Chem. Rev. 1994, 94, 1873–1885

State of the Art in Counterpoise Theory

Frans B. van Duijneveldt,* Jeanne G. C. M. van Duijneveldt-van de Rijdt, and Joop H. van Lenthe

Theoretical Chemistry Group, Debye Institute, Utrecht University, Padualaan 14, 3584 CH Utrecht, The Netherlands

Received May 12, 1994 (Revised Manuscript Received August 5, 1994)

Contents

I. Abstract

This review, covering the period 1987–1993, deals with quantum chemical studies that employ the supermolecular method with some form of counterpoise to calculate the interaction energies of molecular complexes. A theorem is provided showing that the standard counterpoise approach, in which, at a given geometry, energies are evaluated using the full basis set of the complex, yields a pure (i.e. BSSE-free) interaction energy. Artifacts resulting from secondary BSSE have been found to become negligible before the basis set limit of this interaction energy is attained. Alternative methods in which counterpoise is achieved by restricting the fragment description in the calculation of the full complex to the level used for the isolated fragment are formally nearly correct but have been found to give less satisfactory results, mainly because the relevant fragment properties converge only slowly to the basis set limit. Some practical aspects are considered as well, such as the ambiguities that arise in calculating the binding energy of a cluster of molecules.

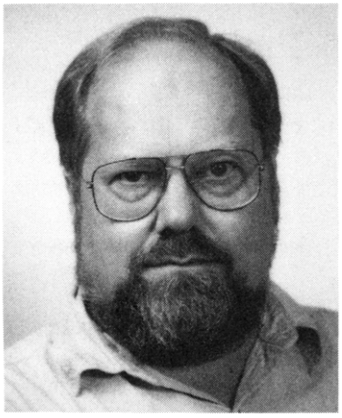
II. Introduction

In the last few years significant progress has been made in the accurate ab initio calculation of the interaction energies of molecular complexes. In some cases the calculated results are now more precise than the available experimental data. Several factors have made this progress possible. First, the accumulated experience with the requirements that must be satisfied by the (one-electron) basis set has made it possible to converge the interaction energy at a given level of theory to the basis set limit, using basis sets of manageable size. Second, the methods that are currently available to allow for electron correlation effects are sufficiently powerful to keep the errors that are inevitably made at this level (barring cases like He_2 where full-CI is a viable option[1,2]) within controllable limits.

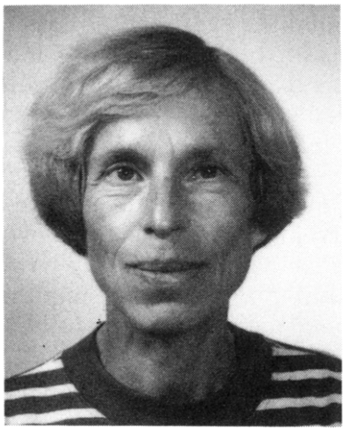
A third area where decisive progress has been made is in developing methodologies specifically aimed at calculating interaction energies. Two main approaches exist in this field, viz. the symmetry-adapted perturbation theory (SAPT) approach,[3,4] in which interaction energies are evaluated directly, and the supermolecular approach, in which interaction energies are obtained as the difference between the total energies of the complex and its constituent parts. The SAPT approach has long suffered from the practical problem that the available programs could evaluate only the simpler of the numerous energy contributions that arise in this theory. But the newer programs are more complete, and accurate results for systems built from two fragments may be within reach. A review of the latest developments is given by Jeziorski et al. in this volume.[4]

The supermolecular approach has several practical as well as conceptual advantages over the SAPT approach. Use is made of standard quantum chemical software, which employs highly efficient algorithms and which is widely available. The approach allows one to study both weakly and strongly interacting systems. The systems may contain any number of fragments and the effects of nonadditivity can be studied with ease. The main problem of this approach has been the uncertainty of how to deal with the so-called basis set superposition error (BSSE), which causes an unphysical lowering of the dimer energy E^{AB} as the dimer forms. Calculating

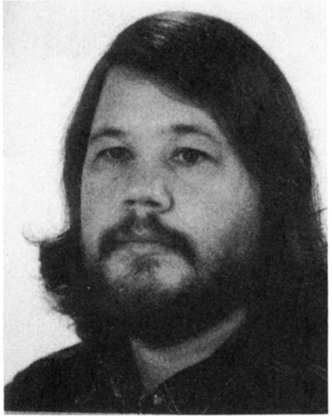
0009-2665/94/0794-1873$14.00/0



Frans B. van Duijneveldt was born in The Hague in 1941. He received his bachelor's degree in chemistry from Utrecht University in 1963. He spent two years at the University of Sheffield with J. N. Murrell, who initiated him in the theory of intermolecular forces. After obtaining his Ph.D. in 1969, he spent a year with E. Clementi, working on complexes and basis sets. He was appointed a lecturer in theoretical chemistry at Utrecht University in 1973 and has been a full professor there since 1980.



Jeanne G. C. M. van de Rijdt was born in Rosmalen, The Netherlands, in 1942. She received her bachelor's degree in chemistry from the University Utrecht in 1966. Since that time she has been working (only part-time) in collaboration with Frans B. van Duijneveldt on hydrogen-bonded systems. She focused her interest mainly on the accuracy of supermolecular calculations. The results, covering a period of about 20 years, were summarized in her Ph.D. thesis in 1994.



Joop H. van Lenthe was born in Velp, The Netherlands, in 1951 and obtained his Ph.D. at Utrecht University. He did postdoctoral work as a Ramsay memorial fellow with Gabriel G. Balint-Kurti in Bristol (England) and Vic. R. Saunders at SRC laboratory in Daresbury (England). In 1989 he was a visiting Professor at the University of Arkansas in Fayetteville (with Prof. Peter Pulay). He is now a senior staff member at Utrecht University. His research interests are in the area of quantum chemical methods and programs. He is one of the authors of the GAMESS-UK program package.

the interaction energy by the counterpoise method[5,6] has been proposed as a strategy to overcome such problems, but it has long been thought that this method, while perhaps reasonable, is basically unsound.

In this short review our aim is to summarize some key arguments in the field of counterpoise theory and to discuss the most recent advances which show that the counterpoise (CP) method is not merely a reasonable device for correcting the basis set superposition error but a fundamentally correct approach to the evaluation of differential quantities, such as interaction energies.

III. Matters of Definition

In the supermolecular method, the interaction energy of a complex AB can be defined as the difference

$$\Delta E(R) = E^{\mathrm{AB}}(R) - E^{\mathrm{A}} - E^{\mathrm{B}} \qquad (1)$$

where R is the A-B distance. For brevity, we suppress all other intermolecular geometrical parameters. For simplicity, we have assumed that the quantum mechanical method used to obtain E^{AB}, E^{A}, and E^{B} is size-consistent, i.e. for large separations E^{AB} reduces to the sum $E^{\mathrm{A}} + E^{\mathrm{B}}$. In (1) E^{A} and E^{B} are assumed to be evaluated using the A basis set for E^{A} and the B basis set for E^{B}. A ΔE obtained in this way will be denoted as $\Delta E^{\mathrm{no\ CP}}$.

In actual calculations one might obtain ΔE by following the lowering of E^{AB}, as the interfragment distance is reduced from infinity to the equilibrium distance R_e, where E^{AB} reaches a minimum. In fact, this is the standard procedure in the gradient (and higher derivative)-based optimization algorithms provided in packages like Gaussian and GAMESS. It is now well-recognized that the result one obtains for ΔE in this way is too negative, because as R decreases not only is the interaction switched on but also the monomers present in AB can start using the one-electron basis set of their partner in the complex, thereby providing an additional stabilization that has nothing to do with the ΔE one is interested in. The error resulting from this has been termed the basis set superposition error (BSSE).[7] Its size is usually not small compared to ΔE, and so the ab initio prediction of potential energy surfaces with quantitative accuracy is only possible if BSSE can effectively be removed or avoided.

It is perhaps appropriate to emphasize that the usage of the partner basis [the so-called basis set extension (BSE)[8]] is not itself an error, for it actually improves the wave function of each monomer. There is ample evidence that the description of almost every physical component of the interaction energy is improved by it. Rather, the error in the above procedure is a matching or balancing error, resulting from the fact that one compares E^{AB} at distances where usage of partner orbitals plays a role, to E^{AB} at infinity, where it does not. The matching at the one-electron level can be restored and the matching error avoided by calculating the interaction energy from

$$\Delta E^{\mathrm{CP}}(R) = E^{\mathrm{AB}}(R) - E^{\mathrm{A\{AB\}}}(R) - E^{\mathrm{B\{AB\}}}(R) \quad (2)$$

where $E^{\mathrm{A\{AB\}}}$ and $E^{\mathrm{B\{AB\}}}$ are monomer energies obtained using the full dimer basis {AB} at the particular AB geometry one is studying. The {B} basis in the $E^{\mathrm{A\{AB\}}}$ calculation and the {A} basis in the $E^{\mathrm{B\{AB\}}}$ calculation are called ghost basis sets. The basis-set matching embodied in (2) has been termed *function counterpoise* by Boys and Bernardi,[6] who originally proposed the use of the counterpoise (CP) method (2) by noting that to evaluate the effect of a perturbation (in this case, the interaction) one should not make any changes to the functional space, as the perturbation is switched on.

By inspection, there is no matching problem in (2), and so (2) is free from BSSE in the sense in which this term was originally proposed.[7] Applying (2) means that the occurrence of BSSE is avoided, and there is no need to explicitly define or calculate a quantity called BSSE. (We postpone a further discussion of the physical significance of the interaction energy ΔE^{CP} given by (2) till section IV.)

However, many routine calculations on molecular complexes do not use (2) but simply follow $E^{\mathrm{AB}}(R)$ to its minimum, which is equivalent to the use of eq 1. At given points of the potential energy surface generated in this way one may then want to assess the size of the error incurred by using (1). Since (2) is the matched counterpart of (1), it follows that the matching error in (1) is

$$\mathrm{BSSE} = E^{\mathrm{A\{AB\}}}(R) + E^{\mathrm{B\{AB\}}}(R) - E^{\mathrm{A}} - E^{\mathrm{B}} \quad (3)$$

and this is the definition of BSSE most widely employed in the literature. The same quantity has also been termed "orbital basis inconsistency" (OBI) error,[9] for reasons clear from the above.

It should be realized that matching errors may not only be present at the level of the orbital basis set, but at the level of the n-electron configuration set as well.[10] The (usually very small) error in ΔE resulting from this may be called "configuration basis inconsistency" (CBI) error[9] or configuration set superposition error (CSSE). CSSE, like BSSE, is overlap-dependent and hence rapidly decreases with increasing R. Unlike the BSSE, CSSE will not vanish as the one-electron basis {AB} approaches completeness. Further details are discussed in section IVE.

A. The Overcorrection Debate

Over the years a debate has evolved centering on the question whether (3) is a sensible assessment of the error in (1). There are widespread feelings that (3) overestimates the error in (1). The doubts have arisen because $E^{\mathrm{A\{AB\}}}$ and $E^{\mathrm{B\{AB\}}}$ in (2) are evaluated using the full basis set of the dimer, i.e. including the orbitals on the ghost molecule that are to be occupied as the dimer forms, whereupon they will no longer be available for improving the partners energy.[11] Consequently, the matching in (2) was felt to be imprecise, and the ΔE of (2) was expected to be more repulsive than it should be. It was proposed[12] that instead of the above scheme—called full counterpoise (FCP) in this context—a more appropriate CP scheme would be one—called virtual counterpoise (VCP)—in which the monomer energies are calculated in a basis that contains the ghost virtual orbital space but not the ghost occupied orbitals. This issue has been definitely settled in a number of studies which critically compared the performance of the VCP and FCP schemes.[13,14] In ref 13, using He_2 as an example, ΔE^{FCP}, ΔE^{VCP}, and $\Delta E^{\mathrm{no\ CP}}$ were calculated at the CEPA-1 level in a sequence of basis sets. Each basis CR*n*DS*m* consisted of a CR part and a DS part. For each basis, independent BSSE-free perturbation calculations were made of the dispersion energy $E^{20}{}_{\mathrm{disp}}$ as given by SAPT. These were used to make a perturbation estimate of the BSSE-free interaction energy, to be expected for each of the basis sets used. In a recent paper, Gutowski et al.[15] improved this perturbation estimate by also calculating the BSSE-free correlated first-order interaction energy E^1 for each basis set.

Table 1. A Comparison of Uncorrected (No CP), Virtuals-Only Corrected (VCP), and Fully Corrected (FCP) CEPA-1 Interaction Energies for He_2 with BSSE-Free Perturbation Theory Estimates ($R = 5.6a_0$)

	interaction energies, K				
basis[a]	no CP	VCP	FCP	estimated[b]	estimated[c]
CR0DS2	−10.29	−7.66	−7.44	−7.74	−7.33
CR0DS4	−39.67	−12.09	−8.81	−8.79	−8.81
CR4′DS2	−8.48	−8.31	−8.28	−8.30	−8.30
CR4′DS4	−9.82	−9.29	−9.19[d]	[−9.19]	[−9.19]

[a] CR0 and CR4′ are 4s1p and 8s4p3d sets, respectively, optimized for intra-atomic correlation. DS2 and DS4 are 1p1d and 2p1d1f1g low-exponent sets optimized for the dispersion energy. [b] Perturbation estimate based on E_{disp}.[13] [c] Perturbation estimate based on E_{disp} and E^1.[15] [d] Value used in calibrating the estimated columns.

A summary of the results is given in Table 1. One notes that the FCP scheme yields results that are close to the BSSE-free perturbation estimates, especially the more recent extended one, while the VCP scheme yields interaction energies that are too attractive, especially in cases where the BSSE is large. For basis CR0DS4 the VCP scheme even yields a binding energy that is larger than the experimental value of −11 K, whereas the CEPA-1 method is known to be unable to fully recover all the dispersion attraction in this system. The VCP scheme must therefore be basically wrong.

It was then recognized[13,14] that the nonavailability of the partners-occupied orbitals is part of the dimer physics that one is trying to describe; viz. it is the result of Pauli's exclusion principle, leading to repulsive exchange terms in ΔE. To assess the size of these repulsions it is imperative to compare the dimer energy to a monomer reference energy where the to-be-occupied orbital space is still fully available, that is, to monomer energies evaluated using the full basis set of the dimer *including* the ghost occupied orbitals.

Thus, in reviewing the overcorrection debate up to 1987 it was concluded[8,16] that the original basis for the overcorrection concept was wrong. The sparse evidence for overcorrection that had been presented till then could all be traced to faulty reasoning. Today, we see no reason to depart from these views and indeed—as we argue in later sections—the soundness of the CP recipe is now more apparent than ever.

In spite of these developments, however, the overcorrection philosophy has survived over the years and even now is still surprisingly popular.[1,17-25] (This list of quotes is not exhaustive.) The current literature abounds with statements that "CP overcorrects the BSSE in (1)", that the "CP method was used to *estimate* the BSSE in (1)",—implying that the removal in (2) is not precise—and that "it is prudent to assume that the correct interaction energy [for method X in basis Y] will be bracketed by $\Delta E^{\mathrm{no\ CP}}$ and ΔE^{CP}". In short, CP-corrected results are still viewed with scepticism.

That so many authors stick to an unfounded and disproven concept is regrettable (for it seriously detracts from the predictive power of current quantum chemical practice), but it is perhaps not too surprising, in view of the long history of the subject. There is, moreover, another misconception that keeps the overcorrection idea alive, viz. the expectation that the CP recipe should produce a result that is closer to the exact ΔE for a given system. This is clearly a most unreasonable expectation, since the dimer basis will usually not be complete, and the quantum mechanical methods used in evaluating the energies in (2) will usually be approximate. Thus, in judging calculated interaction energies one should clearly distinguish between the basis set superposition error (BSSE) and basis set (and configuration set) incompleteness errors (BSIE).[26] BSSE is a result of the {AB} basis being more complete than {A} alone or {B} alone, but removal of BSSE will not remove the incompleteness of {AB}, and so the CP method will only give high-accuracy results if sufficient care is taken in choosing the basis set and the computational method.

B. A New Definition of BSSE?

A BSSE definition entirely different from (3) has very recently been put forward by Davidson and Chakravorty.[27] Their paper starts with a review that accurately reflects the confusion that prevails in the counterpoise debate. Notably, in their discussion of a number of pathological cases in which ΔE^{CP} is further removed from some desirable value than the uncorrected ΔE, the authors do not make a clear distinction between BSSE and BSIE, thereby creating the false impression that the CP method does not yield a valid interaction energy.

The authors then go on to propose an alternative definition of the BSSE in a finite-basis calculation on system AB. As in the above discussion they take the view that BSSE is an error made in ΔE when the monomer energies are calculated in a basis having fewer functions than are available in the dimer calculation. However instead of using the combined {AB} basis considered in the above discussions, they define BSSE in the context of an enlarged basis {ABC} where {C} is *the orthogonal complement* to {AB} such that {ABC} is a complete basis. Their BSSE is then defined, for molecule A, (omitting the minus sign in ref 27) as

$$\mathrm{BSSE}^{\mathrm{A}} = E^{\mathrm{A}}\{\mathrm{ABC}\} - E^{\mathrm{A}}\{\mathrm{AC}\} \qquad (4)$$

and likewise for molecule B. They consider that the correct dimerization energy, free of the BSSE (4), is the one in which both E^{AB} and the monomer energies are all evaluated in the {ABC} basis, which is simply the counterpoise prescription (2), but now applied at the level of the {ABC} basis. Note that for the hypothetical case {AB} itself is a complete basis, the new BSSE definition reduces to the standard result of eq 3. For the more usual case that {AB} is incomplete, the authors provide $(\mathrm{HF})_2$ and $(\mathrm{H_2O})_2$ sample calculations showing that for the basis sets they employ their prescription yields a BSSE which is larger than that of the standard recipe. This finding is not unexpected for it is well known that enlarging a given basis may lead to increased BSSE or to decreased BSSE, depending on the basis one starts from and on the type of enlargement (e.g. see ref 13) (cf. the He_2 results presented in Table 1).

On the whole this new definition does very little to resolve the dilemmas outlined before. In setting up their definition, the authors invoke the standard CP recipe (2), applied at the complete-basis level. At this level it is easy to see that this recipe is the only valid choice. However, complete-basis calculations are not a practical proposition, and it would be of much more interest to know whether the CP recipe remains valid at the level of the {AB} as well. This question remains unanswered. Furthermore, as argued before, if one is prepared to apply the counterpoise recipe at the {AB} level, there is no need to introduce or evaluate a quantity called BSSE. There is even less point in knowing how large the BSSE might have been in the hypothetical case that one had employed a basis more complete than {AB}, especially since the size of the BSSE carries no information on the quality of a given ΔE^{CP} result. We are forced to conclude that this new definition of BSSE is superfluous, and one may only hope that its introduction will not further increase the confusion surrounding the CP recipe.

IV. Evidence That the Counterpoise Method Is a Rigorously Correct Procedure

In this section we ask to what extent (2), which defines ΔE^{CP}, rigorously yields a pure interaction energy for a given system. We do this not by analyzing possible errors in (1), but by direct investigation of the implications of (2).

As stated above, the only valid criterion for judging the correctness of ΔE^{CP} is whether it is close to (or perhaps identical with) the result that should have been expected for the basis set and ab initio method employed in the supermolecular calculation. Thus, "the problem in judging the CP approach is in knowing the right answer".[28] This "right answer" is *not*, in general, the exact ΔE that would result from an exact solution of the Schrödinger equation, because of the remaining incompleteness errors in ΔE^{CP} (BSIE).

One way of checking the correctness of the CP approach has been to study a given complex in a series of basis sets which differ markedly in the BSSE, while reasonable interaction energies (reasonable for these sets) can be guessed with some confidence. Such studies have been presented by Meyer et al.,[29] by Szczesniak and Scheiner,[30] and more recently by Tao and Pan.[20-22] In most cases the CP method gave results close to those expected. Tao and Pan concluded that for the smaller of their basis sets the CP results suffered from an overcorrection of the BSSE, but this is an unjustified conclusion since they started from the assumption that the effect on ΔE from adding different basis functions to a given root basis is additive, which is far from true.[31,32]

A. A Counterpoise Theorem for Full-CI Wave Functions

We here present a direct proof of the correctness of (2) by partitioning ΔE^{CP} into first-order and higher order components, (ΔE^{HL} and $\Delta E^{\text{higher order}}$, respectively) and by relating these to their counterparts in SAPT theory, which are known to be pure interaction energies and which are known to be BSSE-free.

This confrontation of two methodologies is most easily started at the level of the first-order interaction energy (first-order in V, see below), using X-level descriptions for the monomer and the dimer, where X = SCF, CI, CEPA, MPn, etc. Starting from the X-level unperturbed monomer wave functions ψ_0^{A} and ψ_0^{B} and using their antisymmetrized product $A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}$ as a zeroth-order dimer wave function, the supermolecular first-order dimer energy, usually referred to as the Heitler–London (HL) dimer energy, is

$$E_{\mathrm{AB}}^{\mathrm{HL}} = \frac{\langle A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}|H|A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\rangle}{\langle A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}|A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\rangle} \qquad (5)$$

Using $[H,A] = 0$ and $H = H^{\mathrm{A}} + H^{\mathrm{B}} + V$, where $H^{\mathrm{A}} + H^{\mathrm{B}}$ is the sum of the free-monomer Hamiltonians, and V is the intermolecular perturbation (the same as in Londons theory), this reduces to

$$E_{\mathrm{AB}}^{\mathrm{HL}} = \frac{\langle A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}|H^{\mathrm{A}} + H^{\mathrm{B}} + V|\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\rangle}{\langle A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}|\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\rangle} \qquad (6)$$

which in turn may be written as

$$E_{\mathrm{AB}}^{\mathrm{HL}} = \frac{\langle A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}|V|\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\rangle}{\langle A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}|\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\rangle} + E^{\mathrm{A}} + E^{\mathrm{B}} + \Delta \qquad (7)$$

where the first term at the right-hand side is the (BSSE-free) first-order perturbation interaction energy $E^{1,\mathrm{SAPT}}$ as obtained in symmetry-adapted perturbation theory (SAPT).[3] The monomer energies E^{A} and E^{B} are the expectation values of H^{A} and H^{B}, while the final Δ term, which has been called zeroth-order exchange term,[33] arises because ψ_0^{A} and ψ_0^{B} usually are not precisely eigenfunctions of H^{A} and H^{B}, respectively.

We now arrive at the usual step in supermolecular calculations where the interaction energy (in this case the Heitler–London or first-order supermolecular interaction energy ΔE^{HL}) is obtained by subtracting monomer energies from the dimer energy, viz.

$$\Delta E^{\mathrm{HL}} = E_{\mathrm{AB}}^{\mathrm{HL}} - E^{\mathrm{A}} - E^{\mathrm{B}} = E^{1,\mathrm{SAPT}} + \Delta \qquad (8)$$

Several important observations can be made at this stage. Firstly, by inspection of (6) and (7), $\Delta = 0$ if exact monomer wave functions are used in constructing $A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}$. This is the basic reason why it is possible to get pure interaction energies (such as $E^{1,\mathrm{SAPT}}$ in the present case) simply by subtracting monomer energies from a supermolecular dimer energy.

Secondly, it follows from a theorem derived by Chalasinski and Gutowski[34] that Δ will also be zero in the much more important case—from the practical point of view—that $A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}$ is built from full-CI wave functions for A and B, *employing for each of them the full dimer basis set*. This implies that the monomer energies in (7), which are subtracted in getting (8), must also be evaluated in the full dimer basis set, and so one operates here precisely according to the CP approach. The only difference with (2) is that we here consider zeroth-order dimer wave functions. (Note that there is no requirement that the dimer basis should be a complete set.)

Since $\Delta = 0$ in (8) we have proved, for the finite-basis full CI case, that the first-order supermolecular energy ΔE^{HL}, being equal to $E^{1,\mathrm{SAPT}}$, is a pure interaction energy.

Turning now to the higher order supermolecular energy $\Delta E^{\text{higher order}}$, it would be cumbersome to equate it explicitly to the corresponding BSSE-free SAPT expressions, for the full-CI $\Delta E^{\text{higher order}}$ is a variational quantity, and so the SAPT expressions would have to be summed to infinite order. However, since in (7) and (8) we use DCBS descriptions, the improvements to the monomer full-CI wave functions achievable by employing the partner basis are already fully present in the starting wave function $A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}$. A further optimization of $A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}$ in the dimer calculation, to take into account the physical perturbations present in the dimer, will then give energy changes that are interpretable only as a pure interaction energy. Therefore, not only ΔE^{HL} but also the full-CI supermolecular interaction energy

$$\Delta E^{\text{full CI}} = E^{\text{AB,full CI}} - E^{\text{A,full CI}} - E^{\text{B,full CI}} \qquad (9)$$

will be a pure interaction energy provided one subtracts monomer energies obtained in the full dimer basis set. This completes the proof that at the full-CI level the counterpoise method does provide a pure, BSSE-free interaction energy.

In proving that (9) is a pure interaction energy, because $\Delta = 0$, it is essential that monomer descriptions are used that employ the entire dimer basis, that is, *including* the "to be occupied" orbitals of the ghost molecule. Thus the basic assumptions of the virtual-only-CP scheme, and of the thesis that CP must overcorrect the error in eq 1, are again found to be incorrect. A final implication of the above results is that every term in the interaction energy that one obtains is described at the level of the chosen dimer basis set. If the results are somehow unsatisfactory one should not blame the CP method, but rather proceed by improving the dimer one-electron basis set (cf. also the discussion of secondary BSSE in section V).

B. Numerical Evidence

The arguments presented above have recently been numerically confirmed[15] by calculating the (BSSE-

Table 2. Test of the Numerical Accuracy of the CP Recipe in CEPA-Intra Calculations on He_2 ($R = 5.6a_0$)

	$\Delta E^{\text{CEPA-intra}}$, K		
basis[a]	no CP	CP	PT estimate from eq 10
CR0DS2	7.93	10.778	10.838
CR0DS4	−20.14	10.719	10.764
CR2DS2	9.74	10.447	10.448
CR2DS4	8.37	10.441	10.443
CR4′DS2	10.23	10.432	10.432
CR4′DS3	10.00	10.429	10.430
CR4′DS4	9.80	10.429[b]	[10.429]

[a] See Table 1 for details. [b] Used in calibrating the final column.

free) first-order SAPT interaction energy $E^{1,\text{SAPT}}$ of two (full-CI) correlated He atoms for the CRnDSm sequence of basis sets which have markedly different BSSE when used in supermolecular calculations. In the absence of programs capable of calculating $E^{\text{HL}}_{\text{AB}}$ for correlated wave functions, these $E^{1,\text{SAPT}}$ values were compared to those of the counterpoise-corrected CEPA-1 interaction energy obtained from calculations in which the intercorrelating (dispersion-type) doubly-excited configurations had been omitted from the dimer wave function, while the intracorrelating double excitations that introduce BSSE had been kept. This interaction energy $\Delta E^{\text{CEPA-intra}}$ is dominated by the desired ΔE^{HL}, which is repulsive for He_2, but it contains in addition a small higher order energy due to the relaxation of the monomer electron distributions in the field of the other monomer. Its value was estimated to be −0.207 K for the larger basis sets.

Since, according to (8), ΔE^{HL} should equal $E^{1,\text{SAPT}}$ for the present (DCBS) full-CI monomer descriptions, it follows that a reasonable BSSE-free perturbation estimate for $\Delta E^{\text{CEPA-intra}}$ should be

$$\Delta E^{\text{CEPA-intra}} \approx E^{1,\text{SAPT}} - 0.207\ \text{K} \qquad (10)$$

Selected results from ref 15 are given in Table 2. To put these results in perspective, a column $\Delta E^{\text{CEPA-intra,no CP}}$ is included as well. For the larger basis sets, where the small $\Delta E^{\text{higher order}}$ has become stable, the CP-corrected results follow the perturbation estimate to within 0.002 K. That is, to machine precision. Since the BSSE for these larger sets still varies from 0.2 to 2.1 K it follows that the CP-corrected energies must have been fully free of BSSE, in accordance with the theorem of the previous section.

C. The Case of MCBS SCF Monomer Descriptions

Turning now to more accessible monomer descriptions than the full-CI approach, let us first consider the case of MCBS SCF descriptions, which we will encounter in section VII. In this case the (MCBS) counterpoise recipe leading to the first-order interaction energy ΔE^{HL} of (8) is to subtract MCBS SCF monomer energies from a HL dimer energy (5) constructed using the MCBS SCF occupied orbitals {occA} and {occB} of A and B. Fröman and Löwdin[35] have shown that in this case Δ is of the order S^2, where S is a typical overlap integral between the occupied orbitals of A and B. Since S may be as large as 0.1−0.3, Δ is not expected to be small.

As an example, we quote some results for He_2 that were obtained using a 10s GTO basis for He.[14] The SCF MCBS results at $R = 5.6a_0$ were

$$\Delta E^{\text{HL}} = 30.06\ \mu\text{H} \quad E^{1,\text{SAPT}} = 28.22\ \mu\text{H}$$
$$\Delta = 1.83\ \mu\text{H}$$

showing that Δ is too large to ignore.

In this case it is much more difficult to decide whether ΔE^{HL} can be regarded as a pure interaction energy than it was in the DCBS full-CI case. According to (8), ΔE^{HL} equals the sum of $E^{1,\text{SAPT}}$, which is a pure interaction energy, and Δ, which at first sight is not, since it is a matrix element over H^{A} and H^{B} rather than over V. However, it has been noted[36,37] that adding Δ to $E^{1,\text{SAPT}}$ gives a result much closer to the complete-basis SCF result (viz. in the present He_2 case, ΔE^{HL}(s-limit) = 30.69 μH[14]), and so Δ has been interpreted as a correction to the exchange-repulsion term arising from the inaccuracy of the MCBS SCF wave functions.

This rather ad hoc interpretation has later[14] been refined as follows. Making use of the fact that for the SCF case $A\psi_0^{\text{A}}\psi_0^{\text{B}}$ is invariant to transformations among the orbitals {occA, occB}, the dimer energy E^{HL} of (5) can be *reinterpreted* as the dimer energy for two SCF monomers A and B, whose SCF orbitals are optimized in the basis {occA, occB}, rather than in the MCBS basis alone. This will lead to slightly lower monomer SCF energies E^{A} and E^{B} than before (in the present example the lowering was 0.008 μH), and so ΔE^{HL} of (8) will be slightly more repulsive than before (viz. ΔE^{HL}{occA, occB} = 30.07 μH). However, the most striking results are those for the reoptimized SCF orbitals, in which one has $\Delta \approx 0$ (for reasons to be discussed below) and $E^{1,\text{SAPT}} \approx 30.07$ μH, so that ΔE^{HL} now practically equals $E^{1,\text{SAPT}}$, which is a pure interaction energy.

This discussion shows that the occurrence of a sizeable Δ in the original MCBS data is a signal that there exist lower energy monomer descriptions than the original MCBS SCF energies which are still compatible with the dimer description $A\psi_0^{\text{A}}\psi_0^{\text{B}}$. When used in (7) these will yield a more repulsive ΔE^{HL}, which is now interpretable as a pure interaction energy (cf. Cammi et al.[38] and ref 16 for further discussions). The difference with the simpler ΔE^{HL} can be quite large, especially if the monomer basis sets are small, as shown in ref 38 and Table VIII of ref 16.

The final ΔE^{SCF} contains, in addition to ΔE^{HL} discussed above, a relaxation energy, $\Delta E^{\text{higher order}}$, which is much more difficult to analyze. However, the DCBS data to be discussed below suggest that $\Delta E^{\text{higher order}}$ will in practice very nearly be a pure interaction energy. Our overall conclusion is therefore that the usual CP recipe applied to SCF calculations constrained to the MCBS level (i.e. the subtraction of MCBS SCF monomer energies E^{A} and E^{B} from a MCBS-constrained SCF dimer energy) yields a reasonably pure interaction energy, $\Delta E^{\text{SCF,CP}}$, which will be somewhat too low compared to that of the refined recipe where ΔE is obtained by subtracting SCF monomer energies E^{A} and E^{B} obtained in the {occA, occB} orbital space.

D. The Case of DCBS HF Monomer Descriptions

Standard supermolecular dimer SCF calculations allow full freedom to the monomer description in the dimer wave function, and so the analysis of ΔE^{CP} in its components ΔE^{HL} and $\Delta E^{\mathrm{higher\ order}}$ should now start from DCBS SCF monomer descriptions. It has been shown (Groen and van Duijneveldt, quoted in ref 34) that in this case, just as in the case of exact Hartree–Fock monomer descriptions,[39] Δ will be of the order S^4, where S is a typical overlap integral between the occupied orbitals of A and B. Δ may therefore be expected to be small, but only a few calculated values are known to us. From a footnote in ref 37 one finds for He_2 at $R = 5.6a_0$ a value Δ (SCF, 10 s set) ≈ 0.003 μH, which is negligibly small compared to other errors in this type of calculation. For a near-equilibrium geometry of $(H_2O)_2$, Rybak et al.,[40] using the requisite formulas for $E^{1,\mathrm{SAPT}}$ derived by Jeziorski et al.[41] and using dimer-basis monomer wave functions, have recently calculated $E^{1,\mathrm{SAPT}}$ at the Hartree–Fock level, finding $E^{1,\mathrm{SAPT}} = -2.12$ kcal/mol. For the present discussion we have calculated the corresponding Hartree–Fock $E_{\mathrm{AB}}^{\mathrm{HL}}$ result (this is the zeroth-iteration dimer energy in the dimer SCF calculation), using the same basis set and geometry, and we obtained $\Delta E^{\mathrm{HL}} = -2.09$ kcal/mol.[42] Thus, $\Delta = 0.03$ kcal/mol in this example, an ambiguity that is comparable to the basis set incompleteness error but much smaller than the error made in this calculation by not accounting for electron correlation effects. This Δ value, already small at the HF level, is bound to decrease rapidly as soon as one introduces some level of CI in the monomer description.[34] These two examples show that, for all practical purposes, CP-corrected ΔE^{HL} values may be viewed as pure first-order interaction energies between monomers described at the DCBS level, for systems ranging from He_2 to $(H_2O)_2$.

The full ΔE^{SCF} contains, in addition to ΔE^{HL}, a $\Delta E^{\mathrm{higher\ order}}$ term which again is difficult to analyze. However, convincing numerical evidence showing that in DCBS SCF work $\Delta E^{\mathrm{higher\ order}}$ will very nearly be the pure interaction energy as given by SAPT has recently been provided by Cybulski and Chalasinski.[43] These authors performed parallel SCF and BSSE-free SAPT calculations on the system $He-Li^+$ at a distance $R = 10a_0$. At this distance the overlap-dependent exchange energies, including Δ, are vanishingly small. The first-order (electrostatic) energy ought also to be small and only $\Delta E^{\mathrm{higher\ order}}$ is large, being due to polarization of the He in the Li^+ field. In the SAPT calculations this induction energy was evaluated up to the fourth order in V, using DCBS monomer wave functions. The SCF calculations are subject to BSSE, which is still large at this distance. A selection of the results is shown in Table 3. The results show that for both basis sets ΔE^{CP} is astonishingly close to E^{SAPT}. It follows that ΔE^{CP}, like E^{SAPT} is a pure interaction enrgy. It is also clear that the BSSE that is still present in $\Delta E^{\mathrm{no\ CP}}$ was fully removed by applying the CP recipe. The results finally illustrate that even though ΔE^{CP} is a pure interaction energy, this ΔE result may still be quite poor. For example, the first-order energy obtained for the 31G* basis is clearly much too low. This arises because at the DCBS level the He atom acquires a small dipole moment (cf. section V). Only by using larger basis sets can one guarantee that ΔE^{CP} will not only be pure (i.e. free from BSSE) but also accurate.

Table 3. Comparison of CP and No-CP SCF Interaction Energies with E^{SAPT} for $He-Li^+$ [43] ($R = 10a_0$)

	basis 31G*	large basis
$E^{\mathrm{SAPT,first\ order}}$, μH	−20.317	−0.052
$E^{\mathrm{SAPT,higher\ order}}$, μH	−21.202	−67.601
$E^{\mathrm{SAPT,total}}$, μH	−41.519	−67.653
$\Delta E^{\mathrm{SCF,no\ CP}}$, μH	−126.133	−67.775
$\Delta E^{\mathrm{SCF,CP}}$, μH	−41.512	−67.665

The same paper[43] also contained MP2 calculations on $He-Li^+$, and for these too the agreement of the CP corrected data with the appropriate SAPT energies was excellent.

E. Configuration State Counterpoise Procedure (CSCP)

It is actually possible to redefine the monomer descriptions that correspond to a given dimer SCF calculation in such a way that here, as in the full-CI case, the zeroth-order exchange term Δ becomes zero. The monomer wave functions should then be taken to be monomer full-CI wave functions in the limited orbital space {occA, occB}. These orbitals should be optimized to minimize the energy $E^{\mathrm{A}} + E^{\mathrm{B}}$ in this description. The antisymmetrized product $A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}$ of these limited-space full-CI wave functions is identical to a single-determinant wave function formed from the reoptimized occupied SCF orbitals of A and B, which when used in (5–8) will yield $\Delta = 0$, and so $\Delta E^{\mathrm{HL}} = E^{1,\mathrm{SAPT}}$ is a pure interaction energy. Moreover, since all monomer energy improvements that are compatible with a one-determinant dimer wave function are already fully present in this $A\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}$, a subsequent dimer SCF optimization starting from this wave function will yield a pure $\Delta E^{\mathrm{higher\ order}}$ interaction energy.

Hence the overall interaction energy

$$\Delta E^{\mathrm{CSCP}} = E^{\mathrm{AB,SCF}} - E^{\mathrm{A,limited\ full\text{-}CI}} - E^{\mathrm{B,limited\ full\text{-}CI}} \qquad (11)$$

is rigorously an interaction energy.

We have labeled this procedure "configuration state counterpoise" (CSCP)[2] to distinguish it from the usual counterpoise at the SCF level which has

$$\Delta E^{\mathrm{CP}} = E^{\mathrm{AB,SCF}} - E^{\mathrm{A,SCF}} - E^{\mathrm{B,SCF}} \qquad (12)$$

(Of course, all quantities in (11) and (12) are to be evaluated in the full dimer basis.) The difference between the results (12) and (11) defines the "configuration set superposition error" (CSSE) residing in (12) because one here employs for the monomers a configuration set (i.e. a single-configuration wave function) that does not precisely match the n-electron dimer description, resulting in a nonzero Δ. In order to avoid this CSSE one must use a higher level CI description for the monomers than one employs in the dimer calculation.

The size of the CSSE will be some fraction of the difference between the monomer full-CI energies in the full DCBS and MCBS basis sets, i.e. it will be a fraction of the size of the ordinary BSSE at the full-CI level. Since BSSE at the CI level can be quite large, it may seem that CSSE is a problem as well. However, there is evidence that significant contributions to the CI-level BSSE arise only from double, or at most quadruple, excitations to ghost orbitals.[2] This is also apparent from the rapid decrease of the BSSE in calculations on $(H_2O)_2$ at the consecutive MP2, MP3, and MP4 levels of theory.[32] Thus, not only the value of Δ but also the size of the CSSE will rapidly decrease from values at the Hartree–Fock level, once a sufficient level of electron correlation is introduced. As a rule no explicit correction for CSSE should therefore be necessary.

An exception to this rule has been encountered[9,10] in calculations on He_2 employing the interacting correlated fragments (ICF) approach. In one example, the dimer calculation employed a CASSCF reference space built, in addition to the 1s orbitals, from the most important correlating orbitals of each He atom, viz. 2s, $2p_x$, $2p_y$, $2p_z$. For the corresponding monomers one has the option to employ a CAS description including only the atoms own correlating orbitals or a CAS description employing the full active orbital set of the dimer. Only the latter choice was found to give adequate results, since it prevents what we here call CSSE.

V. Basis Set Extension Effects on the Components of ΔE

According to the analysis in section IV the counterpoise approach yields interaction energies in which each contributing term is described at the DCBS level. Such results may differ significantly from the corresponding MCBS results, as was first pointed out by Urban and Hobza.[44] The changes when going to the DCBS description were later designated as higher order basis set superposition effects[45] but are also referred to as secondary BSSE,[46] which is somewhat misleading, since extending a basis set is not in itself an error. The evidence obtained in later years suggests that the use of the DCBS description has a beneficial effect on monomer polarizabilities[45] and on the exchange, dispersion, and polarization interaction energies.[16,8,47] Dimer centered basis sets are more complete for these quantities than are MCBS sets. By contrast, the electrostatic component of ΔE may be affected adversely.[14,43,45,48] This is related to the symmetry lowering experienced by a monomer in the dimer basis set which gives rise to spurious dipoles such as components perpendicular to the 2-fold axis in a water monomer. The modification (at the DCBS level) of moments which are nonzero already in an MCBS description may be equally troublesome.

A recent analysis of the correlated electrostatic interaction energy, E_{coul}, in He_2 showed[15] that the electron–electron repulsion term and the electron–nucleus attraction term are both severely distorted in a DCBS description, but the errors cancel almost precisely and reasonable results were found for the total E_{coul}. In the same study it was also found that the diffuse polarization functions that a basis must contain to give a good description of the dispersion energy tend to give an exchange repulsion energy that is too high if the basis lacks corresponding high-exponent functions. A similar finding had been reported earlier by Meyer and Frommhold.[49]

Table 4. Effect of Basis-Set Extension on the SCF First-Order Interaction Energies (μH) and on the SCF and CEPA Dipole Moments[a] (au) of $(H_2O)_2$ (Geometry M2[31])

basis set[b]	$\Delta E^{\mathrm{HL}}_{\mathrm{DCBS}}$	$\Delta E^{\mathrm{HL}}_{\mathrm{MCBS}}$	$\mu^{\mathrm{AB'}}_{\mathrm{SCF}}$	$\mu^{\mathrm{BA'}}_{\mathrm{SCF}}$	$\mu^{\mathrm{AB'}}_{\mathrm{CEPA}}$	$\mu^{\mathrm{BA'}}_{\mathrm{CEPA}}$
DZP	−2399	−3280	0.794	0.807	0.741	0.762
DZPPc	−2048	−2769	0.768	0.780	0.696	0.715
EZPPc	−2089	−2269	0.784	0.787	0.726	0.729
LPPc	−2069	−2178	0.784	0.785	0.726	0.728
EZPPcB	−2012	−2204	0.785	0.787	0.726	0.730
LPPcB	−1991	−2149	0.784	0.785	0.726	0.729
EZPPcBF	−1973	−2001	0.785	0.787	0.728	0.731
EZPPPBFD	−1948	−2023	0.780	0.781	0.721	0.723

[a] The superscript AB′ denotes that the A dipole was evaluated in the full dimer basis, etc. The proton donor is labeled A, the acceptor B. [b] DZ, ES, EZ, and L denote progressively larger sp and s sets on O and H, respectively. P, PPc, and PPP denote single, double, and triple sets of polarization functions d^{O} and p^{H}. F is a set of f^{O} functions, D a set of d^{H} functions, and B is a set of bond functions on H-O.

The role of basis-set extension effects has recently also been investigated for $(HF)_2$[47,50] and for $(H_2O)_2$.[31] A selection of the $(H_2O)_2$ results is given in Table 4. The DCBS and MCBS values for ΔE^{HL} are seen to converge to the same limiting value, their difference being gradually reduced for larger basis sets. The DCBS series was found to converge much more smoothly and quickly to the basis-set limit than the MCBS series. This leads to the important conclusion that methods that try to avoid BSSE by maintaining an MCBS-level description throughout the dimer calculation (cf. section VII) will have difficulty in reaching the basis set limit. In this context, a relevant conclusion of the $(HF)_2$ study was that the diffuse basis functions usually designated with the symbol "+" take the MCBS results close to the DCBS values, which themselves are much less sensitive to the addition of such functions. In the $(H_2O)_2$ study, the dipole moment differences between the donor and acceptor molecules (which reflect the artefacts of using DCBS monomer descriptions) became vanishingly small as the basis grows larger before the dipole moment itself converges to its basis-set limit (cf. Table 4). It was concluded from this that adjustments to ΔE^{CP}[16] to correct for artefacts introduced at the DCBS level are unnecessary. This concurs with a similar study by Szczesniak and Scheiner[51] on the complexes of Li^+ with NH_3 and H_2O which illustrated the possibility of reducing the MCBS–DCBS differences to very small values by employing Huzinaga's well-tempered basis sets.[52]

VI. Recent Criticisms of the Counterpoise Approach

A. Mayer's Criticism

The conclusion of section IV that the counterpoise recipe is a rigorous one is seemingly in conflict with the conclusions, drawn by Mayer and co-workers from a series of analytical model studies,[53,54] that ΔE^{CP} is subject to a hidden additivity assumption and contains some "extraneous" terms, one of which is due to the supposedly spurious occupied-to-occupied delocalization taking place in the monomer + ghost calculations.

It has recently been shown that these objections partly arose because in the model studies ΔE^{CP} was analyzed starting from an MCBS description for the unperturbed monomers.[55] These problems disappear when similar model systems are studied[43,55] starting from DCBS descriptions for the monomers. As noted in section IIIA, the occupied-to-occupied terms in the ghost calculations, far from being spurious, are necessary to guarantee a correct evaluation of exchange repulsion effects.

The remainder of the problems noted by Mayer et al. (e.g. the appearance of spurious dipole moments in a DCBS description) are basis-set extension effects on ΔE as discussed in section V. These problems are not to be ignored, but they do not constitute a strong argument against the use of the CP approach. In fact, several authors using the BSSE-free SAPT method, while they are free to employ MCBS descriptions for the fragments in a complex, have chosen to employ DCBS descriptions for this purpose (e.g. see the work of Szalewicz and co-workers[40,56]).

B. Numerical Problems

Cook et al.,[57] when performing SCF + MP2 calculations on the alanine dimer in a 6-31G** basis observed that applying the CP method led to a highly repulsive ΔE value. In analyzing this problem[57,58] they proposed that the error originates from the fact that in the monomer + ghost calculations the double excitations included in the MP2 step use a larger excitation space than is available to the monomer present in the dimer (since excitations to the occupied MO's on the partner molecule are then Pauli-forbidden). Noga and Vibok[59] have criticized the CP method at the correlated level for precisely the same reason. Cook et al. tried to identify the offending orbitals (termed ghost virtual orbitals) but independent calculations have shown[55] that omitting these from the monomer + ghost calculation does not solve the problem.

It seems clear that Cook et al.'s interpretation of the problem is incorrect. From sections III and IV, it follows that the inclusion of the fully occupied + virtual orbital space of the ghost, far from generating errors, is essential for getting a proper interaction energy. Moreover, if something is basically wrong in the CP approach at the MP2 level, it should have shown up in some other of the numerous MP2 studies that have been published to date. Thus, if Cook et al.'s results were really too repulsive (which remains to be confirmed) it must have had some other cause. One possibility that suggests itself is the occurrence of near linear dependencies in the monomer + ghost SCF orbitals, which degrade the following MP2 step.

VII. Alternative Ways of Avoiding BSSE

Motivated by the seemingly endless debate in the literature about the validity of the counterpoise approach, several authors have sought to restrict the description of the monomers in a supermolecular dimer calculation in such a way that usage of the partner orbitals for improving the monomers own energy is avoided from the outset. The monomer energies embodied in E^{AB} are then obtained at the MCBS level, and so by subtracting MCBS monomer energies, one obtains a ΔE that seems free of matching errors. Actually, this is a straightforward application of the counterpoise concept, except that MCBS descriptions are used throughout, instead of the DCBS descriptions of eq 2. This type of approach looks attractive at first sight, but several problems have turned up in practice, which we discuss below.

A problem shared by all these methods in which (part of) the monomer wave function is described in MCBS, while the full dimer Hamiltonian is used for calculating the dimer energy, is that the zeroth-order exchange term Δ is potentially large. For example, a HF-level description of this type would have a Δ of the order of S^2,[16] as opposed to the order S^4 result that obtains when DCBS descriptions are used (cf. section IV). Consequently, as explained for the SCF case in section IVC, the procedure used by these authors to obtain ΔE, viz. to subtract MCBS monomer energies from an MCBS-constrained dimer energy, does *not* yield a pure interaction energy. The ΔE obtained will be noticeably more attractive than the pure ΔE that can be obtained by subtracting monomer energies in the {occA, occB} space. The difference will disappear only in the limit that the MCBS basis approaches the basis set limit, for the S^2 component of Δ will then go to zero.

A. Methods Avoiding BSSE at the HF Level

Exploiting a method originally described by Stoll et al.,[60] Cullen[26] has recently performed supermolecular SCF calculations on several hydrogen-bonded complexes in which the monomer orbitals in the dimer calculation were expanded in the monomers own basis set only (strictly monomer MO approach, SMMO). The method is closely related to the (strictly local) valence bond approach advocated some time ago by Cooper et al.[61] and by Collins and Gallup.[62] Cullen obtained several interesting results in this way. For example, he found that the SMMO ΔE's were consistently above (less negative than) the results obtained using the standard counterpoise approach (and, clearly, still more above the uncorrected ΔE of (1)). Cullen's interpretation of this result, largely confirmed by a later more detailed analysis,[55] was that ΔE^{SMMO} lacks the attractive contribution from charge-transfer (or charge-delocalizing) excitations from the occupied MO's of one monomer to the virtuals of the other, and in fact by comparing his data to the standard counterpoised ΔE^{CP} Cullen was able to estimate this somewhat elusive contribution to ΔE, finding values ranging from nearly zero to several kilocalories per mole depending on the system, the intermolecular separation R, and the basis set. The missing CT energy in ΔE^{SMMO} hardly became less by using larger basis sets, and so there is no hope that for hydrogen-bonded complexes interaction energies accurate to within 0.1 kcal/mol or so can readily be obtained by the SMMO (or strictly local VB) method.

As expected from the theory of CT effects, the missing CT energy was found to decay very rapidly with R. In other words, ΔE^{SMMO} and ΔE^{CP} become virtually identical at some R, usually larger than R_e. Interestingly, the BSSE of (3) was still large at this R. To the extent that SMMO is free of BSSE it then follows that ΔE^{CP} was also free of BSSE, in agreement with the conclusions of section IV.

A related proposal[63] to obtain BSSE-free SCF interaction energies by constraining the monomer description in the dimer calculation has been found to show some defects[55,64,65] and has not yet led to useful results.

A potentially more powerful method, aimed at avoiding only those basis-set extension effects in the dimer calculation that give rise to BSSE, is the chemical Hamiltonian approach (CHA) of Mayer and co-workers. Several variants have been proposed, of which the CHA/CE variant[53,66] is considered to be the most accurate, and the CHA/F variant[67-69] is more convenient to use.

In the CHA approach, the monomers in the dimer are not allowed to improve their own energy by using the partner basis, but mixing of A and B orbitals induced by the intermolecular terms in the dimer Hamiltonian does take place, and so, in contrast to the SMMO case, charge transfer effects are accounted for. Once the dimer wave function has been obtained, the dimer energy is calculated as an expectation value over the full dimer Hamiltonian. According to the detailed analysis by Gutowski and Chalasinski[55] the Hartree–Fock level CHA interaction energy then comprises a first-order interaction energy at the MCBS level, and a higher order (or deformation) interaction energy that is given at the DCBS level.

The HF level and MP2 level CHA/CE results for He_2 reported by Noga and Vibok[59] have been compared to the corresponding results in the same basis sets obtained by the standard counterpoise method both by the original authors[59] and by Gutowski and Chalasinski.[55] The differences between the two sets of results were found to be large in comparison to the binding energy of He_2. Noga and Vibok ascribed the differences to flaws in the CP approach. Gutowski and Chalasinski pointed out, however, that the CP results were very reasonable in comparison to known results in much larger basis sets, whereas the CHA/CE results were quite unreasonable and ill-behaved as a function of distance. The results for $(HF)_2$ reported in the same paper[59] are also suspect, since they show an alarming lack of repulsion at short distances, not only in the SCF step but also in the MP2 step.

Valiron et al.[69] have recently performed a similar comparison at the SCF level for a number of hydrogen-bonded complexes. In these examples, the CHA/F results for nine different basis sets and at a range of intermolecular separations were compared to the corresponding standard CP results. Although the comparisons were presented only in graphical form, the differences between the two approaches can be seen to be quite small (typically 0.1–0.4 kcal/mol), especially for the larger basis sets, which were of polarized triple-ζ quality. Valiron et al. concluded that the remaining small differences are due to the "spurious occupied-to-occupied delocalization" inherent in the ghost calculations of the CP approach.

However, as discussed before, this aspect of the ghost calculations is an essential ingredient of an accurate ΔE calculation. A more likely explanation of the differences is that a MCBS-level description of the first-order interaction energy is employed in CHA/F while a DCBS-level description is used in the CP results. According to the discussion in sections IVC and V, the use of MCBS descriptions can easily give rise to differences of the magnitude encountered here. As one approaches a complete basis, the difference between the MCBS and DCBS descriptions is expected to disappear before the BSSE becomes zero, and this is precisely the pattern shown by the CHA/F and CP results of Valiron et al.

On the whole it appears that for these H-bonded systems the differences between the HF-level CHA/F and CP results are small compared to the errors associated with the use of incomplete basis sets and the neglect of correlation effects.

B. Methods Avoiding BSSE at the Correlated Level

An attractive way to analyze the contribution of electron correlation effects to ΔE is to start from a description at the single-configuration level (e.g. the dimer SCF wave function) in which the (occupied) orbitals are localized on the two fragments involved. Double replacement configurations may then be classified as contributing to the intramolecular correlation in fragment A or in fragment B (when both replaced electrons originate from the occupieds of that fragment) or as intercorrelating (dispersion-type) configurations when one electron comes from A and one from B. A well-known class of CI methods based on such a partitioning is the interacting correlated fragments (ICF) approach developed by McLean and co-workers.[9] The same idea has recently been used in calculations at the CEPA level,[15,49] at the MRCI level,[70] at the MP2 level[25,71,72] and in the so-called extended group function models.[73,74]

In each of these papers the partitioning of the space of excited configurations was used to partition the correlation interaction energy according to

$$\Delta E^{\mathrm{CI}} = \Delta E^{\mathrm{intra}} + \Delta E^{\mathrm{inter}} \qquad (13)$$

where the intra contributions are defined by subtracting the correlation energy of fragments A and B from the energy contribution due to the corresponding excitations in the dimer. In calculations employing for the dimer the full (Hartree–Fock) virtual space for all three types of excitation BSSE will enter the $\Delta E^{\mathrm{intra}}$ terms if one subtracts MCBS monomer energies. BSSE will be avoided if DCBS descriptions are used.

It has been recognized long ago by Liu and McLean[7] that in this type of approach one could prevent BSSE from entering the calculated ΔE also by omitting from the dimer calculation those intracorrelating configurations that use orbitals of the partner fragment. This idea has been implemented in several of the more recent studies by partitioning the dimer virtual space in parts corresponding to A and B, respectively. Kapuy and Kozmutza[72] carried out a Boys localization of the dimer (Hartree–Fock) virtuals for this purpose, but subsequent calculations showed that the localized virtual space did not correspond closely enough to that of the isolated monomers to permit the omission of the excitations to the virtual space of the partner molecule. In the papers by Meyer and Frommhold,[49] Saebo et al.,[25] and Røeggen,[73,74] the monomers own basis set (after suitable orthogonalization, if desired) was used to generate the virtual space of A in the dimer calculation. This guarantees a good matching to the (MCBS) virtual space of the free monomers.

The most clear-cut results obtained in this way are the $(H_2O)_2$ MP2-level results reported by Saebo et al.[25] These authors used a sequence of four basis sets in an attempt to reach converged results for ΔE. They also performed independent SAPT-type calculations to monitor the dispersion energy provided by their MP2 descriptions. Their local ("BSSE-free") MP2 interaction energy was roughly constant for their sequence of basis sets, from which they concluded that convergence had been reached and that the corresponding CP-corrected results, which showed less attraction, suffered from overcorrection of the BSSE. Although their data deserve further study, both conclusions seem premature, since in fact from their data it follows that the ΔE^{inter} results were still converging to more negative values and the ΔE^{intra} to more repulsive values even for their largest basis. This points to difficulties in converging an MCBS description of ΔE^{intra} to the basis set limit that are not observed in the DCBS description.[31]

VIII. Practical Points

A. Geometry Optimization and Vibrational Frequencies

One of the useful features of current quantum chemical program packages is the option of automated optimization, using analytical derivative techniques, of the geometry (R) of a complex with or without concomitant optimization of the intramolecular geometrical parameters (r). Such methods operate on the uncorrected total energy $E^{AB}(R,r)$ of the complex, and so the results are contaminated with BSSE. There is no formal problem in carrying out such a calculation while avoiding the BSSE that enters the intermolecular interaction energy. The function that should then be minimized is, in stead of E^{AB},[75-77]

$$E(R,r) = E_{\text{def}}(r) + \Delta E^{\text{CP}}(R,r) \qquad (14)$$

where $E_{\text{def}}(r)$ is the energy required to reach a particular deformed geometry (r) of the free monomers, while $\Delta E^{\text{CP}}(R,r)$ is the counterpoised interaction energy when these deformed monomers approach to some complex geometry R. E_{def} can be calculated in calculations entirely separate from those of ΔE^{CP}, using basis sets and computational schemes that are optimal for this purpose. (This is actually an advantage compared to the case where one optimizes E^{AB} since the description of E^{AB} must then simultaneously be adequate for intramolecular distortions and for intermolecular interactions.) Since analytical derivatives for all energies entering (14) have already been implemented in current programs, there is no fundamental problem in designing automated optimization algorithms based on (14), but no such algorithm has yet been implemented. The application of (14) therefore remains rather laborious, and no fully optimized structures, using (14), for complexes of polyatomic molecules have yet been reported.

Nevertheless, information on the distortion of potential surfaces caused by optimizing E^{AB} rather than (14) is gradually coming available. In a study of Ne_2 and $(CO_2)_2$, Eggenberger et al.[78] have noted the much too short equilibrium distances that result when BSSE is not corrected for. Apparently, the effect of BSSE dominates over all other errors that might have distorted the surface, such as the underestimation of the dispersion energy. For water dimer, similar shortenings have been reported.[31,79] These shortenings were exceptionally large upon the addition of bond functions in the intermolecular overlap region,[31] and so this type of basis set improvement (it improves mainly the description of the dispersion attraction[31,80-82]) can only be admitted when using (14). (The CP method offers no problems in dealing with bondfunctions or any other unconventional basis set.) More conventional improvements of the basis, such as the choice of progressively larger members of the family of aug-cc-pVXZ sets,[83] might be expected to produce a systematic increase of the uncorrected R_e from values which are too short to values approaching the experimental one, but recent experiences with water dimer suggest that the convergence may in fact be irregular and unpredictable.[84] By contrast, for water dimer[31] the use of (14) produced a smooth convergence from too long R_e values to a final value that after vibrational averaging agrees to within 0.005 Å with Odutola and Dyke's experimental result.[85] To illustrate these points a selection of the equilibrium distances and the corresponding binding energies for $(H_2O)_2$ is shown in Table 5.

The effect of BSSE on calculated vibrational frequencies can also be avoided by using (14) rather than the uncorrected E^{AB}. For hydrogen-bonded complexes it has been found that the errors at the SCF level are small. But at the correlated level BSSE leads to OH vibrational frequency shifts (red shifts) that are too large[86] and to an imprecise prediction of the position of hot bands and combination bands associated with the simultaneous excitation of an intermolecular and an intramolecular mode.[87,88]

B. Ambiguities in the Calculated Binding Energies of *n*-mers

The simplest way of forming a trimer is by the process A + B + C → ABC, and the CP approach to calculating the ΔE for this process would be to use the trimer basis for all fragments. The formation of a trimer ABC can also be done in steps such as A + B → AB, followed by AB + C → ABC. If one adopts the CP method in calculating the binding energies for each individual step, then in the second step one would employ the trimer basis {ABC} for all fragments involved. But in the first step one has two choices, viz. to calculate all fragment energies in the {AB} set or to calculate all fragment energies in the

Table 5. Convergence to the Basis-Set Limit of the Equilibrium Binding Energy (kcal/mol) and O–O distance (Å) for $(H_2O)_2$ for Several Basis Sets[a]

	SCF		SCF + MP2	
basis set	*R*	Δ*E*	*R*	Δ*E*
MCY′[79]	3.05 (3.04)	−3.8 (−4.0)	2.99 (2.90)	−4.3 (−5.9)
(5,4,1/3,1)[95]	3.04 (2.99)	−4.04 (−5.14)		
DZP′	3.04	−4.16	3.04	−4.35
ESP	3.03 (3.01)	−3.89 (−4.26)	2.98 (2.84)	−4.50 (−6.03)
ESPB	3.03 (3.01)	−3.95 (−4.66)	2.97 (2.55)	−4.71 (−12.50)
EZPPcB	3.03 (3.02)	−3.80 (−4.10)	2.96 (2.63)	−4.61 (−8.07)
EZPPPBFD	3.05 (3.03)	−3.76 (−4.06)	2.94 (2.80)	−4.68 (−8.21)

[a] The values between parentheses were obtained without CP correction. Taken from ref 31. See Table 4 for details of the basis sets employed in the last five rows.

{ABC} set. Both choices adhere to the CP principle, but it has been found[89−91] that the two choices for the first step give different Δ*E*'s and hence different overall Δ*E*'s as well. If one considers the alternative path A + C → AC followed by AC + B → ABC, then again two choices can be made. From the point of view of thermodynamics, the overall binding energy should be independent of the chosen path, but only the choice to calculate all individual energies in basis {ABC} will yield the same overall Δ*E* as that for the first path.[91] Thus the use of the {ABC} set for all fragments was recommended for the sake of consistency. Likewise, in larger clusters, ΔE^{CP} should preferably be calculated by using monomer energies evaluated in the full cluster basis (although sets on distant ghosts may make a tiny contribution in practice[90,91]).

One may wonder about the physical significance of the various overall Δ*E* values that could have been obtained by making different choices. Since the CP method is followed in all variants, all Δ*E*'s can rightfully be considered as "pure interaction energies" for system ABC. The reason that the results can be different must therefore be that the different basis sets, such as {AB} or {ABC} when studying the step A + B → AB, are of different quality in describing the physics of this step. Thus the differences are a symptom of lingering basis set incompleteness, and they are an indication of the error margin in the final Δ*E*, as compared to the result in a complete basis. Note that the ambiguities are not inherent to the use of the CP approach, as they would also arise when applying a BSSE-free method such as SAPT.

IX. Conclusion and Outlook

Counterpoise methods do not yield exact interaction energies in one stroke. However they can give a pure interaction energy that is free of BSSE. This allows the user to focus on improving the description of the physics of the interaction without having to worry about the size of BSSE as well. In this way, interaction energies converged to the basis set limit have now been obtained for systems ranging from He_2 to $(H_2O)_2$.[9,31,50,51,70] Similar attempts to converge *uncorrected* interaction energies to the basis set limit[1,32,92] have been less successful, even though very large basis sets (necessary to suppress BSSE) were employed. The alternative BSSE-avoiding schemes discussed in section VII (with the exception of the Hartree–Fock level CHA/F model) have also not been very successful in reaching good accuracy, mainly because restricting (part of) the monomer description to remain at the MCBS level necessitates the use of excessively large MCBS basis sets before the components of Δ*E* will converge.

An intriguing aspect of the CP approach that will need further exploration is that the relative stability of isomers may be different at the uncorrected and corrected levels.[93,94] Other areas for future work are the development of CP-based algorithms for automatic geometry optimization, and the development of CP techniques suitable for open-shell interactions. This would open the possibility of applying a rigorous CP method within molecules and thus of studying weak interactions within molecules, such as internal hydrogen bonds.

Acknowledgments. We thank Dr. M. Gutowski (Utah) and Prof. G. Chalasinski (Warsaw) for many enlightening discussions on the subject of counterpoise. We thank Dr. T. van Mourik (Utrecht) for permission to quote some of her MRCI results prior to publication. We thank the referees for suggestions to improve the manuscript.

References

(1) Woon, D. E. *J. Chem. Phys.* **1994**, *100*, 2838.
(2) van Mourik, T. Thesis, Utrecht, 1994.
(3) Jeziorski, B.; Kolos, W. *Molecular Interactions*; Wiley: Chichester, 1982; Vol. 13, pp 1.
(4) Jeziorski, B.; Moszynski, R.; Szalewicz, K. *Chem. Rev.* **1994**, *94*, this issue.
(5) Jansen, H. B.; Ros, P. *Chem. Phys. Lett.* **1969**, *3*, 140.
(6) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(7) Liu, B.; McLean, A. D. *J. Chem. Phys.* **1973**, *59*, 4557.
(8) Chalasinski, G.; Gutowski, M. *Chem. Rev.* **1988**, *88*, 943.
(9) Liu, B.; McLean, A. D. *J. Chem. Phys.* **1989**, *91*, 2348.
(10) Vos, R. J.; van Duijneveldt, F. B.; van Lenthe, J. H. *Mol. Phys.* **1989**, *67*, 1011.
(11) Johansson, A.; Kollman, P.; Rothenberg, S. *Theor. Chim. Acta* **1973**, *29*, 167.
(12) Daudey, J. P.; Claverie, P.; Malrieu, J. P. *Int. J. Quantum Chem.* **1974**, *8*, 1.
(13) Gutowski, M.; van Lenthe, J. H.; Verbeek, J.; van Duijneveldt, F. B.; Chalasinski, G. *Chem. Phys. Lett.* **1986**, *124*, 370.
(14) Gutowski, M.; van Duijneveldt, F. B.; Chalasinski, G.; Piela, L. *Mol. Phys.* **1987**, *61*, 233.
(15) Gutowski, M.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H.; van Duijneveldt, F. B. *J. Chem. Phys.* **1993**, *98*, 4728.
(16) van Lenthe, J. H.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *Adv. Chem. Phys.* **1987**, *69*, 521.
(17) Eggenberger, R.; Gerber, S.; Huber, H.; Searles, D. *J. Phys. Chem.* **1992**, *96*, 6104.
(18) Åstrand, P. O.; Wallqvist, A.; Karlström, G. *J. Chem. Phys.* **1991**, *95*, 6395.
(19) Mezei, M.; Dannenberg, J. J. *J. Chem. Phys.* **1991**, *95*, 6396.
(20) Tao, F.; Pan, Y. *J. Phys. Chem.* **1991**, *95*, 3582.
(21) Tao, F.; Pan, Y. *J. Phys. Chem.* **1991**, *95*, 9811.
(22) Tao, F.; Pan, Y. *J. Phys. Chem.* **1991**, *96*, 5815.
(23) Yang, J.; Kestner, N. R. *J. Phys. Chem.* **1991**, *95*, 9214, ib. 9221.

(24) Del Bene, J. E. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 527.
(25) Saebo, S.; Tong, W.; Pulay, P. *J. Chem. Phys.* **1993**, *98*, 2170.
(26) Cullen, J. M. *Int. J. Quantum Chem. Symp.* **1991**, *25*, 193.
(27) Davidson, E. R.; Chakravorty, S. J. *Chem. Phys. Lett.* **1994**, *217*, 48.
(28) Loushin, S. K.; Liu, S. Y.; Dykstra, C. E. *J. Chem. Phys.* **1986**, *84*, 2720.
(29) Meyer, W.; Hariharan, P. C.; Kutzelnigg, W. *J. Chem. Phys.* **1980**, *73*, 1880.
(30) Szczesniak, M. M.; Scheiner, S. *J. Chem. Phys.* **1986**, *84*, 6328.
(31) van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *J. Chem. Phys.* **1992**, *97*, 5019.
(32) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.
(33) Varandas, A. J. C. *Chem. Phys. Lett.* **1980**, *69*, 222.
(34) Chalasinski, G.; Gutowski, M. *Mol. Phys.* **1985**, *54*, 1173.
(35) Fröman, A.; Löwdin, P.-O. *J. Phys. Chem. Solids* **1962**, *23*, 75.
(36) Murrell, J. N.; Varandas, A. J. C. *Mol. Phys.* **1975**, *30*, 223.
(37) Gutowski, M.; Chalasinski, G.; van Duijneveldt-van de Rijdt, J. G. C. M. *Int. J. Quantum Chem.* **1984**, *26*, 971.
(38) Cammi, R.; Bonaccorsi, R.; Tomasi, J. *Theor. Chim. Acta* **1985**, *68*, 271.
(39) Landshoff, R. *Z. Phys.* **1936**, *102*, 201.
(40) Rybak, S.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1991**, *95*, 6576.
(41) Jeziorski, B.; Bulski, M.; Piela, L. *Int. J. Quantum Chem.* **1976**, *10*, 281.
(42) van Duijneveldt-van de Rijdt, J. G. C. M. Thesis, Utrecht, 1994.
(43) Cybulski, S. M.; Chalasinski, G. *Chem. Phys. Lett.* **1992**, *197*, 591.
(44) Urban, M.; Hobza, P. *Theor. Chim. Acta* **1975**, *36*, 215.
(45) Karlström, G.; Sadlej, A. *Theor. Chim. Acta* **1982**, *61*, 1.
(46) Sokalski, W. A.; Roszak, S.; Hariharan, P. C.; Kaufman, J. J. *Int. J. Quantum Chem.* **1983**, *23*, 847.
(47) Chalasinski, G.; Szczesniak, M. M. *Chem. Rev.*, published in this issue.
(48) Fowler, P. W.; Buckingham, A. D. *Mol. Phys.* **1983**, *50*, 1349.
(49) Meyer, W.; Frommhold, L. *Phys. Rev.* **1986**, *A33*, 1791.
(50) Cybulski, S. M.; Chalasinski, G.; Moszynski, R. *J. Chem. Phys.* **1990**, *92*, 4357.
(51) Szczesniak, M. M.; Scheiner, S. *Collect. Czech. Chem. Chem. Commun.* **1988**, *53*, 2214.
(52) Huzinaga, S.; Klobukowski, M. *J. Mol. Struct. (Theochem)* **1988**, *167*, 1.
(53) Mayer, I.; Surjan, P. R. *Int. J. Quantum Chem.* **1989**, *36*, 225.
(54) Mayer, I.; Turi, L. *J. Mol. Struct. (Theochem)* **1991**, *227*, 43.
(55) Gutowski, M.; Chalasinski, G. *J. Chem. Phys.* **1993**, *98*, 5540.
(56) Szalewicz, K.; Cole, S. J.; Kolos, W.; Bartlett, R. J. *J. Chem. Phys.* **1988**, *89*, 3662.
(57) Cook, D. B.; Sordo, T. L.; Sordo, J. A. *J. Chem. Soc., Chem. Commun.* **1990**, *2*, 185.
(58) Cook, D. B.; Sordo, J. A.; Sordo, T. L. *Int. J. Quantum Chem.* **1993**, *48*, 375.
(59) Noga, J.; Vibok, A. *Chem. Phys. Lett.* **1991**, *180*, 114.
(60) Stoll, H.; Waggenblast, G.; Preuss, H. *Theor. Chim. Acta* **1980**, *57*, 169.
(61) Cooper, D. L.; Gerratt, J.; Raimondi, M. *Adv. Chem. Phys.* **1987**, *69*, 319.
(62) Collins, J. R.; Gallup, G. A. *Mol. Phys.* **1983**, *49*, 871.
(63) Sadlej, A. J. *J. Chem. Phys.* **1991**, *95*, 6705.
(64) Mayer, I. *J. Chem. Phys.* **1992**, *97*, 5257.
(65) Sadlej, A. J. *J. Chem. Phys.* **1992**, *97*, 5259.
(66) Mayer, I.; Surjan, P. R.; Vibok, A. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 281.
(67) Mayer, I.; Vibok, A. *Int. J. Quantum Chem.* **1991**, *40*, 139.
(68) Vibok, A.; Mayer, I. *Int. J. Quantum Chem.* **1992**, *43*, 801.
(69) Valiron, P.; Vibok, A.; Mayer, I. *J. Comput. Chem.* **1993**, *14*, 401.
(70) Vos, R. J.; van Lenthe, J. H.; van Duijneveldt, F. B. *J. Chem. Phys.* **1990**, *93*, 643.
(71) Vos, R. J.; Hendriks, R.; van Duijneveldt, F. B. *J. Comput. Chem.* **1990**, *11*, 1.
(72) Kapuy, E.; Kozmutza, C. *J. Chem. Phys.* **1991**, *94*, 5565.
(73) Røeggen, I.; Skullerud, H. *J. Phys. B.* **1992**, *25*, 1795.
(74) Røeggen, I.; Reza Ahmadi, G.; Wind, P. A. *J. Chem. Phys.* **1993**, *99*, 277.
(75) Emsley, J.; Hoyte, O. P. A.; Overill, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 3303.
(76) Smit, P. H.; Derissen, J. L.; van Duijneveldt, F. B. *J. Chem. Phys.* **1978**, *69*, 4241.
(77) Maggiora, G. M.; Williams, I. H. *J. Mol. Struct.* **1982**, *88*, 23.
(78) Eggenberger, R.; Gerber, S.; Huber, H.; Searles, D. *Chem. Phys. Lett.* **1991**, *183*, 223.
(79) Newton, M. D.; Kestner, N. R. *Chem. Phys. Lett.* **1983**, *94*, 198.
(80) Gutowski, M.; Verbeek, J.; van Lenthe, J. H.; Chalasinski, G. *Chem. Phys.* **1987**, *111*, 271.
(81) van Lenthe, J. H.; Vos, R. J.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *Chem. Phys. Lett.* **1988**, *143*, 435.
(82) Tao, F.; Pan, Y. *J. Chem. Phys.* **1992**, *97*, 4989.
(83) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
(84) Xantheas, S. S.; Dunning, T. H. *J. Chem. Phys.* **1993**, *99*, 8774.
(85) Odutola, J. A.; Dyke, T. R. *J. Chem. Phys.* **1980**, *72*, 5062.
(86) van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *J. Comput. Chem.* **1992**, *13*, 399.
(87) Bouteiller, Y.; Behrouz, H. *J. Chem. Phys.* **1992**, *96*, 6033.
(88) Bouteiller, Y. *Chem. Phys. Lett.* **1992**, *198*, 491.
(89) Wells, B. H.; Wilson, S. *Chem. Phys. Lett.* **1983**, *101*, 429.
(90) Hermansson, K. *J. Chem. Phys.* **1988**, *89*, 2149.
(91) Turi, L.; Dannenberg, J. J. *J. Phys. Chem.* **1993**, *97*, 2488.
(92) Woon, D. E. *Chem. Phys. Lett.* **1993**, *204*, 29.
(93) Kochanski, E.; Prissette, J. *Nouv. J. Chim.* **1980**, *4*, 509.
(94) Tsai, C. J.; Jordan, K. D. *Chem. Phys. Lett.* **1993**, *213*, 181.
(95) Diercksen, G. H. F.; Kraemer, W. P.; Roos, B. O. *Theor. Chim. Acta* **1975**, *36*, 249.