac{\Delta \rho_{\text{Pauli}}(\vec{r}_1) \rho_A(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \iint \frac{\Delta \rho_{\text{Pauli}}(\vec{r}_1) \rho_B(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \iint \frac{\Delta \rho_{\text{Pol}}(\vec{r}_1) \rho_A(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \iint \frac{\Delta \rho_{\text{Pol}}(\vec{r}_1) \rho_B(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \frac{1}{2} \iint \frac{\rho_{\text{XC}, A}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \frac{\rho_{\text{XC}, B}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \frac{1}{2} \iint \frac{\rho_{\text{XC}, AB}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \frac{1}{2} \iint \frac{\Delta \rho_{\text{XC}}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \sum_{I=1}^{N_A} \sum_{J>I}^{N_A} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \\
& + \sum_{I=1}^{N_B} \sum_{J>I}^{N_B} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} + \sum_{I=1}^{N_A} \sum_{J=1}^{N_B} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad (7)
\end{aligned}$$

On the other hand, the summation of the energies of the isolated systems A and B is given by

$$\begin{aligned}
E_A + E_B = & -\frac{1}{2} \int \nabla^2 \rho_A(\vec{r}_1, \vec{r}_1')_{r_1'=r_1} d\vec{r}_1 \\
& -\frac{1}{2} \int \nabla^2 \rho_B(\vec{r}_1, \vec{r}_1')_{r_1'=r_1} d\vec{r}_1 \\
& + \int \hat{v}_{N_A} \rho_A(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_{N_B} \rho_B(\vec{r}_1) d\vec{r}_1 \\
& + \frac{1}{2} \iint \frac{\rho_A(\vec{r}_1) \rho_A(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \frac{1}{2} \iint \frac{\rho_B(\vec{r}_1) \rho_B(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \frac{1}{2} \iint \frac{\rho_{\text{XC}, A}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \frac{1}{2} \iint \frac{\rho_{\text{XC}, B}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \sum_{I=1}^{N_A} \sum_{J>I}^{N_A} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} + \sum_{I=1}^{N_B} \sum_{J>I}^{N_B} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad (8)
\end{aligned}$$

where all of the terms are contained explicitly within eq 7. The difference between eqs 7 and 8 is then the interaction energy, E_{int} , between A and B, expressed in terms of the deformation densities and unperturbed densities of the isolated systems. By defining the electrostatic potential created by the electrons and nuclei of molecules A and B (isolated) as

$$\hat{v}_A(\vec{r}_1) = \hat{v}_{N_A}(\vec{r}_1) + \int \frac{\rho_A(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_2 \quad (9)$$

$$\hat{v}_B(\vec{r}_1) = \hat{v}_{N_B}(\vec{r}_1) + \int \frac{\rho_B(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_2 \quad (10)$$

and grouping terms depending on the unperturbed densities and deformation densities, it is possible to separate E_{int} into different contributions with clear physical meaning (eqs 11–15).

$$E_{\text{int}} = E_{\text{elec}} + E_{\text{exch}} + E_{\text{rep}} + E_{\text{pol}} \quad (11)$$

$$\begin{aligned}
E_{\text{elec}} = & \int \hat{v}_{N_A} \rho_B(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_{N_B} \rho_A(\vec{r}_1) d\vec{r}_1 \\
& + \iint \frac{\rho_A(\vec{r}_1) \rho_B(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \sum_{I=1}^{N_A} \sum_{J=1}^{N_B} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad (12)
\end{aligned}$$

$$E_{\text{exch}} = \frac{1}{2} \iint \frac{\rho_{\text{XC}, AB}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \quad (13)$$

$$\begin{aligned}
E_{\text{rep}} = & \int \hat{v}_A \Delta \rho_{\text{Pauli}}(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_B \Delta \rho_{\text{Pauli}}(\vec{r}_1) d\vec{r}_1 \\
& + \frac{1}{2} \iint \frac{\Delta \rho_{\text{Pauli}}(\vec{r}_1) \Delta \rho_{\text{Pauli}}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \iint \frac{\Delta \rho_{\text{Pauli}}(\vec{r}_1) \rho_A(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \iint \frac{\Delta \rho_{\text{Pauli}}(\vec{r}_1) \rho_B(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& - \frac{1}{2} \int \nabla^2 \Delta \rho_{\text{Pauli}}(\vec{r}_1, \vec{r}_1')_{r_1'=r_1} d\vec{r}_1 \quad (14)
\end{aligned}$$

$$\begin{aligned}
E_{\text{pol}} = & \int \hat{v}_A \Delta \rho_{\text{Pol}}(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_B \Delta \rho_{\text{Pol}}(\vec{r}_1) d\vec{r}_1 \\
& + \frac{1}{2} \iint \frac{\Delta \rho_{\text{Pol}}(\vec{r}_1) \Delta \rho_{\text{Pol}}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \iint \frac{\Delta \rho_{\text{Pol}}(\vec{r}_1) \rho_A(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \iint \frac{\Delta \rho_{\text{Pol}}(\vec{r}_1) \rho_B(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + \iint \frac{\Delta \rho_{\text{Pauli}}(\vec{r}_1) \Delta \rho_{\text{Pol}}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
& + -\frac{1}{2} \int \nabla^2 \Delta \rho_{\text{Pol}}(\vec{r}_1, \vec{r}_1')_{r_1'=r_1} d\vec{r}_1 \\
& + \frac{1}{2} \iint \frac{\Delta \rho_{\text{XC}}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \quad (15)
\end{aligned}$$

The terms given above are classified as follows:

- (i) Electrostatic term, E_{elec} , which exclusively depends on the nuclear charge and one-electron density distributions of the isolated systems, accounting for the eventual presence of effective charges and multipole moments
- (ii) Exchange term, E_{exch} , depending exclusively on the unperturbed intermolecular exchange-correlation density
- (iii) Repulsion term, E_{rep} , depending on the deformation of the monomers' one-electron densities associated with the Pauli exclusion principle
- (iv) Polarization term, E_{pol} , depending on the deformation of the electron densities due to the electron polarization. In

Table 1. Comparison of Electrostatic and Exchange-Repulsion Energies for Water, Hydrogen Fluoride, and Methane Dimers Obtained at the SCF, MP2, and CCSD Levels Using the New Fragmentation Scheme and the SAPT Method (All Values in kJ mol^{−1})

	(H ₂ O) ₂			(HF) ₂			(CH ₄) ₂		
	SCF	MP2	CCSD	SCF	MP2	CCSD	SCF	MP2	CCSD
<i>E</i> _{elec}	−33.51	−33.39	−32.64	−26.40	−25.56	−25.19	−0.84	−1.00	−0.92
<i>E</i> _{elec} (SAPT)	−33.51	−33.30	−32.68	−26.44	−25.44	−25.19	−0.84	−1.05	−0.96
diff (%)	0.02	0.36	0.14	0.03	0.57	0.00	3.10	2.25	3.93
<i>E</i> _{x-rep}	26.69	32.09	33.72	18.33	23.14	24.60	3.22	3.35	3.51
<i>E</i> _{x-rep} (SAPT)	26.40	30.92	31.46	18.20	22.51	22.84	3.22	3.60	3.72
diff (%)	1.06	3.72	7.20	0.70	2.92	7.87	0.63	6.72	5.16

turn, the polarization energy can also be partitioned into one-electron density and exchange-correlation density terms

3. COMPUTATIONAL DETAILS

Implementation of eqs 11–15 has been performed in a program written in the Fortran language. In its current version, the program requires as input the information of the molecular orbital coefficients and the one-electron and two-electron integrals for basis functions. The Gaussian 03 program¹² provides the input information for the example calculations presented in this work. Then, the program computes the different density matrices, expressed in terms of basis functions, required for the calculation of the energy terms. The calculation of the exchange and repulsion energies is the most delicate step, and further details about their computation are given in and .

At the SCF level, the different energy terms that constitute the polarization energy are obtained from the one-electron and the exchange deformation densities. Since the total interaction energy and all its components are calculated analytically, differences between the interaction energy calculated using the supermolecular approach and that obtained as a summation of its energy components have been found to be negligible.

On the contrary, at the post-SCF level, the exchange-correlation energy term of the polarization energy is obtained as the difference between the total interaction energy and the summation of the remaining energy components. This shortcut avoids the arduous task of computing the two-electron reduced density matrices at the post-SCF level and relies on the accuracy of the calculation of the electrostatic and exchange-repulsion energies (see next section for details).

We have checked our method in three typical complexes such as water, hydrogen fluoride, and methane dimers. The 6-311++G-(2d,2p) basis set was employed in the calculations of water and hydrogen fluoride dimers. Since a good description of the methane dimer potential energy surface requires a larger basis set, we have employed for this system the aug-cc-pVQZ basis set. Energy decomposition was performed using Hartree–Fock (HF), MP2, MP4, CCD, CCSD, and QCISD electron densities.

4. EXAMPLES

Comparison with Perturbation Approaches. Although the new fragmentation can be applied on any kind of atomic or molecular interaction (covalent, ionic, van der Waals, etc.), the most interesting application is, undoubtedly, the study of weak intermolecular interactions. Perturbation and hybrid approaches

provide a solid background for the physical interpretation of the interaction energy in intermolecular complexes. Terms arising from perturbation approaches can be classified as electrostatic, exchange, and polarization, where the latter can be split up into pure induction and dispersion energies at the second-order perturbation level.

In this section, we will merge as far as possible the energy terms of eqs 11–15 with those arising from the perturbation approaches. We will start with the simplest case of SCF electron densities to further extend it to the more general case of correlated post-SCF densities.

The physical interpretation of the energy terms given in eq 11 becomes clear when the electron densities are obtained at the HF level. The electrostatic term is the classical intermolecular Coulombic interaction between electrons and nuclei of different monomers. As long as we deal with Hartree–Fock electron densities, the intramonomer correlation effects are not taken into account (in this section, we will employ the term “uncorrected” for those energy terms that do not include electron correlation corrections).

$$E_{\text{elec}}^{\text{unc}} = \int \hat{v}_{N_A} \rho_B^{\text{HF}}(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_{N_B} \rho_A^{\text{HF}}(\vec{r}_1) d\vec{r}_1 + \iint \frac{\rho_A^{\text{HF}}(\vec{r}_1) \rho_B^{\text{HF}}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \sum_{I=1}^{N_A} \sum_{J=1}^{N_B} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad (16)$$

This is exactly the same energy as the electrostatic energy obtained with Morokuma’s method, and also the same as the electrostatic energy obtained from the hybrid methods that employ the Hartree–Fock interaction energy. The Hartree–Fock electrostatic energies calculated using the new fragmentation and the SAPT-HF method are shown in Table 1 for water, hydrogen fluoride, and methane dimers. As one can see, differences in the values obtained by both methodologies are negligible.

At the HF level, the exchange-correlation density contains exclusively the electron exchange part. Thus, $E_{\text{exch}}^{\text{unc}}$ gives exactly the exchange part of the uncorrected exchange-repulsion energy.

$$E_{\text{exch}}^{\text{unc}} = \frac{1}{2} \iint \frac{\rho_{X,AB}^{\text{HF}}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \quad (17)$$

This is one important advantage of using electron densities to represent the interaction energy, it is possible to separate exchange energy from repulsion, which is not possible using

perturbation methods. The Hartree–Fock exchange and repulsion energy terms obtained in this work are also compared in Table 1 with the exchange-repulsion energies obtained using SAPT-HF. As in the case of electrostatic energies, the summation of the exchange plus repulsion terms gives the same results as the SAPT-HF method for the exchange-repulsion energy. As expected for interactions between closed-shell systems, the exchange part is negative, whereas the repulsion part is positive and larger in absolute value. The intermolecular exchange energy stabilizes the complex, but the Pauli repulsion exerted by electrons with the same spin in the intermolecular region overtakes the exchange energy, giving rise to a net destabilization. Details about the calculation of $\rho_{X,AB}^{\text{HF}}(\vec{r}_1, \vec{r}_2)$, and $\Delta\rho_{\text{Pauli}}^{\text{HF}}(\vec{r}_1)$ are given in .

Since the dispersion energy is not accounted for at the HF level, the polarization term (eq 15) gives directly the uncorrected induction energy. However, in this case the induction energy also reflects the exchange correction that arises in the perturbation methods.

$$\begin{aligned}
 E_{\text{ind}}^{\text{unc}} = & \int \hat{v}_A \Delta\rho_{\text{Pol}}^{\text{HF}}(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_B \Delta\rho_{\text{Pol}}^{\text{HF}}(\vec{r}_1) d\vec{r}_1 \\
 & + \frac{1}{2} \iint \frac{\Delta\rho_{\text{Pol}}^{\text{HF}}(\vec{r}_1) \Delta\rho_{\text{Pol}}^{\text{HF}}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
 & + \iint \frac{\Delta\rho_{\text{Pol}}^{\text{HF}}(\vec{r}_1) \rho_A^{\text{HF}}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
 & + \iint \frac{\Delta\rho_{\text{Pol}}^{\text{HF}}(\vec{r}_1) \rho_B^{\text{HF}}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
 & + \iint \frac{\Delta\rho_{\text{Pauli}}^{\text{HF}}(\vec{r}_1) \Delta\rho_{\text{Pol}}^{\text{HF}}(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \\
 & + -\frac{1}{2} \int \nabla^2 \Delta\rho_{\text{Pol}}^{\text{HF}}(\vec{r}_1, \vec{r}_1')_{r_1'=r_1} d\vec{r}_1 \\
 & + \frac{1}{2} \iint \frac{\Delta\rho_X^{\text{HF}}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \quad (18)
 \end{aligned}$$

Summarizing, all energy terms obtained with the new fragmentation scheme have physical interpretation in terms of traditional electrostatic, exchange-repulsion, and induction energies derived from perturbation theory at the HF level.

The use of correlated post-SCF densities incorporates the dynamic electron correlation effect into the interaction energy. This evidently improves the results but complicates the physical interpretation of the energy fragmentation. The dispersion energy, which is intrinsically related to the dynamic electron correlation, appears to be unavoidably distributed within the polarization term. On the contrary, the electrostatic term still has a clear-cut physical meaning as the inclusion of electron correlation does not change its nature but incorporates the effect of the intramonomer dynamic electron correlation. The electrostatic term calculated at the correlated level is now the sum of the Hartree–Fock electrostatic energy plus the intramonomer correlation correction to the electrostatic energy. This term can be viewed as the “corrected” electrostatic energy.

$$\begin{aligned}
 E_{\text{elec}}^{\text{corr}} = & \int \hat{v}_{N_A} \rho_B(\vec{r}_1) d\vec{r}_1 + \int \hat{v}_{N_B} \rho_A(\vec{r}_1) d\vec{r}_1 \\
 & + \iint \frac{\rho_A(\vec{r}_1) \rho_B(\vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 + \sum_{I=1}^{N_A} \sum_{J=1}^{N_B} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad (19)
 \end{aligned}$$

The electrostatic energies obtained at different post-SCF levels are compared in Table 1 with the electrostatic energies obtained with SAPT at the MP2 and CCSD levels for the reference dimers. As one can see, the MP2 and CCSD electrostatic energies obtained with the new fragmentation scheme are almost the same as those calculated with SAPT.

On the other hand, the corrected exchange energy can also be obtained straightforwardly from the unperturbed intermolecular exchange-correlation density (see for its calculation). This can be viewed as the unperturbed intermolecular exchange density corrected by the intramonomer electron correlation.

$$E_{\text{exch}}^{\text{corr}} = \frac{1}{2} \iint \frac{\rho_{X,AB}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_2 - \vec{r}_1|} d\vec{r}_1 d\vec{r}_2 \quad (20)$$

The Pauli repulsion can also be obtained separately as in the case of Hartree–Fock densities. As mentioned in , the best way to compute the deformation density associated with the Pauli repulsion is through a weighted orthogonalization procedure¹³ of the natural orbitals of the monomers. One can compare in Table 1 the summation of the exchange plus Pauli repulsion energies obtained from the new fragmentation and the exchange-repulsion energies calculated with SAPT at the MP2 and CCSD levels. Results obtained by both methodologies are very similar, demonstrating the good performance of the weighted orthogonalization in the calculation of the exchange-repulsion energy. Analyzing the exchange and the Pauli repulsion energies separately, it can be observed that their absolute values go up as the degree of electron correlation increases, following the sequence HF < MP2 < CCD < CCSD \approx QCISD \approx MP4, which reflects an increase of the overlapping between the monomers’ electron densities with the electron correlation.

The disadvantage of using correlated densities in the new energy fragmentation is the apparent nonseparability of the polarization term. Thus, one can only speak “a priori” of polarization energy, including here the induction and dispersion and their exchange-correlation corrections. Separation of polarization energy into induction and dispersion seems to have only physical meaning within the second-order perturbation theory. In fact, for higher order perturbation theories, the induction and dispersion terms are not completely separable, and coupled induction-dispersion energies appear already at third-order perturbation theory.¹⁴ We are currently developing a procedure for merging the second-order RSPT with the new fragmentation scheme in order to get the induction energy from the rest of polarization energy at the post-SCF level.¹⁵

Energy Fragmentation vs Deformation Density Plots. Together with other local properties of the electron density,¹⁶ deformation density plots can be employed to rationalize at the qualitative level the stability of hydrogen bonding,¹⁷ stacking,¹⁸ or anion- π complexes.¹⁹ These deformation density plots are also frequently employed to evaluate the strength of chemical bonds.^{20,21} In the case of intermolecular interactions, deformation density plots are more properly obtained as the difference between the one-electron density of the complex and the summation of the one-electron densities of the noninteracting monomers. In the calculation, the monomers are placed at the same position that they occupy in the complex. This deformation density includes the effect that all of the interaction energy terms exert on the electron density distribution upon complexation. Thus, the effects of

Table 2. Interaction Energy Components for Water, Hydrogen Fluoride and Methane Dimers Obtained at SCF and Different Post-SCF Levels Using the New Fragmentation Scheme (All Values in kJ mol^{-1})

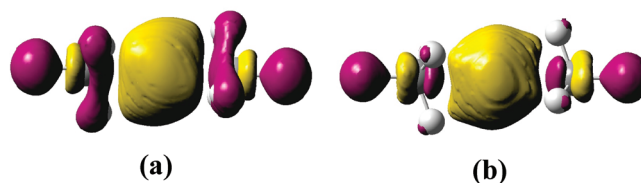
	SCF	MP2	CCD	CCSD	QCISD	MP4
(H ₂ O) ₂						
E_{elec}	−33.51	−33.39	−32.72	−32.64	−32.59	−32.68
E_{x}	−44.89	−60.08	−56.99	−57.57	−57.82	−57.91
E_{rep}	71.59	92.17	89.66	91.29	92.22	91.67
$E_{\text{x-rep}}$	26.69	32.09	32.64	33.72	34.35	33.76
E_{pol}	−8.87	−17.57	−17.91	−19.12	−19.71	−19.08
	−19.41 ^a	−39.12 ^a	−39.20 ^a	−40.96 ^a	−41.84 ^a	−41.09 ^a
	10.54 ^b	21.55 ^b	21.38 ^b	21.84 ^b	22.13 ^b	22.01 ^b
E_{int}	−15.73	−18.91	−17.82	−17.99	−17.95	−17.95
(HF) ₂						
E_{elec}	−26.40	−25.56	−25.27	−25.19	−25.15	−25.19
E_{x}	−33.39	−48.24	−44.89	−46.65	−47.15	−47.20
E_{rep}	51.71	71.38	68.20	71.30	72.68	72.22
$E_{\text{x-rep}}$	18.33	23.14	23.35	24.64	25.52	25.02
E_{pol}	−7.91	−14.10	−14.27	−15.69	−16.57	−15.94
	−8.95 ^a	−28.03 ^a	−26.61 ^a	−29.71 ^a	−31.05 ^a	−30.33 ^a
	1.05 ^b	13.93 ^b	12.34 ^b	14.02 ^b	14.56 ^b	14.39 ^b
E_{int}	−15.98	−16.48	−16.19	−16.23	−16.11	−16.07
(CH ₄) ₂						
E_{elec}	−0.84	−1.00	−0.92	−0.92	−0.92	−0.96
E_{x}	−7.82	−12.76	−12.30	−12.43	−12.47	−12.51
E_{rep}	11.09	16.11	15.65	15.94	16.02	15.94
$E_{\text{x-rep}}$	3.22	3.35	3.35	3.51	3.56	3.43
E_{pol}	−0.17	−3.56	−3.18	−3.39	−3.43	−3.35
	−2.13 ^a	−7.57 ^a	−7.57 ^a	−7.91 ^a	−7.99 ^a	−7.78 ^a
	1.92 ^b	4.02 ^b	4.39 ^b	4.48 ^b	4.52 ^b	4.44 ^b
E_{int}	2.18	−1.17	−0.75	−0.84	−0.84	−0.88

^a One-electron density contribution to polarization. ^b Exchange-correlation density contribution to polarization.

exchange-repulsion and polarization cannot be separated a priori. This entails some problems for the analysis of dispersive interactions.

As an illustrative example, it is well-known that dispersion plays a key role in the stabilization of methane complexes.^{22–24} So, the Hartree–Fock interaction energy for the dimer is 0.52 kcal mol^{-1} , whereas the CCSD interaction energy is $-0.20 \text{ kcal mol}^{-1}$ according to the values collected in Table 2. Looking at the deformation density of Figure 1, one can see that the differences between HF and CCSD plots are negligible, and an explanation of the stabilization of the methane dimer from its deformation energy is not possible, even on a qualitative level.

On the other hand, we can confirm that the stabilization of the methane dimer at the post-SCF level mainly stems from the polarization energy, which is almost zero at the HF level (see values in Table 2). In the new energy partitioning, the deformation density can be separated into deformation density due to Pauli repulsion and deformation density due to electron polarization. Both contributions are represented separately in Figure 2 for the three reference complexes at the HF and CCSD levels. It is clear from these plots that the difference in

**Figure 1.** Total deformation density plots of the methane dimer obtained at the SCF (a) and CCSD (b) levels. Isosurface value is $4 \times 10^{-5} \text{ au}$.

the polarization energy obtained at the post-SCF level, which is associated with dispersion, is also reflected on the deformation density in a larger accumulation of electron density in the intermolecular region.

The effect of dispersion on water and hydrogen fluoride dimers is also significant. Thus, the CCSD polarization energies are around twice the Hartree–Fock energies. However, its effect on the deformation density is negligible for these complexes (see Figure 2). This is due to the large permanent electric dipoles of water and hydrogen fluoride that induce additional large dipoles, which are sufficiently well described even at the HF level. These large induced dipoles overshadow any other possible perturbations of the complex electron density.

It is also interesting to look at the different contributions to the polarization energy separately (see Table 2). Thus, the net complex stabilization due to the electron polarization comes exclusively from the change in the electron–electron and electron–nuclei Coulombic interactions (deformation of the one-electron density), whereas the change in the exchange–correlation energy always results in a destabilization of the complex. Use of correlated methods stresses this trend.

On the other hand, as mentioned before, the Pauli repulsion energy increases at the post-SCF level due to the larger overlapping between the monomers' electron densities. This can also be deduced from the deformation density plots of Figure 2 (see the Pauli repulsion contribution), which reflect a larger depletion of electron density in the intermolecular region at the post-SCF level.

5. CONCLUDING REMARKS AND FUTURE DEVELOPMENTS

An exact partitioning of the intermolecular interaction energy using one-electron and exchange–correlation densities and their deformations upon the complexation process has been presented. The methodology, which can be applied at the SCF and any post-SCF computational level, allows partitioning the interaction energy of an atomic or molecular pair into electrostatic, exchange, repulsion, and polarization terms, without significant computational cost. The slowest computational step is the previous calculation of the corresponding electron density matrices of the unperturbed systems and the complex, which can be done using any quantum chemical program package.

The particular case of weak intermolecular interactions has been treated in detail by comparison with the energy partitioning arising from perturbation methods. Uncorrelated and correlated densities have been analyzed separately, finding that the electrostatic, exchange–repulsion, and induction energy terms are identified with those obtained from the new fragmentation at the SCF and post-SCF levels. We are currently implementing a procedure to separate the induction energy from the dispersion

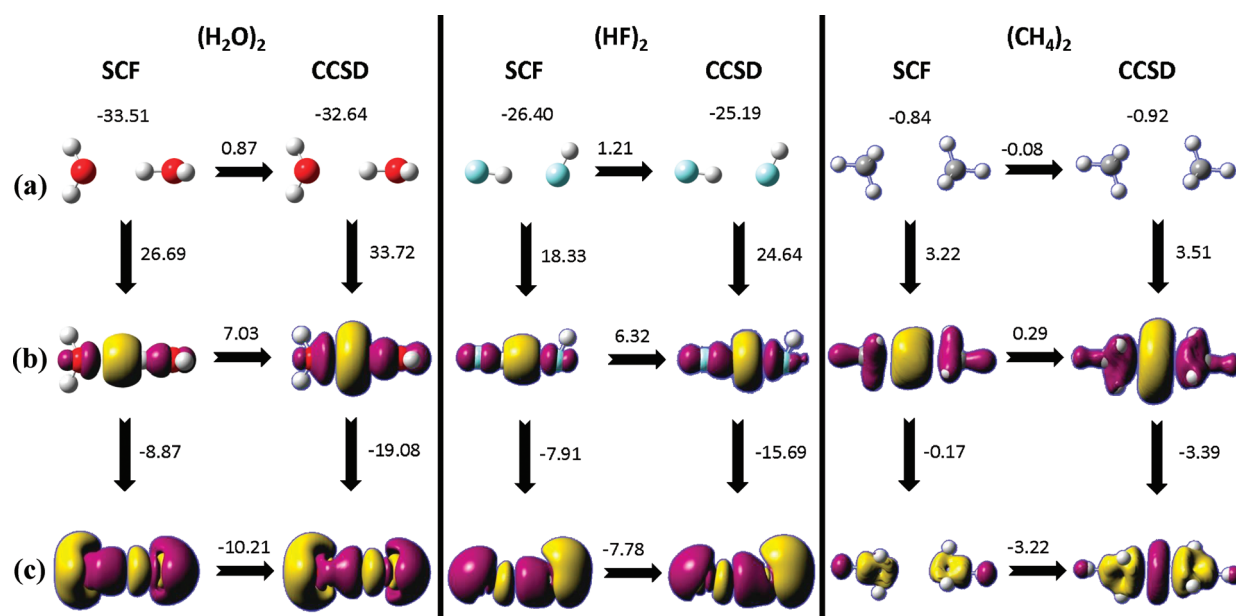


Figure 2. Deformation densities together with the energies (in kJ mol^{-1}) associated with the electrostatic (a), exchange-repulsion (b), and polarization (c) terms for water, hydrogen fluoride, and methane dimers. SCF and CCSD results are shown, and differences between them are indicated on the corresponding horizontal arrow. Isosurface values are 2×10^{-4} au for HF and H_2O and 4×10^{-5} au for CH_4 . All energy values are in kJ mol^{-1} .

energy by merging the second-order RSPT with the new fragmentation scheme.

A bridge between qualitative deformation density plots and quantitative measures of the interaction energy components can be established within the framework of this new partitioning scheme, providing a graphical and very intuitive interpretation of the complex formation.

We are currently extending the method to the case of more than two molecules, which will provide insight into the nature of cooperative effects.

APPENDIX A. CALCULATION OF $\rho_{X,AB}^{\text{HF}}(\vec{r}_1, \vec{r}_2)$ AND $\Delta\rho_{\text{PAULI}}^{\text{HF}}(\vec{r})$

At the HF level, the spin-free two-electron density can be obtained by eq 21:

$$\rho^{\text{HF}}(\vec{r}_1, \vec{r}_2) = \rho^{\text{HF}}(\vec{r}_1)\rho^{\text{HF}}(\vec{r}_2) + \rho_X^{\text{HF}}(\vec{r}_1, \vec{r}_2) \quad (21)$$

where the electron exchange density, $\rho_X^{\text{HF}}(\vec{r}_1, \vec{r}_2)$, represents the difference between the nonconditioned and conditioned probability of finding an electron in r_1 when another electron of the same spin is found in r_2 . In other words, it accounts for the static correlation of the movement of an electron due to the presence of a second electron of the same spin imposed by the Pauli's exclusion principle.

The electron exchange density can be expanded in the spin orbital basis, which for the case of restricted Hartree–Fock calculations and orthogonal basis adopts the form of eq 22:

$$\rho_X^{\text{HF}}(\vec{r}_1, \vec{r}_2) = -2 \sum_{i=1}^{\text{NOO}} \sum_{j=1}^{\text{NOO}} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) \quad (22)$$

where NOO refers to the number of occupied orbitals. In turn, when the orbitals are constructed as a linear combination of a set

of basis functions, χ_{μ} , the electron exchange density can be written as

$$\begin{aligned} \rho_X^{\text{HF}}(\vec{r}_1, \vec{r}_2) &= -2 \sum_{\mu=1}^{\text{NBF}} \sum_{\nu=1}^{\text{NBF}} \sum_{\lambda=1}^{\text{NBF}} \sum_{\sigma=1}^{\text{NBF}} D_{\mu\nu} D_{\lambda\sigma} \chi_{\mu}(\vec{r}_1) \chi_{\lambda}(\vec{r}_2) \chi_{\nu}(\vec{r}_1) \chi_{\sigma}(\vec{r}_2) \end{aligned} \quad (23)$$

where **D** represents the 1-electron reduced density matrix (1-RDM). The matrix elements of the 1-RDM are given by:

$$D_{\mu\nu} = \sum_{i=1}^{\text{NOO}} C_{\mu,i} C_{\nu,i} \quad (24)$$

For the particular case of an unrelaxed intermolecular complex, the electron exchange density can be expressed in terms of the monomers' molecular orbitals and partitioned into three different terms:

$$\begin{aligned} \rho_X^{\text{HF}}(\vec{r}_1, \vec{r}_2) &= -2 \sum_{i=1}^{\text{NOO}_A} \sum_{j=1}^{\text{NOO}_A} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) - 2 \sum_{i=1}^{\text{NOO}_B} \sum_{j=1}^{\text{NOO}_B} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) + \rho_{X,AB}^{\text{HF}}(\vec{r}_1, \vec{r}_2) \end{aligned} \quad (25)$$

The first two terms are the Hartree–Fock intramonomer electron exchange densities (the first two terms in eq 5), whereas the third term is the Hartree–Fock intermolecular electron exchange density. The latter results from the antisymmetrization of the product of unrelaxed wave functions of the monomers and represents the part of the two-electron density due to the electron exchange between different monomers. The calculation of this term from the unrelaxed

orbitals of the monomers has the inconvenience of these two sets of orbitals being nonorthogonal to each other. It is then necessary first to orthogonalize these orbitals in order to get an expression for the electron exchange density equivalent to eq 22. We have employed in this work the Lowdin's *symmetric orthogonalization* procedure.²⁵ Thus, denoting the new set of orthogonal orbitals with the superscript "oo", the electron exchange density can be written as

$$\rho_X^{\text{HF}}(\vec{r}_1, \vec{r}_2) = -2 \sum_{i=1}^{\text{NOO}} \sum_{j=1}^{\text{NOO}} \phi_i^{\text{oo}}(\vec{r}_1) \phi_j^{\text{oo}}(\vec{r}_2) \phi_j^{\text{oo}}(\vec{r}_1) \phi_i^{\text{oo}}(\vec{r}_2) \quad (26)$$

and the intermolecular electron exchange density can be obtained by merging eqs 25 and 26:

$$\begin{aligned} \rho_{X,AB}^{\text{HF}}(\vec{r}_1, \vec{r}_2) = & -2 \sum_{i=1}^{\text{NOO}_A} \sum_{j=1}^{\text{NOO}_B} \phi_i^{\text{oo}}(\vec{r}_1) \phi_j^{\text{oo}}(\vec{r}_2) \phi_j^{\text{oo}}(\vec{r}_1) \phi_i^{\text{oo}}(\vec{r}_2) \\ & + 2 \sum_{i=1}^{\text{NOO}_A} \sum_{j=1}^{\text{NOO}_A} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) \\ & + 2 \sum_{i=1}^{\text{NOO}_B} \sum_{j=1}^{\text{NOO}_B} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) \\ & + 2 \sum_{i=1}^{\text{NOO}_A} \sum_{j=1}^{\text{NOO}_A} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) \\ & + 2 \sum_{i=1}^{\text{NOO}_B} \sum_{j=1}^{\text{NOO}_B} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) \end{aligned} \quad (27)$$

Using basis functions, the intermolecular electron exchange density is then given by

$$\begin{aligned} \rho_X^{\text{HF}}(\vec{r}_1, \vec{r}_2) = & -2 \sum_{\mu=1}^{\text{NBF}} \sum_{\nu=1}^{\text{NBF}} \sum_{\lambda=1}^{\text{NBF}} \sum_{\sigma=1}^{\text{NBF}} (D_{\mu\nu}^{\text{oo}} D_{\lambda\sigma}^{\text{oo}} - D_{\mu\nu}^A D_{\lambda\sigma}^A \\ & - D_{\mu\nu}^B D_{\lambda\sigma}^B) \chi_{\mu}(\vec{r}_1) \chi_{\lambda}(\vec{r}_2) \chi_{\nu}(\vec{r}_1) \chi_{\sigma}(\vec{r}_2) \end{aligned} \quad (28)$$

where the superindex in the 1-RDMs denotes the set of orbitals employed for its calculation and NBF refers to the number of basis functions.

From the orbital orthogonalization proposed above, one can also obtain, in terms of the 1-RDMs, the one-electron deformation density associated to the Pauli repulsion.

$$\Delta \rho_{\text{Pauli}}^{\text{HF}}(\vec{r}) = 2 \sum_{\mu=1}^{\text{NBF}} \sum_{\nu=1}^{\text{NBF}} (D_{\mu\nu}^{\text{oo}} - D_{\mu\nu}^A - D_{\mu\nu}^B) \chi_{\mu}(\vec{r}) \chi_{\nu}(\vec{r}) \quad (29)$$

APPENDIX B. CALCULATION OF $\rho_{X,AB}(\vec{r}_1, \vec{r}_2)$ AND $\Delta \rho_{\text{PAULI}}(\vec{r})$ AT THE POST-SCF LEVEL

Similarly to eq 21, the exchange-correlation density for a closed-shell electron system can be written in general as

$$\rho_{XC}(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1, \vec{r}_2) - \rho(\vec{r}_1) \rho(\vec{r}_2) \quad (30)$$

In turn, the two-electron density, $\rho(\vec{r}_1, \vec{r}_2)$, can be written in terms of the two-electron reduced density matrix (2-RDM) in the space of the basis functions:

$$\rho(\vec{r}_1, \vec{r}_2) = 2 \sum_{\mu=1}^{\text{NBF}} \sum_{\nu=1}^{\text{NBF}} \sum_{\lambda=1}^{\text{NBF}} \sum_{\sigma=1}^{\text{NBF}} D_{\mu\nu\lambda\sigma} \chi_{\mu}(\vec{r}_1) \chi_{\lambda}(\vec{r}_2) \chi_{\nu}(\vec{r}_1) \chi_{\sigma}(\vec{r}_2) \quad (31)$$

where **D** represents here the 2-RDM.

For the strict calculation of $\rho_{X,AB}(\vec{r}_1, \vec{r}_2)$, it is then necessary to compute the matrix elements of the 2-RDMs for the isolated monomers and for the unrelaxed complex. This is not a simple task, especially for large systems. As an alternative to the computation of the 2-RDMs, one can approximate the exchange-correlation densities in terms of natural orbitals and their occupation numbers. In this work, we have chosen the approximate form of the exchange-correlation density derived from the Pauli exclusion principle,²⁶ which was found to provide accurate results in atomic energy calculations.²⁷

$$\rho_{XC}(\vec{r}_1, \vec{r}_2) = -2 \sum_{i=1}^{\text{NNO}} \sum_{j=1}^{\text{NNO}} n_i^{1/2} n_j^{1/2} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) \quad (32)$$

In eq 32, n_i and n_j denote the occupation numbers of the orbitals i and j and NNO refers to the number of natural orbitals.

As in Hartree–Fock, the electron exchange-correlation density for the unrelaxed complex can be expressed in terms of the monomers' natural orbitals and partitioned into three different terms using the expression 32.

$$\begin{aligned} \rho_{XC}(\vec{r}_1, \vec{r}_2) = & -2 \sum_{i=1}^{\text{NNO}_A} \sum_{j=1}^{\text{NNO}_A} n_i^{1/2} n_j^{1/2} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) \\ & - 2 \sum_{i=1}^{\text{NNO}_B} \sum_{j=1}^{\text{NNO}_B} n_i^{1/2} n_j^{1/2} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) \\ & + \rho_{XC,AB}(\vec{r}_1, \vec{r}_2) \end{aligned} \quad (33)$$

In eq 33, the first two terms are the intramonomer electron exchange-correlation densities, and the last term is the intermolecular electron exchange-correlation density. As in Hartree–Fock, the intermolecular term results from the antisymmetrization of the wave function product of the unperturbed monomers and represents the part of the 2-electron density due to the electron exchange between different monomers. However, one must follow a different orthogonalization procedure to that of Hartree–Fock for the calculation of the intermolecular term from the natural orbitals of the monomers. Since the weight of each orbital is given by its occupation number (its square root in this case), one can use a weighted orthogonalization procedure¹³ to get a new set of orthogonalized orbitals. The weighted orthogonalization procedure followed in this work resembles that of Weinhold and co-workers²⁸ and also requires an additional diagonalization of the occupation matrix to get the final set of natural orbitals.²⁹ After the orthogonalization, one gets a transformation matrix that transforms both the orbitals and their occupation numbers. Thus, the exchange-correlation density can be expressed in terms of the new orthogonalized orbitals:

$$\begin{aligned} \rho_{XC}(\vec{r}_1, \vec{r}_2) = & -2 \sum_{i=1}^{\text{NNO}} \sum_{j=1}^{\text{NNO}} (n_i^{\text{oo}})^{1/2} (n_j^{\text{oo}})^{1/2} \phi_i^{\text{oo}}(\vec{r}_1) \phi_j^{\text{oo}}(\vec{r}_2) \phi_j^{\text{oo}}(\vec{r}_1) \phi_i^{\text{oo}}(\vec{r}_2) \end{aligned} \quad (34)$$

where, as in the previous appendix, they are denoted by the superscript “oo”. The intermolecular part is then given by

$$\begin{aligned} & \rho_{XC, AB}(\vec{r}_1, \vec{r}_2) \\ &= -2 \sum_{i=1}^{NNO} \sum_{j=1}^{NNO} (n_i^{oo})^{1/2} (n_j^{oo})^{1/2} \phi_i^{oo}(\vec{r}_1) \phi_j^{oo}(\vec{r}_2) \phi_j^{oo}(\vec{r}_1) \phi_i^{oo}(\vec{r}_2) \\ &+ 2 \sum_{i=1}^{NNO_A} \sum_{j=1}^{NNO_A} n_i^{1/2} n_j^{1/2} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) \\ &+ 2 \sum_{i=1}^{NNO_B} \sum_{j=1}^{NNO_B} n_i^{1/2} n_j^{1/2} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) \end{aligned} \quad (35)$$

In practice, eq 35 is calculated in terms of basis functions:

$$\begin{aligned} \rho_X^{HF}(\vec{r}_1, \vec{r}_2) &= -2 \sum_{\mu=1}^{NBF} \sum_{\nu=1}^{NBF} \sum_{\lambda=1}^{NBF} \sum_{\sigma=1}^{NBF} (1/2 D_{\mu\nu}^{oo} 1/2 D_{\lambda\sigma}^{oo} - 1/2 D_{\mu\nu}^A 1/2 D_{\lambda\sigma}^A - 1/2 D_{\mu\nu}^B 1/2 D_{\lambda\sigma}^B) \\ &\chi_{\mu}(\vec{r}_1) \chi_{\lambda}(\vec{r}_2) \chi_{\nu}(\vec{r}_1) \chi_{\sigma}(\vec{r}_2) \end{aligned} \quad (36)$$

where in general the matrix elements of $1/2 \mathbf{D}$ are given by

$$1/2 D_{\mu\nu} = \sum_{i=1}^{NNO} n_i^{1/2} C_{\mu, i} C_{\nu, i} \quad (37)$$

and $C_{\mu, i}$ represents the coefficient of the basis function μ in the orbital i .

Similar to Hartree–Fock, the post-HF deformation density associated with the Pauli repulsion can be obtained from the weighted orthogonalization procedure as

$$\Delta \rho_{\text{Pauli}}(\vec{r}) = 2 \sum_{\mu=1}^{NBF} \sum_{\nu=1}^{NBF} (D_{\mu\nu}^{oo} - D_{\mu\nu}^A - D_{\mu\nu}^B) \chi_{\mu}(\vec{r}) \chi_{\nu}(\vec{r}) \quad (38)$$

where in general the density matrix elements contain also the corresponding occupation numbers.

$$D_{\mu\nu} = \sum_{i=1}^{NNO} n_i C_{\mu, i} C_{\nu, i} \quad (39)$$

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