J. Phys. Chem. A **1998,** *102,* 5997−6003

Local Treatment of Electron Correlation in Molecular Clusters: Structures and Stabilities of $(H_2O)_n$, $n = 2-4$

Martin Schütz, Guntram Rauhut, and Hans-Joachim Werner*

Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

Received: February 16, 1998; In Final Form: May 6, 1998

The structures and stabilities of small water clusters are studied by local electron correlation methods. It is demonstrated that the local treatment eliminates basis set superposition errors (BSSEs) to a large extent and thus allows BSSE-free geometry optimizations. Results for various basis sets are presented which show that the interaction energies and structural parameters obtained by local second-order Møller−Plesset perturbation theory (LMP2) without counterpoise correction are in close agreement with counterpoise-corrected conventional MP2 results. Furthermore, a partitioning of the LMP2 energies of $(H_2O)_n$, $n = 2-4$, into different excitation classes is reported, which underlines the importance of ionic contributions as well as intramolecular correlation for hydrogen-bonded clusters. The results of this analysis are compared with previous data obtained by symmetry-adapted perturbation theory (SAPT).

1. Introduction

Weak forces acting between individual molecules play a key role in a large variety of chemical and biological processes, e.g., enzymatic reactions as well as protein and DNA folding. *Molecular clusters*, i.e., isolated aggregates of a number of interacting molecules, represent appropriate model systems to study intermolecular forces: They can be synthesized in molecular beam experiments and characterized by a broad palette of laser spectroscopical methods.[1−3] Furthermore, small molecular clusters fall into the range of applicability of ab initio quantum chemistry. Yet the accurate description of intermolecular forces is still a difficult problem. Most of the calculations adopt the *supermolecular approach*, where the interaction energy of the cluster is obtained as the difference between the total energies of the cluster and all noninteracting monomers. The major advantage of this procedure is that standard methods and codes can be used for such calculations. Moreover, already a Hartree−Fock (HF) calculation of the cluster provides a reasonable description of electrostatic and induction effects. However, the supermolecular approach is known to be sensitive to basis set extension effects, in particular to *basis set superposition errors* (BSSEs). A remedy to this problem, the so-called *counterpoise correction* (CP), was proposed almost 30 years ago,[4] but still is (to some extent at least) controversial (for a review on this topic see ref 5). In any case, the CP correction is computationally costly, since it requires (n+1) calculations in the composite basis (spanned by the basis functions on all n monomers), rather than a single one.

Alternative methods that take into account the specific nature of intermolecular interactions, i.e., intermolecular perturbation methods, have been developed as well. One of the most successful advancements here is the *symmetry-adapted perturbation theory* (SAPT),[6,7] which takes care of exchange effects between interacting monomers and includes intramonomer correlation effects by virtue of a double perturbation theory, where the intermolecular interaction operator V and the intramonomer correlation operator W act as perturbations. Perturbational approaches such as SAPT are BSSE free by construction and also provide naturally a partitioning of the interaction energy into physically meaningful quantities such as the electrostatic-, induction-, dispersion-, and exchange-repulsion components, similar to those occurring in a partitioning scheme developed by Morokuma.[8] However, due to its double perturbation character, it is not straightforward to apply SAPT to clusters involving a larger number of monomers.

Recently, Handy et al.[9] studied the water dimer using DFT methods. They found reasonable agreement with more accurate ab initio calculations, but the deviations of calculations with different functionals were of the same order as the correlation contribution itself. This is not surprising, since the present density functionals do not account for dispersion contributions, which are substantial components of intermolecular forces. Therefore, in our opinion, DFT methods are unsuitable for *accurate* studies of molecular clusters.

In supermolecular calculations the HF contribution to the interaction energy converges rather quickly with increasing basis set size. The HF basis set limit is normally closely approached for larger basis sets, which are required for an appropriate description of intermolecular correlation effects. This also means that the BSSE at the HF level becomes rather insignificant for such basis sets. On the other hand, the dispersion energy, which is a pure electron correlation effect, converges only very slowly with basis set size,[10] and the CP correction is much larger at the correlated level. The latter problem can be avoided by using *local correlation methods*,[11−13] which eliminate the BSSE at the correlated level to a large extent, as was shown previously by Saebø et al.,[14] Hampel and Werner,[15] and Pedulla et al.[16] The primary goal for the development of local correlation methods was to reduce the steep dependence of the computational cost on the size of the chemical system for high-level electron correlation methods and thus to open a path for accurate treatments of larger molecules. The avoidance of the BSSE is a nice side effect, which results from the restriction of the correlation space of an electron pair to basis functions in the spacial vicinity of the two localized MOs involved. This means that functions from remote centers cannot contribute with their tails to improve the basis set flexibility, which is the primary source of the BSSE. The underlying concept of local

S1089-5639(98)01168-2 CCC: $15.00

TABLE 1: $(H_2O)_2$ Interaction Energies for Hartree−Fock and Different Levels of Electron Correlation, Calculated with Several Basis Sets of the aug-cc-pVXZ Family. The $(H_2O)_2$ Geometry of Ref 34 with an Intermolecular Distance $R = 2.895$ Å Was Used. All Values Are Given in kcal/mol

	aug-cc-pVDZ			aug-cc-pVTZ			aug-cc-pVQZ		
method	ΔE	ΔE_{CP}	δ_{CP}	ΔE	ΔE_{CP}	δ_{CP}	ΔE	ΔE_{CP}	δ_{CP}
HF	−3.75	−3.50	0.252	−3.57	−3.49	0.077	−3.56	−3.53	0.030
MP2	−5.16	−4.30	0.859	−5.11	−4.63	0.477	−5.04	−4.80	0.237
LMP2	−4.27	−4.14	0.126	−4.53	−4.48	0.048	−4.73	−4.71	0.013
MP4(SDQ)	−4.93	−4.09	0.839	−4.89	−4.44	0.448	−4.79	−4.60	0.184
LMP4(SDQ)	−4.06	−3.93	0.131	−4.35	−4.29	0.060	−4.53	−4.51	0.019
CCSD	−4.92	−4.09	0.827	−4.89	−4.45	0.447			
LCCSD	−4.06	−3.93	0.133	−4.36	−4.30	0.060			

correlation methods is now well-understood and used by several research groups.[12,13,15,17−19] Efficient integral direct implementations of local Møller−Plesset perturbation (MP2−4) and coupled cluster (CCSD) theory became recently available[20] in the MOLPRO[21] program package.

Usually, the first step in a molecular cluster study is to locate the relevant minimum-energy structures on the inter/intramolecular potential energy surface (PES). For three reasons such optimizations are very difficult to perform: First, the number of local minima grows exponentially with the cluster size,[22] and finding the global minimum[23] is a severe problem. Second, due to the coupling of inter- and intramolecular degrees of freedom, optimizations are notoriously difficult to converge, even if one starts in the vicinity of the global minimum. This problem can be minimized by the use of symmetry-adapted internal coordinates.[24,25] Third, the common post-HF gradient methods are tainted with BSSE. This could be avoided by optimizing CP-corrected energies, which would require separate gradient calculations for the supermolecule and all fragments. Due to the high cost of such a procedure, BSSE effects are often discarded in optimizations of molecular clusters, or accounted for a posteriori on the intermolecular PES only, by computing a series of CP-corrected energies along selected intermolecular coordinates.

Very recently, we have developed a method for computing analytical gradients for local MP2 (LMP2).[26] This offers a new efficient way to determine BSSE-free geometries. This method, which is outlined in section 2, has been applied in the present work. The size of the remaining BSSE is investigated in section 3.1. In section 3.2 we report LMP2 water dimer structures for a series of different basis sets which were optimized including the coupling of all degrees of freedom. For water clusters the correlation contributions to the interaction energy beyond second order are small due to a cancellation of the components of higher order single/double and disconnected quadruple excitations with the fourth-order perturbational estimate of the connected triples.[27−29] The MP2 level thus is well-suited for a treatment of such clusters.

The local correlation concept offers another interesting prospect in the context of intermolecular interactions: Due to the local character of both the occupied and virtual orbitals, the correlation contribution to the intermolecular interaction energy can be partitioned into individual contributions of different excitation classes. This provides some physical insight into the nature of intermolecular forces. In section 3.3 we present such a partitioning scheme and report results for LMP2 calculations on $(H_2O)_n$, $n = 2−4$.

2. Methods

In local correlation methods[11−13,15] the occupied molecular orbitals are localized, but kept orthonormal. We have used the Pipek−Mezey localization[30] for all calculations reported in this paper. The virtual orbitals are obtained from the atomic orbitals (AOs) by projecting out the occupied space. The nonorthogonal projected functions obtained in this way are inherently localized. To each localized MO $|\phi_i\rangle$ a subset $[i]$ (*orbital domain*) of the projected orbitals is assigned. The domains were selected as described by Boughton and Pulay,[31] using a selection criterion of 0.015 (in various applications[15] this value was found to be more appropriate for larger basis sets than the value of 0.02 proposed by Boughton and Pulay, but in the present case there is no difference). The correlation space of an electron pair (ij) (the so-called *pair domain* $[ij]$) is the union of the orbital domains $[i]$ and $[j]$. Linear dependencies are removed separately for each pair domain by deleting one projected function for each small eigenvalue (threshold 10^{-4}) of the overlap matrix of the subspace $[ij]$. For numerical reasons, the projected functions arising from the oxygen 1s functions were deleted from all domains (for details see ref 15). The domains were determined at a large intermolecular distance of the two water molecules and then kept fixed for all other geometries. This avoids any steps on the potential energy surface due to changes of the domains and thus guarantees a smooth potential energy surface.

Analytical energy gradients for local MP2 were computed using a new program recently developed.[26] The theory is somewhat more complicated than for conventional MP2 gradients, since additional terms arise from the nonorthogonality of the projected functions and the fact that the correlation space for each orbital pair is different. Furthermore, the geometry dependence of the localization matrix has to be taken into account by solving a set of *coupled perturbed localization* (CPL) equations.[26] However, the additional effort is negligible and outweighed by savings due to the local approximation.

In the present study we used the augmented correlation consistent basis sets of Dunning[32] (aug-cc-pVXZ) for X = D (double-ζ) to X = Q (quadruple-ζ). These correspond to the original cc-pVXZ sets[33] augmented by one diffuse function for each angular momentum. All calculations have been performed with the MOLPRO package of ab initio programs.[21]

3. Results and Discussion

3.1. Basis Set Superposition Error in Local Correlation Methods. As already mentioned, local correlation methods eliminate the incremental BSSE at the correlated level to a large extent. Table 1 compares local and canonical $(H_2O)_2$ interaction energies with (ΔE_{CP}) and without (ΔE) counterpoise correction (δ_{CP}), computed at the HF, MP2, MP4(SDQ), and CCSD levels, respectively. All interaction energies were obtained at the CCSD(T)/aug-cc-pVTZ dimer geometry reported in ref 34. It is evident from Table 1 that the incremental BSSE arising from electron correlation is reduced for all local methods by about 1 order of magnitude. In fact, the δ_{CP} values for the individual local correlation methods are even *smaller* than the HF values, indicating that the incremental BSSE at the correlated level is

TABLE 2: $(H_2O)_2$ O−O Distances R, Interaction Energies ΔE, and Relaxation Energies E_{rlx} Obtained with MP2 and LMP2 for Different Basis Sets. The Corresponding CP-Corrected Values of R Reported in Ref 35 Are Also Given. ΔE Values in Parentheses Refer to Interaction Energies Without CP Correction. The Distances and Energies Are Given in Å and kcal/mol, Respectively

	MP2			LMP2				MP2[a]
basis	R	ΔE^b	E_{rlx}	R	ΔE^b	E_{rlx}	ΔR	R
cc-pVDZ	2.909	−3.64(−7.47)	0.03	2.951	−3.70(−6.73)	0.02	0.041	
cc-pVTZ	2.907	−4.37(−6.09)	0.04	2.955	−4.20(−5.40)	0.03	0.048	
cc-pVQZ	2.902	−4.67(−5.49)	0.04	2.933	−4.52(−5.07)	0.03	0.022	
aug-cc-pVDZ	2.917	−4.43(−5.26)	0.03	2.975	−4.32(−4.42)	0.03	0.058	2.975
aug-cc-pVTZ	2.907	−4.71(−5.18)	0.04	2.940	−4.59(−4.63)	0.03	0.033	2.933
aug-cc-pVQZ	2.902	−4.86(−5.09)	0.04	2.925	−4.77(−4.78)	0.03	0.023	2.918[c]

[a] From ref 35. [b] Relaxation energies E_{rlx} of the monomers are already included. [c] This result corresponds to a constrained optimization of the O−O separation, with the remaining coordinates kept at their optimized aug-cc-pVTZ values.

negative. This effect can be explained as follows: At large intermolecular distances the domains are identical to the ones in individual water molecules. As the intermolecular distance decreases, the occupied orbitals of the two fragments begin to overlap, and the projected orbitals of fragment A get some tails near molecule B, which are not effective to correlate the electrons in A. Vice versa, the projected orbitals of fragment B have some contributions of basis functions at fragment A, but these are not taken into account to correlate the electrons in A. Thus, the correlation space of A is slightly deteriorated (and vice versa for fragment B). However, this effect is rather small, typically half the magnitude of the SCF BSSE, and therefore the total BSSE (SCF + LMP2) is about half the SCF BSSE. We have also tested the effect of selecting different domains at the equilibrium structure of the cluster and for the fragments. The effect was found to be very small ($\leq$0.025 kcal/mol) and thus not considered further.

Usually, one would anticipate that the BSSE is large with diffuse basis sets. However, in the present case the opposite is true, since the diffuse functions have significant contributions in the Hartree−Fock wave functions. The SCF BSSE is reduced by a factor of about 10 when using the aug-cc-pVXZ instead of the cc-pVXZ basis sets. For instance, at the optimized LMP2 structures one finds the following SCF CP corrections: cc-pVDZ, 2.22 kcal/mol; aug-cc-pVDZ, 0.22 kcal/mol; cc-pVQZ, 0.34 kcal/mol; aug-cc-pVQZ, 0.03 kcal/mol. It is therefore mandatory to use diffuse basis sets for calculations on water clusters.

3.2. Geometries. As discussed above, the availability of analytical local MP2 gradients offers an easy and efficient way to obtain structures of molecular clusters that are virtually free of BSSE. Table 2 compares the optimized O−O distances R of $(H_2O)_2$ between canonical and local MP2 for a series of different basis sets. In the following we use the notation METHOD/BASIS/CP, where the suffix CP is added for counterpoise-corrected results. The individual distances correspond to fully optimized dimer structures, i.e., with both inter- and intramolecular degrees of freedom relaxed. The length of the intermolecular hydrogen bond is elongated by 0.06−0.02 Å, depending on the basis set quality, when going from a canonical to a local description of electron correlation. As anticipated, the (uncorrected) LMP2 distances are quite close to the corresponding MP2/CP values of Xantheas,[35] which are also given in Table 2. There is a remaining discrepancy between the LMP2 and the MP2/CP distances of ref 35, the LMP2 values being 0.007 Å longer in the cases of aug-cc-pVTZ and aug-cc-pVQZ. One possible explanation for this could be the intrinsic lack of certain ionic excitations in the local correlation treatment, as will be discussed in the subsequent section. Another reason for the deviations could be the fact that the MP2/aug-cc-pVQZ/CP value reported in ref 35 was obtained in a constrained optimization, where all but the R coordinate were kept at their optimum MP2/aug-cc-pVTZ/CP values, while our LMP2/aug-cc-pVQZ result was obtained by fully optimizing all degrees of freedom.

TABLE 3: Structural Parameters of the Translinear C_s $(H_2O)_2$ Geometry Obtained from Full MP2 and LMP2 Geometry Optimizations Using the aug-cc-pVTZ and aug-cc-pVQZ Basis Sets without CP Correction. For the Definition of the Parameters see Figure 1. The Corresponding Interaction Energies Are Also Given, for Convenience (cf. Table 2). All Values Are Given in Å, deg, and kcal/mol without Zero-Point Corrections (See Text)

	aug-cc-pVTZ		aug-cc-pVQZ		aut-cc-pVTZ	model potentials	
	MP2	LMP2	MP2	LMP2	DFT/B3LYP[a]	NEMO[c]	ASP[e]
r_1	0.960	0.961	0.958	0.958	0.961	0.958[d]	0.957[d]
r_2	0.969	0.969	0.967	0.966	0.970	0.958[d]	0.957[d]
Θ_1	104.5	104.4	104.7	104.6	105.4	104.5[d]	104.5[d]
r_3	0.962	0.963	0.960	0.960	0.963	0.958[d]	0.957[d]
Θ_2	104.5	104.5	104.6	104.7	105.5	104.5	104.5[d]
R	2.907	2.940	2.902	2.925	2.917	2.88	2.98
β_1	5.6	5.7	6.0	6.0	5.3	4.4	0.0
β_2	123.4	123.5	122.8	122.8	123.3	121	117
ΔE	−4.71	−4.63	−4.86	−4.78	−4.50[b]	−4.71	−4.68

[a] From ref 40. [b] No CP correction, but estimated to complete basis set limit. [c] From ref 41. [d] Kept fixed at the respective free water values. [e] From ref 42.

Table 2 shows that the local and CP-corrected O−O distances R are more sensitive to basis set extensions than the uncorrected ones. In particular the CP-uncorrected MP2/aug-cc-pVDZ result of $R = 2.917$ Å is essentially identical to the MP2/aug-cc-pVQZ/CP value, while the MP2/aug-cc-pVDZ/CP and (uncorrected) LMP2/aug-cc-pVDZ values are too large by about 0.05 Å. The BSSE observed for this latter basis is still quite large even at the HF level, as is evident from Table 1. The good prediction of R using this rather small basis is most probably due to a cancellation of errors. As was discussed in ref 10, the missing dispersion energy is approximately compensated by the BSSE. Comparison of our uncorrected MP2 geometries with the CP-corrected ones of ref 35 shows that even with the aug-cc-pVQZ basis the BSSE effect on the intermolecular distance is quite large (0.016 Å), while the uncorrected LMP2 values are close to the CP-corrected MP2 values. It appears that the most reliable way to obtain very accurate cluster structures is to perform a series of local or CP-corrected geometry optimizations for a hierarchy of basis sets and to extrapolate from these to inifinite basis set size.

Table 3 compiles the complete set of independent geometrical parameters for the translinear C_s structure of $(H_2O)_2$, as obtained by full MP2 and LMP2 optimizations and employing the aug-cc-pVTZ and aug-cc-pVQZ basis sets, respectively (the struc-

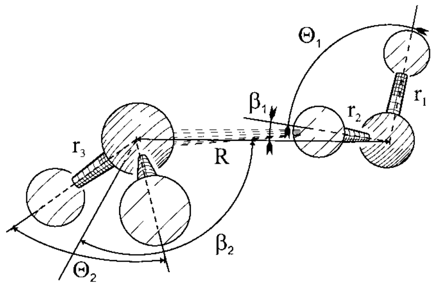

Figure 1. Minimum-energy structure of the water dimer. The trans-linear hydrogen-bonding arrangement has C_s symmetry. The intermolecular coordinates are R, the O−O distance; β_1, the bonding angle between the donor O−H bond and the O−O bond vector; and β_2, the inclination angle between the plane of the acceptor monomer and the O−O bond vector.

tural parameters are defined in Figure 1. All coordinates apart from R are well-converged already with the aug-cc-pVTZ basis. Furthermore, the discrepancies between LMP2 and canonical MP2 appear to be small for all coordinates except R. The latter naturally is the one that is most affected by BSSE. The experimental values available in the literature for the O−O distance R and the binding energy D_0 amount to $R = 2.976$ Å[36] and $D_0 = 3.59$ kcal/mol,[37] respectively. The ZPE values as obtained by quantum diffusion Monte Carlo (QDMC)[38] or by the NEMO/ZPVE approach[39] range between 1.8 and 2.1 kcal/mol. The anharmonic correction to the O−O distance is large, i.e., in the range 0.05−0.1 Å.[39] One should note here, however, that the computation of anharmonic corrections in floppy molecules is a nontrivial task, due to the potentially strong coupling between the intermolecular (and eventually intramolecular) modes. These properties are very sensitive to subtleties of the PES and hence depend strongly on the model potential that is used.[39] Nevertheless, with an estimate of $\Delta E_\infty = 5.0$ kcal/mol for the complete (one-particle and N-particle) basis set limit,[10] which now is established on the theoretical side, and an estimate of 1.8 kcal/mol at the lower edge of the range for the ZPE, one would arrive at an upper limit for the binding energy D_0 of 3.2 kcal/mol, 0.4 kcal/mol below the experimental result. On the basis of these calculations, one might be tempted to question the accuracy of the experimental D_0 value, which was obtained from thermal conductivity measurements.

Table 3 also compares the MP2 and LMP2 structural parameters and interaction energies of the present work with the corresponding values as obtained by density functional theory (using the popular hybrid functional B3-LYP),[40] as well as with two of the most successful model potentials available today, i.e., the NEMO[41] and the ASP[42] water potentials. Both of these potentials include nonadditive induction effects, which are important in water clusters. The NEMO potential compares also very well with ab initio data for structural parameters, relative energies, and vibrational frequencies of larger water clusters. For a detailed discussion of the performance of the NEMO potential and a comparison with ab initio calculations on the water trimer and tetramer clusters we refer to ref 43.

3.3. Partitioning of the Interaction Energy. The local character of occupied and virtual orbitals in the local correlation treatment also offers the appealing possibility to decompose the intermolecular interaction energy of molecular clusters into individual contributions of different excitation classes. Separating excitations from individual LMOs into the corresponding orbital domains along the boundaries of the individual monomer subunits, the following substitution classes can be distinguished, as displayed in Figure 2.

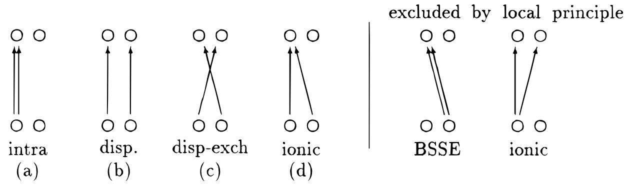

Figure 2. Schematic representation of the different double excitation classes of local correlation methods in the context of intermolecular interactions. The lower and upper circles represent different monomers in the ground and excited states, respectively. The arrows symbolize the corresponding excitations. The different excitation classes a−d are explained in the text.

(a) Intramonomer double substitutions $i \rightarrow [i\, i']$, $i' \rightarrow [i\, i']$: the LMOs i, i' and their pair domain are all located on the same monomer of the cluster. These substitutions describe *intramolecular correlation* effects.

(b) Simultaneous single excitations on two different monomers $i \rightarrow [i]$, $j \rightarrow [j]$: the LMOs i, j and the related orbital domains $[i]$, $[j]$ are localized on different monomers. This substitution class is responsible for the *dispersive coupling* between the individual monomers.

(c) Cross excitations transferring one electron from an occupied LMO of monomer A to the correlating space of monomer B and vice versa, i.e., $i \rightarrow [j]$, $j \rightarrow [i]$: This substitution class can be related to *dispersion exchange* effects.

(d) *Ionic* substitutions transferring one electron from an occupied LMO of monomer A to the correlating space of monomer B, coupled with a single excitation on monomer B, i.e., $i \rightarrow [j]$, $j \rightarrow [j]$.

(d′) *Ionic* substitutions transferring one electron from an occupied LMO of monomer B to the correlating space of monomer A, coupled with a single excitation on monomer A, i.e., $i \rightarrow [i]$, $j \rightarrow [i]$.

Doubly ionic substitutions, i.e., $i \rightarrow [j]$, $i' \rightarrow [j]$ as well as ionic substitutions of the type $i \rightarrow [i]$, $i' \rightarrow [j]$ are automatically excluded by construction in the local correlation method. The former are mainly responsible for the occurrence of BSSE in conventional calculations (it is postulated here that the main portion of the BSSE at the correlated level is caused by double excitations to the distant monomer to improve the description of *intramolecular* correlation). To omit this type of substitutions is hence desirable, as was discussed above. However, the latter substitutions may contribute to some extent to the interaction energy, in particular of hydrogen-bonded clusters. Table 4 compares the LMP2 interaction energies and correlation contributions of some smaller water clusters in the aug-cc-pVTZ basis with the corresponding conventional MP2 calculations after CP correction. The local calculations are consistently lacking 10−15% of the correlation contribution to the interaction energy, and this deficiency is most probably due to the neglect of these latter ionic substitutions.

We note that in the calculations of Saebø et al.[14] the local calculations gave significantly larger interaction energies than the conventional CP-corrected ones, i.e., 4.79 vs 4.57 kcal/mol at the MP2 level, for their best basis set. Since the authors reported CP corrections at the SCF level only, one cannot definitely rule out that there was a significant BSSE left at the correlated level in their calculations. Usually, the BSSE of local calculations is very small (cf. Table 1 of the present work). However, if the domains are determined at finite distances, it may happen that some projected functions, which belong to the redundant set in the asymptotic domains, are not eliminated from the pair domains. Such functions would have significant components on the second monomer, since the virtual space of

TABLE 4: Partitioning of Local MP2 Interaction Energy of Small Water Clusters According to the Different Excitation Classes As Discussed in the Text. ΔE_{SCF} and ΔE_{corr} Are the SCF and (L)MP2 Contributions to the Interaction Energy (Including Counterpoise Correction), Respectively, $\Delta E_{tot} = \Delta E_{SCF} + \Delta E_{corr}$ Is the Total Interaction Energy, and δ_{CP} Are the Corresponding Counterpoise Corrections. All Values Are Given in kcal/mol

	aug-cc-pVDZ LMP2	aug-cc-pVTZ LMP2	aug-cc-pVQZ LMP2	aug-cc-pV5Z LMP2	aug-cc-pVTZ MP2
			$(H_2O)_2$		
ΔE_{SCF}	−3.80	−3.69	−3.68	3.68	−3.69
ΔE_{corr}	−0.55	−0.93	−1.12	−1.19	−1.06
ΔE_{tot}	−4.35	−4.62	−4.80	−4.86	−4.75
E_{disp}	−0.96	−1.03	−1.06	−1.05	
$E_{disp-exch}$[a]	−0.01	+0.01	+0.06	+0.08	
E_{ionic}	−0.75	−1.11	−1.30	−1.35	
$E_{ionic,acc}$[b]		−0.34		−0.38	
$E_{ionic,don}$[c]		−0.77		−0.96	
$E_{intra-corr}$	+1.17	+1.20	+1.18	+1.13	
δ_{CP}(SCF)	+0.22	+0.07	+0.03	0.01	+0.07
δ_{CP}(tot)	+0.10	+0.04	+0.01	+0.03	+0.45
			$(H_2O)_3$		
ΔE_{SCF}	−10.87	−10.97	−11.07		−10.97
ΔE_{corr}	−2.34	−3.53	−4.09		−4.12
ΔE_{tot}	−13.21	−14.50	−15.16		−15.09
E_{disp}	−3.57	−3.76	−3.74		
$E_{disp-exch}$[a]	−0.04	+0.01	+0.18		
E_{ionic}	−2.86	−3.83	−4.46		
$E_{intra-corr}$	+4.13	+4.04	+3.93		
δ_{CP}(SCF)	+0.79	+0.20	+0.08		+0.20
δ_{CP}(tot)	+0.46	+0.14	+0.03		+1.25
			$(H_2O)_4$		
ΔE_{SCF}	−20.25	−20.59			−20.59
ΔE_{corr}	−3.92	−6.13			−7.04
ΔE_{tot}	−24.17	−26.72			−27.63
E_{disp}	−5.78	−5.97			
$E_{disp-exch}$[a]	−0.14	+0.08			
E_{ionic}	−6.11	−8.14			
$E_{intra-corr}$	+8.12	+7.90			
δ_{CP}(SCF)	+1.28	+0.38			+0.38
δ_{CP}(tot)	+0.69	+0.27			+2.31

[a] Only those terms of $E^{(20)}_{disp-exch}$ are included that involve "cross" substitutions, i.e., substitutions of the type $i \rightarrow [j]$, $j \rightarrow [i]$, where i and j are localized MOs on different monomers. [b] Substitutions of the type $i \rightarrow [j]$, $j \rightarrow [j]$, where i and j are localized MOs on the H-donor and H-acceptor monomers, respectively. [c] Substitutions of the type $i \rightarrow [i]$, $j \rightarrow [i]$, where i and j are localized MOs on the H-donor and H-acceptor monomers, respectively.

the first monomer is already spanned by those functions that are nonredundant in the asymptotical domains. As a result, the local correlation contribution to the interaction energy would be contaminated by a significant portion of BSSE.

In the work by Saebø et al. all orbital domains extend over the whole monomer, which is a further difference from the present work, yet this does not explain the fact either that their local interaction energies are larger than the conventional ones after CP correction.

Table 4 also compiles the individual contributions of the LMP2 interaction energies of $(H_2O)_n$ ($n = 1-4$), based on a decomposition into the substitution classes (a−d′) as described above. Results for the aug-cc-pVXZ (X = D−5) are given. For the dimer the corresponding LMP2 structures reported in Table 3 are used. The trimer and tetramer structures were taken from refs 44 and 45, respectively. The individual components were obtained by distinguishing intra- and intermolecular pairs and by decomposing *intermolecular* double excitation amplitudes $\tilde{T}^{ij}_{\mu\nu}$ along the orbital domain boundaries by simply zeroing out the other blocks of these matrixes.

The intramolecular correlation contribution $E_{intra-corr}$ comprises the SAPT components E^{12}_{pol} (second-order intramonomer correlation correction to the electrostatic energy), E^{22}_{ind} (second-order intramonomer correlation to the induction energy), and E^{12}_{exch} (second-order intramonomer correlation correction to the exchange repulsion), i.e., $E_{intra-corr} \approx E^{12}_{pol} + E^{22}_{ind} + E^{12}_{exch}$. For the water dimer these SAPT components amount to +0.4, −0.4, and +1.2 kcal/mol, respectively;[7,46] hence the sums of these components are very close to the $E_{intra-corr}$ values reported in Table 4, which seem to be quite stable with respect to basis set extensions.

On the other hand, the dispersion energy E_{disp} is not directly comparable with the SAPT counterpart E^{20}_{disp} (the second-order dispersion energy between two HF monomers). Since the reference wave function for LMP2 is derived from a fully antisymmetrized HF wave function of the whole cluster, most of the dispersion exchange contributions are already included in E_{disp}, namely those that reshuffle electrons between occupied orbitals of two different monomers. In our calculations the dispersion exchange contribution only corresponds to simultaneous cross excitations from monomer A into the correlation space of monomer B and vice versa, i.e., excitation class c. The effect of these excitations seems to be negligibly small. On the other hand, in SAPT the (attractive) dispersion and (repulsive) dispersion exchange contributions occur as separate terms.[47] The E^{20}_{disp} values are therefore substantially more negative than the E_{disp} values of Table 4, i.e., for the dimer −1.5 to −2.0 kcal/mol vs −1.0 to −1.1 kcal/mol, depending on the basis set. On the other hand, the E_{disp} values of the present work are reasonably close to the dispersion contributions as they occur in intermolecular model potentials such as NEMO (i.e., −1.18 kcal/mol for the dimer and −3.87 kcal/mol for the trimer).[41,43] The latter are estimated using a London-type formula with a damping function[48] introduced to account for the mutual overlap of the monomer wave functions, i.e., exchange effects.

As is evident from Table 4, ionic substitutions (d,d′) play an important role in water clusters at equilibrium distances. This was already observed earlier by Saebø and Pulay.[49,50] Saebø et al.[14] showed that only 70% of the correlation contribution to the interaction energy of $(H_2O)_2$ was recovered when ionic substitutions were excluded from the wave function. In the present work both ionic and purely dispersive substitutions are allowed simultaneously in the wave function, with the ionic components becoming even more prominent: Dispersive and ionic contributions now appear to have about the same weight. It is also interesting to note that the ionic components are considerably more sensitive to extensions of the basis set than the dispersive components, which turn out to be fairly stable.

The decomposition of individual $\tilde{T}^{ij}_{\mu\nu}$ amplitudes along the orbital domain boundaries carries some arbitrariness, since the functions of the two orbital domains are not mutually orthogonal. However, a different partitioning scheme that uses projectors[15] to project individual amplitudes from their pair domains onto the individual orbital domains (which is nonadditive in the intermolecular energy components) shows a very similar picture, namely that the dispersive and ionic components are of equal importance.

Model potentials such as the NEMO or ASP water potentials, which are based on intermolecular perturbation theory of SCF monomer wave functions, naturally neglect intramolecular correlation effects as well as ionic contributions. Both turn out to be sizable, as was demonstrated above. However, there seems to be a fortuitous cancellation between $E_{\text{intra}-\text{corr}}$ and E_{ionic}, as is evident from Table 4. This seems to be an important reason for the success of these potentials, when it comes to the modeling of water−water interactions at close-to-equilibrium distances. However, at larger distances this cancellation probably no longer holds, since E_{ionic} vanishes rapidly with increasing intermonomer distance. So one has to be careful when using such potentials on more remote sections of the potential energy surface.

4. Summary and Conclusions

Besides its computational savings the local treatment of electron correlation provides some conceptual advantages over conventional approaches, which are especially useful in the context of intermolecular interactions. In the present paper it was demonstrated for the example of the water dimer that local correlation energies, and more importantly local energy gradients, are hardly contaminated by basis set superposition errors (BSSEs). This opens an efficient route for BSSE-free geometry optimizations of molecular clusters, since local MP2 (LMP2) gradients are computationally not more demanding than their conventional equivalent. It has been demonstrated[26,51] that intramolecular coordinates and vibrational frequencies are only slightly affected by the local approximation. Small differences from conventional methods have also been traced to a reduction of BSSE.

The local correlation concept also offers the possibility for a partitioning of the intermolecular interaction energy into individual contributions arising from different excitation classes. This renders some physical insight into the nature of intermolecular forces. In the present work such a partitioning of the interaction energy was carried out for a series of small water clusters $(H_2O)_n$, $n = 2-4$. It turns out that for these *hydrogen-bonded* systems *ionic* contributions are of similar importance as *dispersive* ones and moreover that the former show a stronger dependence on the basis set than the latter. It was also observed that LMP2 underestimates the correlation contribution to the interaction energy by 10−15%, relative to canonical MP2 after counterpoise correction. This lack of interaction energy may be related to the omission of certain types of *ionic* excitations in the local correlation treatment. It appears, however, that this neglected component is considerably smaller than the basis set truncation error, e.g., at the level of the aug-cc-pVTZ basis, or errors of the MP2 approximation itself.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft in the “Schwerpunktprogramm Molekulare Cluster” and by the EU in the TMR network FMRX-CT96-088. Further support from the Fonds der Chemischen Industrie and the BASF AG is gratefully acknowledged.

References and Notes

(1) Pugliano, N.; Cruzan, J. D.; Loeser, J. G.; Saykally, R. J. *J. Chem. Phys.* **1993**, *98*, 6600.
(2) Saykally, R. J.; Blake, G. A. *Science* **1992**, *257*, 1937.
(3) Liu, K.; Brown, M. G.; Carter, C.; Saykally, R. J.; Gregory, J. K.; Clary, D. C. *Nature* **1996**, *381*, 501.
(4) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(5) van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873.
(6) Jeziorski, B.; Moszynski, R.; Szalewicz, K. *Chem. Rev.* **1994**, *94*, 1887.
(7) Rybak, S.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1991**, *95*, 6576.
(8) Morokuma, J. *Chem. Phys.* **1971**, *55*.
(9) Mok, D. K. W.; Handy, N. C.; Amos, R. *Mol. Phys.* **1997**, *92*, 667.
(10) Schütz, M.; Brdarski, S.; Widmark, P.-O.; Lindh, R.; Karlström, G. *J. Chem. Phys.* **1997**, *107*.
(11) Pulay, P. *Chem. Phys. Lett.* **1983**, *100*, 151.
(12) Saebø, S.; Pulay, P. *J. Chem. Phys.* **1987**, *86*, 914.
(13) Saebø, S.; Pulay, P. *Annu. Rev. Phys. Chem.* **1993**, *44*, 213.
(14) Saebø, S.; Tong, W.; Pulay, P. *J. Chem. Phys.* **1993**, *98*, 2170.
(15) Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1996**, *104*, 6286.
(16) Pedulla, J. M.; Vila, F.; Jordan, K. D. *J. Chem. Phys.* **1996**, *105*, 11091.
(17) Murphy, R. B.; Beachy, M. D.; Friesner, R. A.; Rignalda, M. N. *J. Chem. Phys.* **1995**, *103*, 1481.
(18) Reynolds, G.; Martinez, T. J.; Carter, E. A. *J. Chem. Phys.* **1996**, *105*, 6455.
(19) Rauhut, G.; Pulay, P.; Werner, H.-J. *J. Comput. Chem.*, in press.
(20) Schütz, M.; Lindh, R.; Werner, H.-J. Submitted to *Mol. Phys.*
(21) MOLPRO is a package of ab initio programs written by Werner, H.-J.; Knowles, P. J. with contributions from Almlöf, J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Lindh, R.; Lloyd, A. W.; Meyer, W.; Mura, M. E.; Nicklass, A.; Peterson, K.; Pitzer, R.; Pulay, P.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Taylor, P. R.; and Thorsteinsson, T.
(22) Hoare, M. R. *Adv. Chem. Phys.* **1979**, *40*, 49.
(23) Hartke, B. *Chem. Phys. Lett.* **1996**, *258*, 144.
(24) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550.
(25) Fischer, T. H.; Almlöf, J. *J. Phys. Chem.* **1992**, *96*, 9768.
(26) El Azhary, A.; Rauhut, G.; Pulay, P.; Werner, H.-J. *J. Chem. Phys.* **1998**, *108*, 5185.
(27) Klopper, W.; Schütz, M.; Lüthi, H. P.; Leutwyler, S. *J. Chem. Phys.* **1995**, *103*, 1085.
(28) Schütz, M.; Klopper, W.; Lüthi, H. P.; Leutwyler, S. *J. Chem. Phys.* **1995**, *103*, 6114.
(29) Klopper, W.; Schütz, M. *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 469.
(30) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916.
(31) Boughton, J. W.; Pulay, P. *J. Comput. Chem.* **1993**, *14*, 736.
(32) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
(33) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
(34) Halkier, A.; Koch, H.; Jørgensen, P.; Christiansen, O.; Beck Nielsen, I. M.; Helgaker, T. *Theor. Chem. Acc.* **1997**, *97*.
(35) Xantheas, S. S. *J. Chem. Phys.* **1996**, *104*, 8821.
(36) Odutola, J. A.; Dyke, T. R. *J. Chem. Phys.* **1980**, *72*.

(37) Curtiss, L. A.; Frurip, D. J.; Blander, M. *J. Chem. Phys.* **1979**, *71*.

(38) Franken, K. A.; Dykstra, C. E. *J. Chem. Phys.* **1994**, *100*.

(39) Åstrand, P.-O.; Karlström, G.; Engdahl, A.; Nelander, B. *J. Chem. Phys.* **1994**, *102*.

(40) Kim, K.; Jordan, K. D. *J. Phys. Chem.* **1994**, *98*.

(41) Åstrand, P.-O.; Wallqvist, A.; Karlström, G. *J. Chem. Phys.* **1994**, *100*.

(42) Millot, C.; Stone, A. *J. Mol. Phys.* **1992**, *77*, 439.

(43) Engkvist, O.; Forsberg, N.; Schütz, M.; Karlström, G. *Mol. Phys.* **1997**, *90*, 277.

(44) Schütz, M.; Bürgi, T.; Leutwyler, S.; Bürgi, H. B. *J. Chem. Phys.* **1993**, *99*, 5228; **1994**, *100*, 1780 (E).

(45) Schütz, M.; Klopper, W.; Lüthi, H. P.; Leutwyler, S. *J. Chem. Phys.* **1995**, *103*, 6114.

(46) Mas, E. M.; Szalewicz, K. *J. Chem. Phys.* **1996**, *104*, 7606.

(47) Hess, O.; Caffarel, M.; Huiszoon, C.; Claverie, P. *J. Chem. Phys.* **1990**, *92*, 6049.

(48) Tang, K. T.; Toennis, J. P. *J. Chem. Phys.* **1984**, *80*.

(49) Saebø, S.; Pulay, P. *Chem. Phys. Lett.* **1985**, *113*, 13.

(50) Saebø, S.; Pulay, P. *J. Chem. Phys.* **1988**, *88*, 1884.

(51) Rauhut, G.; El Azhary, A.; Eckert, F.; Schumann, U.; Werner, H.-J. *Spectrochim. Acta*, in press.