Comparison of semiempirical and ab initio QM decomposition analyses for the interaction energy between molecules

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Abstract

A decomposition analysis of the interaction energy of molecular complexes using both semiempirical (PM3) and ab initio methods shows major differences. Whereas electrostatic stabilization accounted for a significant part of the interaction by ab initio theory, the electrostatic energy in semiempirical theory was mainly repulsive. This difference has major implications for intuitive models of intermolecular interactions, particularly in light of recent AM1 and PM3 energy decomposition calculations suggesting that charge transfer and polarization provides the binding energy of molecular clusters, including protein-solvent systems. © 2002 Published by Elsevier Science B.V.

1. Introduction

The idea of decomposing the QM energy of intermolecular systems into physically meaningful quantities has its origins in chemical intuition [1]. Terms such as electrostatic, repulsion, delocalization, charge transfer, polarization and dispersion are used to describe movements of electronic charge density that may occur when molecules interact and the nature of forces that are binding the molecules together. However, there is no unique way to divide the total energy of interaction of molecular complexes into these various components. The methods pioneered by Morokuma [2,3] have assigned Hartree–Fock wavefunctions to most of these terms (except for dispersion which is a correlation effect). However, later methods [4,5] gave rise to different definitions for many of these terms. The differences between these methods decrease as the molecules are moved further apart, and are apparent mainly for strong intermolecular interactions such as H bonds or donor–acceptor

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complexes [6]. Recently, van der Vaart and Merz [7] defined a scheme whereby the total interaction energy (E_{int}) is the sum of only three terms, electrostatic, polarization and charge transfer:

$$E_{int} = E_{ele} + E_{pol} + E_{ct}. \tag{1}$$

A unique feature of this approach is that, unlike the former wavefunction-based decomposition schemes, it can be applied to the semiempirical MNDO, AM1 and PM3 methods [8–10] in addition to density functional and ab initio methods. It is also linear scaling so it can be applied to large systems such as proteins. Within the semiempirical AM1 and PM3 approximations the scheme has been applied to small H-bonded bimolecular complexes and large water clusters [7]. It was also used to analyse the interactions between solvent water and a protein [11]. In each case the electrostatic component (E_{ele}) was predicted to be positive, i.e. this scheme suggests that electrostatic models cannot provide any binding energy for the intermolecular interactions being considered. This result is surprising, as it appears to be at variance with the general conclusion obtained from modelling studies and energy decomposition analysis based on ab initio calculations [12–20], and with recent experience in the development of hybrid semiempirical QM and molecular mechanics methods [21,22].

There have been a number of detailed studies [23–25] comparing the semiempirical and ab initio methods, and attempts have been made to specifically correct the semiempirical methods for various H-bonding scenarios [26–29]. The main conclusion from these studies is that for many H-bonded systems a semiempirical approach can be found that compares well with accurate ab initio calculations. However, the underlying semiempirical approximation itself remains prone to unsystematic errors and is, therefore, not always reliable. To our knowledge, there appears to have been no direct comparison of electrostatic interactions between molecules in the semiempirical and ab initio methods based on energy decomposition schemes. In order to determine whether the results obtained by van der Vaart and Merz [7,11] were likely an artefact of the semiempirical methods used, we have conducted a comparative

semiempirical (PM3) and ab initio study on a number of H-bonded and donor–acceptor systems. We also briefly discuss the possible origins of any such differences.

2. Methods

Consider two discrete molecules A and B with V_{AB} as the Hamiltonian for the coulomb interaction of the electrons and nuclei on molecule A with those of molecule B. As a starting point, energy decomposition schemes usually consider the interaction of the two molecules with monomeric wavefunctions [6] to obtain the electrostatic component (E_{ele}) of the interaction energy. Note that as the monomeric wavefunctions are assumed to be unchanged on interaction there is no intermixing of the molecular orbitals on A and B. The expectation value of V_{AB} in terms of the monomeric wavefunctions Ψ_A^0 and Ψ_B^0 is then given by

$$E_{ele} = \langle \Psi_A^0 \Psi_B^0 | V_{AB} | \Psi_A^0 \Psi_B^0 \rangle. \tag{2}$$

This expression is of course equivalent to the coulomb interaction between two classical charge densities $\rho_A = \Psi_A^0 \Psi_A^0$ and $\rho_B = \Psi_B^0 \Psi_B^0$. In semiempirical methods where an explicit form of the wavefunction is not defined for the purposes of computing matrix elements of the various terms in the Hamiltonian, a different approach has to be taken. One approach is that developed by van der Vaart and Merz [7] specifically designed for, though not limited to, large systems such as proteins. In the present work we are only concerned with small bimolecular complexes and so have opted for using a rather more simplified scheme.

If in the semiempirical method $\mathbf{W}$ is the array of two-center two-electron repulsion integrals and $\mathbf{S}$ is the overlap matrix of atomic orbitals (assumed orthogonal), then setting $\mathbf{W}_{AB} = \mathbf{0}$ and $\mathbf{S}_{AB} = \mathbf{0}$ (i.e. zero matrix elements between atomic orbitals of A and B) ensures that the Fock matrix connecting A and B, $\mathbf{F}_{AB}$, is zero and hence we obtain $\mathbf{P}_{AB} = \mathbf{0}$ for the corresponding density matrix between A and B. Note that as the two-center core-electron attractions and core–core repulsions are also expressed in terms of elements of the electron repulsions, $\mathbf{W}_{AB} = 0$ ensures that there are no

coulomb interactions between molecules A and B. We can then compute the SCF density matrix for the non-interacting monomers at any intermolecular separation, i.e. the monomers will have the same density matrix as if they were infinitely separated. If we obtain such a density ($\mathbf{P}^0$) at the equilibrium separation of the two molecules in the complex, we can compute the electrostatic contribution to the binding energy simply as

$$E_{ele} = E(\mathbf{W}_{AB}, \mathbf{P}^0) - E(\mathbf{W}_{AB} = \mathbf{0}, \mathbf{P}^0), \tag{3}$$

where $E(\mathbf{W}_{AB}, \mathbf{P}^0)$ is the total energy calculated using $\mathbf{P}^0$, and $E(\mathbf{W}_{AB} = \mathbf{0}, \mathbf{P}^0)$ gives the total energy of the non-interacting molecules. Using $\mathbf{P}^0$, only the coulomb integrals contribute to the interaction between monomer charge densities, and Eq. (3) can be expressed in terms of the electron–core and electron–electron (E_{elec}) and core–core (E_{core}) interaction terms

$$E_{ele} = E_{elec} + E_{core}, \tag{4}$$

$$\begin{aligned} E_{elec} = &\sum_{\mu \in A} \sum_{v \in A} P^0_{\mu v} \sum_{i \in B} -Z_i(\mu v | s_i s_i) \\ &+ \sum_{\mu \in B} \sum_{v \in B} P^0_{\mu v} \sum_{i \in A} -Z_i(\mu v | s_i s_i) \\ &+ \sum_{\mu \in A} \sum_{v \in A} P^0_{\mu v} \sum_{\lambda \in B} \sum_{\sigma \in B} P^0_{\lambda \sigma}(\mu v | \lambda \sigma), \end{aligned} \tag{5}$$

$$E_{core} = \sum_{i \in A} \sum_{j \in B} Z_i Z_j (s_i s_i | s_j s_j) g(R_{ij}), \tag{6}$$

where Z are the core charges (nuclei plus inner shell electrons), $(\mu v | \lambda \sigma)$ are the usual two-center two-electron integral approximations, and $g(R_{ij})$ is a function of the interatomic distance [8,9].

In the present study we need not be concerned with the individual definitions of polarization, charge transfer or exchange repulsion, as these are known to depend strongly on the decomposition scheme [6]. Indeed, due to the lack of an explicit wavefunction, it is doubtful whether all of these terms can be adequately defined within semiempirical theory. However, given the definition of the electrostatic term in Eqs. (2) and (3), these remaining terms can be combined into a single energy which may be called the deformation term. This deformation term is due to rearrangement of electrons when molecules A and B interact and includes all exchange effects, polarization of the monomers, and charge transfer between A and B. Also, for the purposes of this comparison between semiempirical and ab initio methods, it is not necessary to consider the effect of changes in the monomer geometries or electron correlation on complex formation. The complex geometries were first fully optimized to obtain the total energy $E_{complex}$ and a total interaction energy computed as

$$E_{int} = E_{complex} - E_{monomers}, \tag{7}$$

where the monomers' energy $E_{monomers}$ was calculated at the optimized geometries in the complex. Thus, we do not need to consider the optimized geometries for the non-interacting monomers. By definition, the change in energy due to deformation of the electronic charge density in the complex is then given by

$$E_{def} = E_{int} - E_{ele}. \tag{8}$$

Although our focus will be primarily on the analysis of the electrostatic interaction, there is another factor which affects the ab initio results for the total energy difference (E_{int}) and, hence, E_{def}, namely the BSSE [30]. This factor needs to be considered whenever atomic orbital basis sets are used to calculate the energies of molecular complexes. This correction does not apply to the semiempirical methods, and, therefore, should be taken into account when comparing the two approaches. We have estimated the BSSE in the ab initio calculations using a standard counterpoise (ghost-orbital) correction [30].

The semiempirical calculations were carried out using MOPS [31]. In the present work we report only results using the PM3 method, as the AM1 method is expected to behave similarly. The GA-MESS program [32] was used for the ab initio calculations at the Hartree–Fock level using the 6-31+G** basis set.

3. Results and discussion

The results of the energy decomposition analysis for the H-bonded systems are given in Table 1. As expected in the case of H-bonded systems, electrostatic interactions at the ab initio (HF/

Table 1
PM3 and ab initio HF/6-31+G** energy decomposition analysis (kcal/mol) for the H-bonded complexes

H-bonded $A \cdots B$	E_{ele}		E_{def}		E_{int}	
	PM3[a]	6-31+G**	PM3	6-31+G**	PM3	6-31+G**
$N_2 \cdots HF$	3.3 (0.0)	−2.0	−3.4	0.6	−0.1	−1.4
$N_2 \cdots HCN$	0.2 (0.0)	−1.0	−0.8	0.2	−0.6	−0.8
$N_2 \cdots HNC$	0.2 (0.0)	−1.6	−1.0	0.4	−0.8	−1.2
$HCN \cdots HF$	8.4 (−5.2)	−9.1	−12.8	2.7	−4.4	−6.4
$HCN \cdots HCN$	8.6 (−4.0)	−5.8	−13.0	1.4	−4.4	−4.4
$HCN \cdots HNC$	8.8 (−4.3)	−7.9	−13.9	2.0	−5.1	−5.9
$H_2O \cdots H_2O$	7.5 (−4.4)	−8.9	−10.3	3.8	−2.8	−5.1
$CH_3NH_2 \cdots H_2O$	10.7 (−5.0)	−11.5	−13.5	5.4	−2.8	−6.1
$CN^- \cdots HF$	3.8 (−14.7)	−35.7	−22.1	9.7	−18.3	−26.0
$CN^- \cdots HCN$	4.1 (−15.2)	−28.0	−29.8	6.0	−25.7	−22.0
$HO^- \cdots HF$	−2.5 (−24.9)	−49.3	−21.5	9.8	−24.0	−39.5
$HO^- \cdots HCN$	−2.6 (−22.9)	−49.9	−29.2	11.4	−31.8	−38.5
$HS^- \cdots HCN$	4.7 (−20.9)	−16.5	−27.1	0.9	−22.4	−15.6
$Cl^- \cdots H_2O$	10.2 (−16.3)	−16.8	−28.3	4.0	−18.1	−12.8
$CH_3NH_3^+ \cdots H_2O$	0.5 (−14.0)	−22.9	−13.3	5.1	−12.9	−17.8
$CH_3COO^- \cdots H_2O$	2.0 (−16.7)	−27.0	−17.9	7.5	−15.9	−19.5
$CH_3COO^- \cdots C(NH_2)_3^+$	−67.1 (−114.3)	−143.1	−54.7	20.9	−121.8	−122.2

[a] Results in parentheses are coulomb interaction energies calculated from an atomic-charge model for the monomers in the PM3 approximation.

6-31+G**) level provide a large contribution to the binding energy. The remainder term E_{def} tends to be much smaller and is always positive, due to the inclusion of the Pauli repulsions. This is in stark contrast to the semiempirical (PM3) results, which are qualitatively similar to the results obtained by van der Vaart and Merz [7,11] in that the coulombic energy of interaction is usually a repulsive term. The binding in the semiempirical approxi-

mation then comes mainly from the deformation terms. The electrostatic component is significantly negative only for the interaction between ion pairs [$CH3COO^- \cdots C(NH_2)_3^+$], although it is only half the magnitude of the corresponding ab initio term. In the donor–acceptor systems also (Table 2), the electrostatic interactions calculated at the ab initio level provide an important contribution to the binding energy. However, the remainder term is

Table 2
PM3 and ab initio HF/6-31+G** energy decomposition analysis (kcal/mol) for the donor–acceptor complex

Donor–acceptor $A \cdots B$	E_{ele}		E_{def}		E_{int}	
	PM3[a]	6-31+G**	PM3	6-31+G^{**b}	PM3	6-31+G^{**c}
$BH_3 \cdots NH_3$	121.8 (−15.4)	−89.9	−191.3	57.4 (55.1)	−57.0	−32.5
$BH_3 \cdots PH_3$	97.4 (−9.3)	−64.1	−182.9	42.3 (41.1)	−85.5	−21.8
$BH_3 \cdots AsH_3$	80.8 (−4.4)	−53.3	−121.6	37.0 (31.9)	−40.8	−16.3
$AlH_3 \cdots NH_3$	41.0 (−13.6)	−67.8	−106.7	38.1 (36.7)	−65.7	−29.7
$AlH_3 \cdots PH_3$	55.2 (−14.2)	−35.0	−126.2	20.4 (20.1)	−71.0	−14.6
$AlH_3 \cdots AsH_3$	17.3 (−2.3)	−31.4	−51.3	22.2 (17.4)	−34.0	−12.2
$GaH_3 \cdots NH_3$	25.9 (3.0)	−71.1	−148.9	48.9 (43.8)	−123.0	−22.2
$GaH_3 \cdots PH_3$	49.5 (18.1)	−41.1	−348.0	29.8 (25.8)	−298.5	−11.3
$GaH_3 \cdots AsH_3$	61.7 (3.4)	−40.3	−224.6	31.1 (21.4)	−162.9	−9.2

[a] Results in parentheses are coulomb interaction energies calculated from an atomic-charge model for the monomers in the PM3 approximation.
[b] Corrected for BSSE. The uncorrected results are given in parentheses.
[c] Corrected for BSSE.

much larger than in the H-bonded complexes, reflecting stronger Pauli repulsions. This does not mean that the polarization and charge transfer types of effects are negligible. It is well known that polarization and charge transfer also contribute to the binding energy of molecular complexes [6]. Note, however, that the BSSEs, which only affect E_{int} and hence E_{def}, lead to an over estimation of the charge transfer effect. In the present calculations using the 6-31+G** basis, BSSE corrections of < 0.5 kcal/mol for non-ionic complexes and up to 1 kcal/mol for H-bonded complexes involving ionic species were obtained. In relative terms, corrections of these magnitudes are not very significant for the H-bonded systems. However, the BSSEs for the donor–acceptor complexes ranged from as little as 0.3 kcal/mol for $AlH_3 \cdots PH_3$ up to as high as 10 kcal/mol for $GaH_3 \cdots AsH_3$. The BSSE-corrected E_{int} and E_{def} values are given in Table 2. Thus, although the counterpoise method [30] gives only a rough estimate of the BSSE correction, for many of the donor–acceptor complexes the effects of charge transfer on the interaction energy are predicted to be significantly less than the uncorrected results for E_{def} in Table 2, further emphasising the relative importance of electrostatic stabilization.

As a further test of the semiempirical method, we computed E_{ele} from a simple atomic-charge representation of the monomers. The results are given in parentheses under E_{ele} in Tables 1 and 2. The atomic charges were obtained using a method [33] based on a least-squares fit to the semiempirical (PM3) approximation of the molecular electrostatic potential (MEP). Clearly, if the MEP reflects a realistic molecular-charge distribution we would expect a degree of stabilization from the coulomb energy of interaction between the MEP-derived atomic charges. The charge model results in Tables 1 and 2 show such stabilization except for complexes involving GaH_3. At the PM3 level, the Ga atom is incorrectly predicted to have a negative partial charge, and, hence, we obtain a repulsive coulomb interaction from the atomic-charge model for the GaH_3 complexes. Note also the energy for the N_2 complexes (Table 1) for this model is formally zero due to zero atomic charges for the N_2 molecule.

It is clear from the results presented in Tables 1 and 2 that there are large discrepancies between semiempirical and ab initio electrostatic interaction terms. The question then is what are the likely origins of these differences? To the extent that both represent interactions between molecules with frozen charge densities, i.e. the molecules' charge distributions at infinite separation, Eqs. (2) and (3) are analogous. However, whether the coulomb integrals, Eq. (5), bear direct comparison with the ab initio ones is questionable [34]. Note that in the semiempirical approximation the two-center coulomb integrals themselves assume simple parametric forms and contain contributions due to parameterization of the semiempirical Hamiltonian, i.e. their values may be modified to compensate for other approximations. For example, the semiempirical Fock matrix implicitly assumes an orthonormal atomic orbital (OAO) basis. Although orthogonalization affects atomic orbitals, and, hence, integrals and Fock matrix elements, it is largely neglected in the MNDO, AM1 and PM3 methods. As these effects appear to be important and cannot be fully corrected in the parameterization of these methods, additional terms need to be included in the Fock matrix elements to be properly described in a OAO basis. These orthogonalization corrections are particularly important for obtaining a correct description of the one-electron two-center resonance terms and valence–core interactions [35]. The parameters in these empirically-based QM methods are thus highly interrelated, depending on the underlying approximations, and consequently individual terms may bear little relationship to corresponding ab initio quantities.

To investigate the origin of the large deformation term E_{def} in the semiempirical method (Table 1), we have partitioned the total energy into intramolecular $(E_A + E_B)$ and intermolecular (E_{AB}) contributions for molecules A and B in the H-bonded complexes. This partition is exact in semiempirical methods as the energy can be expressed rigorously in terms of one- and two-center atomic contributions. Thus E_{AB} can be interpreted as an interaction energy, analogous to E_{int}, Eq. (7). The interaction energy E_{AB} can be further partitioned into resonance (J), exchange (K) and cou-

Table 3
PM3 resonance (J), exchange (K) and coulomb (C) components of the intermolecular energy E_{AB} (kcal/mol), and the total binding energy ΔE_{bind} (kcal/mol), for H-bonded A $\cdots$ B complexes

H-bonded A $\cdots$ B	J	K	C	E_{AB}[a]	ΔE_{bind}[b]
$N_2 \cdots HF$	−6.5	−1.4	3.3	−4.6	−0.06
$N_2 \cdots HCN$	−1.5	−0.3	0.1	−1.7	−0.63
$N_2 \cdots HNC$	−1.7	−0.3	0.1	−2.0	−0.74
$HCN \cdots HF$	−24.6	−6.8	9.1	−22.3	−4.2
$HCN \cdots HCN$	−24.9	−7.8	9.2	−23.5	−4.1
$HCN \cdots HNC$	−26.2	−8.1	9.4	−24.9	−4.8
$H_2O \cdots H_2O$	−20.2	−3.9	7.5	−16.6	−2.8
$CH_3NH_2 \cdots H_2O$	−26.1	−7.3	11.2	−22.2	−2.6
$CN^- \cdots HF$	−38.9	−13.6	10.8	−41.7	−17.4
$CN^- \cdots HCN$	−49.0	−20.2	11.4	−57.8	−23.1
$HO^- \cdots HF$	−36.3	−9.8	0.4	−45.8	−23.4
$HO^- \cdots HCN$	−43.9	−13.8	−3.9	−61.5	−29.8
$HS^- \cdots HCN$	−46.4	−13.7	4.2	−55.9	−20.6
$Cl^- \cdots H_2O$	−50.7	−15.0	16.5	−49.1	−16.8
$CH_3NH_3^+ \cdots H_2O$	−24.5	−6.2	2.2	−28.4	−12.7
$CH_3COO^- \cdots H_2O$	−32.2	−8.7	6.2	−34.7	−15.4
$CH_3COO^- \cdots C(NH_2)_3^+$	−87.3	−33.4	−38.6	−159.4	−118.5

[a] $E_{AB} = J + K + C$ (at optimized complex geometry).
[b] $\Delta E_{bind} = E_{complex} - E_{monomers}$ ($E_{complex}$ at optimized complex geometry and $E_{monomers}$ at optimized monomer geometry); ($\Delta E_{bind} - E_{AB}$) = change in monomer energies on complex formation.

lomb (C) terms. These components are given in Table 3 for the relaxed charge density (**P**) in the H-bonded complexes. Note that if the monomer (unrelaxed) charge densities (**P**^{0}) are used, J and K are zero and the coulomb term (C) corresponds exactly to E_{ele} defined by Eq. (3). Indeed, the coulomb terms in Table 3 are found to be qualitatively similar to E_{ele} in Table 1, i.e. mostly positive. Thus, polarization of the monomer charge densities does not appear to account for the large deformation contribution. Also, comparing E_{int} in Table 1 with ΔE_{bind} in Table 3 it can be seen that relaxing the monomer geometries in the complex has a relatively small effect on the interaction energy. It is clear from the results in Table 3, however, that the resonance (R) terms contribute most to the deformation energy, with the exchange (K) terms also making a significant contribution.

4. Conclusions

The present study of the electrostatic interaction between molecules has revealed critical differences between the semiempirical and ab initio QM results. It would appear that recent energy decomposition calculations [7,11] based on semiempircal methods place too much emphasis on the importance of reorganization of electronic charge (polarization and charge transfer) at the expense of electrostatic stabilization that arises from the interaction between monomeric charge densities. In the present work we found that the semiempirical QM coulomb terms are very often repulsive, whereas, we stress, it is known from accurate ab initio calculations that electrostatics should provide a significant binding energy contribution. We also found that the large electronic reorganization energy that provides the H-bonding energy in the semiempirical method arises predominantly from the resonances terms. Consequently, we conclude that the semiempirical methods are not generally suitable for the decomposition analysis of intermolecular interactions into physically meaningful terms.

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