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# The origin of deficiency of the supermolecule second-order Møller-Plesset approach for evaluating interaction energies

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Calculations for the complex of thymine and adenine are used to show that the supermolecule second-order Møller-Plesset perturbation theory (MP2) approach for evaluating interaction energies fails in certain cases because of the behavior of one of its components: the uncoupled Hartree-Fock dispersion energy. A simple approach for correcting the MP2 supermolecule interaction energies is proposed. It focuses on correcting a relatively small difference between the MP2 and coupled cluster interaction energies, which is a very appealing feature of the new approach considering a benchmark role played by coupled cluster results. © 2007 American Institute of Physics.

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Despite its limitations, second-order Møller-Plesset perturbation theory (MP2) remains an important approach for evaluating interaction energies, particularly of large molecules for which high-level calculations can be extremely time consuming. However, since it is known that the MP2 approach fails for certain important classes of intermolecular complexes and since high-level calculations can be prohibitively time consuming in certain cases, the only way to obtain any results is to use an approximate method, which corrects the deficiencies of the MP2 approach. To our knowledge, no such approach has been proposed so far, although we should mention recent attempts to develop methods based on density-functional theory (DFT) that could perform better than MP2. For example, Johnson and Becke<sup>1</sup> highlight the fact that their approach “performs twice as well as basis-set extrapolated MP2 theory for dispersion-bound complexes, with minimal computational cost.” Hesselmann *et al.*<sup>2</sup> also showed that for stacked configurations of nucleic acid bases, a combination of DFT and symmetry-adapted perturbation theory (SAPT) performs better than the MP2 method. Johnson and Becke, as well as Hesselmann *et al.*, were clearly concerned with the development of the DFT approaches rather than with answering the question about the origin of failure of the MP2 approaches. Nonetheless, the development of a reliable DFT approach could benefit from the explanation of why, in certain cases, the MP2 results are very similar to high-level calculations, but in other cases are different.

In this communication we will use the results for both stacked and hydrogen bonded configurations of the thymine-adenine complex to first illustrate the limitation of the MP2 approach and then to explain them. Stacked configurations of nucleic acid bases are examples of dispersion-bound complexes for which the MP2 approach fails. Interestingly, however, the MP2 approach works very well for the hydrogen bonded configurations of nucleic acid bases. To our knowledge, there have been no attempts to explain why a method

works well for one geometry, but fails for another geometry of the same complex.

All geometries considered here can be easily generated using the procedure described in Ref. 3 and monomer geometries that can be found on the Internet (<http://pubs.acs.org>) as supporting information for Ref. 3. In every case, the center of mass of the thymine molecule is at the origin of Cartesian coordinates. Hydrogen bonded geometries are obtained by placing the center of mass of adenine on the  $x$  axis at a distance  $R$ , and using the following Euler angles to rotate the two bases: thymine,  $\phi=75^\circ$ ,  $\theta=180^\circ$ , and  $\chi=0^\circ$  and adenine,  $\phi=0^\circ$ ,  $\theta=180^\circ$ , and  $\chi=0^\circ$ . For the stacked configurations of the complex, all Euler angles are set to zero, and the center of mass of adenine is placed on the  $z$  axis at a distance  $R$ .

The supermolecule MP2 interaction energies ( $\Delta E^{\text{MP2}}$ ) as well as the supermolecule results obtained by using single and double excitation coupled-cluster theory with noniterative treatment of triple excitations [CCSD(T)] [ $\Delta E^{\text{CCSD(T)}}$ ] are given in Table I. All results were obtained with the 6-31G\*(0.25) basis set,<sup>4</sup> which was small enough so that the CCSD(T) calculations could be performed. All interaction energies and their components were obtained by using the

TABLE I. The supermolecule MP2 and CCSD(T) interaction energies (in kcal/mol) obtained with the 6-31G\*(0.25) basis set for the indicated configurations of the thymine-adenine complex.

Method	Stacked	H bonded
	$R=3.00 \text{ \AA}$	$R=5.50 \text{ \AA}$
MP2	-6.11	19.13
CCSD(T)	-2.69	20.19
	$R=3.40 \text{ \AA}$	$R=6.15 \text{ \AA}$
MP2	-8.95	-11.91
CCSD(T)	-7.10	-12.07
	$R=5.00 \text{ \AA}$	$R=7.00 \text{ \AA}$
MP2	-2.09	-5.89
CCSD(T)	-1.82	-6.04

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basis set of the entire complex. Calculations were performed with MOLPRO 2000 (Ref. 5) and TRURL 98 (Ref. 6) packages.

We emphasize that the CCSD(T) calculations for the T-A complex even in a basis set such as 6-31G\*(0.25) are very time consuming. This should become more apparent when the cost of the iterative CCSD calculations or the noniterative triples is considered. It is well known that the most expensive step of the latter correction scales as  $o^3v^4$ , where  $o$  and  $v$  denote the number of occupied and virtual orbitals. Using the frozen-core approximation to speed up the calculations results in  $o=49$  and  $v=220$ . To perform a comparable calculation, for example, for the water dimer ( $o=8$ ),  $v$  would have to be equal to 856. Even if a large basis set, such as aug-cc-pV5Z, was used for the water dimer  $v$  would only be 564. We also stress that the use of the 6-31G\*(0.25) basis set allowed us to compare our approximate methods with rigorous CCSD(T) results, unlike the CCSD(T) interaction energies that can be found, for example, in Ref. 2, which are only estimates based on large basis set MP2 calculations and smaller basis set CCSD(T) calculations. Such an approximation is not always a good one, as everyone can easily verify by running a few tests.

For each configuration we present the results for three distances which represent three points on the one-dimensional potential energy cuts through the multidimensional potential energy surfaces. The middle distance corresponds to an approximate minimum on the one-dimensional potential energy curve so, obviously, the shortest distance represents a point on the repulsive inner wall, and the longest distance represents a point on the outer wall of the curve. As can be seen, the MP2 and CCSD(T) results for the H-bonded configuration differ only slightly. On the other hand, the results for stacked configurations clearly show that the MP2 approach overestimates the attractive interaction, although at longer distances the MP2 and CCSD(T) curves approach one another. It is well known that for stacked configurations the interaction energy is attractive because of the dispersion energy, but at longer distances, the electrostatic energy becomes more important than the dispersion energy.

Ideally, the explanation of the differences between the MP2 and CCSD(T) results should be achieved by using a rigorous energy partitioning procedure. Unfortunately, to our knowledge, such a procedure is not yet available for the CCSD(T) approach. The differences between  $\Delta E^{\text{MP2}}$  and  $\Delta E^{\text{CCSD(T)}}$  at long distances can be analyzed by comparing properties of the separate molecules at these two levels of theory, but this should not be confused with the rigorous partitioning of the interaction energy. Of importance is the fact that the MP2 calculation is the starting point of the CCSD(T) procedure, so one has to try to understand the nature of the relatively small difference between the two approaches. On the other hand, in DFT approaches do not share any similarities with the CCSD(T) method. In this work the CCSD(T)-MP2 difference will be analyzed in terms of the dipole polarizabilities, dispersion coefficients, and eventually nonexpanded dispersion energies.

In Table II, we present the values of the three diagonal components of dipole polarizabilities ( $\alpha$ ) of thymine and adenine obtained with the 6-31G\*(0.25) basis set. Of particular

TABLE II. Diagonal components of dipole polarizability (in  $e^2a_0^2E_h^{-1}$ ) obtained with the 6-31G\*(0.25) basis set and the indicated methods.

Method	Component		
	xx	yy	zz
Thymine			
UCHF	78.57	71.09	44.88
TDHF	93.09	74.81	40.14
MP2	101.05	78.35	41.14
CCSD(T)	100.64	78.18	41.06
Adenine			
UCHF	99.69	92.08	48.68
TDHF	105.77	89.62	40.95
MP2	111.39	97.75	41.82
CCSD(T)	110.65	96.88	41.86

importance is the difference between the uncoupled Hartree-Fock (UCHF) and the time-dependent Hartree-Fock (TDHF) values of the perpendicular (zz) component of polarizability. This difference tells us about the importance of the response effects which in the present case are clearly more important than the correlation effects which can be gauged by comparing the difference between the TDHF and MP2 or CCSD(T) results. The shortcomings of the UCHF approach for evaluating dipole polarizabilities are well known, but the method and how it compares to more sophisticated approaches are of interest because the nonexpanded UCHF dispersion energy contributes to the supermolecule  $\Delta E^{\text{MP2}}$ .<sup>7</sup> The fact that the UCHF value of  $\alpha_{zz}$  is visibly greater than the values obtained with the other three methods contributes to the deficiency of the MP2 approach for describing stacking interactions. However, it is not the most important effect.

A better understanding of dispersion interactions is accomplished by evaluating dispersion coefficients. We do not give them explicitly, although, of course, they are available upon request, but mention only the asymptotic ratio of the expanded UCHF/TDHF dispersion energies evaluated for the H bonded and stacked configurations described earlier. These ratios are 1.237 for the H bonded and 1.358 for the stacked configuration, so at very long distances the UCHF dispersion energies are significantly greater in magnitude than the TDHF results. It is clear that static polarizabilities alone do not predict such a significant effect, particularly for the H-bonded configuration, so, obviously, frequency dependence of polarizabilities also plays an important role.

Unfortunately, neither the dipole polarizabilities in Table II nor the asymptotic dispersion energies fully explain the trends that we observe for the supermolecule results in Table I, although we do have an explanation of why the MP2 approach overestimates the magnitude of the attractive stacking interactions. This starts with the wrong description of the perpendicular (zz) component of polarizability by the UCHF approach, is then magnified for dispersion coefficients and, not surprisingly, is also observed for supermolecule results. What remains unclear is why the effect at distances given in Table I is smaller than the asymptotic one for the stacked configurations and why for the H-bonded configurations the MP2 and CCSD(T) results are so similar.

TABLE III. The nonexpanded UCHF ( $\epsilon_{\text{disp}}^{\text{UCHF}}$ ) and TDHF ( $\epsilon_{\text{disp}}^{\text{TDHF}}$ ) dispersion energies (in kcal/mol) obtained with the 6-31G\*(0.25) basis set for the indicated configurations of the thymine-adenine complex.

Method	Stacked	H bonded
	$R=3.00 \text{ \AA}$	$R=5.50 \text{ \AA}$
$\epsilon_{\text{disp}}^{\text{UCHF}}$	-26.04	-23.95
$\epsilon_{\text{disp}}^{\text{TDHF}}$	-20.91	-21.93
	$R=3.40 \text{ \AA}$	$R=6.15 \text{ \AA}$
$\epsilon_{\text{disp}}^{\text{UCHF}}$	-13.24	-6.68
$\epsilon_{\text{disp}}^{\text{TDHF}}$	-10.45	-6.40
	$R=5.00 \text{ \AA}$	$R=7.00 \text{ \AA}$
$\epsilon_{\text{disp}}^{\text{UCHF}}$	-1.41	-1.60
$\epsilon_{\text{disp}}^{\text{TDHF}}$	-1.02	-1.50

A satisfactory explanation of these problems is achieved only when we evaluate the nonexpanded dispersion energies. In Table III, we present the UCHF and TDHF nonexpanded dispersion energies found for the same configurations that we considered in Table I.

As can be seen, the UCHF ( $\epsilon_{\text{disp}}^{\text{UCHF}}$ ) and TDHF ( $\epsilon_{\text{disp}}^{\text{TDHF}}$ ) nonexpanded dispersion energies are much closer to each other compared to the asymptotic ratios given earlier. Smaller UCHF/TDHF ratios of nonexpanded dispersion energies at short distances and the fact that they slowly increase to the asymptotic ratios imply an important role of higher-rank polarizabilities as well as the penetration effects. The latter were recently shown to play a very important role for electrostatic interactions,<sup>8</sup> but they are as important for dispersion interactions.

The modification of the UCHF/TDHF ratio for the non-expanded dispersion energies is much greater for the H-bonded configurations. For example, at  $R=6.15 \text{ \AA}$  the UCHF/TDHF ratio is only 1.044 compared to the asymptotic value of 1.237. For the stacked configuration at  $R=3.40 \text{ \AA}$ , the ratio is 1.267 compared to the asymptotic value of 1.358. These results give us a hint that the dispersion energy is the origin of the differences between the MP2 and CCSD(T) approaches, because the trend is similar to that found for the supermolecule results given in Table I. A simple replacement of  $\epsilon_{\text{disp}}^{\text{UCHF}}$  in  $\Delta E^{\text{MP2}}$  by the corresponding  $\epsilon_{\text{disp}}^{\text{TDHF}}$  value, improves agreement with  $\Delta E^{\text{CCSD(T)}}$  only for stacked configurations. However,  $\epsilon_{\text{disp}}^{\text{TDHF}}$  is not a precise component of  $\Delta E^{\text{CCSD(T)}}$ . The unknown CCSD(T) dispersion energy,  $\epsilon_{\text{disp}}^{\text{CCSD(T)}}$  has not been calculated so far, but, fortunately, we could use the estimated CCSD(T) dispersion coefficients which were recently reported for the nucleic acid bases<sup>9</sup> to try to estimate it. We make the assumption that the unknown  $\epsilon_{\text{disp}}^{\text{CCSD(T)}}$  behaves like  $\epsilon_{\text{disp}}^{\text{TDHF}}$  rather than  $\epsilon_{\text{disp}}^{\text{UCHF}}$ . The estimated  $\epsilon_{\text{disp}}^{\text{CCSD(T)}}$  is obtained by scaling  $\epsilon_{\text{disp}}^{\text{TDHF}}$  by the asymptotic CCSD(T)/TDHF ratio evaluated for a specific configuration by using dispersion coefficients. For the 6-31G\*(0.25) basis set, the asymptotic CCSD(T)/TDHF ratios are 1.061 for the stacked configuration and 1.068 for the H-bonded configuration. The reader can easily verify that by subtracting  $\epsilon_{\text{disp}}^{\text{UCHF}}$  given in Table III from the supermolecule MP2 results given in Table I and then adding to that difference  $\epsilon_{\text{disp}}^{\text{TDHF}}$  from

TABLE IV. The estimated CCSD(T) interaction energies (in kcal/mol) obtained by replacing the UCHF dispersion energy in the supermolecule  $\Delta E^{\text{MP2}}$  by a scaled TDHF dispersion energy.

Method	Stacked	H bonded
	$R=3.00 \text{ \AA}$	$R=5.50 \text{ \AA}$
CCSD(T)	-2.26	19.67
	$R=3.40 \text{ \AA}$	$R=6.15 \text{ \AA}$
CCSD(T)	-6.80	-12.07
	$R=5.00 \text{ \AA}$	$R=7.00 \text{ \AA}$
CCSD(T)	-1.76	-5.90

Table III, scaled by either 1.061 or 1.068, we do get the results presented in Table IV. As can be seen, the estimated  $\Delta E^{\text{CCSD(T)}}$  given in Table IV are in much better agreement with the actual CCSD(T) results presented in Table I than the MP2 results. A very similar estimated  $\epsilon_{\text{disp}}^{\text{CCSD(T)}}$  can be obtained by assuming that the difference between the supermolecule MP2 and CCSD(T) results is due to the difference between dispersion energies. By adding the difference between  $\Delta E^{\text{CCSD(T)}}$  and  $\Delta E^{\text{MP2}}$  to  $\epsilon_{\text{disp}}^{\text{UCHF}}$ , we obtain  $\epsilon_{\text{disp}}^{\text{CCSD(T)}}$  which is very similar to the one obtained by scaling  $\epsilon_{\text{disp}}^{\text{TDHF}}$  by the asymptotic CCSD(T)/TDHF ratio.

Our calculations for other systems such as water, methane, or benzene dimers, as well as the rare gas dimers, also allow us to explain why in certain cases the MP2 and CCSD(T) results are so similar, while in other cases they are so different. In all cases the dispersion energy plays a decisive role in the explanation of the observed trend. We also performed calculations for the same configurations of the cytosine-guanine complex as Hesselmann *et al.*<sup>2</sup> and our approach produces results in better agreement with the estimated  $\Delta E^{\text{CCSD(T)}}$  than the SAPT-DFT approach.<sup>2</sup> With the aug-cc-pVDZ basis set, the results (in kcal/mol) are follows: H-bonded configuration, -28.69 (MP2), -29.15 [estimated CCSD(T)], -28.14 (SAPT-DFT), and -29.98 (new approach) and stacked configuration, -18.53 (MP2), -16.71 [estimated CCSD(T)], -15.69 (SAPT-DFT), and -16.30 (new approach). Of importance is the fact that for the H-bonded configuration the MP2 approach performs better than SAPT-DFT, although, of course, some caution is needed as comparison is made with the estimated CCSD(T) results. These results provide an additional illustration that our approach is promising and the idea that the difference between the supermolecule MP2 and CCSD(T) interaction energies is, at least in some cases, due to the difference in dispersion energy, deserves further exploration.

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