New Intermolecular Benchmark Calculations on the Water Dimer: SAPT and Supermolecular Post-Hartree–Fock Approaches

P. REINHARDT,[1,2] J.-P. PIQUEMAL[1,2]

[1]*Laboratoire de Chimie Théorique, UPMC Univ Paris 06, UMR 7616, Case Courrier 137, 4 Place Jussieu, F-75005 Paris, France*

[2]*Laboratoire de Chimie Théorique, CNRS, UMR 7616, Case Courrier 137, 4 Place Jussieu, F-75005 Paris, France*

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ABSTRACT: In this contribution, we propose accurate intermolecular benchmarks for the 10 standardized water dimers initially proposed by van Duijneveldt et al., following a study by Smith et al. (J Chem Phys, 1990, 92, 1240). Using the popular triple-zeta aug-cc-pVTZ basis set, symmetry-adapted perturbation theory (SAPT) computations have been performed and compared with supermolecular post-Hartree–Fock techniques up to most recent explicitly correlated methods. Effects of approximated inclusion of third-order corrections to induction and exchange-induction energies are discussed. As SAPT results are close to the best available ab initio ones, detailed analysis of the available individual SAPT contributions to the interaction energy confirms that electron correlation acts not only on its long-range dispersion part but also on its separated physical components. This permits to assess the validity of the usual HF+Dispersion model as approximation to add pure correlation effects to orbital-based interaction schemes. The study proposes extensive benchmark data in a Supporting Information part to provide useful data for the development and the test of new force field energy functions for water. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 109: 3259–3267, 2009

Key words: energy decomposition scheme; intermolecular interaction energy; force fields; electronic correlation; water dimer

Correspondence to: J.-P. Piquemal; e-mail: jpp@lct.jussieu.fr or P. Reinhardt; e-mail: peter.reinhardt@upmc.fr

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1. Introduction

Within the past recent years, intermolecular energy decomposition analysis (EDA) schemes [1–11] have been shown to be very useful techniques to design new generation molecular mechanics potentials ([12–19] and references therein). Indeed, following a "bottom up" approach [15, 19], each one of the different physical components of the interaction energy can be unraveled giving solid grounds for the reparametrization of existing force fields or the definition of new functional forms. In 2003, van Duijneveldt et al. [20], using the double zeta IOM basis set [21], proposed a series of EDA benchmarks for the water dimer [22] based on 10 standardized geometries extracted from a high-level correlated potential energy surface, calculated by Smith et al. [22(a)]. According to the authors, such set should be the perfect test to evaluate the accuracy of existing force fields and their ability to accurately reproduce the different components of the interaction energy. In this contribution, we propose to come back to these water dimers, still using state of the art EDA techniques but coupled to a larger triple-zeta basis set, namely the popular au-cc-pVTZ [23]. Indeed, this basis set has been used recently ([17, 24] and references therein) by several groups to build accurate water models including the polarizable AMOEBA water model [25]. We propose here a detailed analysis of the components of the interaction energy using the symmetry-adapted perturbation theory (SAPT) approach [3] up to coupled cluster singles and doubles (CCSD) corrections.

Beyond the detailed SAPT analysis, we present reference data for supermolecular post-Hartree–Fock (HF) calculations as well, ranging from second-order perturbation theory to most recent explicitly correlated methods. With these reference data at hand, we may assess the validity of approximate interaction schemes as the HF+Dispersion (HFD) approach [26, 27].

The further organization of the article is the following: after a brief exposition of the systems, the used methods, and notations, we will focus on several characteristic results and give an index to the Supporting Information (available in the online version of this article). The HFD model is discussed in a separate section, and all purely technical details are collected in an appendix.

2. Systems, Methods, and Definitions

2.1. CHARACTERIZATION OF THE DIMER SYSTEMS

The 10 dimer geometries have been selected by Smith et al. [22(a)] and van Duijneveldt et al. [20] as extremal points of the total-energy surface of the water dimer system. The most stable configuration actually known was obtained and studied with a different objective by Klopper et al. [28] and is not part of the present set. The same holds for the water dimer in the benchmark S22 dimer set of Hobza and coworkers [29]. The first of the present 10 structures is quite close to these two.

All the dimer systems are depicted in Figure 1. The first three ones present a classical hydrogen bond with one hydrogen atom pointing to the oxygen of the other water molecule. Systems 6 to 10 are symmetric orientations, and system No. 4 and 5 belong to the C_i and C_2 symmetry groups, respec-

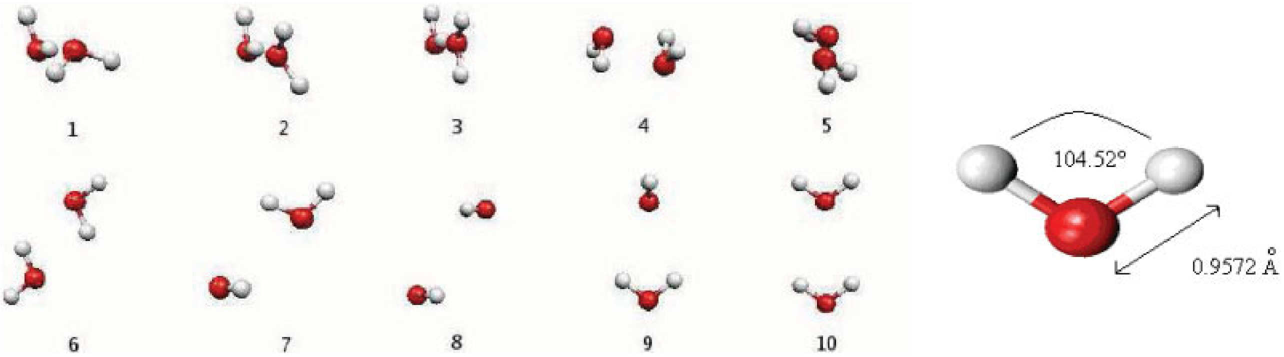

FIGURE 1. Representation of the 10 considered water dimers and the common internal geometry of the water monomer for all dimer systems. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tively. System 2 is a linear water dimer of C_1 symmetry (see Refs. 20 and 22 for details).

Contrary to Smith's optimized monomer geometries for each dimer, but in line with the study of van Duijneveldt et al. [20], we use the same fixed monomer geometries throughout the whole study. This geometry is an experimental structure [20] with an intramolecular angle of 104.52° and an O—H bond length of 0.9572 Å. This choice is motivated on one hand by the fact that the parameterization of force fields for water–water interactions does not necessarily treat water molecules as flexible units, and on the other hand to render interaction contributions comparable from one to another dimer system without having to take into account additional internal relaxation or geometrical deformation energies.

2.2. SAPT DECOMPOSITION

As already introduced, the aug-cc-pVTZ basis set has been used for all calculations, which becomes for SAPT calculation accessible today, but was out of interest and computationally too demanding with this benchmark method when the dimer sets were established. This has changed in the last years in the sense that the aug-cc-pVTZ set is now a more routinely used one, motivating the diffusion of new reference data.

SAPT consists of a multiple perturbation series with the intramolecular and the intermolecular perturbation operator, augmented by corresponding exchange terms. The starting point is the independent monomer wave functions, which means that this method is not an approximation to full configuration interaction (CI) total energies in the same basis set. Even convergence of the SAPT expansion not assured [30]. Nevertheless, because of the fact that the starting point is well defined and the interaction energy, very tiny compared with total energies, is calculated directly step by step without differences of large total energies, the method has become a reference for energy decomposition schemes, permitting to ascribe classical terms as electrostatics, induction, and dispersion to the individual contributions.

We organized the vast amount of SAPT results (several levels are available, see Ref. 3 for details) in the Supporting Information of this article. In principle, SAPT does not use a completely antisymmetrized wave function for the dimer. The HF interaction energy, with orthogonalized molecular orbitals, includes, therefore, an electrostatic part, an exchange-repulsion part, and the full intermolecular induction series of a SAPT calculation, together with terms taking into account orbital relaxation through the interaction. These parts are easily identifiable, so a hybrid method has been proposed and used with success, replacing the sum of the enumerated contributions by the HF interaction energy, much simpler to calculate. Intramolecular correlation and the dispersion parts are added to this, leading to the so-called SAPT(hybrid) method [3]. For separating induction and the rest (electrostatics and exchange-repulsion), and for comparing the validity of the SAPT(hybrid) approach, we give these data separately in second and third order. The third-order exchange-induction term is, however, not available, and we propose an approximation, maintaining the ratio induction/exchange-induction from the second-order terms [8]. The same estimation is used to obtain the $E^{22}{}_{\text{(exch-ind)}}$ contribution from $E^{22}{}_{\text{(ind)}}$, $E^{20}{}_{\text{(ind,resp)}}$, and $E^{20}{}_{\text{(exch-ind,resp)}}$. Response-corrected terms [3] are available and included, leading to the following decomposition of the total SAPT interaction energy into a SCF-like part and a correlation part.

$$\begin{aligned}\text{SAPT (SCFlike},r) &= E^{10}{}_{\text{pol}} + E^{10}{}_{\text{exch}} + E^{20}{}_{\text{(ind,resp)}} + E^{20}{}_{\text{(exch-ind,resp)}}\end{aligned}$$

$$\begin{aligned}\text{SAPT(SCF, Paris)} &= \text{SAPT(SCF,resp\}} \\ &\quad + E^{30}{}_{\text{ind}}\,(1 + E^{20}{}_{\text{(exch-ind,resp)}}/E^{20}{}_{\text{(ind,resp)}})\end{aligned}$$

$$\begin{aligned}\text{SAPT(Corr)} &= E^{12}{}_{\text{(pol,resp)}} + E^{13}{}_{\text{(pol,resp)}} + E^{1}{}_{\text{exch(CCSD)}} \\ &\quad + E^{22}{}_{\text{(ind)}} + E^{22}{}_{\text{(exch-ind)}} + E^{2}{}_{\text{disp}} + E^{20}{}_{\text{(exch-disp)}}\end{aligned}$$

This leads us to three SAPT total interaction energies, combining the correlation part with either the second- or third-order SAPT(SCF) or the HF interaction energy ΔE(HF), abandoning the construction of an entirely difference-dedicated calculation in the latter case.

$$\begin{aligned}\text{SAPT(2nd order)} &= \text{SAPT(SCFlike},r) \\ &\quad + \text{SAPT(Corr)}\end{aligned}$$

$$\text{SAPT (hybrid)} = \boldsymbol{\Delta}\, E(\text{HF}) + \text{SAPT(Corr)}$$

$$\text{SAPT(Paris)} = \text{SAPT(SCF, Paris)} + \text{SAPT(Corr)}$$

$E^{10}{}_{\text{pol}}$ denotes the HF electrostatic interaction of the independent monomer charge distributions, which includes both the long-range multipolar part and the short-range penetration energy because of overlapping charge distributions. $E^{12}{}_{(\text{pol,resp})} + E^{13}{}_{(\text{pol,resp})}$ are the sum of second- and third-order intramolecular correlation corrections on the first-order intermolecular electrostatic interaction $E^{10}{}_{\text{pol}}$.

$E^{10}{}_{\text{exch}}$ corresponds to the HF first-order exchange-repulsion energy, which can be corrected up to the CCSD level ($E^{1}{}_{\text{exch(CCSD)}}$) by intramolecular correlation contributions. $E^{20}{}_{(\text{ind,resp})} + E^{20}{}_{(\text{exch-ind,resp})}$ are associated, respectively, to the HF induction (equivalent to Ziegler's so-called delocalization energy [2], which also corresponds to the sum of polarization and charge transfer terms in Morokuma-like schemes [1]) and exchange-induction values, respectively (intramolecular correlation is included through the addition of $E^{22}{}_{(\text{ind})} + E^{22}{}_{(\text{exch-ind})}$). The London dispersion energy is computed as a sum of dispersion ($E^{2}{}_{\text{disp}}$) and exchange-dispersion $E^{20}{}_{(\text{exch-disp})}$ components. The direct term ($E^{2}{}_{\text{disp}}$) is the sum of $E^{20}{}_{\text{disp}} + E^{21}{}_{\text{disp}} + E^{22}{}_{\text{disp}}$ including intramolecular correlation on the second-order intermolecular dispersion term, whereas intramolecular correlation is absent from the exchange-dispersion part. We neglect all higher order terms [8].

2.3. SUPERMOLECULAR-CORRELATED CALCULATIONS

In contrast to the decompositions available in SAPT, the supermolecular correlation methods furnish only total interaction energies. The discussion on decomposition schemes in localized orbitals and for orbital-based methods as density functional theory (DFT) is still under way, but will not be addressed or used here. Interested readers may find details on these propositions and results in Refs. [6–10].

For intermolecular interaction, the results of the second-order Møller–Plesset perturbation theory, in general, are very close to the more elaborated ones, and we add fourth-order interaction energies as well. In fourth order, triple excitations participate to the total energy, and we emphasize their contribution for comparison with the coupled-cluster results.

More sophisticated correlation methods are based on the variational principle, but have to be corrected for the so-called size-extensivity error, as the pure variational CI scheme in singly and doubly substituted determinants (CISD) does not scale correctly with the number of electrons and is thus of little interest for determining interaction energies. CI-derived, but size-consistent methods are among others the coupled-electron pair approximation (CEPA-0) [31], the averaged coupled pair functional (ACPF) [32], and the more recent averaged quadratic coupled-cluster approach (AQCC) [33]. These three cited methods result from shifting the diagonal of the CISD matrix by, respectively, E_{Corr} (CEPA-0), by $(1 - 2/n)\, E_{\text{Corr}}$ (ACPF) or $[(n - 2)(n - 3)/n(n - 1)]\, E_{\text{Corr}}$ (AQCC) while maintaining the CISD eigenvalue problem algorithm [34]. n is hereby the number of correlated electrons. These CI-based methods are all approximations to the more complicated coupled-cluster theory using single and double excitations (CCSD), which nowadays, together with the perturbational estimation of triple excitations (CCSD(T)) have become a kind of standard in wave function-based correlation methods. For intermolecular interactions, it has proven that the triples contributions contain important parts, coupling dynamical correlation with orbital relaxation.

All these methods are well documented in the literature and are implemented in all main quantum chemistry codes. For this reason, we present the data for all of these. Recently, in the quest for linear-scaling algorithms, local correlation methods emerged, and we will give some results in the appropriate section on these. However, we do not include these data in our Supporting Information, as the local methods depend significantly on the localization scheme used and the additional computational parameters used, at least to a degree beyond our aim for reproducible data.

The explicitly correlated methods (F12-MP2, F12-CCSD, and F12-CCSD(T), where an explicit term taking into the account the electron–electron cusp is included) are very recently available, and for their documentation and more global assessment, we refer to the publication of Marchetti and Werner [35]. We have to remind as well for these that results may depend on the computational parameterization and the implementation in the Molpro package [36], as these methods are not yet available in a standard fashion. However, the published results of Marchetti and Werner [35] suggest that results obtained with the F12-CCSD(T) method are absolutely converged with respect to the basis set and should present the most precise reference for total-energy calculations. The weaker dependence on basis sets arises from the correlation term $\exp(-\beta\ r_{12})$, not included in the Full CI model, the most complete description of the correlation space within a given basis set and the expansion in excited determinants.

TABLE I
Total interaction energies in kcal/mol for the 10 water dimers.

	1	2	3	4	5	6	7	8	9	10
RHF	−3.53	−3.16	−3.18	−2.62	−2.44	−2.44	−2.04	−0.71	−2.00	−1.53
MP2	−4.65	−4.17	−4.15	−3.94	−3.74	−3.72	−2.94	−1.10	−2.72	−1.94
ACPF	−4.57	−4.09	−4.06	−3.87	−3.64	−3.60	−3.00	−1.20	−2.80	−2.02
CCSD(T)	−4.68	−4.19	−4.16	−3.98	−3.75	−3.72	−3.08	−1.24	−2.86	−2.06
SAPT (Hybrid)	−4.85	−4.39	−4.37	−4.11	−3.91	−3.90	−3.17	−1.28	−3.02	−2.22
SAPT (Paris)	−5.23	−4.72	−4.70	−4.46	−4.21	−4.17	−3.41	−1.37	−3.34	−2.42

All results are counterpoise corrected and include all electrons in the correlation calculations. The SAPT values are the SAPT(hybrid) and SAPT(Paris) ones of the Supporting Information. All data are in kcal/mol.

The same holds for instance for Quantum Monte-Carlo reference data, which never can be met by standard correlation methods (viable approximations to Full CI) as the limit is beyond the Full CI description. This is why we do not include the F12 results in the reference data collection, but give an explicit table in the appropriate section.

2.4. INDEX TO THE SUPPORTING INFORMATION

In the accompanying Supporting Information, we give in a first entry all positions of the water dimers used in this study, together with nuclear repulsion energies and HF total energies for the monomers and the dimer systems. A second section presents the detailed SAPT decomposition for each system, in a first section the SCF-like terms and different summations, secondly pure correlation terms, inaccessible by HF, and a third one with the total interaction energies of the different combinations with the possible SCF-like terms.

A third set of tables contains the overall interaction energies with respect to the different post-HF methods enumerated in the previous section. All interaction energies are in kcal/mol and corrected for the basis-set superposition error (BSSE) via the counterpoise scheme [37], that is, we calculate the dimer and the corresponding monomers in the complete basis set of the dimer system.

Results may differ a little when including the O1s core electrons in the correlation treatment. For the SAPT procedure, all electrons are taken into account throughout, and when discussing results we only address all-electron calculations. For the supermolecular data, freezing the core orbitals amounts to a loss of interaction energy of about 0.02 kcal/mol.

3. Results

3.1. TOTAL INTERACTION ENERGIES: SAPT AND SUPERMOLECULAR POST-HF APPROACHES

From the data in the Supporting Information, we present in Table I a subset, namely, RHF, MP2, ACPF, CCSD(T), SAPT(Paris), and SAPT(hybrid) total interaction energies. Correlation is important for all systems, ranging from about 1.2 kcal/mol (first three systems) to 0.5 kcal/mol (systems 8 and 10) for the interaction energies. We see that MP2/ACPF/CCSD(T) produces one common set of interaction energies, whereas SAPT(hybrid) and SAPT-(Paris) give slightly higher values, consistently 0.2 and 0.5 kcal/mol larger, respectively. We arrive thus at a nearly complete description of the overall interaction energy from electrostatic, induction, and dispersion terms together with intramolecular correlation and corresponding exchange contributions. In that sense, we may attribute for instance the SAPT dispersion term to the physically independent "classical" dispersion interaction, to which we will come back later. SAPT(Paris) results demonstrate that the equivalence of the sum of electrostatics, exchange, and induction to the HF interaction energy is valid within 0.3 kcal/mol for these systems, despite the limit of the induction expansion and the approximation for the complete antisymmetrization operator [3]. The Supporting Information shows that the third-order induction contribution has the same size as the second-order one, approximate third-order induction and exchange-induction terms are essential energies closer to the HF value.

TABLE II

Interaction energies for the nonstandard methods.

Method/system	1	2	3	4	5	6	7	8	9	10
LMP2	−4.46	−3.95	−3.90	−3.75	−3.75	−3.49	−2.82	−1.05	−2.59	−1.84
F12-MP2	−4.87	−4.38	−4.35	−4.16	−3.94	−3.92	−3.10	−1.16	−2.89	−2.06
F12-CCSD	−4.62	−4.15	−4.13	−3.92	−3.69	−3.67	−3.02	−1.18	−2.83	−2.06
F12-CCSD(T)	−4.84	−4.33	−4.30	−4.13	−3.89	−3.86	−3.19	−1.28	−2.97	−2.15
SAPT (hybrid)	−4.85	−4.39	−4.37	−4.11	−3.91	−3.90	−3.17	−1.28	−3.02	−2.22
SAPT (Paris)	−5.23	−4.72	−4.70	−4.46	−4.21	−4.17	−3.41	−1.37	−3.34	−2.42

LMP2 as localized MP2, and F12 for the explicitly correlated methods taking into account the electron–electron cusp. From the variants proposed by Marchetti and Werner [35], we took the F12b-CCSD(T) and F12-MP2/3C(FIX) ones. The last row repeats the SAPT data from the previous table. All data are in kcal/mol.

Remarkably (but not new) is the closeness of MP2 and CCSD(T), even without inclusion of triple excitations for the former. MP2 neglects simultaneously contributions to the correlation energy from dimer and monomer systems, and we have as well a cancellation of errors because of using HF orbital energies for denominators and missing higher excitations in the numerators.

3.2. RESULTS FOR LOCAL MP2 AND EXPLICITLY CORRELATED METHODS

In this section, we give some results for nonstandardized methods as implemented in the Molpro program package. As the HF wave function is invariant upon orbital rotations leaving the separation between occupied and virtual orbitals untouched, second-order perturbation theory may be formulated as an eigenvalue problem similar to CEPA-0 in a set of localized orbitals [38, 39]. Without any further approximations, the MP2 energy in canonical orbitals is exactly reproduced. The method becomes interesting in the context of linear-scaling correlation methods [40] using nonorthogonal virtual orbitals and distance-dependent cutoff criteria. Results then become weakly dependent on the way the approximations are implemented and how the set of localized occupied orbitals is generated. The table shows that results indeed coincide well with the data obtained with canonical orbitals sets. The linear-scaling issue is, of course, in this context less important. Schütz et al. [41] demonstrated that furthermore the basis-set superposition error can be significantly reduced with the LMP2 implementation, making geometry optimizations much less expensive that with the standard counterpoise correction.

For showing that our calculated interaction energies are not only valid in this particular basis set, we carried out explicitly correlated calculations as well, the results of which are included in Table II. As stated the comparison with methods approximating Full CI is not so direct, but nevertheless the coincidence of SAPT with the most elaborate F12-CCSD(T) is quite striking.

3.3. IMPORTANCE OF TRIPLE EXCITATIONS

From the data concerning supermolecular post-HF methods, MP4 and the CCSD(T) results show the importance of triple excitations of the various dimer systems, ranging from 0.06 to 0.2 kcal/mol (Table III). This is much more than the difference between MP2 and CCSD(T), and between ACPF and CCSD(T), underlining the cancellation of errors for the methods not including triple excitations at all.

If we look at total energies, not energy differences, we found that for instance for the first system, the ACPF total energy lies halfway between MP2 and CCSD(T): 152.697 a.u. (MP2), −152.711 a.u. (ACPF), and −152.724 a.u. (CCSD(T)). Nevertheless, the interaction energy differs by nearly 0.1 kcal/mol between ACPF and CCSD(T) and only by 0.03 kcal/mol between MP2 and CCSD(T).

Interestingly, the F12-CCSD(T) yields exactly the same contributions of triple excitations to the interaction energy as does CCSD(T), showing perhaps the importance of the orbital relaxation (single excitations) in combination with diagrams of the dynamical correlation (double excitations).

TABLE III
Contribution of the triple excitations to the interaction energy for MP4, CCSD(T), and F12-CCSD(T), in kcal/mol.

	1	2	3	4	5	6	7	8	9	10
T in MP4	−0.20	−0.18	−0.17	−0.21	−0.20	−0.19	−0.14	−0.08	−0.11	−0.06
T in CCSD(T)	−0.22	−0.19	−0.18	−0.22	−0.20	−0.19	−0.17	−0.10	−0.14	−0.09
T in F12-CCSD(T)	−0.22	−0.19	−0.18	−0.22	−0.20	−0.19	−0.17	−0.10	−0.14	−0.09

4. VALIDITY OF THE HFD APPROXIMATION

As it has been shown earlier, electron correlation does not act only by addition of a dispersion contribution to the uncorrelated HF energy, each component is modified by its related correlation correction. For example, the exchange contribution benefits from the CCSD correction, being more repulsive, whereas correlation diminishes the stabilization of the electrostatic contribution $E^{10}{}_{\text{pol}}$. On the opposite, the induction component is enhanced by correlation. In other words, there is a transfer of the origin of the stabilization of the overall interaction energy between first order (electrostatic and exchange repulsion) as exchange-repulsion becomes more repulsive and electrostatic less attractive and second order (induction and dispersion) when correlation is added.

In these conditions, what can we think of the usual [26, 27] HFD approximation? In this approximation, the supermolecular HF energy is supplemented by an empirical dispersion including parameters fitted on the difference of a correlated method to HF energy. Introduced many years ago by Hepburn et al., this approach is still popular [42–46] within DFT offering an affordable access to van der Waals interactions. It has also been largely used in molecular modeling to supplement expression fitted on HF EDA decomposition.

Figure 2 displays a comparison of the SAPT dispersion (summed to the exchange-dispersion component) to the difference of selected post-HF methods (including MP2, MP4, and CCSDT) to the uncorrelated HF values. First, one can see that the order of magnitude of the energies is not conserved as dispersion + exchange-dispersion appears at least twice as large as the others quantities. Moreover, the slopes are also slightly different. Indeed, all post-HF methods already include the summed effects that we have mentioned (for instance the increase of exchange-repulsion), which does not necessarily vary like the dispersion itself in $1/R^n$. That way, when dealing with the HFD approach, one perturbs the nature of the added "dispersion like" contribution, which will then diverge from the "true" dispersion contribution. The empirical correction will have to correct the HF values for all correlation effects, not only at long-range (dispersion) but also at short range (for instance exchange-repulsion, difference in short-range electrostatic penetration, or even exchange-induction).

5. Conclusions

We proposed extensive SAPT benchmarks on selected geometries of the water dimer, which could help force fields developers to improve the quality of their models. The chosen SAPT level, coupled to the aug-cc-pVTZ basis set, has been shown to give equivalent or better results than high-quality supermolecular post-HF computa-

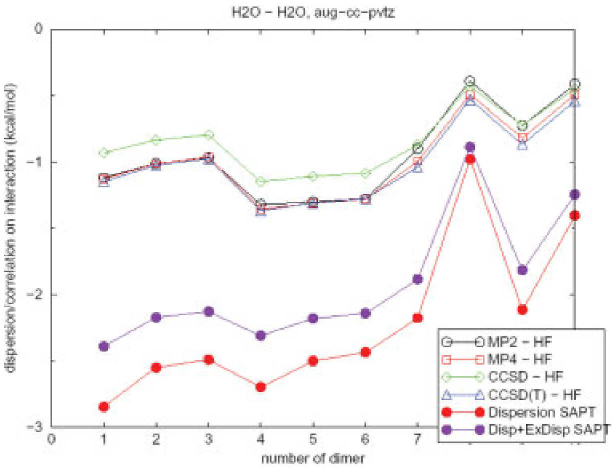

FIGURE 2. Comparison of correlation/dispersion energy components computed at several levels. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tions, which should provide interesting reference computations for the different physical contributions to the interaction energy. Our approximations suggest that third-order SAPT corrections to the induction/exchange-induction terms are generally not negligible. Our results also show that addition of electron correlation cannot be simply approximate by the addition of a dispersion-like correction as many effects are then merged. Such computations could be then used to improve DFT-D (DFT+dispersion) models, where an empirical correction is added to recover van der Waals interactions.

Appendix: Technical Details of the Calculations

The SAPT calculation has been performed with the SAPT package [47], coupled for the integral generation and the preceding HF calculations to the Dalton 1.0 package [48]. For a single dimer, the computer time on a DEC Alpha workstation was about 6 h, using ~25 Gbytes of disk space, because of the large number of bielectronic integrals in the nonorthogonal basis sets in SAPT. For the post-HF correlation calculations, Molpro [36] has been used in the versions 2002.7 (MP2, LMP2 with standard settings of internal parameters, CI-based methods, Coupled-Cluster) and 2008.1 (F12 methods). For these calculations, we spent about 40 min on a modern Core2Duo system on a single processor, with about 2 GB of disk space.

The aug-cc-pvtz basis set has been used in spherical harmonics with five angular *d* functions and seven angular *f* functions per radial functions. For the conversion of atomic units to kcal/mol, we used the factor 627.51 kcal/mol for one a.u.

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