

A Hirshfeld Partitioning of the MP2 Correlation Energy: Method and Its Application to the Benzene Dimers

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ABSTRACT: In this work a method is presented for the partitioning of MP2 correlation energies through a grid-space partitioning using the iterative Hirshfeld weight function. The correlation energies are partitioned into mono- and diatomic contributions using two alternative schemes, which allow different levels of parallelization. The method is tested on a set of 24 molecules containing various atoms, leading to the conclusion that, while the numerical results of the two schemes slightly differ, the chemical information contained in them is similar. The method is subsequently applied to the analysis of the interaction energy of three benzene dimers.

1. INTRODUCTION

The appeal in studying the energy of a system lies in its hold on information, such as bonding, stability, and reactivity. The information provided by an energy calculation can be greatly enriched if the total energy can be partitioning into chemically meaningful components. An obvious way of partitioning the energy within a correlated ab initio method is to do it for the Hartree–Fock and correlation energy separately. Since a number of energy partitioning schemes are available for the Hartree–Fock energy,^{1–10} the present paper focuses on the correlation energy partitioning.

Since the energy expression depends on the level of theory, the number and the nature of various contributions differ accordingly. In particular, within the range of the correlated ab initio methods, such as Møller–Plesset¹¹ perturbation theory and coupled clusters,^{12,13} the quality of the energy obtained is determined by the sophistication level of the correlation energy expression. For a closed-shell system, the correlation energy can be expressed through the amplitude τ_{ij}^{ab} in eq 1:

$$E_c = \sum_{ij} \sum_{ab}^{\text{occ virt}} \tau_{ij}^{ab} [2(ia|jb) - (ib|ja)] \quad (1)$$

where i and j denote occupied molecular orbitals, a and b are virtual molecular orbitals, and $(ia|jb)$ are two-electron repulsion integrals. Although this expression is, strictly speaking, of a nonlocalized nature, it is tempting for a chemist to rationalize it in terms of atomic and bond (diatomic) contributions, in order to extract chemical information about the system.

Therefore, several methods have been developed in the past decade for the partitioning of correlation energies.^{14–22} These methods can be divided into two major categories. The first one includes methods based on a population analysis partitioning,^{14–17} where one makes use of the linear combination of atomic orbitals (LCAO) expansion of the molecular orbitals and rewrites eq 1 in terms of a sum over atomic orbitals with common centers, thus partitioning the total correlation energy into a sum of mono- and diatomic contributions.^{14–16} On the other hand, for variational methods such as configuration interaction (CI), the two-electron

energy can be partitioned directly using the second-order density matrix Γ :¹⁷

$$E_{ee} = \sum_{ijkl} \Gamma_{ijkl} (ij|kl) \quad (2)$$

where E_{ee} contains both the correlation energy as well as the two-electron Hartree–Fock energy contributions. The methods of the second category are based on a partitioning in the three-dimensional physical space,^{3,18–21} where the two-electron integrals $(ia|jb)$ are partitioned into mono- or diatomic contributions by inserting the atomic weight functions into the integral. In this case, too, one can make use of either eqs 1¹⁸ or 2.^{19–21}

This broad collection of methods reflects the nonuniqueness of partitioning, which is due to the lack of a quantum mechanical “atomic Hamiltonian” within a molecule. Therefore, none of the wabove-mentioned methods can be a priori declared superior to the others. The usefulness of each method is to be judged by practical criteria, such as the consistency of the results with the chemical knowledge and intuition. For instance, when partitioning the total energies into diatomic contributions, one would desire the values to be comparable with dissociation energies for bonding interactions, to increase with the bond multiplicity, and to provide clearly different values for bonding and nonbonding interactions.

In this work, we propose to partition the correlation energy of the second-order Møller–Plesset method (MP2) through the use of the Hirshfeld method,^{23–25} which has proved to be useful for the analysis of a broad gamma of properties, including the energy at Hartree–Fock⁹ and density functional theory (DFT) levels.²⁶ A short description of the Hirshfeld method, together with the outline of our methodology for the partitioning of the MP2 correlation energy into mono- and diatomic contributions is presented in Section 2, followed by some details on the implementation in Section 3 and by a discussion of the results on a limited set of 24 molecules in Section 4. An application of the method to the interaction energy of three benzene dimers is

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presented in Section 5. Finally, Section 6 contains the summary and the conclusions of this work.

The correlation energy decomposition can be used in two manners. First, for the systems in which the electron correlation essentially determines the molecular structure (such as van der Waals complexes), the decomposition can be applied as such to understand which pairwise interactions are more important than the others. On the other hand, the correlation energy decomposition can be used for any molecule on the top of a suitable Hartree–Fock energy decomposition (for instance, according to ref 9). This gives rise to a total correlated energy decomposition.

2. METHOD

The Hirshfeld method allows to partition molecular properties into atomic contributions through insertion of a normalized weight function into the integral that determines the property in question. For instance, the population of atom A is determined by the following expression:

$$N_A = \int w_A(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} = \int \rho_A(\mathbf{r})d\mathbf{r} \quad (3)$$

where $\rho(\mathbf{r})$ is the molecular density and $w_A(\mathbf{r})$ is the atomic weight function. The total number of electrons is recovered by summation over all the atoms, since the atomic weight functions at each point \mathbf{r} sum to one:

$$N = \sum_A \int w_A(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} = \int \left(\sum_A w_A(\mathbf{r})\right)\rho(\mathbf{r})d\mathbf{r} \quad (4)$$

In the classic version of the Hirshfeld method (H-C),²³ the weight function of each atom is constructed from the free-atom densities $\rho_A^{[0]}(\mathbf{r})$ normalized by a superposition of the free-atom densities of all the atoms in the molecule, referred to as “promolecule”:

$$w_A^{\text{H-C}}(\mathbf{r}) = \frac{\rho_A^{[0]}(\mathbf{r})}{\sum_B \rho_B^{[0]}(\mathbf{r})} \quad (5)$$

These free-atom densities are obtained from a self-consistent field (SCF) calculation on an isolated atom in its spectroscopic ground state with the same basis set as used in the calculation of the electron density of the molecule. This form of a weight function assumes that the atoms within the molecules resemble the free spherically symmetric neutral atoms. Since this choice is somewhat arbitrary, an improved iterative version of the Hirshfeld method (H-I) was developed by Bultinck et al.,²⁵ in which the promolecule is constructed from densities of atoms which resemble actual atoms in the molecule rather than free atoms. This is achieved through an iterative procedure, where the weight function at the n -th iteration is constructed from the atomic densities obtained in the previous iteration:

$$w_A^{[n]}(\mathbf{r}) = \frac{\rho_A^{[n-1]}(\mathbf{r})}{\sum_B \rho_B^{[n-1]}(\mathbf{r})} \quad (6)$$

where $\rho_A^{[n-1]}(\mathbf{r}) = w_A^{[n-1]}(\mathbf{r})\rho(\mathbf{r})$ and $w_A^{[1]}(\mathbf{r}) = w_A^{\text{H-C}}(\mathbf{r})$ is the classic Hirshfeld weight function. Here, $\rho_A^{[n-1]}(\mathbf{r})$ is an atomic

density which integrates to the number of electrons $N_A^{[n-1]}$ calculated in the previous iteration as

$$N_A^{[n-1]} = \int w_A^{[n-1]}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \quad (7)$$

Since $N_A^{[n-1]}$ is generally a noninteger number, this is achieved by interpolating between the densities of atoms with the upper bound integer of $N_A^{[n-1]}$ and the lower bound integer of $N_A^{[n-1]}$ number of electrons. This procedure is repeated until convergence, at which point the converged atomic weight functions become the H-I weight functions. The practical details of the iterative procedure can be found in ref 25.

The partitioning of a two-electron integral can be obtained by inserting the Hirshfeld atomic weight function into the two-electron integral as follows:

$$\begin{aligned} (ia|jb) &= \sum_A (ia|jb)^A \\ &= \sum_A \int w_A(\mathbf{r}_1)\varphi_i(\mathbf{r}_1)\varphi_a(\mathbf{r}_1) \left[\int \frac{\varphi_j(\mathbf{r}_2)\varphi_b(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \right] d\mathbf{r}_1 \end{aligned} \quad (8)$$

The integral in square brackets can be easily evaluated at each gridpoint \mathbf{r}_1 using analytical formulas for nuclear attraction integrals, which allows avoiding double numerical integration. A similar partitioning of the two-electron integral was employed by Imamura et al.¹⁸ However, those authors used the Becke weight function²⁷ rather than the Hirshfeld partitioning. More importantly, Imamura et al. only decompose the amplitude in the correlation energy expression (eq 1), which leads to a correlation energy expressed by a sum of monatomic contributions only. In contrast, we prefer to partition also the two-electron integrals in the second multiplier of eq 1 in order to obtain both mono- and diatomic terms. Eventually, this yields the following MP2 correlation energy partitioning into diatomic contributions $E_{\text{MP2}}^{\text{AB}}$ and monatomic ones $E_{\text{MP2}}^{\text{AA}}$:

$$E_{\text{MP2}} = \sum_A E_{\text{MP2}}^{\text{AA}} + \sum_{A < B} E_{\text{MP2}}^{\text{AB}} \quad (9)$$

where

$$E_{\text{MP2}}^{\text{AB}} = 2 \sum_i^{\text{occ}} \sum_a^{\text{virt}} \sum_j^{\text{occ}} \sum_b^{\text{virt}} \frac{(ia|jb)^A [2(ib|ja)^B - (ib|ja)^B]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (10)$$

and

$$E_{\text{MP2}}^{\text{AA}} = \sum_i^{\text{occ}} \sum_a^{\text{virt}} \sum_j^{\text{occ}} \sum_b^{\text{virt}} \frac{(ia|jb)^A [2(ia|jb)^A - (ib|ja)^A]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (11)$$

Here ε_i is the orbital energy of the i -th molecular orbital. The factor 2 in eq 10 is due to symmetric nature of the expression: $E_{\text{MP2}}^{\text{AB}} = E_{\text{MP2}}^{\text{BA}}$.

A closer look at eq 10 reveals an alternative expression for the $E_{\text{MP2}}^{\text{AB}}$ energy contribution. Indeed, since $(ia|jb) = (ai|bj)^*$, a similar but not equivalent diatomic correlation energy expression $E_{\text{MP2}}^{\text{AB}}$ can be defined:

$$E_{\text{MP2}}^{\text{AB}} = 2 \sum_a^{\text{virt}} \sum_i^{\text{occ}} \sum_b^{\text{virt}} \sum_j^{\text{occ}} \frac{(ai|bj)^A [2(ai|bj)^B - (aj|bi)^B]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (12)$$

The difference between the two definitions lies in the terms $(ib|ja)^B$ and $(aj|bi)^B$, which are not equivalent since the atomic weight function of atom B is inserted in the left-hand side of the integral (eq 8). This involves integration over \mathbf{r}_1 in $\int w_B(\mathbf{r}_1)\varphi_i(\mathbf{r}_1)\varphi_b(\mathbf{r}_1) \int \varphi_j(\mathbf{r}_2)\varphi_a(\mathbf{r}_2)r_{12}^{-1}d\mathbf{r}_2d\mathbf{r}_1$ in the former and in $\int w_B(\mathbf{r}_1)\varphi_a(\mathbf{r}_1)\varphi_j(\mathbf{r}_1) \int \varphi_i(\mathbf{r}_2)\varphi_b(\mathbf{r}_2)r_{12}^{-1}d\mathbf{r}_2d\mathbf{r}_1$ in the latter.

Partitioning the MP2 correlation energy according to eq 10 can be interpreted in terms of pair correlation energies e_{ij} :

$$E_{MP2} = \sum_{ij}^{occ} e_{ij} \quad (13)$$

where

$$e_{ij} = \sum_{ab}^{virt} \frac{(ia|jb)[2(ia|jb)] - (ib|ja)]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (14)$$

$$= \sum_{ab}^{virt} \frac{(ai|bj)[2(ai|bj)] - (aj|bi)]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (15)$$

Partitioning e_{ij} into diatomic contributions according to eq 10 can be regarded as decomposing the i -th occupied orbital to atoms A and B while summing over the occupied j . The alternative expression in eq 12, on the other hand, decomposes i to atom A on the left-hand side of the product in the e_{ij} expression, but both i and j are decomposed to atom B on the right-hand side of the product. From this perspective, eq 12 is less theoretically sound than eq 10 but, as will be shown later, is better suited for parallelization while producing similar results.

Yet another option would be to consistently decompose orbital i to atom A and orbital j to atom B, which leads to the expression:

$$\tilde{E}_{MP2}^{AB} = 2 \sum_i^{occ} \sum_a^{virt} \sum_j^{occ} \sum_b^{virt} \frac{(ia|jb)^A [2(jb|ia)^B - (ja|ib)^B]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (16)$$

However, since expression 16 is considerably more computationally demanding, we will focus on eqs 10 and 12 for the rest of this article.

3. COMPUTATIONAL DETAILS

The calculation of all diatomic contributions in eqs 10 and 12 is computationally demanding, since each of the integrals $(ia|jb)^A$ has to be evaluated numerically. As we would like to be able to apply this method in systems of interest without being overencumbered with size limitations, we implemented an MPI-parallelized code with the following structure (Chart 1):

Chart 1

do i=proc_id,num_occ_orb,numprocs	do a=proc_id,num_virt_orb,numprocs
loop over gridpoints	loop over gridpoints
integrate and store in memory	integrate and store in memory
(ia jb) ^A for all a, j, b and A	(ai bj) ^A for all i, b, j and A
end loop	end loop
calculate E(i,AB)	calculate E(a,AB)
enddo	enddo
reduce all E(i,AB)'s	reduce all E(a,AB)'s

where the left-hand scheme represents parallelization over the occupied molecular orbitals i , according to eq 10, while the right-hand scheme represents parallelization over the virtual molecular orbitals a according to eq 12. Here $E(i,AB)$ and $E(a,AB)$ are the contributions of the i -th molecular orbital into E_{MP2}^{AB} and of the a -th molecular orbital into E_{MP2}^{AB} , respectively.

$$E(i,AB) = (2 - \delta_{AB}) \sum_a^{virt} \sum_j^{occ} \sum_b^{virt} \frac{(ia|jb)^A [2(ia|jb)^B - (ib|ja)^B]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (17)$$

$$E(a,AB) = (2 - \delta_{AB}) \sum_i^{occ} \sum_b^{virt} \sum_j^{occ} \frac{(ai|bj)^A [2(ai|bj)^B - (aj|bi)^B]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (18)$$

The possibility to calculate $E(i,AB)$ and $E(a,AB)$ is the key feature of the parallelization scheme; this cannot be achieved for expressions, such as eq 16. Although the right-hand scheme will always result in a larger total CPU time, the number of numerical integrations to be performed being larger (since there are always more virtuals than occupied), it allows a much higher degree of parallelization. For instance, an ethylene molecule calculated with the aug-cc-pVDZ basis set has 8 occupied and 72 virtual molecular orbitals. In the first version of the method the calculation can be parallelized over a maximum of 8 processes, while in the second version the calculation can be run over 72 processes. In the latter case, the wall-clock time of the calculation will be effectively reduced by a factor of 72 compared to a single-process run of the same code, since the communication needed between the processors is minimal, requiring only the transmission of a symmetric matrix holding the $E(a,AB)$ energies.

The geometries of the 24 small molecules examined in Section 4 were optimized with the Gaussian03²⁸ program at the MP2/aug-cc-pVDZ level. The full MP2 formalism was used throughout the work. The geometries of the three benzene dimers examined in Section 5 are obtained from ref 30, and the interaction energies where calculated using the Gaussian03²⁸ program at the MP2/6-31++G** level. The partitioning of the correlation energies was performed using the STOCK program.²⁴ For the sake of comparison, the Ayala–Scuseria energies¹⁴ were calculated using another program written by the authors.

4. TEST CALCULATIONS

The MP2 correlation energies of a set of 24 molecules were calculated and partitioned using the two alternative methods described above. Table 1 gives the monatomic contributions E_{MP2}^{AA} (eq 10) and E_{MP2}^{AA} (eq 12) to the correlation energies, while Table 2 contains the diatomic contributions E_{MP2}^{AB} and E_{MP2}^{AB} of bonded atoms. The contributions of nonbonded atoms will be discussed at a later stage. For both partitioning schemes, the total correlation energies are reconstructed from eq 9 with an accuracy of 0.01 kcal/mol.

As seen from Table 1, the monatomic values depend strongly on the atom type, getting more negative in the order $H < B < C < N < F < O < Cl$. For a given type of atom, the energies are influenced by the bonding with the neighboring atoms. For instance, the correlation energy of a hydrogen atom becomes less negative for $H(B) > H(C) > H(Cl) > H(N) > H(O) > H(F)$, suggesting that the absolute value of the correlation energy decreases with increasing polarity of the bond. The hybridization

Table 1. Monoatomic Energies $E_{\text{MP2}}^{\text{AA}}$ and $E_{\text{MP2}}^{\text{AA}'} (eqs 10 and 12, respectively)$ Calculated Using the Aug-cc-pVDZ Basis Set^a

	H		B		N		C		O		X	
	$E_{\text{MP2}}^{\text{AA}}$	$E_{\text{MP2}}^{\text{AA}'}$	$E_{\text{MP2}}^{\text{AA}}$	$E_{\text{MP2}}^{\text{AA}'}$	$E_{\text{MP2}}^{\text{AA}}$	$E_{\text{MP2}}^{\text{AA}'}$	$E_{\text{MP2}}^{\text{AA}}$	$E_{\text{MP2}}^{\text{AA}'}$	$E_{\text{MP2}}^{\text{AA}}$	$E_{\text{MP2}}^{\text{AA}'}$	$E_{\text{MP2}}^{\text{AA}}$	$E_{\text{MP2}}^{\text{AA}'}$
BH ₃	−7.90	−7.46	−20.75	−19.72								
B ₂ H ₆	−7.44 (2B)	−7.06 (2B)	−26.46	−26.76								
	−7.95 (1B)	−7.49 (1B)										
CH ₄	−5.79	−5.34					−58.94	−57.58				
C ₂ H ₆	−6.30	−5.84					−59.10	−57.58				
C ₂ H ₄	−6.10	−5.63					−60.69	−59.15				
C ₂ H ₂	−5.23	−4.77					−63.44	−67.81				
C ₆ H ₆	−6.71	−6.22					−65.24	−63.51				
H ₂ O	−2.63	−2.36							−124.13	−123.62		
CH ₃ OH	−6.55(C)	−6.08(C)					−59.79	−52.27	−125.75	−124.97		
	−6.34(C⋯O)	−5.87(C⋯O)										
	−3.17(O)	−2.87(O)										
CH ₃ OCH ₃	−6.76(C)	−6.29(C)					−55.63	−54.09	−128.51	−127.51		
	−6.43(C⋯O)	−5.96(C⋯O)										
H ₂ CO	−6.68	−6.21					−48.11	−46.62	−127.54	−126.67		
HCO ₂ H	−7.01(C)	−6.52(C)					−43.01	−41.58	−129.78	−129.01		
	−2.75(O)	−2.49(O)							−127.39(H)	−126.67(H)		
CO ₂							−37.63	−36.23	−129.61	−128.88		
CO							−45.79	−44.84	−125.48	−124.54		
NH ₃	−3.74	−3.40			−97.85	−96.95						
CH ₃ NH ₂	−6.44(C⋯N)	−5.96(C⋯N)			−98.68	−97.57	−55.89	−54.33				
	−6.70(C)	−6.22(C)										
	−4.62(N)	−3.89(N)										
N ₂ H ₄	−4.40	−4.03			−96.01	−94.82						
cis-N ₂ H ₂	−5.10	−4.68			−92.80	−91.50						
trans-N ₂ H ₂	−4.87	−4.46			−92.88	−91.59						
N ₂					−87.88	−86.53						
HF	−1.90	−1.69									−134.95	−134.74
HCl	−5.11	−4.69									−92.67	−92.24
CH ₃ F	−6.21	−5.75					−51.92	−50.49			−137.71	−137.29
CH ₃ Cl	−6.07	−5.62					−59.75	−58.27			−94.19	−93.64

^a All values are in kcal/mol. H(X) denotes a hydrogen atom bonded with atom X. H(X⋯Y) denotes a hydrogen atom bonded with atom X and sterical interaction with atom Y.

state of the atoms, the hybridization of the neighboring atoms, and the weak interactions also influence the correlation energy, although to a smaller extent. For example, the correlation energy of H increases on going from ethane to acetylene by 1.07 kcal/mol but decreases on going from NH₃ to *cis*-N₂H₂ by 1.44 kcal/mol, when calculated using eq 10. Similar trends are observed for the heavier atoms. For example, the absolute value of the monatomic correlation energy of carbon increases from ethane to acetylene but decreases when going from CH₃OCH₃ to CO₂. These variations are found to correlate strongly for the H atoms with the in the atomic charges calculated with the iterative Hirshfeld method from the MP2 density, as shown in Figure 1, where all hydrogen atoms present the molecules in Table 1 where included. For heavier atoms, the general trend persists but is less pronounced: A value of $R = 0.87$ is found for C atoms and an even lower value for O and N. This is hardly surprising since one cannot expect a straightforward connection between a nonlocal property as correlation and a local property of condensed density. The correlation found for the H atoms can be explained by the fact that the $E_{\text{MP2}}^{\text{H}}$ property can be seen as a special case

among the monatomic correlation energies, since it describes the correlation energy of an atom containing only one electron. This “self-correlating” property can be rationalized as follows: Consider the symmetric H₂ molecule described by a minimal basis set, such that there is only one doubly occupied molecular orbital i and one virtual orbital a . The monatomic correlation energy of atom H₁ is then given by:

$$E_{\text{MP2}}^{\text{H}} = \frac{(ia|ia)^{\text{H}_1}(ia|ia)^{\text{H}_1}}{2(\epsilon_i - \epsilon_a)} \quad (19)$$

Since both of the atoms are symmetric, the weight function of both atoms is identical, and the orbitals are equally delocalized over both atoms, so $E_{\text{MP2}}^{\text{H}_1} = E_{\text{MP2}}^{\text{H}_2}$ and, due to the factor 2 in the definition in eq 10, $E_{\text{MP2}}^{\text{H}_1} = 1/2 E_{\text{MP2}}^{\text{H}_1 \text{H}_2}$. Now consider a hypothetical molecule HX, still in the framework of the minimal basis set, where X still contains only one electron but is more electronegative. Then the orbital i is more localized on X. Evidently, $E_{\text{MP2}}^{\text{H}}$ will decrease and so will the atomic population of H. Thus, an increase in electronegativity of neighboring atoms causes a decrease of the

Table 2. Diatomic Energies $E_{\text{MP2}}^{\text{AB}}$ and $E'_{\text{MP2}}^{\text{AB}}$ (eqs 10 and 12, respectively) Calculated Using the Aug-cc-pVDZ Basis Set^a

	BH		CH		CC		NH		NN	
	$E_{\text{MP2}}^{\text{AB}}$	$E'_{\text{MP2}}^{\text{AB}}$	$E_{\text{MP2}}^{\text{AB}}$	$E'_{\text{MP2}}^{\text{AB}}$	$E_{\text{MP2}}^{\text{AB}}$	$E'_{\text{MP2}}^{\text{AB}}$	$E_{\text{MP2}}^{\text{AB}}$	$E'_{\text{MP2}}^{\text{AB}}$	$E_{\text{MP2}}^{\text{AB}}$	$E'_{\text{MP2}}^{\text{AB}}$
BH ₃	−5.27	−5.96								
B ₂ H ₆	−5.34(1B)	−5.97(1B)								
	−3.90(2B)	−4.15(1B)								
CH ₄			−6.05	−6.73						
C ₂ H ₆			−5.62	−6.30	−7.74	−8.49				
C ₂ H ₄			−5.46	−6.15	−13.65	−15.03				
C ₂ H ₂			−5.01	−5.67	−22.87	−25.21				
C ₆ H ₆			−4.84	−5.53	−9.42	−10.42				
CH ₃ OH			−5.21(C)	−5.94(C)						
			−5.06(C...O)	−5.78(C...O)						
CH ₃ OCH ₃			−5.12(C)	−5.85						
			−5.02(C...O)	−5.73(C...O)						
H ₂ CO			−4.81	−5.57						
HCO ₂ H			−3.97	−4.74						
NH ₃							−5.84	−6.44		
CH ₃ NH ₂			−5.28(C)	−6.01(C)			−5.29	−5.91		
			−5.15(C...N)	−5.85(C...N)						
N ₂ H ₄							−4.96	−5.61	−6.98	−7.97
cis-N ₂ H ₂							−4.71	−5.40	−15.95	−17.71
trans-N ₂ H ₂							−4.55	−5.22	−16.25	−18.04
N ₂									−32.79	−35.48
CH ₃ F			−5.19	−5.92						
CH ₃ Cl			−5.16	−5.86						
	CN		OH		OC		XH		XC	
	$E_{\text{MP2}}^{\text{AA}}$	$E'_{\text{MP2}}^{\text{AA}}$	$E_{\text{MP2}}^{\text{AA}}$	$E'_{\text{MP2}}^{\text{AA}}$	$E_{\text{MP2}}^{\text{AA}}$	$E'_{\text{MP2}}^{\text{AA}}$	$E_{\text{MP2}}^{\text{AA}}$	$E'_{\text{MP2}}^{\text{AA}}$	$E_{\text{MP2}}^{\text{AA}}$	$E'_{\text{MP2}}^{\text{AA}}$
H ₂ O			−5.04	−5.55						
CH ₃ OH			−4.30	−4.84	−6.15	−6.95				
CH ₃ OCH ₃					−4.74	−5.54				
H ₂ CO					−13.69	−15.14				
HCO ₂ H			−3.90	−4.35	−6.44	−7.22				
					−11.48	−12.76				
CO ₂					−12.70	−14.09				
CO					−22.00	−23.89				
CH ₃ NH ₂	−7.60	−8.46								
HF							−4.34	−4.76		
HCl							−6.73	−7.57		
CH ₃ F									−4.58	−5.24
CH ₃ Cl									−7.44	−8.32

^a All values are in kcal/mol.

monatomic correlation energy. Since this picture is too simplistic for heavier atoms, the correlation factor is lower in this case. For carbon atoms, a reasonably strong correlation of $R = 0.96$ (Figure 2) is found between the monatomic correlation energies and the change in atomic population due to correlation, defined as

$$N_{\text{A}}^{\text{corr}} = \int w_{\text{A}}(\mathbf{r})(\rho^{\text{MP2}}(\mathbf{r}) - \rho^{\text{SCF}}(\mathbf{r}))\mathrm{d}\mathbf{r} \quad (20)$$

The diatomic correlation energy contributions depend strongly on the bond multiplicity. The correlation energy varies between 4 and 8 kcal/mol for a single bond, 13 to 18 kcal/mol for

a double bond, and 22 to 25 kcal/mol for a triple bond (or even more for the N₂ molecule) for all the atoms in the examined set of molecules. The value obtained for the C–C bond in benzene is quite encouraging, since it is situated between the value for ethane and ethylene.

The dependence on bond multiplicity can be explained by the energy denominator in eqs 10 and 12. When passing from a single to a double to a triple bond, the diatomic component increases strongly due to a much smaller gap between the π -orbitals compared to that between σ -orbitals. Within the same bond type and multiplicity, the values are influenced by the

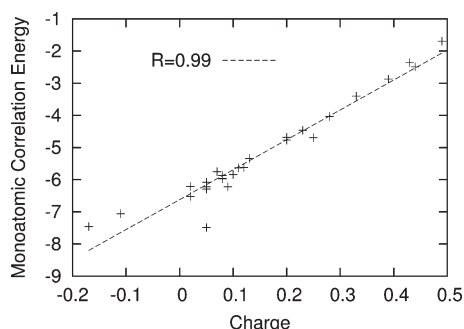


Figure 1. The correlation between the Hirshfeld atomic charge (in au) and the monatomic MP2 correlation energy (in kcal/mol) $E_{\text{MP2}}^{\text{AA}}$ (eq 11) of the H atoms.

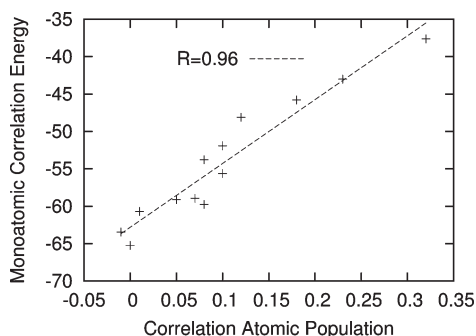


Figure 2. The correlation between the change in the atomic population due to correlation N_A^{corr} (eq 20) (in au) and the monatomic MP2 correlation energy (in kcal/mol) $E_{\text{MP2}}^{\text{AA}}$ (eq 11) of the C atoms.

chemical surrounding. For instance, the absolute values for the C–H bond decrease on going from ethane to acetylene, with the absolute values for methane being larger than for ethane and for benzene lower than for acetylene.

The values calculated using eqs 10 and 12 differ by about 0.5 kcal/mol for the mono- and diatomic energies involving the H atom and up to 3 kcal/mol for correlation energies of the heavier atoms. In general, the monatomic energies $E_{\text{MP2}}^{\text{AA}}$ are slightly less negative than $E_{\text{MP2}}^{\text{AA}}$. Correspondingly, the diatomic energies $E_{\text{MP2}}^{\text{AB}}$ are larger in absolute values than $E_{\text{MP2}}^{\text{AB}}$. Despite these small numerical differences, the trends discussed above are equivalent in both partitioning schemes.

The basis set dependence of the method is summarized in Table 3. Only the mono- and diatomic values calculated using eq 12 are shown, as the basis set dependence of both partitioning schemes is similar. Table 3 also reports the total correlation energy for each basis set. One can see that the MP2 correlation energy is significantly undermined when polarization functions are excluded, while the addition of diffuse functions has only a minor effect. The difference between the Pople double- and triple- ζ basis sets amounts to 20% of the total correlation energy calculated with the triple- ζ basis set, while the values obtained with the aug-cc-pVDZ basis set are situated in between. Comparing the aug-cc-pVDZ values with the values obtained with the largest Pople basis set shows that while the monatomic energies of the former are slightly higher, the diatomic energies are lower. This effect is especially pronounced for the energies of the C, N, and O atoms. Overall, the addition of polarization functions appears to result in the most significant improvement.

In order to compare our scheme with other partitioning techniques, in Table 3 we give the values obtained using the Ayala–Scuseria¹⁴ method, calculated with the 6-31G* basis set. These results indicate that not only the numerical values of the mono- and diatomic energies differ but also, in some cases, the trends as well. For example, the relation between the diatomic correlation energy and the bond multiplicity, as discussed above, is not present in the Ayala–Scuseria method.

In most molecules examined here, the sum of the monatomic energies and diatomic energies of the bonding interactions comprises more than 95% of the total correlation energy. The diatomic contributions between two nonbonded atoms are limited, in absolute values, to less than 0.05 kcal/mol between two H atoms, 0.5 kcal/mol for an H atom interaction with a heavier atom, and 1.0 kcal/mol between two heavier atoms. Three exceptions to this rule are present in the 24 molecules studied here, which concern 2 nonbonding interactions between O atoms in HCO₂H and CO₂ and a nonbonding interaction between B atoms in diborane. The diatomic correlation energies for these three pairs are summarized in Table 4, calculated using various basis sets. While $E_{\text{MP2}}^{\text{OO}}$ for the O···O interaction in both molecules decreases in absolute value with increasing the basis set and may therefore be expected to become less significant at the complete basis set limit, the situation is reversed for the B···B interaction. This is probably related to an exchange interaction, which also emerges indirectly in bond orders between nonbonded X···Z atoms in the case of three-center two-electron X–Y–Z bonds.³¹

5. INTERACTION ENERGY OF BENZENE DIMERS

In the previous section we have demonstrated that both schemes (eqs 10 and 12) provide chemically meaningful mono- and diatomic correlation energies. In this section we will focus on applying the method to benzene dimers. The energetics of this system is largely determined by dispersion interaction, which cannot be correctly described neither by Hartree–Fock nor by most density functionals. As mentioned in Section 2, the scheme based on eq 10 is theoretically more sound. However, since the scheme based on eq 12 is much more easily parallelizable, and in light of the quality of the results obtained in the previous section, the CPU-intensive calculations on the benzene dimers were carried out within the second scheme.

The structures of three benzene dimers in the sandwich, parallel displaced, and T-shaped configurations are shown in Figure 3. The geometries optimized at QCISD(T)/aug-cc-pVTZ level were taken from ref 30. The calculations of the MP2 correlation energy were performed using the 6-31++G** basis set. Since the MP2 method overestimates dispersion interaction in the benzene dimer³² and the 6-31++G** basis set is not large enough to fully reproduce the correlation energy, the results only represent a qualitative picture of the interaction energy of these dimers. This qualitative picture is, however, sufficient for our goal, since the chemical information that can be obtained from a partitioning method is confined in the trends, rather than the exact values. For each of the geometries, the total MP2 energy was calculated for the dimer and for each of the monomers using the BSSE correction. Since Tables 1 and 2 already report values of the total mono- and diatomic correlation energies of benzene, we will discuss only the contribution of correlation energy to the interaction energy of the dimers. Table 5 lists the interaction energy at Hartree–Fock and MP2 levels as well as the contributions of the monatomic correlation energies (E^{C} and E^{H}), the intramolecular diatomic correlation

Table 3. Mono- and Diatomic Correlation Energies Calculated Using eq 12 with Various Basis Sets^a

	6-31G	6-31G**	6-31++G**	6-311	6-311G**	6-311++G**	aug-cc-pVDZ	Ayala–Scuseria
CH ₄								
C	−38.59	−60.14	−59.86	−50.69	−70.42	−69.65	−57.58	−55.42
H	−3.25	−4.93	−5.15	−3.45	−5.2	−5.45	−5.34	−5.15
CH	−2.74	−6.13	−6.12	−2.83	−6.56	−6.53	−6.73	−6.84
total	−63.09	−105.56	−106.27	−76.40	−118.84	−119.04	−107.56	−105.56
C ₂ H ₆								
C	−39.46	−59.59	−60.01	−57.78	−69.93	−69.97	−57.58	−55.32
H	−3.72	−5.62	−5.63	−3.93	−5.87	−5.93	−5.84	−6.93
CC	−2.37	−7.19	−7.32	−2.65	−8.38	−8.25	−8.49	−9.99
CH	−2.55	−5.87	−5.87	−2.65	−6.20	−6.19	−6.30	−6.93
total	−119.87	−198.03	−199.50	−147.00	−224.16	−224.58	−200.73	−198.04
C ₂ H ₄								
C	−41.00	−60.56	−61.27	−53.73	−71.15	−71.50	−59.15	−61.23
H	−3.67	−5.43	−5.43	−3.86	−5.65	−5.69	−5.63	−4.95
CC	−7.89	−14.14	−13.88	−7.95	−14.90	−14.65	−15.03	−8.22
CH	−2.38	−5.69	−5.66	−2.48	−6.00	−5.97	−6.15	−7.04
total	−115.59	−181.85	−183.05	−142.43	−206.19	−206.74	−183.15	−181.85
NH ₃								
N	−60.17	−93.43	−95.33	−74.97	−108.85	−109.71	−96.95	−85.55
H	−2.01	−3.06	−3.25	−2.10	−3.11	−3.40	−3.40	−4.38
NH	−2.46	−5.79	−5.78	−2.65	−6.06	−6.01	−6.44	−6.89
total	−73.86	−120.55	−123.03	−89.51	−136.96	−138.57	−127.24	−120.55
N ₂ H ₄								
N	−61.71	−91.74	−93.73	−76.12	−106.49	−107.92	−94.82	−87.39
H	−2.53	−3.87	−3.83	−2.68	−3.95	−3.98	−4.03	−4.46
NN	−1.08	−6.81	−7.00	−1.34	−7.37	−7.21	−7.97	−7.78
NH	−1.99	−5.22	−5.12	−2.17	−5.40	−5.29	−5.61	−6.34
total	−143.21	−228.48	−232.46	−173.71	−259.84	−262.46	−238.97	−228.47
HCO ₂ H								
H(C)	−4.28	−6.56	−6.37	−4.52	−6.77	−6.60	−6.52	−5.12
H(O)	−1.72	−2.49	−2.36	−1.77	−2.48	−2.43	−2.49	−3.69
C	−29.41	−43.65	−44.28	−41.00	−52.04	−52.67	−41.58	−49.64
O	−85.57	−117.58	−120.42	−102.95	−140.48	−142.39	−129.06	−118.69
O(H)	−81.76	−115.84	−118.29	−98.66	−139.36	−140.97	−126.67	−111.07
CO(1)	−1.61	−6.64	−6.81	−1.64	−6.65	−6.68	−7.22	−6.07
CO(2)	−6.96	−12.45	−12.10	−6.81	−12.44	−12.10	−12.76	−8.43
CH	−1.96	−4.82	−4.54	−1.92	−4.83	−4.60	−4.74	−5.98
OH	−1.30	−4.05	−3.99	−1.47	−4.03	−3.95	−4.35	−5.82
total	−217.05	−316.77	−322.15	−263.35	−371.85	−375.38	−338.79	−316.77

^a The rightmost column lists the values obtained with the Ayala–Scuseria (ref 14) method with the 6-31G** basis set.

energies ($E_{\text{intra}}^{\text{CC}}$, $E_{\text{intra}}^{\text{HH}}$ and $E_{\text{intra}}^{\text{CH}}$) and the intermolecular diatomic correlation energies ($E_{\text{inter}}^{\text{CC}}$, $E_{\text{inter}}^{\text{HH}}$ and $E_{\text{inter}}^{\text{CH}}$) to the interaction energies. These quantities are defined as follows

$$E^{\text{A}} = E_{\text{MP2}}^{\text{AA}}(\text{dimer}) - E_{\text{MP2}}^{\text{AA}}(\text{monomer}) \quad (21)$$

$$E_{\text{intra}}^{\text{AB}} = E_{\text{MP2}}^{\text{AB}}(\text{dimer}) - E_{\text{MP2}}^{\text{AB}}(\text{monomer}) \quad (22)$$

$$E_{\text{inter}}^{\text{AB}} = E_{\text{MP2}}^{\text{AB}}(\text{dimer}) \quad (23)$$

The calculations were performed according to eq 12.

As seen from Table 5, the correlation energy is essential for correct description of the bonding in the benzene dimers. The interaction energies of all three configurations are positive when calculated using the Hartree–Fock method. The MP2 method predicts the parallel-displaced configuration to be the most stable with an interaction energy of −2.24 kcal/mol, followed by the sandwich configuration with an interaction energy of −2.02 kcal/mol, and the T-shaped configuration with an interaction energy of −1.43 kcal/mol. This order is in agreement with the QCISD-(T)/aug-cc-pVTZ interaction energy reported by Janowski et al.,³⁰ although our MP2/6-31++G** values are somewhat

Table 4. Significant Diatomic Correlation Energies (in kcal/mol) between Nonbonding Atoms Calculated Using eqs 10 and 12

	6-31G	6-31G**	6-31++G**	6-311	6-311G**	6-311++G**	aug-cc-pVDZ
OO(HCO ₂ H)	−1.69(−1.79)	−1.33(−1.41)	−1.44(−1.55)	−1.79(−1.70)	−1.36(−1.43)	−1.45(−1.55)	−1.61(−1.73)
OO(CO ₂)	−6.66(−6.34)	−4.03(−4.05)	−3.94(−3.99)	−6.59(−6.27)	−4.02(−4.05)	−3.93(−3.97)	−3.83(−3.90)
BB(B ₂ H ₆)	−1.93(−2.19)	−3.70(−4.15)	−3.90(−4.37)	−1.97(−2.28)	−4.02(−4.16)	−4.18(−4.68)	−4.11(−4.59)

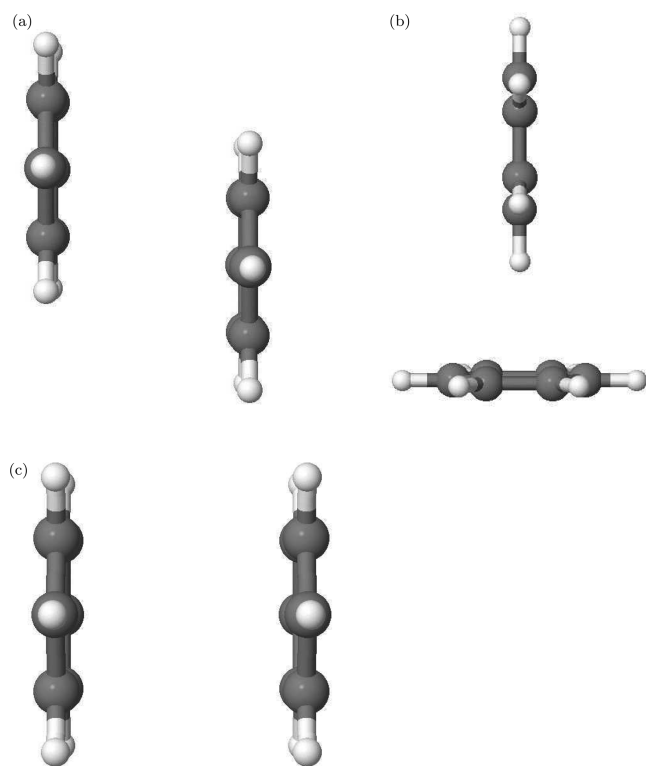


Figure 3. Three benzene dimers used in this work.

underestimated due to a limited basis set size. The MP2 correlation energy is found to be the highest in the parallel displaced dimer and the lowest in the T-shaped dimer, despite the fact that the largest overlap between the π -orbitals is present in the sandwich dimer.

The partitioned correlation energy reveals that due to dispersion interaction in the dimer, the intramolecular diatomic contributions are partially shifted to the monatomic contributions. For example, in the parallel-displaced dimer, the monatomic correlation energies increase by up to 11.4 kcal/mol per benzene moiety, while the diatomic correlation energies within a benzene moiety decrease by up to 6.7 kcal/mol. The net change in correlation energy within a moiety is negative, amounting to an average 80% of the total correlation energy contribution to the interaction energy. The rest of the correlation energy is assigned to the intermolecular diatomic correlation energies. The largest values are found for the C–C interactions in the parallel displaced and sandwich dimers and the C–H interactions in the T-shaped dimer.

Since the physical phenomenon responsible for the negative interaction energy of the benzene dimers is the dispersion interaction between the electronic densities of the two benzene moieties, we are especially interested in the distribution of the pairwise interactions from which these intermolecular correlation

Table 5. Interaction Energies of Three Benzene Dimers Calculated at the Hartree–Fock (E^{HF}) and MP2 (E^{MP2}) Levels of Theory with the 6-31++G** Basis Set and the Contributions of the Monoatomic Correlation Energies (E^{C} and E^{H}), the Intramolecular Diatomic Correlation Energies ($E_{\text{intra}}^{\text{CC}}$, $E_{\text{intra}}^{\text{HH}}$, and $E_{\text{intra}}^{\text{CH}}$), and the Intermolecular Diatomic Correlation Energies ($E_{\text{inter}}^{\text{CC}}$, $E_{\text{inter}}^{\text{HH}}$, and $E_{\text{inter}}^{\text{CH}}$) to the Interaction Energies^a

	parallel displaced	sandwich	T-shaped
E^{HF}	3.69	3.51	1.02
E^{MP2}	−2.24	−1.43	−2.02
E^{corr}	−5.94	−4.95	−3.04
E^{C}	−9.59	−8.08	−5.55
E^{H}	−1.84	−1.58	−1.56
sum	−11.44	−9.67	−7.12
$E_{\text{intra}}^{\text{CC}}$	4.44	3.69	3.10
$E_{\text{intra}}^{\text{HH}}$	0.03	0.02	0.02
$E_{\text{intra}}^{\text{CH}}$	2.20	1.77	1.69
sum	6.67	5.48	4.81
$E_{\text{inter}}^{\text{CC}}$	−0.74	−0.53	0.05
$E_{\text{inter}}^{\text{HH}}$	−0.06	−0.03	−0.07
$E_{\text{inter}}^{\text{CH}}$	−0.39	−0.22	−0.73
sum	−1.19	−0.78	−0.74

^a Calculated with eqs 21–23. All values are in kcal/mol.

energy contributions consist. These values contain the most important information on the nature of the intermolecular dispersion interaction. The small values are in agreement with the recent findings of Contreras-García et al.³³ that the region of the noncovalent dispersion interaction was found to lie between the two monomers, where the electron density ρ is smaller than 0.02 au and the reduced gradient $|\nabla\rho| \cdot \rho^{-4/3}$ is greater than 0.7 au. As discussed in Section 4, small values of electron density inevitably lead to relatively small intermolecular diatomic correlation energy contributions.

The sum of the intermolecular correlation energy contributions is the largest in the parallel-displaced dimer, which is the most stable dimer of the three configurations examined here. Figure 4 illustrates the major pairwise interactions between the three symmetrically nonequivalent carbon and hydrogen atoms. The strongest intermolecular interactions (solid lines on Figure 4) total to −0.06 kcal/mol and occur between carbon atoms separated by 3.6 Å. Interactions of −0.03 kcal/mol (dotted lines on Figure 4) which occur between carbon atoms separated by an average of 3.9 Å and between carbon and hydrogen atoms separated by an average 3.5 Å. The weakest interactions shown here are −0.02 kcal/mol and occur between carbon atoms separated by 4.2 Å. In the sandwich dimer, where one has only one symmetrically nonequivalent carbon and hydrogen atoms, the strongest intermolecular interactions of −0.03 kcal/mol are

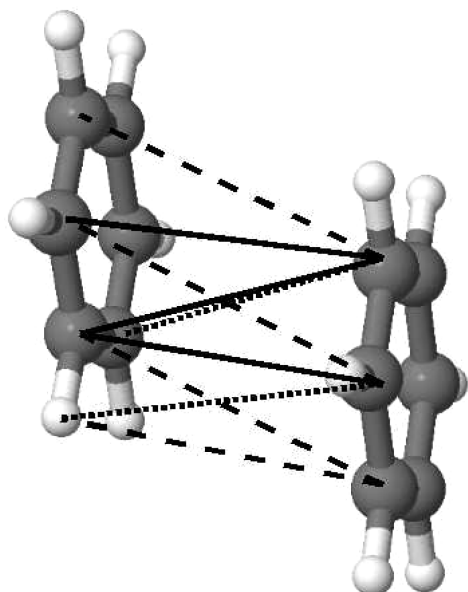


Figure 4. Main intermolecular pairwise interactions $E_{\text{inter}}^{\text{AB}}$ (eq 23) in the parallel-displaced benzene dimer. Strongest interactions (≥ -0.06 kcal/mol) are represented by solid lines, intermediate interactions (-0.03 kcal/mol) are dotted lines, and the weakest interactions (< -0.02 kcal/mol) are shown by dashed lines.

found between two nearest carbon–carbon atoms, which are separated by 3.9 \AA . The second strongest interaction of -0.02 kcal/mol is found between a carbon atom and its two neighbors, separated by 4.2 \AA . The intermolecular interactions between the carbon and hydrogen atoms are all smaller than -0.01 kcal/mol, and as in the case of parallel-displaced dimer, no significant interactions are found between the hydrogen atoms. In the T-shaped, most of the intermolecular interaction energy can be attributed to the six C–H interactions between the H atom of the upper benzene monomer in Figure 2, which is closest to the lower benzene monomer, and the six C atoms in the lower monomer. Each of these six interactions amounts to -0.1 kcal/mol, almost twice as strong as the strongest C–C interaction in the parallel-displaced monomer. The strong interaction is in accordance with the short C–H distance, which amounts to 2.8 \AA . The clear connection between the distance and the intermolecular diatomic interactions is in correspondence with the known R^{-6} dependence of the dispersion interaction.

6. SUMMARY AND CONCLUSIONS

In conclusion, we have proposed a method for partitioning of MP2 correlation energy using the Hirshfeld method. It can be used either on the top of an existing Hartree–Fock energy decomposition or on its own right. Two alternative partitioning schemes were presented, with one of the schemes having a better theoretical foundation but the other allowing a better degree of parallelization. In spite of different formulations, both schemes produce only slightly different numerical results but show the same trends for diatomic and monatomic energies. The correlation energy partitioning can be either performed on its own right or done as a complement to an existing Hartree–Fock energy partitioning, which results in a partitioning of the total correlated energy.

The basis set dependence of the partitioning method is similar to that of the MP2 method itself: A limited basis set was found to undermine the energies, while including polarization functions leads to a major improvement. The monatomic correlation energies were found to depend strongly on the type of the atom. For hydrogen, the monatomic correlation energy is in line with the atomic charge. This does not hold for heavier atoms. The diatomic energies for bonded atoms depend mostly on the bond multiplicity and reflect the strength of the bond between the two atoms. The diatomic contributions of non-bonding interatomic interactions are found to be negligible in most cases, with exception of systems where exchange interactions between nonbonding atoms are present.

Finally, the method was applied for the analysis of the interaction energies of benzene dimers. The intermolecular interactions were found to be determined mainly by the distance between the atoms, with C–C interactions being stronger than C–H interactions for equal distance and H–H interactions being always negligible.

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