WEAKLY BONDED SYSTEMS

J. H. VAN LENTHE, J. G. C. M. VAN DUIJNEVELDT-VAN DE RIJDJT and F. B. VAN DUIJNEVELDT

Rijksuniversiteit Utrecht, Vakgroep Theoretische Chemie, Padualaan 8, De Uithof, Utrecht, The Netherlands

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I. INTRODUCTION

The foundations for our present understanding of intermolecular forces were laid in the first decades of this century. First, Keesom, Debye and Fakkenhagen elucidated the role played by permanent electric moments and polarizabilities. After the advent of quantum mechanics, Heitler and London identified the exchange forces which keep molecules apart, and London discovered the dispersion forces which explained such puzzling phenomena as the condensation of noble gases.

The quantitative evaluation of the corresponding interaction energies had to await the development of computers and ab initio systems in the 1960s. By the early 1970s it was apparent that self-consistent field (SCF) theory provides a reasonably accurate description of hydrogen-bonded complexes like (H₂O)₃, while theories that explicitly account for electron correlation must be used for systems which are predominantly bound by dispersion forces, such as He-H₂ and He₂. Rapid developments in both hardware and software have since taken place and ab initio calculations on weakly bound systems are now routinely being carried out. Useful information is gathered in this way and the potential surfaces obtained find application in simulation studies of liquids, solids and various solvation problems.

The precision of present-day ab initio results is not very high, however. This is evident from the discrepancies between results obtained in different calculations on the same system. Worse still, calculations which introduce methodological improvements do not always lead to better agreement with experiment. The water dimer provides a case in point. Hartree–Fock (HF) calculations in a 6-31 + G(d) basis, which by many would be regarded as of good quality, yield $\Delta E = 5.4$ kcal mol$^{-1}$ at $R = 2.96$ Å, both in good agreement ($5.4 \pm 0.7$ kcal mol$^{-1}$, $2.98 \pm 0.01$ Å). Improvement of the basis set (at the HF level) spoils the agreement, yielding $3.8$ kcal mol$^{-1}$ at $3.05$ Å. Keeping the same basis, but introducing correlation at the second-order Møller–Plesset (MP2) level spoils the agreement the other way, yielding about $7$ kcal mol$^{-1}$ at $2.90$ Å. (Clearly a combination of these two improvements yields more perspective.)

The conclusion to be drawn from these and many similar observations is that good agreement frequently comes about through a cancellation of errors, and in the absence of foreknowledge about the behaviour of these errors in any particular example, this severely detracts from the predictive power of ab initio theory.

There are a number of applications for which a theory with increased predictive power in weakly bonded molecular-beam experiments or potential energy (hazardous) tasks is truly predictive absolutely. The possibility of both intra- and intermolecular forces, theoretically understood of weakly bonded systems, may also help to clarify any apparent lack of the correct ordering of phenomena and their relevance.

Our aim in this book is to describe the methods, and to hope that this will contribute to the advancement of the field. The problems which methods of calculation like correlated many-body perturbation theories (CPEA), or the limited basis set of ab initio calculations, are not adequately corrected for? Is it not a grand and promising prospect of calculations and predictions? Of course, our outlook, and work in the field, is not as we would wish it to be, but progress continues.
predictive power would be most welcome. The wealth of experimental data on weakly bonded systems that has been gathered, primarily in various molecular-beam experiments, can only be adequately interpreted if precise potential energy surfaces are available. It is a laborious (and somewhat hazardous) task to assemble such potentials in an empirical manner, and a truly predictive theory would speed up the interpretation process considerably. The possibility of calculating potential energy surfaces as a function of both intra- and intermolecular degrees of freedom will be especially helpful in studying various vibration and relaxation processes, leading to a better understanding of the kinetics and thermodynamics of the system. Many weakly bonded systems have potential surfaces with several local minima and only a theory in which all errors are under control may be expected to yield a correct ordering of the associated binding energies, etc. Finally, the theory should be able to provide accurate information on three-body effects in view of their relevance to bulk simulations.

Our aim in this review is to highlight the main problems in current ab initio methods, and to discuss ways of surmounting these problems, in the hope that this will contribute to the formulation of a theory with larger predictive power. The problems to be discussed are the following. First, which of the current methods of allowing for electron correlation, e.g. Möller–Plesset (MP) theory, many-body perturbation theory (MBPT), coupled electron-pair approximations (CEPA), are adequate? Secondly, which errors are caused by the use of limited basis sets? Finally, can basis-set superposition errors be avoided or corrected for? One might sympathize with the authors of the following quotation: 'In general except for the case of He₂, there is no immediate prospect of calculating an accurate potential.' Paradoxically, it turns out that He₂ is one of the more difficult systems to treat accurately, and on the whole, our outlook, expressed in the final section, is definitely more optimistic.

Since we focus on methodological problems, little space will be devoted to the properties and peculiarities of specific systems. Many of these are discussed in the book by Hobza and Zahradník. Ab initio calculations on hydrogen-bonding systems have recently been reviewed by Beyer et al. Interactions between non-polar molecules were treated by van der Avoird et al., while noble-gas interactions were covered in the monograph by Maitland et al.

The ability to obtain accurate potential energy surfaces is only a first step towards a full description of weakly bonded systems. A next step must be the determination of the intermolecular vibrational modes, in order to interpret the wealth of spectroscopic data available for these systems, and in order to estimate the zero-point vibrational energy correction that must be applied before calculated binding energies can be compared to experimental enthalpies of formation. The appropriate force constants and frequencies are routinely produced at the harmonic level by the more recent ab initio program packages that employ gradient techniques, such as GAUSSIAN 80 and
GAMESS. The vibrational data obtained in this way should, however, be used with care, since many weakly bonded systems exhibit large-amplitude motions (especially when simple hydrides are involved) which cannot be accurately modelled at the harmonic level. Indeed, the very concept of the ‘equilibrium structure’ of such complexes, while formally valid, loses much of its significance, and a much larger section of the surface must be sampled than is customary for ordinary molecules. Appropriate techniques for evaluating vibrational wavefunctions beyond the harmonic level have been reviewed by Le Roy et al. and very recently by Briels et al. and the interested reader is referred to these.

A final aspect not considered here is the search for analytical fits to potential energy surfaces given in numerical form on a grid of points, or, more generally, the development of simple models that can be applied to larger systems where the direct evaluation of $\Delta E$ by ab initio methods becomes impracticable. Recent activities in this field include the use of the distributed multipole model for predicting the equilibrium structures of van der Waals complexes. The legitimacy of applying electrostatics has been questioned, but in view of the well documented performance of the electrostatic model in rationalizing geometries of complexes these criticisms seem to be unjustified. Mention should also be made of the so-called test-particle model in which a nitrogen atom is used as a probe to determine the parameters of the repulsive $\exp(-R)$ terms in a site-site potential model that should be applicable to large molecules. Work along these lines can contribute to a better understanding of molecular liquids and molecular solids.

II. COMPONENTS OF THE INTERACTION ENERGY

Knowledge of the separate terms that make up the interaction energy of a given complex can be useful for a variety of reasons. It helps to understand why the complex is formed, in relation to properties of the separate molecules. But it also offers a way of checking the accuracy of a calculation by requiring that not only the total energy but also its components must become stable with respect to further improvements in the description of the system. Finally, a knowledge of the separate terms facilitates the search for accurate fitted analytical potential energy functions, which is a necessary step if the results are to find further use in simulations of larger systems. Detailed reviews on these energy terms are available.

A. Long-range Interactions

The energy components are most naturally divided into long-range and short-range terms. The long-range terms may be defined in terms of London’s perturbation theory leading to electrostatic, induction and dispersion effects.

$$V = \sum \alpha \Delta \mu \cdot \Delta \mu$$

where $V$ = Hamiltonian, $\Delta \mu$ = dipole moments, $\alpha$ = dipole–dipole interaction parameter, $\Delta \mu$ = electric dipole moment of $\alpha$-molecule. The simplest energy term being used; second order.

Alternatively, this can be described by a variety of methods. There are nearly converged intermolecular potentials in second order. For example, a dipole–dipole interaction for each first-row atom.

The induction and dispersion interactions are all in second-order terms which describe the interaction between two moments and vice versa.

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dispersed energies. For molecules with Hamiltonians $H^A$ and $H^B$ and unperturbed ground-state wavefunctions $\Psi^A_0$ and $\Psi^B_0$ the first-order electrostatic Coulomb energy is given by

$$E_{\text{Coul}} = \langle \Psi^A_0 | V | \Psi^B_0 \rangle$$

(1)

where $V = H^{AB} - H^A - H^B$ collects all intermolecular electrostatic interaction operators. At long range $E_{\text{Coul}}$ may be written as a sum of the dipole–dipole, dipole–quadrupole, … interactions between the molecular permanent multipole moments, by invoking the multipole expansion of $V$ with respect to one origin in A and one in B. Several definitions for these moments are currently being used; see Refs 13, 43 and 44 for recent summaries.

Alternatively, distributed multipole expansions or distributed point-charge descriptions may be employed in which charges or multipoles are placed at a variety of centres in the molecule$^{28,29,45-49}$. These have the advantage that a nearly converged multipole energy can be obtained even at a relatively short intermolecular separation, and without requiring multipoles of very high order. For example, models with a charge on each hydrogen atom, a charge and a dipole on each bond centre, and a charge plus dipole plus quadrupole on each first-row atom can give excellent results$^{28,29,45,49}$.

The induction and dispersion energies arising from mutual polarization are in second-order perturbation theory given by

$$E_{\text{ind}} = \sum_s \left| \langle \Psi^A_0 | V | \Psi^B_0 \rangle \right|^2 \quad \text{(B by A)}$$

$$E_{\text{ind}} = \sum_s \left| \langle \Psi^B_0 | V | \Psi^A_0 \rangle \right|^2 \quad \text{(A by B)}$$

(2)

which describes the energy lowering due to polarization of B in the field of A and vice versa, and

$$E_{\text{disp}} = \sum_r \sum_s \left| \langle \Psi^A_0 | V | \Psi^B_0 \rangle \right|^2$$

(3)

which describes the energy lowering associated with polarization by instantaneous fluctuations in the charge distributions of A and B. Here, $\Psi^A_0$ and $\Psi^B_0$ are unperturbed singly excited wavefunctions of the monomers. At long range, the multipole expansion of $V$ leads to expressions for $E_{\text{ind}}$ (B by A) in terms of the permanent moments of A and the static polarizabilities of B$^{13,50}$. (When the perturbation theory is carried beyond second order, the hyperpolarizabilities come into play as well$^{40}$.) Similarly, $E_{\text{disp}}$ may be reduced, by applying the Casimir–Polder relation, to a closed expression involving the dynamic (i.e. frequency-dependent) polarizabilities $\alpha(\omega)$ of the separate molecules$^{49}$. This approach offers the advantage that once the $\alpha(\omega)$ have been obtained for a series of molecules, the corresponding $C_s$ coefficients in the $R^{-4}$ expansion of
the dispersion energy for any given pair of these molecules can be evaluated by a simple integration. In the past, experimental data were used in constructing the $\alpha_{\text{d}}$ functions\textsuperscript{31}, but more recently efficient \textit{ab initio} techniques have been developed to evaluate $\alpha_{\text{d}}$ at the (TDCHF) and at the correlated level\textsuperscript{52–54}.

The applicability of these one-centre multipole-expanded methods to larger molecules is limited, since the convergence will be poor. Descriptions involving bond–bond or atom–atom interactions have therefore been proposed in the past\textsuperscript{11,12}. A rigorous method to distribute a molecule’s polarizability over more than one centre has been described very recently\textsuperscript{56}. Similar in spirit is a method in which the $V$-expanded numerators in Eq. (3) are replaced by interactions between transition multipoles at well chosen centres\textsuperscript{57}. Finally, we mention a recent method to evaluate (3) at the TDCHF level, but avoiding the expansion of $V$\textsuperscript{58,59}. This should in principle be applicable to large molecules, but the computational effort involved is large unless further approximations are made\textsuperscript{58,59}.

B. Short-range Effects: Penetration

In the study of weakly bound systems the range of distances around the van der Waals minimum is usually the one of primary interest. Here the performance of the long-range terms in their multipole-expanded forms is somewhat problematic. First, the multipole series may not converge sufficiently fast or not at all and, secondly, penetration effects become non-negligible.

While the convergence problem may be somewhat alleviated by using distributed multipole descriptions, the penetration effects can only be recovered by switching to expressions invoking $V$ in its unexpanded form. The origin of the penetration effects is the different $R$ dependence of electron–electron, electron–nuclear and nuclear–nuclear electrostatic interactions as the charge clouds penetrate one another. For $R \rightarrow 0$ the latter term tends to infinity, whereas the other interaction terms remain finite, and hence the sum of these terms deviates from the multipole result, in which all charges are treated on an equal footing. Although the precise form taken by the penetration energy would seem to depend on the description chosen for the multipole series\textsuperscript{50} there is agreement that penetration effects are far from negligible. For example, $E_{\text{coul}}$ for the cyclic geometry of HCOOH dimer at $R_c$, which equals 36.2 kcal mol$^{-1}$, contains about 5.5 kcal mol$^{-1}$ penetration attraction\textsuperscript{61}. Also, from the data in Table 2 of Ref. 62 one may deduce that for linear (HF)$_2$ with $R = 5.0$ a.u., penetration accounts for about 0.0015 hartree out of a total $E_{\text{coul}}$ of 0.0101 hartree. However, penetration effects fall off exponentially with distance and at $R = 6.0$ a.u., just outside the van der Waals minimum, they account for less than $3\%$ of $E_{\text{coul}}$ in (HF)$_2$. For extremely diffuse systems, such as LiH, but also for systems with lone pairs pointing in each other’s direction like linear N$_2$–N$_2$, the effects are larger\textsuperscript{62}.

Penetration effects in $E_{\text{disp}}$ too, however, are negligible. The multipole-expanded expressions can be converted to the long-range form

$$E_{\text{exch}} = \mathcal{P}$$

where $\mathcal{P}$ = sum over all pairs, of more pairs here, and two additional exchange terms involving the electron densities $\mathcal{W}_j$ and $\mathcal{W}_k$. $E_{\text{exch}}$ rapidly vanishes as $R \rightarrow 0$ and should be written in the form

$$E_{\text{exch}} = \mathcal{P}$$

In second order, $E_{\text{exch}}$ to be retained. For example, in the case shown in Eq. (3) in the text.

The term $\Delta E$ in all formulae refers to the ground state of AB.

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The term $\Delta E$ in all formulae refers to the ground state of AB.
Penetration effects also occur in the second-order long-range terms and in $E_{\text{disp}}$ they lead to reduced attraction compared to the multipole-expanded result. The effects may be accounted for by using Eqs (2) and (3) in non-expanded form or (in the case of $E_{\text{disp}}$) by applying suitable damping functions to the long-range $C_{\alpha}/R^n$ terms.

C. Short-range Effects: Exchange

London’s perturbation theory was formulated on the basis of the unperturbed product states $\psi^A_0 \psi^B_0$ that are eigenfunctions of $H^A + H^B$. These states do not satisfy the Pauli principle (the electrons of A being distinguishable from those of B) and hence at short $R$ one must adopt a different approach. The remedy is to use antisymmetrized states $\mathcal{A}\psi^A_0 \psi^B_0$ which, however, are not eigenfunctions of $H^A + H^B$. The form of perturbation theory that can deal with these problems is now known as symmetry-adapted perturbation theory (SAPT)\textsuperscript{41}. It may be formulated in such a way that $\Delta E$ comprises, in addition to each long-range term, a corresponding exchange term. The most important of these is the first-order exchange energy $E_{\text{exch}}$ in the majority of complexes is the main repulsive term and takes the form

$$E_{\text{exch}} = \frac{\langle \mathcal{A}\psi^A_0 \psi^B_0 | V | \psi^A_0 \psi^B_0 \rangle - \langle \psi^A_0 \psi^B_0 | V | \psi^A_0 \psi^B_0 \rangle \langle \mathcal{A}\psi^A_0 \psi^B_0 | \psi^A_0 \psi^B_0 \rangle}{\langle \mathcal{A}\psi^A_0 \psi^B_0 | \psi^A_0 \psi^B_0 \rangle}$$

(4)

where $\mathcal{P} = (\mathcal{A} - 1)$ is a sum of permutation operators exchanging one, two or more pairs of electrons between A and B. Each additional exchange introduces two additional overlap densities in the integrals and so the $O(S^2)$ single-exchange terms dominate in (4). Owing to the presence of these overlap densities $E_{\text{exch}}$ decreases exponentially with increasing distance, and it is this rapidly varying repulsion which keeps molecules apart. For later reference it should be mentioned that the total first-order interaction energy may be written in the form

$$E^{(1)} = E_{\text{Coul}} + E_{\text{exch}} = \frac{\langle \mathcal{A}\psi^A_0 \psi^B_0 | V | \psi^A_0 \psi^B_0 \rangle}{\langle \mathcal{A}\psi^A_0 \psi^B_0 | \psi^A_0 \psi^B_0 \rangle}$$

(5)

In second order one has the $E_{\text{exch-ind}}$ and $E_{\text{exch-disp}}$ energies which were found to be repulsive in the few systems for which they have been evaluated\textsuperscript{68}. For example, in Ne$_2$ they quench some 5% of the non-expanded $E_{\text{disp}}$ (as given by (3)) in the region of the van der Waals minimum.

D. Charge-transfer Energy

The terms defined in (1)-(5) provide a complete description (to second order) of $\Delta E$ in any complex. Now there are many complexes in which the ground state of AB acquires some ionic character $A^+ B^-$. Formally, this transfer of a
single electron may be viewed as a special case of polarization of A by B, and hence the resulting energy lowering, the charge-transfer energy \( E_{CT} \), forms part of \( E_{ind} \), Eq. (2). However, \( E_{CT} \) depends quadratically on overlap densities between A and B and hence its \( R \) dependence is more like that of \( E_{exch-ind} \) than that of \( E_{ind} \) itself. For these reasons \( E_{CT} \) is often discussed separately from \( E_{ind} \), in combination with the \( E_{exch-ind} \) terms.

### E. Intramolecular Correlation Effects

Most of the previous discussion has tacitly assumed the availability of the exact eigenfunctions of A and B. These are usually not available, and (1)–(5) may thus in principle be calculated by using wavefunctions \( \psi_A \), etc., determined in the self-consistent field (SCF) or configuration-interaction (CI) approximations. Indeed, \( E_{corr} \), evaluated from SCF monomer wavefunctions is one of the terms arising in the current energy partitioning schemes for SCF interaction energies \( E_{corr} \). Estimates of \( E_{disp} \), to be added to SCF interaction energies, are as a rule obtained by using \( \psi_0^{SCF} \phi_0^{SCF} \) as the unperturbed product state \( \psi_0 \). A formal justification of these procedures has been given in the double-perturbation variant of SAPT \( ^{11} \) in which the sum of the monomer Fock operators is used as \( H^0 \), rather than \( H^0 + H^0 \). The difference \( (H^0 + H^0 - H(Fock)) \) is treated as a second perturbation, and can be used to estimate correlation corrections to (1)–(5) as given at the SCF level. Alternatively, these correlation corrections may be determined by inserting CI wavefunctions directly into (1)–(5). In this way it has been shown, for example, that intramolecular correlation in He leads to an increase of about 10% in the He–He first-order exchange energy \( ^{72} \). Similar calculations have been performed for Be–Be \( ^{73} \) and for H–H \( ^{74} \) and depending on the case both increase and decrease of \( E_{exch} \) were observed.

### F. Energy Components in the Supermolecular Approach

In the supermolecular approach the interaction energy \( \Delta E \) of a complex is obtained by evaluating the total energy \( E_{AB} \) of the AB supermolecule using method X (X = SCF, CI, CEP, MPn, CPF, ...) and subtracting the energy of the monomers:

\[
\Delta E^X = E_{AB}^X - E_A^X - E_B^X
\]

The connection with the perturbation method may be made by assuming the exact eigenfunctions \( \psi_A^0 \) and \( \psi_B^0 \) to be available. Using \( \mathcal{A} \psi_A^0 \psi_B^0 \) as a zeroth-order dimer wavefunction the dimer energy is obtained as

\[
E_{AB}^{HL} = \frac{\langle \mathcal{A} \psi_A^0 \psi_B^0 | H | \mathcal{A} \psi_A^0 \psi_B^0 \rangle}{\langle \mathcal{A} \psi_A^0 \psi_B^0 | \mathcal{A} \psi_A^0 \psi_B^0 \rangle}
\]

This quantity is equal to \( \langle \mathcal{A} \psi_A^0 \psi_B^0 | [H, \mathcal{A}] \psi_A^0 \psi_B^0 \rangle \), from which \( \Delta E_{HL} \) can be obtained using \( H^0 \psi_A^0 \psi_B^0 \), which is seen to be equivalent to (7) one now has:

\[
\Delta E_{HL} = \Delta E_{AB} - \Delta E_A - \Delta E_B
\]

where \( \Delta E_{HL} \) is identical to \( \Delta E_{AB} \) because SCF or any other approximation in which \( \Delta E_{HL} \) is calculated. The use of \( \Delta E_{HL} \) is analogous to expanding a calculable quantity called Landau–Gorylnski in terms of indistinguishable wavefunctions of a finite set at zero temperature and subsequently correcting for the necessity of general wavefunctions as a corrections. Such corrections can be better approximated in an improved basis. (Extensive tests show \( E_{AB}^{HL}(SCF) \) leads to.

From these considerations a reasonable approximation is to use Eq. (6) into the supermolecular approach, for example, according to (7).
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This quantity will be referred to as the dimer Heitler–London energy. Using \( [H, \mathcal{A}] = 0 \) and \( H = H^0 + V \) it may be reduced to

\[
E_{\text{HL}}^{\text{AB}} = \frac{\langle \mathcal{A} \psi_A^0 \psi_B^0 | H^0 + V | \psi_A^0 \psi_B^0 \rangle}{\langle \mathcal{A} \psi_A^0 \psi_B^0 | \psi_A^0 \psi_B^0 \rangle}
\]

(8)

from which the Heitler–London (first-order) interaction energy is found to be, using \( H^0 \psi_A^0 \psi_B^0 = (E_A + E_B) \psi_A^0 \psi_B^0 \),

\[
\Delta E_{\text{HL}} = E_{\text{HL}}^{\text{AB}} - E_A - E_B = \frac{\langle \mathcal{A} \psi_A^0 \psi_B^0 | V | \psi_A^0 \psi_B^0 \rangle}{\langle \mathcal{A} \psi_A^0 \psi_B^0 | \psi_A^0 \psi_B^0 \rangle}
\]

(9)

which is seen to be identical with the perturbation result \( E^{(1)} \) of Eq. (5).

1. The SCF Case

Going one step further, one may analyse the case of an SCF (i.e. single-configuration) dimer calculation. The zeroth-order wavefunction \( \psi_A^0 \psi_B^0 \) is equivalent to a single configuration, and hence is a valid first step to consider before going on to the converged dimer SCF wavefunction. Substituting it in (7) one now finds (with \( E_A + E_B = E^0 \))

\[
\Delta E_{\text{HL}} = E_{\text{HL}}^{\text{AB}} - E_A - E_B = \frac{\langle \mathcal{A} \psi_A^0 \psi_B^0 | V | \psi_A^0 \psi_B^0 \rangle}{\langle \mathcal{A} \psi_A^0 \psi_B^0 | \psi_A^0 \psi_B^0 \rangle} + \frac{\langle \mathcal{A} \psi_A^0 \psi_B^0 | H^0 | \psi_A^0 \psi_B^0 \rangle - E^0 \langle \psi_A^0 \psi_B^0 | \psi_A^0 \psi_B^0 \rangle}{\langle \mathcal{A} \psi_A^0 \psi_B^0 | \psi_A^0 \psi_B^0 \rangle} = E^{(1)} + \Delta
\]

(10)

where \( E^{(1)} \) takes the same form as (5), but the second term (\( \Delta \)) is not zero because SCF functions are not eigenfunctions of \( H \). The presence of \( \Delta \) means that \( \Delta E_{\text{HL}} \), unlike \( E^{(1)} \), cannot be regarded as a pure interaction energy, and so the use of \( \Delta E_{\text{HL}} \) seems problematical. However, this view is too pessimistic. By expanding \( \mathcal{A} \) it can be shown that for exact Hartree–Fock solutions the so-called Landshoff terms in \( \Delta^{7,8} \) are zero, and only some very small terms of \( O(S^4) \) remain.\(^{76} \) Hence at the Hartree–Fock limit \( \Delta E_{\text{HL}} \) and \( E^{(1)} \) will be almost indistinguishable.\(^{77} \) For the more common case that \( \psi_A^0 \) is determined in a finite set at A and \( \psi_B^0 \) in a finite set at B, \( \Delta \) will be of \( O(S^4) \) and so will not necessarily be small.\(^{78} \) However, it has been shown\(^{79} \) that \( \Delta \) may be regarded as a correction for the incompleteness of the monomer basis sets, \( \Delta E_{\text{HL}} \) being a better approximation to the exact \( \Delta E_{\text{HL}} \) than is \( E^{(1)} \) evaluated in the same finite bases. (Extensions of this result are possible which involve a reinterpretation of \( E_{\text{HL}}^{\text{AB}} \) (SCF) leading to \( \Delta = O(S^4) \), but this point will be taken up in Section VI.)

From the previous discussion it follows that at the SCF level \( \Delta E_{\text{HL}} \) is a reasonable tool for partitioning SCF interaction energies obtained from Eq. (6) into terms which correspond to those obtained in the perturbation approach. In the usual partitioning schemes\(^{36,69} \) \( \Delta E_{\text{HL}} \) itself is partitioned according to

\[
\Delta E_{\text{HL}} = E_{\text{exch}} + E_{\text{cont}}
\]

(11)
where $E_{\text{cor}}$ is evaluated from (1) by inserting monomer SCF functions. Next, the energy gained in the SCF process, starting from $E^{\text{ex}}_{\text{AB}}$ (Eq. (7)) is called the ‘second-order energy’ or ‘delocalization energy’

$$\Delta E^{(2)} = E^{\text{SCF}}_{\text{AB}} - E^{\text{ex}}_{\text{AB}}$$

which may be further partitioned by separate calculation of $E_{\text{ind}}$ and, in some schemes, $E_{\text{ct}}$ \cite{36}. In the present review we use

$$\Delta E^{(2)} = E_{\text{ind}} + E_{\text{ctx}}$$

where $E_{\text{ind}}$ is evaluated perturbationally (Eq. (2)) and $E_{\text{ctx}}$ collects $E_{\text{ct}}$ and $E_{\text{ctx-ind}}$, all of which are short-range terms. Note that since we are dealing with a variational method, $\Delta E^{(2)}$ will contain not only second-order but higher-order effects as well.

The total SCF interaction energy is given by

$$\Delta E^{\text{SCF}} = \Delta E^{\text{HL}} + \Delta E^{(2)}$$

In the form derived here it will be contaminated with the basis-set superposition error (BSSE) (cf. Section V). Moreover, since dispersion energy is a correlation effect, $\Delta E^{\text{SCF}}$ will not contain $E_{\text{disp}}$.

2. The Better-than-SCF Case

Here we discuss methods X that allow for electron correlation. In most of these, an SCF calculation is performed first, and some degree of CI is performed using $\psi_{\text{SCF}}$ as the reference configuration. Supremum calculation at this level have the advantage over SCF that $E_{\text{disp}}$ can be accounted for, and it becomes possible to obtain correlation corrections to the various terms in Eqs (1)–(4). The rigorous analysis of $\Delta E^{\text{HL}}$ at this level of theory is a complicated problem which has so far received little attention. In fact $\Delta E^{\text{HL}}$ may not be the appropriate first-order energy to consider in the context of methods with a non-variational energy expression (e.g. MP2, MP4, CEPA, ...). Another problem is that the zeroth-order wavefunction $\phi_{\text{X}}$ (i.e., an antisymmetrized product of two singles and doubles CI (CI(SD)) wavefunctions) will usually contain higher excitations than are present in the X description of the dimer, and so an analysis of $\Delta E^{\text{HL}}$ along the lines discussed above is not a valid first step in interpreting the final $\Delta E^{\text{X}}$ answer. This problem can only be rigorously solved by employing a full CI description throughout, but this is clearly impracticable. It may also be approximately solved by employing a size-consistent description (CEPA, (CPF), (CCD)), for here the missing excitations would implicitly be allowed for in calculating the dimer energy. We take up this point in Section III.

Because of these complexities it is customary to partition CI dimerization energies in a different way.

$$\Delta E^{\text{SCF}} = \Delta E^{\text{HL}} + \Delta E^{(2)}$$

where $\Delta E^{\text{HL}}$ can be further partitioned into contributions that can be further analyzed for individual contributions to $\Delta E^{(2)}$.

III. SUPERMOL

The simplest approach is to adjoin the Hartree–Fock result, add the dispersion energy for the whole supermolecule, and neglect those terms which are thus not negligible.

Some methods have been extended to treat II. The integrals have been used in the event of all\(\text{\textsuperscript{70,71,80,81, 82}}\). Variational energies (Møller–Plesset\(\text{\textsuperscript{4,83,84}}\), partitioning\(\text{\textsuperscript{8,9}}\), and the like) have been extended to II.

The inclusion of the supermolecule is accounted for in the less expensive valence CI in which antisymmetry requires only those orbitals that are fully occupied or occupied and which are rather small (so that it approximates the CI(SD) polarization approximation that is applicable). This yields the same as the supermolecule Hamiltonian. The CI then yields the same result as a supermolecule dispersion energy calculation. More accurate results can be obtained using the core Hartree–Fock (CHF) method, which may be used as a supermolecule in this case time.

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energies in a different way, namely as

$$\Delta E^{\text{CI}} = \Delta E^{\text{SCF}} + \Delta E^{\text{corr}}$$

(15)

where $\Delta E^{\text{SCF}}$ can be analysed as indicated above, and $\Delta E^{\text{corr}}$ lumps together the correlation corrections that are achieved in the chosen CI approach. They can be further analysed by partitioning $\Delta E^{\text{corr}}$ into intra- and intermolecular contributions to the interaction energy.

III. SUPERMOLECULAR METHODS FOR CALCULATING INTERACTION ENERGIES

A. Self-consistent Field plus Dispersion Method

The simplest \textit{ab initio} method used to study van der Waals molecules is the Hartree–Fock method. To the Hartree–Fock interaction energy one should add the dispersion energy, which ranges from some 20\% of the dissociation energy for the water dimer to twice the van der Waals well depth for He$_2$, and is thus not negligible. The combined method may be termed SCF + Disp.

Some methods to calculate the dispersion energy were discussed in Section II. The integrals from the supermolecular Hartree–Fock calculation may be used in the evaluation of formula (3) using the non-expanded potential\textsuperscript{6,71,80,81}, yielding the polarization dispersion energy\textsuperscript{82}. Either orbital energies (Müller–Plesset partitioning\textsuperscript{83}) or state energies (Epstein–Nesbet partitioning\textsuperscript{84,85}) may be used in the denominators. This method has recently been extended to open-shell molecules\textsuperscript{86,87}.

The inclusion of exchange corrections to the dispersion energy, not accounted for in the polarization approximation, is achieved in more expensive valence-bond (VB)\textsuperscript{88–91} and CI (dispersion CI)\textsuperscript{92,93} techniques, in which antisymmetrized excited configurations are employed. In these approaches only those configurations are included in the calculation that result from the simultaneous excitation of one electron out of the properly localized occupied states of each monomer. The (repulsive) exchange corrections are rather small (see Section II) and the complexity of these approaches approximates that of more complete CI or VB calculations. Both the polarization approach and the dispersion VB and dispersion CI methods\textsuperscript{92} yield dispersion energies at the uncoupled Hartree–Fock (UCHF) level, the only differences being the choice of expansion functions and zeroth-order Hamiltonian. Though the corresponding infinite order, provided it converges, yields the same result in all these methods, the second-order perturbation dispersion energies may be quite different in different approaches; c.f. Ref. 94. More accurate results are obtained in the variational coupled Hartree–Fock (CHF) method, where the wavefunction adapts in a self-consistent way to the, in this case time-dependent, perturbation. The difference between CHF and
UCHF is called higher-order self-consistency or apparent correlation. To illustrate the differences in the \( C_6 \) van der Waals coefficients in the various approaches we present some values for \( \text{He}_2 \) and \( \text{Ar}_2 \) in Table I. It is seen that the Epstein–Nesbet variant gives results close to experimental values for \( \text{He}_2 \) and \( \text{Ne}_2 \), but that it overestimates \( C_6 \) for heavier systems where the Möller–Plesset variant is closer to experiment. Although an extension of the CHF method avoiding the multipole expansion of \( V \) has been proposed, most existing applications of CHF theory are for long-range dispersion coefficients, so damping functions have to be applied.

The SCF + Disp method is frequently applied since it is relatively cheap and thus allows the calculation of many points on the potential energy surface. A useful potential may be obtained by empirical adjustments to the potential. For example, a damping function may be adjusted using experimental data or various components of a fitted dispersion energy may be scaled to more reasonable values. The Hartree–Fock interaction energy may also be improved, by replacing its multipole and induction components by energies derived from multipoles obtained from better calculations (e.g. CI) or experiment; cf. Refs 78 and 104–107. While these procedures may yield reasonable potentials, we feel that the predictive power of the SCF + Disp approach is limited.

### Table I

<table>
<thead>
<tr>
<th></th>
<th>( \text{He–He} )</th>
<th>( \text{Ar–Ar} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>'Experiment'</td>
<td>1.46256</td>
<td>6596</td>
</tr>
<tr>
<td>MP2</td>
<td>1.12257</td>
<td>74260</td>
</tr>
<tr>
<td>EN</td>
<td>1.45257</td>
<td>7797</td>
</tr>
<tr>
<td>Disp CI/Tamm–Dancoff</td>
<td>1.55258</td>
<td>85258</td>
</tr>
<tr>
<td>TDCHF</td>
<td>1.37258</td>
<td>61259</td>
</tr>
<tr>
<td>CEPA-I</td>
<td>1.37258</td>
<td>58258</td>
</tr>
</tbody>
</table>

B. Second-order Möller–Plesset Theory

The next level of sophistication is to include inter- as well as intra-correlation effects using, as advocated by Pople, a true supermolecular method subject to BSSE (cf. Section V). We restrict our discussion here to the frequently applied second-order variant (MP2).

The dispersion energy (inter-monomer correlation) in the MP2 approach is obtained at the uncoupled Hartree–Fock level, as discussed above. At long range the result is identical to that of the polarization approach using the Möller–Plesset partitioning. No coupling between correlation effects is included in the present calculations.

The intra-molecular energy through

\[
\Psi(0) = \sum_{n, \sigma} \langle n, \sigma | V | n, \sigma \rangle
\]

where \( \Psi(0) \) is the MP2 energy and \( V \) is the dispersion plus all other contributions between Hartree–Fock orbitals are included in the above calculation, which is based on the MP2 method.

From the results of the above calculation (i.e. the first step), the inter-monomer interaction energy is evaluated and a detailed discussion of the reliability of the results is given.

### C. Conclusion

The method of Section II can be used in conjunction with the more sophisticated approaches described above. The above calculations were performed using a few studies at the MP2 level of theory (\( \text{H}_2 \), \( \text{O}_2 \), \( \text{H}_2\text{O} \), \( \text{HF} \), \( \text{Ar–Ar} \), \( \text{O}_2 \)). We mention these studies in the results section as examples.

A major reason for the success of the MP2 method is the use of the extended basis sets to include the correlation energy of the electrons. The resulting calculations are accurate, since the correlation energy is included to the same extent as the exchange energy. The result is essentially equivalent to the exact wave function, which is known to be a major source of the accuracy of the MP2 method.
included in the MP2 approach, so dispersion interaction between uncorrelated (Hartree–Fock) monomers is described.

The intra-monomer correlation affects the (intermolecular) interaction energy through matrix elements of the form

$$\langle \Phi^{(0)}_A \Phi^{(1)}_B | V | \Phi^{(0)}_A \Phi^{(1)}_B \rangle$$

(16)

where $\Phi^{(0)}$ is the Hartree–Fock wavefunction and $\Phi^{(1)}$ is the wavefunction at the MP2 level. This indicates that the MP2 method yields the interaction between Hartree–Fock monomer A and MP2-correlated monomer B and vice versa, which should account for the bulk of the correlation correction to $\Delta E$.

From the results of Dierckx et al.\textsuperscript{111} one may infer that MP2 wavefunctions (i.e., the first-order wavefunction) give in response to a perturbation an interaction energy corresponding to reasonable multipole moments. More detailed research, using large basis sets, is required to establish firmly the reliability of the MP2 approach.

C. Coupled Electron-pair Approximation and Related Methods

The methods discussed so far require a computational time proportional to $n^4$, where $n$ is the number of basis functions used. To go up one level to more sophisticated methods, CI, CEPA or higher-order MBPT, increases the computational time to an $n^6$ dependence. It is therefore not surprising that few studies at this level on larger van der Waals molecules have appeared, e.g., (H$_2$O)$_2$,\textsuperscript{16,93,112–115} N$_2$–N$_2$,\textsuperscript{103} Ne–Na$_2$,\textsuperscript{116} N$_2$–HF, CO–HF, HCN–HF,\textsuperscript{117} Ar–HCl,\textsuperscript{100} (AH)$_2$ complexes (A = N, O, F, P, S, Cl)\textsuperscript{116} and He–O$_2$.\textsuperscript{118} We may expect many more calculations at this level in the near future, as computers become rapidly more powerful.

A major requirement that any method must satisfy, and which is satisfied by all non CI- or VB-like methods discussed previously, is that of size extensivity.\textsuperscript{119,120} This implies that the energy of $n$ non-interacting pairs of electrons should be equal to the sum of the $n$ energies of the electron pairs, e.g. a calculation on the supersystem at infinite distance between the monomers should yield the sum of the monomer energies (size consistency). An intrinsically size-extensive method is a coupled cluster (CC) or CEPA related method.\textsuperscript{94,121,122} The higher-order MBPT approaches may be viewed as approximations to coupled pair methods.\textsuperscript{94} For example, a MBPT calculation employing only double excitations is, if summed to infinite order, equivalent to L-CPMET (CEPAO).\textsuperscript{123} It is not obvious that a few higher orders of Møller–Plesset perturbation theory yield significantly more accurate results, since the convergence of Møller–Plesset perturbation theory is slow,\textsuperscript{124} the perturbation ('electron correlation') being not small. Furthermore, Frisch et al.\textsuperscript{16} show that the third- and fourth-order Møller–Plesset contributions cancel each other approximately. The familiar method of
energies. If the resulting potential energy surface is to be of predictive value (i.e. relative energy of isomers, location of saddle points, vibrational properties), the final calculated interaction energies for geometries of interest should probably be accurate to within about 5%. This figure of 5% amounts to 0.25 kcal mol\(^{-1}\) for dimers like (H\(_2\)O\(_2\)), and to 0.5 K for He\(_2\). Although present-day calculations rarely attain this, it is not unrealistic to expect such accuracy within the next few years.

The requirements that must be met by the basis follow more or less directly from the partitioning of the interaction energy. Briefly, long-range terms \((E_{\text{Coul}}, E_{\text{ind}}, E_{\text{disp}})\) lead to the requirement that electric multipole moments and electric multipole polarizabilities must be accurately represented. The short-range terms, being a direct consequence of overlap effects, require an adequate description of the valence-electron density both close to the nuclei and far away from them. Finally, though the bulk of BSSE can be removed by applying the counterpoise (CP) method (see Section V), there may be lingering artefacts due to the basis-set extension effect\(^{139}\) and in order to reduce these one may wish to choose the basis such that these effects are as small as possible.

Before discussing these requirements in more detail, it should be noted that a very precise description of the core electrons is usually not required, and this has led to various methods in which these are simulated by pseudo-potential methods\(^{140-142}\) and to the freezing of core orbitals in CI calculations. The total energy, being very sensitive to errors in the core region, must certainly not be used as a criterion for choosing basis sets for interaction energy calculations\(^{143}\).

### A. Long-range Terms

Let us consider the long-range terms first. An accurate description of these requires the monomer moments and polarizabilities to be described accurately. However, the precise role played by the relative importance of the dipole, quadrupole, etc., moment depends on the system studied. In polar–polar interactions the dipole–dipole term in \(E_{\text{Coul}}\) has a much larger weight in the final \(\Delta E_{\text{total}}\) than \(E_{\text{disp}}\). Hence for a 5% accuracy in \(\Delta E_{\text{total}}\), the dipole moment \(\mu\) may have to be accurate to 1–2\(\%\) while the error in the polarizability \(\alpha\) may be as large as 10\(\%\). As the systems get less polar, the relative weight of \(E_{\text{Coul}}\) diminishes while that of \(E_{\text{disp}}\) increases. Hence for a relative accuracy of 5% in \(\Delta E_{\text{total}}\), \(\alpha\) may now have to be accurate to 2\(\%\) or even better. A summary of these requirements is given in Table III.

How should one choose the basis to meet these requirements? The use of carefully balanced minimal basis sets has been advocated as a means for producing reasonable dipole moments\(^{144,145}\). Apart from the fact that such sets cannot yield a meaningful estimate of \(E_{\text{disp}}\), the dipole moments obtained in several minimal sets were rather poor. Decontracting the basis, such as to give split valence sp, sp\(^2\), sp\(^3\), etc., or LS coulomb and overlap exponents and flexibility and basis set superposition error, but mostly stay within the limit, whereas a basis set larger than this (Table III) or larger than this (Table IV) is required in order to meet the requirements for the polarization properties required.

Similarly, H, C, and N are common prototypical molecules (C, N, O, P) and their exponents have been tabulated and at the CI level of theory, these are roughly 1.0 for all elements. Dunning’s correlation consistent basis set requires lower exponents and yields higher accuracy.

It is not also possible to test the methods by adding the basis set. This is illustrated in Table V, where a molecule in a complex with a long-range dipole moment is computed. It is found that the bond order is in excellent agreement, especially with the ab initio solution. The polarizability of the basis set is also in excellent agreement, especially with the ab initio solution. The polarizability of the basis set is also in excellent agreement, especially with the ab initio solution.
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TABLE III

Accuracy requirements for molecular electric multipole properties.

<table>
<thead>
<tr>
<th>Type of complex</th>
<th>Typical ΔE_{bound} (μhartree) at equilibrium geometry</th>
<th>Example</th>
<th>Relative importance of long-range terms</th>
<th>Acceptable relative errors (%) in monomer properties*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polar–polar</td>
<td>10000</td>
<td>OH⋯OH</td>
<td>Coul &gt; ind &gt; disp</td>
<td>μ: 2 5 10 15 50</td>
</tr>
<tr>
<td>Polar–non-polar</td>
<td>1000</td>
<td>Cl⋯H⋯Ar</td>
<td>Coul &lt; ind &lt; disp</td>
<td>Ω: 5 15 30 15</td>
</tr>
<tr>
<td>Non-polar–non-polar</td>
<td>100</td>
<td>He⋯He</td>
<td>Coul ≈ ind ≈ disp</td>
<td>Ω: 2 10</td>
</tr>
</tbody>
</table>

*These errors correspond to an accuracy of 5% in ΔE_{bound} at equilibrium geometry.

give split valence or double-zeta (DZ) type basis sets, provides for more flexibility and hence a better description of induction and charge redistribution, but molecular electric properties are inaccurate. For example, SCF DZ dipole moments differ typically by about 0.15 a.u.¹⁴⁶ from the Hartree–Fock limit, whereas for accurate work on polar systems the errors should be less than this (Table III). Increased accuracy can be obtained by adding polarization functions to the basis. For atoms with occupied p shells, dipole properties require d functions, quadrupole properties require f functions, etc. Similarly, H, He, Li and Be need p, d, … functions. The simplest and most common procedure is to add one set of d functions to each ‘heavy’ atom (C, N, O, F) and a set of p functions on each H, and to optimize the orbital exponents by minimization of the total energy. Both at the SCF level¹⁴⁷,¹⁴⁸ and at the CI level¹²⁰,¹⁴⁹ this yields exponent values of roughly 1.0 for μ_{p}, roughly 1.0 for μ_{C,N,O,F} and roughly 0.5 for μ_{He,Ne}, yielding basis sets known as Dunning’s DZP basis, 6–31G**, etc. Cations require higher and anions require lower d exponents⁵⁰. Optimizing the correlation energy itself also yields higher exponents¹²⁹.

It is not always recognized that the improvement of the electric properties by adding these energy-optimized polarization functions is not spectacular. This is illustrated in Table IV, which shows SCF dipole properties for the HF molecule in a number of basis sets. The double-zeta plus polarization (DZP) dipole moment is still 0.05 a.u. too high, and the polarizability perpendicular to the bond direction is less than half the correct value. Far better results can be obtained by adding a second diffuse set of polarization functions¹⁵⁰,¹⁵¹, especially when its exponents are determined by maximizing the dipole polarizability or the dispersion energy¹⁴⁶,¹⁵²,¹⁵³. This is illustrated by the (DZPP) basis in Table IV, which yields μ and x₃ values good enough to allow accurate calculations on dimers. These results are in line with the observation of Kochanski¹⁵⁵ and others¹⁵⁶ that a single set of polarizability-optimized
TABLE IV
SCF dipole properties\(^a\) for the HF molecule \((R = 1.7328a_0)\) in different basis sets\(^b,\)\(^c\).

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Polarization function exponents</th>
<th>(\mu)</th>
<th>(\alpha_1)</th>
<th>(\alpha_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZ</td>
<td>(\alpha_d = 1.0, \alpha_p = 1.0)</td>
<td>0.939</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DZP</td>
<td>(\alpha_d = 0.40, \alpha_p = 0.30)</td>
<td>0.811</td>
<td>4.35</td>
<td>1.71</td>
</tr>
<tr>
<td>(DZP(^*))</td>
<td>(\alpha_d = 0.25, \alpha_p = 0.15)</td>
<td>0.759</td>
<td>5.10</td>
<td>3.46</td>
</tr>
<tr>
<td></td>
<td>(\alpha_d = 0.15, \alpha_p = 0.08)</td>
<td>0.783</td>
<td>5.44</td>
<td>3.83</td>
</tr>
<tr>
<td>DZPP</td>
<td>(\alpha_d = 1.0/0.15, \alpha_p = 1.0/0.08)</td>
<td>0.842</td>
<td>5.42</td>
<td>3.66</td>
</tr>
<tr>
<td>LPP</td>
<td>(\alpha_d = 0.10, \alpha_p = 0.10)</td>
<td>0.764</td>
<td>5.59</td>
<td>4.23</td>
</tr>
<tr>
<td>HF limit(^{129})</td>
<td>(\alpha_d = 0.10, \alpha_p = 0.10)</td>
<td>0.765</td>
<td>5.62</td>
<td>4.34</td>
</tr>
</tbody>
</table>

\(^{a}\)All values are given in atomic units (a.u.).
\(^{b}\)Taken from Ref. 146.
\(^{c}\)Energy-optimized.

DZ = (9s5p/4s) → [4s2p/2s],
L = (13s8p/8s) → [3s3p/2s].

Polarization functions of a given symmetry can account for about 90% of the maximum contribution to \(E_{\text{disp}}\) that can result from that symmetry. In fact, in these papers not \(\alpha_d\) but \(E_{\text{disp}}\) itself was used to optimize the exponents. This leads to exponents slightly higher than those resulting from \(\alpha_d\) optimization. The use of two polarizability optimized sets was found to yield about 99%\(^{9,8,8,157,}\), and this may be the appropriate choice when studying very weak interactions. The triply optimized sets used by Werner and Meyer\(^{129}\) were derived with a similar high accuracy in mind. Other doubly and triply optimized sets have been proposed recently\(^{158}\) but the exponents of these are not low enough to give accurate polarizabilities.

To conclude this section on SCF dipole properties it is instructive to inspect the variation of the DZP results in Table IV with orbital exponent. As mentioned above, energy-optimized exponents (\(\alpha_d = \alpha_p = 1.0\)) yield poor results, and very low exponents (\(\alpha_d = 0.15, \alpha_p = 0.08\)) yield reasonable polarizabilities, but poor moments. There exists, however, an intermediate choice (\(\alpha_d = 0.25, \alpha_p = 0.15\)) for which \(\mu\) and \(\alpha_d\) are simultaneously quite acceptable. The same property was demonstrated to hold for a number of other small molecules and this so-called 'moment-optimized' DZP\(^{146}\) basis was therefore advocated as the smallest set yielding reasonable \(E_{\text{coul}}\) and \(E_{\text{disp}}\) energies for polar dimers.

To illustrate how these basis sets behave in actual calculations, Table V shows the results of SCF + Disp (non-expanded second-order perturbation theory) calculations on the water dimer at a near-equilibrium geometry\(^{107}\).
The results confirm the inadequacy of the unpolarized 4–31G basis and the energy-optimized singly polarized DZP basis set, while DZP is seen to give results close to the ones obtained by the DZPP basis. Table V shows a large BSSE for the DZP basis because the polarization function exponents are not energy-optimized. One therefore has to correct for this BSSE in order to get meaningful interaction energies.

Very accurate dipole polarizabilities require not only the use of suitable polarization functions, but also an enlargement of the so-called ‘isotropic’ part of the basis. This may be achieved by replacing the 6–31G or DZ part of the basis by larger energy-optimized sets such as 6–311G, (11s7p), (13s8p) or one of the larger even-tempered basis sets. A common alternative is to add diffuse s and p functions to a smaller basis. The effect of this basis-set enlargement on the SCF dipole properties of HF is illustrated by the (LPP) entry in Table IV. The changes are rather small, and so it remains to be seen whether these functions are really necessary in dimer calculations, where the orbitals of the partner molecule may (partially) compensate for their absence.

A very similar discussion applies to quadrupole properties as well. The f functions needed for these properties should have their exponents optimized with respect to the contribution of quadrupole transitions to the dispersion energy, or with respect to the quadrupole polarizability, which relates the induced quadrupole moment to an inducing field gradient. Optimal single f exponent have been reported as \( \alpha_f^q = 0.18 \), \( \alpha_f^q = 0.275 \), and \( \alpha_f^q = 0.28 \). These values are 6–8 times lower than the exponents which maximize the contribution of f functions to the total correlated monomer energy, and so, as for d exponents, energy-optimized values are unsuitable. Static quadrupole moments are changed by added f func-
tions but, since the effects are small (e.g. for HF the effect appears to be a reduction of $\Theta$ by about 0.03 a.u.), this puts no further constraints on the exponents that should be chosen.

Our discussion has so far neglected correlation effects on molecular properties. Correlation is known to change dipole moments of small molecules by amounts up to 0.20 a.u. (H$_2$CO, while dipole polarizability components may change by up to 2.3$\text{a}_0^4$(NH$_3$), and so allowing for correlation effects in these properties is necessary in accurate work. Highly correlated wavefunctions require the presence of polarization functions with fairly high exponents in the basis set and so one might expect that such functions are necessary also in dealing with the effects of correlation on electric properties. This turns out not to be the case, however, and reasonable correlation corrections have been obtained in basis sets of the DZPP type and even in the DZP' basis. We should add that correlation corrections to properties are sensitive not only to the basis but also to the method chosen, MP2 and CI(SD) corrections typically deviating by about 20% from the effect found using more accurate methods like MP4 or CEPA.

### B. Short-range Terms

These include the penetration parts of and the exchange corrections to each of the long-range terms (see Section II). By far the most important of these is the first-order exchange energy, $E_{\text{exch}}$, which is mainly responsible for the forces that keep molecules apart. Detailed expressions show that $E_{\text{exch}}$ depends on overlap densities between the occupied orbitals of the separate molecules, as well as on the value of the monomer electrostatic potentials in the overlap region. These potentials will be accurate enough if the basis-set requirements for the long-range terms are met, and so the additional requirement raised by $E_{\text{exch}}$ is that overlap densities be described accurately.

Now an overlap density (like $1s_A(1)1s_B(1)$ in He$_2$) has a high value all the way from nucleus $A$ to nucleus $B$ (since for each point $P$ on the internuclear axis $\exp(-r_{AP})\exp(-r_{BP}) = \exp(-r_{AB})$) and so a correct description of the overlap density requires the monomer orbitals to be numerically accurate over the whole intermolecular region (and not only over the region where the molecules ‘touch’ each other). But in practice the main problems come from the values of the orbitals far from the nucleus. These tend to be underestimated (particularly if Gaussian atomic orbitals are used), since one usually employs energy-optimized basis sets and these are biased towards a good description close to the nuclei.

Several strategies are available to enhance the orbital density in regions far from the nuclei (we only discuss the case of Gaussian type orbitals (GTOs)).

1. An energy-optimized basis of given size (e.g. 9e5p or 4–31G) may be replaced by a large energy-optimized set (e.g. 11s7p or 6–311G) (note that 6–31G length is not available, with the corresponding exponents improved by increasing the number of segments in the basis set).

2. Instead of fitting a single set of exponents, at least a set of exponents was done for He$_2$, He$_3$, and He$_4$, involving a careful determination of the coefficients and the size of the basis set.

3. Instead of using a single basis set, a series of bases can be used for each molecule, e.g. Huzinaga's [5s3p1d] set and the [5s6p1f] set of 6–31G (e.g. a double zeta set, or a double zeta set plus a diffuse orbital). These may provide further correction.

4. An alternative to using atomic orbitals is the so-called effective orbital (EOZ) basis, which contains a smaller number of orbitals that are placed in such a way that the energy is minimized; this is an excellent choice for most calculations, and the energy difference is very small.


6-311G is roughly equivalent to 9s5p). This strategy may be carried to great lengths by switching to energy-optimized even-tempered sets, which are available up to very large size (e.g., 20s10p for Ne162). The main problem with this approach is that most of the added functions are used up to improve the description of the core electrons, and so the 'tail' region of the orbital improves only slowly. By the time that the tail is adequate, a large number of functions (closely spaced in exponent space) are present not only in the core region but also in the valence region. The usual technique of segmented contraction167 will not be effective in reducing the basis to a manageable size since it must not be used for the valence region168.

2. Instead of using energy-optimized sets one might use sets obtained by fitting to accurate Hartree–Fock orbitals169–172. These sets have both the exponents and the expansion coefficients determined by the criterion of a least-squares fit. Relatively small fits can give orbitals with good tails, as was demonstrated in calculations of the first-order interaction energies of He2,170, Be2,171 and Ne2.172. However, in calculating higher-order energies involving charge redistributions, as well as in CI calculations, the expansion coefficients must be given variational freedom and under these circumstances the advantage of these sets over energy-optimized sets of the same size seems to be lost (see below).

3. Instead of using ever larger energy-optimized sets one could use a fairly small energy-optimized set and add diffuse s, p, ... sets whose exponents are chosen as in even-tempered sets, i.e., by extrapolating the geometric progression of exponent values in the original set. As an addition to Huzinaga’s 9s5p sets this has proved useful in dealing with anions and with Rydberg orbitals173. The size of the basis after contraction is [4s3p] or [5s3p] for first-row atoms. More recently, similar extensions with s and p sets on first-row atoms and s on H have been proposed for the 6-31G and 6-311G basis sets158, yielding sets with a size [4s3p] and [5s4p] for first-row atoms. These extensions gave significant changes in calculations on weakly bound complexes involving H bonding or cation–molecule interactions16. For example, the extensions resulted in reduced interaction energies and in changed dimer geometries. The role of the added functions may partly have been to reduce the BSSE and so their effect on BSSE-corrected interaction energies remains to be assessed.

4. An alternative basis combining moderate size with the accuracy of the atomic outer region provided by large energy-optimized basis sets was recently proposed for the O atom in He–O2.87 This so-called extended-zeta (EZ) basis is formed from an energy-optimized 9s5p set161 by replacing the outer s function by two even-tempered more closely spaced s functions, the most diffuse of which is slightly more diffuse than the most diffuse s in the energy-optimized 13s8p set. Similarly the outer two p functions were replaced by three p functions. The resulting set (unlike 13s8p) can be applied...
contracted without significant loss of accuracy to \([5s3p]\), and yields electric moments and polarizabilities of similar accuracy\(^{174}\) as the \((13s8p)\) set in Ref. 146.

5. The final strategy for improving the tail of monomer wavefunctions is of a different kind. It is based on the consideration that the accurate calculation of \(E_{\text{exch}}\) will usually not be the final goal. Rather, one aims at the accurate evaluation of \(E_{\text{total}}\), having an accurate \(E_{\text{exch}}\) as one of its components. From the counterpoise principle (see Section V) it follows that the basis set that decides the accuracy of \(E_{\text{exch}}\) in the final result is not the monomer basis set, as described in points 1–4 above, but the full basis of the dimer. In fact, the presence of the other molecule's orbitals will improve the tail precisely where it matters, viz. in the region where the exchange repulsion comes about. Since basis sets lacking good tails underestimate \(E_{\text{exch}}\), it is to be expected that \(E_{\text{exch}}\) will increase when the dimer set is used in constructing the monomer wavefunctions. This is one of the factors causing changes in the first-order interaction energies for a number of systems when switching from monomer (MBS) to dimer (DBS) basis sets\(^ {104,175-177}\). Note, however, that these energies contain a changed \(E_{\text{Coul}}\) as well, which may or may not be an improvement\(^ {139}\).

The relative merits of strategies 1–5 are illustrated in Table VI, which shows \(E_{\text{Coul}}\) and \(E_{\text{exch}}\) values for \(\text{He}_2\). These results were calculated using Eqs (1) and (4), employing SCF monomer wavefunctions obtained in 10 different monomer basis sets. Entries 1–5 illustrate the use of ever larger energy-optimized sets (strategy 1). \(E_{\text{Coul}}\) and \(E_{\text{exch}}\) are seen to converge to values of \(-4.94\) and \(35.63\) \(\mu\)hartree, respectively. Using MBS gives very slow convergence, but using DBS gives good results (converged to within 5% already at the 8s level). Entry 6 (strategy 2) employs an 8s basis fitted to an accurate Hartree–Fock orbital for \(\text{He}\)^{170}. This is seen to give excellent results already for MBS. However, after redetermining the 8s expansion coefficients variationally, as one is forced to do in a full dimer calculation, the good results are spoilt (entry 7). Both \(E_{\text{Coul}}\) and \(E_{\text{exch}}\) are now overestimated, indicating that the bias in this basis towards low components exaggerates the tail density. Presumably, this type of defect cannot be remedied using DBS, but this was not checked. Strategy 3, the addition of diffuse functions, is illustrated in entries 8 and 9. At the MBS level, there is a clear improvement with respect to the original sets, viz. energy-optimized 5s and 10s. At the DBS level, however, the '10 + 1' basis behaves irregularly\(^ {76}\) and the original 10s DBS data seem more accurate. Although one cannot simply extrapolate these results to more strongly bound systems, it seems fair to say that addition of diffuse functions does not necessarily give a better description.

Finally, entry 10 illustrates the extended-zeta (EZ) basis of strategy 4, a 6s basis in this example. It is seen to give better results than the equally large
<table>
<thead>
<tr>
<th>Calc.</th>
<th>GTO basis</th>
<th>Monomer energy (hartree)</th>
<th>Most diffuse exponent</th>
<th>$E_{\text{Coul}}$</th>
<th>$E_{\text{exch}}$</th>
<th>$E_{\text{Coul}}$</th>
<th>$E_{\text{exch}}$</th>
<th>Ref.</th>
<th>$\delta$ (hartree) from Eq. (22)</th>
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<tr>
<td>1</td>
<td>$4s^b$</td>
<td>2.855 160</td>
<td>0.2980</td>
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<td>178</td>
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<td>2</td>
<td>$5s^b$</td>
<td>2.859 895</td>
<td>0.2446</td>
<td>-1.91</td>
<td>3.15</td>
<td>-4.92</td>
<td>32.76</td>
<td>178</td>
<td>44.30</td>
</tr>
<tr>
<td>3</td>
<td>$8s^b$</td>
<td>2.861 625</td>
<td>0.1642</td>
<td>-4.38</td>
<td>25.27</td>
<td>-5.03</td>
<td>35.38</td>
<td>178</td>
<td>0.39</td>
</tr>
<tr>
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<td>$10s^b$</td>
<td>2.861 672</td>
<td>0.1387</td>
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</tr>
<tr>
<td>5</td>
<td>$20s^c$</td>
<td>2.861 680</td>
<td>0.0989</td>
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<td>35.38</td>
<td>-4.94</td>
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</tr>
<tr>
<td>6</td>
<td>$8s^d$</td>
<td>2.858 875</td>
<td>0.0605</td>
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<td>35.73</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>7</td>
<td>$8s^e$</td>
<td>2.859 462</td>
<td>0.0605</td>
<td>-5.04</td>
<td>37.88</td>
<td>-</td>
<td>-</td>
<td>This work</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>$5s^h + 1s$</td>
<td>2.859 967</td>
<td>0.0990</td>
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<td>This work</td>
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</tr>
<tr>
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<td>$10s^b + 1s$</td>
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<td>35.47</td>
<td>This work, 76</td>
<td>0.03</td>
</tr>
<tr>
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<td>$6s^f$</td>
<td>2.860 088</td>
<td>0.1500</td>
<td>-4.76</td>
<td>31.07</td>
<td>-5.05</td>
<td>35.56</td>
<td>This work</td>
<td>0.21</td>
</tr>
</tbody>
</table>

In the DBS calculations of 1-5, the dimer set contained p sets on both atoms; see Ref. 178.

*Energy-optimized 161.
*GTO basis
*Fitted to HF AO (quoted in Ref. 170).
*As entry 6, but coefficients determined variationally. 0.906, 3.318 825, 1.176, 0.420 and 0.150.
*EZ basis (see text) with exponents 98.124 267, 14.768.
‘5 + 1’ set obtained by simply adding a diffuse function. It is also much better than energy-optimized 6s and, in fact, its quality resembles that of energy-optimized 9s, to which it was modelled. We conclude that this type of basis set shows some promise for high-accuracy work. However, for many purposes, the improvement offered by simply employing the dimer basis set allows one to use more standard basis sets with relatively little risk of inaccuracies in \( E_{\text{exch}} \).

V. THE BASIS-SET SUPERPOSITION ERROR: HISTORICAL BACKGROUND

In a standard dimer calculation the energy of the supersystem (AB) is calculated with the union of the subsystem one-electron basis sets

\[ \chi_{AB} = \chi_A \oplus \chi_B \]  

(18)

In practice, the monomer basis sets are not complete, an obvious exception being the \( ^2\Sigma_u \) \( \text{H}_2 \) van der Waals molecule\(^1\). The extension of the basis set in the dimer then results in a relatively better description of the dimer with respect to the monomers, yielding a correspondingly better energy. If the interaction energy is obtained as the difference of the separately calculated dimer and monomer energies, each with their own basis,

\[ \Delta E_{\text{total}}(R_{AB}) = E_{AB}(\chi_A \oplus \chi_B) - E_A(\chi_A) - E_B(\chi_B) \]  

(19)

this energy contains, in addition to the effect of the physical interactions, the result of the basis-set extension for each monomer. This non-physical energy contribution is commonly known as the basis-set superposition error (BSSE)\(^1\). It was first explicitly considered by Kestner\(^1\) as an explanation for the spurious minimum in the potential energy curve for \( \text{He}_2 \) calculated within the Hartree–Fock approximation by Ransil\(^2\). Earlier the problem was noted by Clementi\(^3\) and cleverly avoided by Jansen and Roos\(^4\), who used what came to be known as the Boys–Bernardi function counterpoise recipe (CP method).

A. The Counterpoise Method

Boys and Bernardi\(^5\) argue that the effect of a perturbation is most accurately calculated if all other parameters in the calculation are kept the same (‘counterpoise’), so that a maximal cancellation of errors is obtained. In the case of a van der Waals molecule, the perturbation is the effect of the nuclei and electrons of one monomer on the other and vice versa. Following Boys and Bernardi’s concept that ‘the full set of expansion functions used in the dimer calculation must also be used in the monomer calculations’, the usual implementation of these ideas is as follows. One calculates the van der Waals interaction energy by computing both the ‘perturbed monomers’ (the dimer calculation...
calculation) and the unperturbed monomers (the isolated monomers) with the same (dimer) basis set:

$$
\Delta E_{\text{total}} = E_{AB}(\chi_A \oplus \chi_B) - E_A(\chi_A) - E_B(\chi_B)
$$

(20)

The calculation of the monomer A energy $E_A(\chi_A)\oplus\chi_B$ is now identical to the dimer calculation except for the number of electrons, which is that of A only, and the charges of the nuclei of monomer B (the ghost), which are set to zero. The monomer energies in the basis $(\chi_A\oplus\chi_B)$ depend on the geometry of the complex, so they must be computed for every point on the van der Waals potential energy surface. The counterpoise procedure requires an increased computational time, which is less than three times the time needed for the original dimer calculation, since the (AO) two-electron integrals are identical in both dimer and monomer calculations and only have to be evaluated once.

"But a less than three times effort is well worth it while if it gives the possibility that much more accurate values of intermolecular interactions may be obtained\(^7\)."

The procedures described above are only valid when a size-consistent method is used to calculate the various energies. Special formulae have therefore been developed\(^8\) to deal with BSSE in CI(SD) calculations, since these lack size consistency. However, it seems preferable to use Eq. (20) as it stands, and to apply size-consistency corrections (cf. Section III.C) to all energies.

**B. Different Interpretations of the Basis-set Superposition Error**

Although it is possible to use Eq. (20) directly, without any explicit consideration of a quantity called BSSE, it is customary to start from Eq. (19) and to consider the correction $\delta$ that would remove the BSSE in (19), viz.

$$
\Delta E(\text{corrected}) = \Delta E(\text{Eq. (19)}) + \delta
$$

$$
= E_{AB}(\chi_A \oplus \chi_B) - E_A(\chi_A) - E_B(\chi_B) + \delta
$$

(21)

If $\Delta E(\text{corrected})$ is taken to be $\Delta E(\text{Eq. (20)})$ then the BSSE correction $\delta$ is seen to be

$$
\delta = \delta^A + \delta^B = E_A(\chi_A) - E_A(\chi_A \oplus \chi_B) + E_B(\chi_B) - E_B(\chi_A \oplus \chi_B)
$$

(22)

Now the right-hand side of Eq. (21) can be read in two different ways. First, $\delta$ may be interpreted as a correction to the monomer energies, i.e. to the reference energy used in estimating the interaction energy. Adopting Eq. (20) as the corrected interaction energy then merely asserts, in true Boys-Bernardi spirit, that $E_A(\chi_A \oplus \chi_B)$ is the proper reference for estimating the effect of the perturbation. The second interpretation of Eq. (21) is that $\delta$ is a correction which removes the unphysical lowering of the monomer energies present in the
dimer energy \( E_{AB}(\chi_A \oplus \chi_B) \). This second interpretation has led to widespread hesitation in accepting Eq. (20), since intuitively it seems clear that the Pauli principle will prevent one component to fully utilize the basis set of the other component in the dimer calculation\(^{188}\). This interpretation has led to a variety of proposals (see below) in which the occupied orbitals of B are excluded from the calculation of \( E_A \) and \( E_B \). The correction \( \delta \) will then usually be smaller than \( \delta^P \).

Johansson et al.\(^{189}\) were the first to conclude that the counterpoise procedure overestimates the basis-set superposition error. They proposed to scale the correction by a factor reflecting the reduced number of ghost virtual orbitals available to a monomer in the dimer situation and obtained good agreement with larger basis sets for their STO-3G SCF calculations on hydrogen-bonded systems. Their idea has had few followers and little success\(^{190,191}\). Nevertheless, their conclusion that the BSSE is overestimated has received widespread acclaim and many authors believe the counterpoise procedure to yield a (high) upper bound\(^{18,103,112,157,188,190-207}\).

C. Alternative Counterpoise Scheme

A rigorous implementation of the idea that the ghost's occupied orbitals should not be available in the monomer calculation was proposed by Daudet et al.\(^{192}\). In their scheme, which one may call virtuals-only CP, the BSSE for monomer A is obtained as

\[
\delta^X = E_A(\chi_A) - E_A(\chi_A \oplus \chi_B^X) \\
\chi_B^X = \chi_B^{\text{ref}} \oplus \chi_B^V
\]  

(23)

Fig. 1 is an attempt to illustrate the differences between the original CP scheme (often denoted as full CP) and the virtuals-only CP scheme. For the sake of argument the dimer wavefunction is assumed to be of the CI(5D) type but the following arguments apply equally to the SCF case, providing the dimer SCF wavefunction is considered to arise by mixing in excited configurations in a reference configuration built from free-monomer MOs.

In the full CP method (Fig. 1a) the dimer and monomer CI calculations are performed in the same manner. The occupied and virtual orbitals for each system are determined in an SCF calculation employing the complete basis set. These orbitals are subsequently employed in the CI calculation.

In the virtuals-only scheme (Fig. 1b) the monomer calculation is performed in the basis of the monomer augmented by the virtual orbitals of the ghost, which are orthogonal to the (absent) occupied orbitals of the ghost. Note that the monomer's own virtuals are not orthogonalized to these (absent) ghost occupied orbitals. The dimer calculation may be either identical to the one of the full CP scheme above or, more in the Boys–Bernardi spirit of using identical function spaces in both dimer and monomer calculations, it may employ suitableraf to be little different. 

Note that the latter, in the linear approximation.

The idea of possibilities in the dimer they chose a monomer calculation to SCF orbitals in the Ar dimer than that calculated reference configuration in the monomer and other procedure was exaggerated well in both schemes will be discarded.

D. Experience

A large number of papers were used to correct
D. Experiences With the Full and Virtuals-only Counterpoise Schemes

A large number of studies are now available in which one or both CP schemes were used to correct for the BSSE. We here present some of the conclusions...
<table>
<thead>
<tr>
<th>Basis</th>
<th>Method</th>
<th>Full</th>
<th>Virtuals-only</th>
<th>No correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H₂O)₂</td>
<td>ΔE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(kcal mol⁻¹)⁴⁶</td>
<td>STO-3G</td>
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<td>-5.16</td>
</tr>
<tr>
<td>Ar-HCl</td>
<td>ΔE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(μhartree)³</td>
<td>Basis I</td>
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<td>-5.58</td>
</tr>
<tr>
<td>(μhartree)³</td>
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<td>-646</td>
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<tr>
<td>(H₂O)₂</td>
<td>ΔE</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(kcal mol⁻¹)¹¹⁵</td>
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<td>-7.22</td>
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</tr>
<tr>
<td></td>
<td>EZPP</td>
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<td>-4.39</td>
<td>-4.91</td>
</tr>
</tbody>
</table>

*R = 5.63 a.u., θ = 60°.
*R(Ar...Cl) = 7.6 a.u., θ = 0°.
*R = 5.60 a.u., θ = 40°.
and opinions that have been put forward in these studies. Some selected results are shown in Table VII. Without discussing these in detail, it is apparent that BSSE corrections can easily be of the same magnitude as the interaction energy itself. Also, even the differences between $\delta^{CP}$ and $\delta^V$ can be of that magnitude.

A feature not apparent from Table VII is that for larger basis sets the CI BSSE may be larger than the SCF BSSE, and it is difficult to remove it by enlarging the basis. Its value may easily reach 50% of the correlation interaction energy. An example of this was provided by Clementi and Habitiz who, correcting only for the SCF BSSE in their Davidson-corrected CI calculations of the water dimer potential energy surface, found a well depth of 5.5 kcal mol$^{-1}$. The second virial coefficient calculated for their surface was a factor of 2 too high, indicating too much attraction. By decreasing the correlation contribution to the interaction energy by an arbitrary factor 0.5 the calculated virial coefficient was brought into good agreement with experiment and the well depth was reduced to 4.7 kcal mol$^{-1}$. Correcting is thus absolutely necessary both in SCF and CI calculations.

We stress that the purpose of a good BSSE correction scheme has to be to yield the true interaction energy corresponding to the quality of the basis set and the method. One should not expect all basis dependencies to be removed nor the experimental result to be reproduced. Comparison with, e.g., the experimental dissociation energy may be misleading. Since the main defect of most basis sets employed in practical calculations is a lack of sufficient polarization functions (cf. Section IV) to reproduce the dispersion energy adequately, the true interaction for those basis sets will be above the experimental result and any scheme that underestimates the BSSE will be favoured in such a comparison.

These considerations are frequently overlooked in studies that claim, on numerical grounds, that $\delta^{CP}$ is an overcorrection, or simply unhelpful. For example, in an SCF study on FH$_2$, Kocjan et al. observed that $\delta^{CP}$ correction of the STO-2G result at the calculated $R_e$ removed all attraction. Their conclusion that $\delta^{CP}$ overcorrects is debatable, however, since $R_e$ was probably so short that a repulsive corrected $\Delta E$ should have been anticipated.

In a recent CI study of Ar–HC$^+$ the present authors compared $\delta^{CP}$ and $\delta^V$ corrected energies with the experimental $\Delta E$ and concluded that $\delta^{CP}$ was too large. However, as argued above, the comparison should have been with the (unknown) true $\Delta E$ in the given method and basis. Finally, a somewhat different approach was taken in a recent SCF study on (HF)$_2$. It was argued that $\delta^{CP}$ correction was unhelpful, since it failed to reduce the range of interaction energies. However, since basis sets ranging from minimal to large as well as polarized were considered, the electric properties were very different.
from case to case and so a wide range of ‘true’ interaction energies should have been anticipated.

There have been a number of SCF studies on polar systems\textsuperscript{78, 107, 208, 209} in which the important contribution of the monomer dipole moment to the attractive interaction\textsuperscript{209} was recognized. By avoiding polarity differences\textsuperscript{107, 208} or by correcting for them\textsuperscript{78, 209} these studies arrived at the conclusion that $\delta^P$ correction brings small-basis results in close agreement with large-basis results. The same conclusion was reached in SCF work on non-polar systems\textsuperscript{175, 209, 210}. However, in the absence of similar work (SCF and CI), using the $\delta^V$ correction, no objective conclusion can be drawn (however, see Section VI).

As noted before, the majority of authors regard $\delta^P$ as an overcorrection, at least in principle, and so it is not surprising that the $\delta^V$ correction—even though it is somewhat harder to implement—has found increasing use in recent years\textsuperscript{36, 90, 128, 143, 192, 195, 197, 199, 203, 206, 211–214}. An approximate version is sometimes employed, intended to reduce the dimension of the ghost calculation already at the AO level. It consists of using only the polarization functions of the ghost\textsuperscript{143, 197, 203} plus possibly the diffuse AOs\textsuperscript{215}. This variant has mainly been applied to cluster calculations\textsuperscript{197, 203, 215} where basis-set size is a premium. Although in a few cases\textsuperscript{128, 197} $\delta^V$ was claimed to give better agreement with experiment than $\delta^P$, it seems fair to say that the results of all $\delta^V$ studies leave the question of the correctness of $\delta^P$ or $\delta^V$ fully open.

This opinion is shared by a number of authors who regard the full counterpoise corrected and the virtuals-only corrected energies as results bracketing the real interaction energy for the basis\textsuperscript{199, 203} or the experimental interaction energy\textsuperscript{214, 216}.

Fundamental support for the $\delta^V$ correction was expressed by Morokuma \textit{et al.}\textsuperscript{36}, who observed that in energy-partitioned SCF calculations the $E_{\text{cr}}$ term became excessive for basis sets subject to large BSSE. They argued that a virtuals-only scheme is the proper one to correct for this. It was noted that the virtuals of the ghost to be included should really be those of the counterpoise-corrected instead of the isolated ghost. This recipe is difficult to implement. However, in their example the difference from the simple recipe was extremely small. Similarly, Hayes and Stone\textsuperscript{199, 213} state that, while only the virtuals of the partner are available in their non-orthogonal second-order perturbation theory, the occupied orbitals may become available in higher orders.

An implicit assumption made in the above work\textsuperscript{36, 90, 213} is that the first-order interaction energy $\Delta E_{\text{HI}}$, when evaluated using monomer wavefunctions in the monomer’s own basis, will be free of BSSE. This assumption was formulated explicitly in a recent letter by Collins and Gallup\textsuperscript{217}. In their opinion $\delta$ should therefore be smaller than $\Delta E_{(1)}$. However, $\delta^P$ was found to be larger than $\Delta E_{(1)}$ in several cases and so they concluded that $\delta^P$ is an overcorrection. We return to this point in Section VI.
E. Ways of Avoiding Basis-set Superposition Errors

To this time no general agreement has been reached in the literature and the problem of how to determine the basis-set superposition error is considered unsolvable by many. Thus methods have been devised to avoid the BSSE either completely or to a large extent.

Non-orthogonal valence-bond (VB) techniques\textsuperscript{89,91,138,179,213,218-220} are most suited to this purpose since the orbital spaces of the two monomers may be separated exactly. The configurations (structures) included in the calculation may be chosen such that no BSSE arises. However, as Wormer\textit{et al.}\textsuperscript{221} pointed out, configurations classified as charge-transfer type in VB calculations also contribute to the BSSE. To omit these configurations is too crude a solution since, as Gallup showed for the BSSE-free $^{3\Sigma^+}$ H\textsubscript{2} van der Waals system\textsuperscript{179}, the charge-transfer energy can be an important component of the interaction energy. In their H\textsubscript{2} calculations Collins and Gallup\textsuperscript{138} avoid the BSSE when a small basis is used, by using for the dimer a reference configuration built from monomer occupied orbitals calculated in the dimer basis set\textsuperscript{78,175}, a recipe in complete agreement with the full counterpoise scheme at SCF level, and obtain a charge-transfer energy in good agreement with large-basis-set results. The BSSE at CI level, caused by double excitations with at least one of the virtuals of the partner involved, is avoidable at little penalty in the VB scheme\textsuperscript{138}. Obviously one may also avoid CI BSSE simply by taking only inter-monomer correlation (dispersion) into account\textsuperscript{88,89,91,92,218,219,221}, but then the important contributions of the intramonomer correlation to the interaction energy, both in the exchange repulsion and in the multipole interaction, are neglected.

Using orthogonal orbitals, the interacting correlated fragments (ICF) method\textsuperscript{133,180,200,222} attempts to avoid the BSSE by combining correlated monomers using a few carefully optimized important configurations for each monomer, and allowing only inter-monomer correlation on top of that. The definition of inter-correlation is a bit troublesome, however, since the monomer orbitals are mixed in the dimer calculation, owing to the orthogonality constraint. The BSSE of the correlated fragments cannot be excluded completely but seems to be negligible where checked\textsuperscript{200,222}.

A less rigorous approach is to hope for cancellation of the BSSE and the effect of omitted (polarization) functions on the dispersion energy\textsuperscript{103,223} or for cancellation of the BSSE and the total dispersion energy. The latter is implicitly assumed if the geometry of a van der Waals complex is optimized within the Hartree–Fock framework\textsuperscript{16,108,224-230} or when uncorrected small-basis SCF results are preferred based on a comparison with experimental data\textsuperscript{15,7,231}. The former is utilized if no BSSE correction is applied to CI or Møller–Plesset perturbation theory results for van der Waals molecules\textsuperscript{16,93,112,232-243}.
Such a cancellation of errors may occur for certain special basis sets, but it can never be complete \textsuperscript{106,244}, since the geometrical dependence of the BSSE may not be expected to be similar to that of the missing interaction energy, e.g., the \( R^{-6}, R^{-8}, \) etc., terms of the dispersion energy \textsuperscript{106}. The BSSE does not even always decrease as the inter-monomer distance increases \textsuperscript{245}. To quote Bolis \textit{et al.} \textsuperscript{244}: ‘Fortuitously the basis-set superposition error can yield interaction energies in agreement with experimental data, however, for internuclear distances that generally disagree with the experimental data’. A right distance combined with the wrong dissociation energy is also found \textsuperscript{225}.

Finally, in view of the current uncertainty with regard to the proper scheme to correct for BSSE, some authors regard the full counterpoise-corrected and the uncorrected interaction energies as results bracketing the real interaction energy for the basis \textsuperscript{188} or the experimental interaction energy \textsuperscript{18,204}. The counterpoise method is sometimes only used as an indication for the reliability of the calculation \textsuperscript{114,206,246,247}. Note, however, that a small BSSE may be due to either a good basis set of the monomer or to a basis on the ghost which is not fitted to improve the energy of the monomer. Wells and Wilson \textsuperscript{202} find that, as the basis set is systematically increased, the BSSE may not monotonically decrease but may instead increase and pass through a maximum before decreasing to its limiting value of zero.

Summarizing, since the basis-set superposition error may be large (that is, comparable to the interaction energy) and since it depends in an erratic way upon basis set and geometry, and affects both CI and SCF calculations and is extremely difficult to avoid without reducing the quality of the calculation, it is of vital importance to arrive at a reliable accepted scheme to correct for it.

VI. JUSTIFICATION OF THE FULL COUNTERPOISE PROCEDURE

In the previous section it became clear that in accurate calculations the BSSE must be corrected for. Although this may be done using the full CP procedure, there are a large number of authors who maintain that \( \delta + \) is an overcorrection. The following arguments for this seem worthy of further consideration:

1. \( \Delta E^{UL} \), involving only occupied MOs cannot contain BSSE, and since \( \delta + \) is sometimes larger than \( \Delta E^{CI} \), it must be an overcorrection.
2. \( \delta \) corrects for the unphysical energy lowering present in \( E^{AB} \) (the total dimer energy) and since occupied MOs are no longer available in the dimer, \( \delta + \) must be an overcorrection. This may be formulated as: in calculating \( \Delta E \) the function spaces must be the same, and since in the dimer there are no excited configurations where electrons of \( A \) enter the occupied orbitals of \( B \), these configurations must also be excluded from the monomer calculation.

Now it is recognized that a number of authors have provided numerical results to apply, such as He\textsubscript{2} in a s-type wavefunction for a true interatomic potential energy calculation.

On the other hand, as mentioned in Section V, many calculations have been obtained with the inclusion of \( A \) and \( B \) in the calculation, the details of which are not given in this article.

A. Conditions for Overcorrection

In Section V, we have shown that \( E^{UL} \) for a dimer or molecule is given by

\[
E^{UL} = E^{A} + E^{B} + \Delta E + \delta \]

The correction \( \delta \) is obtained by subtracting \( \Delta E \) from \( E^{AB} \) and \( \Delta = \Omega(\phi) \) is the difference of the effective Hamiltonian \( \Omega \) and \( \phi \) for the monomer. A and one of the dimers. Now \( \Omega \) and \( \phi \) with an observable.

\[
E^{UL} = E^{A} + E^{B} + \Delta E + \delta \]

We now use the notation \( E^{UL} \) as the interaction energy at the two monomers, for the wavefunction \( \phi \) corresponding to the same configuration as in (25) (this leads to the results in (26)) and in the case of the H-H system, the term—namely, the term—corresponding to the

This shows that for the two terms, \( \delta \) and \( \Delta E \), the corresponding terms in the wavefunction cannot be simply added together, as in the case of the H-H system. This is because the term—namely, the term—corresponding to the

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Now it is hard to prove formally that these arguments are wrong. But a number of recent calculations\textsuperscript{134,178}, both at the SCF and the CEPA level, have provided compelling numerical evidence that \( \delta^{CP} \) is the proper correction to apply, and that \( \delta^{Y} \) undercorrects. This was achieved by studying \( \Delta E \) for \( \text{He}_2 \) in a sequence of basis sets subject to widely different BSSE, while the true interaction energy for a given basis was monitored in independent calculations using perturbation theory.

On the basis of these numerical findings, we offer in this section some observations which in our opinion refute the above objections against the \( \delta^{CP} \) correction. A central role is played by the ghost’s occupied orbitals, since it is the inclusion of these in \( \delta^{CP} \) that has aroused so much criticism.

A. The Heitler–London Interaction Energy \( \Delta E^{HL} \) May Contain Basis-set Superposition Errors

In Section II.F it was shown that the total dimer Heitler–London energy \( E^{HL}_{AB} \) for a dimer wavefunction \( \mathcal{A}\psi^A\psi^B \), where \( \psi^A \) and \( \psi^B \) are SCF wavefunctions for \( A \) and \( B \), may be written as (cf. Eq. (10)):

\[
E^{HL}_{AB} = E_A + E_B + E^{(1)} + \Delta \tag{24}
\]

The corresponding interaction energy \( \Delta E^{HL} \) (Eq. (10)) is obtained by subtracting the reference energy \( E_A + E_B \). Here \( E^{(1)} \) is the first-order energy (5), and \( \Delta = O(S^4) \), hence small, if \( \psi^A \) and \( \psi^B \) are at the Hartree–Fock limit, but \( \Delta = O(S^2) \) when these SCF wavefunctions are obtained in finite basis sets, one at \( A \) and one at \( B \). \( E_A \) and \( \psi^A \) depend only on the occupied orbitals of \( A \); hence with an obvious extension of the notation (24) becomes

\[
E^{HL}_{AB} = E_A(\chi_{A}^{occ}) + E_B(\chi_{B}^{occ}) + E^{(1)}[\psi^A(\chi_{A}^{occ}), \psi^B(\chi_{B}^{occ})] + O(S^2) \tag{25}
\]

We now use a theorem, proved elsewhere\textsuperscript{76,78}, that \( \Delta = O(S^4) \), hence small, not only at the Hartree–Fock limit but also when \( \psi^A \) and \( \psi^B \) are SCF wavefunctions obtained in a finite common (dimer) basis set. Suppose we employ for this purpose the basis \( (\chi_{A}^{occ} \otimes \chi_{B}^{occ}) \). This leaves \( \mathcal{A}\psi^A\psi^B \) and hence \( E^{HL}_{AB} \) unchanged, since it involves mixing of orbitals within a single-determinant wavefunction. Thus instead of (25) one has

\[
E^{HL}_{AB} = E_A(\chi_{A}^{occ} \otimes \chi_{B}^{occ}) + E_B(\chi_{A}^{occ} \otimes \chi_{B}^{occ}) + E^{(1)}[\psi^A(\chi_{A}^{occ} \otimes \chi_{B}^{occ}), \psi^B(\chi_{A}^{occ} \otimes \chi_{B}^{occ})] + O(S^4) \tag{26}
\]

This shows that one and the same dimer energy, viz. \( E^{HL}_{AB} \), can be interpreted in two different ways. The Heitler–London interaction energy \( \Delta E^{HL} \) can correspondingly be obtained by subtracting from \( E^{HL}_{AB} \) the monomer energies in (25) (this is the usual procedure in Morokuma’s energy partitioning\textsuperscript{15}) or those in (26). The latter procedure is clearly preferable, since the dubious \( \Delta \) term—not a pure interaction energy—is smallest in (26).
Comparing the Heitler–London interaction energies corresponding to (25) and (26) one readily finds \(^{178,245}\)

\[
\Delta E^{\text{HI}}(\text{Eq. (26)}) = \Delta E^{\text{HI}}(\text{Eq. (25)}) + \delta^{\text{occ}}
\]  

(27)

where

\[
\delta^{\text{occ}} = E_A(\chi_A^{\text{occ}}) + E_B(\chi_B^{\text{occ}}) - E_A(\chi_A^{\text{occ}} \otimes \chi_B^{\text{occ}}) - E_B(\chi_A^{\text{occ}} \otimes \chi_B^{\text{occ}})
\]

(28)

is a first-order BSSE in \(\Delta E^{\text{HI}}(\text{Eq. (25)})\) due to its use of the inappropriate reference energy \(E_A(\chi_A^{\text{occ}}) + E_B(\chi_B^{\text{occ}})\) (cf. also Ref. 104). This \(\delta^{\text{occ}}\) is identical with \(\Delta^{\text{occ}}\) in Ref. 245.

We note in passing that \(E^{\text{HI}}_{\text{AB}}\) allows even a third interpretation, namely in terms of full CI wavefunctions for A and B, each obtained in the common basis \((\chi_A^{\text{occ}} \otimes \chi_B^{\text{occ}})\) defined above. When combined in the form \(\phi^A \psi^B\) this will yield the same wavefunction as before. Now \(\Delta\) vanishes completely\(^{245}\). (Also, if the monomer CI functions are complete up to \(n\)-fold excitations then the contributions to \(\Delta\) can be related only to higher than \(n\)-fold excitations\(^{248}\).) In this case \(E^{\text{HI}}_{\text{AB}}\) reduces to monomer energies plus a pure interaction energy. These monomer CI energies \(E_A(\chi_A^{\text{occ}} \otimes \chi_B^{\text{occ}})\) will be lower than those in (26) and so the corresponding \(\Delta E^{\text{HI}}\) energy will be more repulsive. This is a true interaction phenomenon, reflecting a decrease in correlation effects when bringing A and B together. In this particular case, the entire correlation energy \(E^\text{CI}(\chi_A^{\text{occ}} \otimes \chi_B^{\text{occ}}) - E_A(\chi_A^{\text{occ}} \otimes \chi_B^{\text{occ}})\) is lost upon dimerization as a result of the Pauli principle, giving rise to increased exchange repulsion in \(\Delta E^{\text{HI}}\). Exactly the same result would be obtained from a non-orthogonal valence-bond study, where each individual monomer is described by a CI function in the basis \((\chi_A^{\text{occ}} \otimes \chi_B^{\text{occ}})\). This example illustrates that a reduction of excited configurations in the dimer situation is not a valid reason to omit configurations from monomer calculations.

Returning to the SCF case, we note that the \(\Delta\) term in \(E^{\text{HI}}_{\text{AB}}\) can also be made small (i.e. \(O(S^4)\)) by using the full dimer basis \((\chi_A \otimes \chi_B)\) in calculating the monomer SCF wavefunctions, i.e. full CP\(^{175}\). This leads to a different \(E^{\text{HI}}_{\text{AB}}\), and a different \(\Delta E^{\text{HI}}\):

\[
E^{\text{HI}}_{\text{AB}}(\chi_A \otimes \chi_B) = E^A(\chi_A \otimes \chi_B) + E^B(\chi_A \otimes \chi_B) + E^{(1)}[\phi^A(\chi_A \otimes \chi_B),
\psi^B(\chi_A \otimes \chi_B)] + O(S^4)
\]

(29)

This recipe may be the only practical option, for example, when bond functions are used on the A–B axis, or when the numerical Hartree–Fock method is employed.

Values of \(\Delta E^{\text{HI}}\) corresponding to (29) have been obtained by several authors\(^{178,144,175–178,249}\). They are sometimes higher, sometimes lower, than those of (25). The difference has been termed BSSE\(^{(1)}\) (Ref. 144), but this is confusing since most of the difference may reside in the different \(E^{(1)}\) energies in (25) and (26). We find it more appropriate to obtain a corrected \(\Delta E^{\text{HI}}\) that is in agreement with \(\Delta E^{\text{SCF}}\), even in the presence of BSSE\(^{(1)}\).

As long as one accepts that BSSE\(^{(1)}\) is a first-order effect, one can then use the difference between \(\Delta E^{\text{HI}}\) and \(\Delta E^{\text{SCF}}\) to correct for the contribution of BSSE\(^{(1)}\). In both the dimer and the monomer, the effect can arise from BSSE\(^{(1)}\) or from BSSE\(^{(2)}\).

Typical results are given in Table I, where the contributions of BSSE\(^{(1)}\) and BSSE\(^{(2)}\) are discussed in detail. In a mono...
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\[ E_{\text{HF}}(\chi_{A}^{\text{occ}} \otimes \chi_{B}^{\text{occ}}) \]  

The use of the inappropriate interpretation, namely in the common basis, in \( \psi_A \otimes \psi_B \) this will yield completely incorrect results. (Also, if the \( n \)-fold excitations are the dominant excitation energy, then the \( n \)-fold excitations will be preferred.) In this section we assume that the interaction energy \( E_{\text{HF}} \) is the sum of the \( n \)-fold independent contributions, and that the \( n \)-fold excitations are the only important interaction energy. This will only be possible when the \( n \)-fold basis sets are used to obtain \( \psi_A \) and \( \psi_B \), i.e. when one employs \( E_{\text{HF}} \) (Eq. (29)) to partition the final \( \Delta E_{\text{HF}} \).

B. Monomer A in Dimer AB Can Recover the Full Counterpoise Correction \( \delta_{\text{CP}} \)

The counterpoise correction can be applied by using (20) directly, without explicit consideration of a quantity called BSSE (cf. Section V.B). If, on the other hand, one sets up the dimer calculation by starting from monomer wavefunctions obtained in the monomer's own basis set, then BSSE will enter the calculation at some stage, and a correction \( \delta \) must be applied to remove it. In the previous section a small part of \( \delta_{\text{CP}} \) (viz. \( \delta_{\text{occ}} \)) was seen to creep in already in \( E_{\text{HF}} \). We now examine how the remainder of \( \delta_{\text{CP}} \) can enter the dimer calculation, even though the occupied orbitals seem 'unavailable'.

By performing the monomer plus ghost calculation in steps, first adding only the ghost occupied MOs, one obtains \( \delta_{\text{occ}} \) (Eq. (28)); likewise, adding only the virtuals, one obtains \( \delta_{\text{vir}} \) (Eq. (23)). Adding the full space of the ghost one finds \( \delta_{\text{CP}} \) (Eq. (22)), which proves to be larger than the sum of \( \delta_{\text{occ}} \) and \( \delta_{\text{vir}} \).

\[ \delta_{\text{total}} = \delta_{\text{CP}} = \delta_{\text{occ}} + \delta_{\text{vir}} + \delta_{\text{occ-vir}} \]

Typical results for these \( \delta \) contributions are shown in Table VIII. The direct contribution of the ghost occupieds (\( \delta_{\text{occ}} \)) is seen to be quite small, but the indirect contributions, viz. the mixing term \( \delta_{\text{occ-vir}} \), can be as large as 60% of \( \delta_{\text{CP}} \). This may be understood as follows.

In a monomer plus ghost calculation, the ghost occupieds and virtuals,
### TABLE VIII

<table>
<thead>
<tr>
<th>SCF</th>
<th>$H_2O \ldots HOH^{2+}$ <em>(R = 2.98 Å)</em></th>
<th>$STO-3G$</th>
<th>4-31G</th>
<th>4-31G</th>
<th>4-31G</th>
<th>(kcal mol$^{-1}$)</th>
<th>$\delta_{CT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.77</td>
<td>1.0</td>
<td>1.64</td>
<td>3.41</td>
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<tr>
<td></td>
<td></td>
<td>0.22</td>
<td>0.39</td>
<td>0.84</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.16</td>
<td>0.21</td>
<td>0.48</td>
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<tr>
<td></td>
<td></td>
<td>0.05</td>
<td>0.58</td>
<td>0.32</td>
<td>0.95</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SCF</th>
<th>$He \ldots He^{1+}$ <em>(R = 5.6a$_0$)</em></th>
<th>4s2p</th>
<th>5s2p</th>
<th>10s2p</th>
<th>(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.26</td>
<td>48.3</td>
<td>5.1</td>
<td>54.7</td>
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<td></td>
<td></td>
<td>0.83</td>
<td>10.3</td>
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<tr>
<td></td>
<td></td>
<td>0.002</td>
<td>0.03</td>
<td>0.006</td>
<td>0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cl</th>
<th>$He \ldots He^{1+}$ <em>(R = 5.6a$_0$)</em></th>
<th>CR0+DS3</th>
<th>CR0+DS5</th>
<th>CR2+DS3</th>
<th>(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>20.2</td>
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</tr>
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<td>0.007</td>
<td>1.22</td>
<td>0.183</td>
<td>1.41</td>
</tr>
</tbody>
</table>

$^\text{aIn Refs 178 and 134, $}\delta_{\text{soc}}$ for molecule A was calculated in the basis ($\chi_A \oplus \chi_B^{\text{soc}}$).$^\text{b}$

The energy of monomer A in the presence of the frozen monomer B is calculated once and the counterpoise principle implies that the correction $-\delta_{\text{soc}} - \delta_{\text{virr}}$ for each monomer B and the dimer needs to be calculated in the presence of the monomer A if it is not impossible to avoid the monomer A from being calculated in the dimer. This will contain some artefacts, allowing for some uncertainty. As seems from Table VIII, the estimate, rather than a proper reference. The sum of van der Waals molecular electron densities$^{198,204}$ is an approximated additive.$^{193,252}$

If, instead of dimer interactions, the Bernardi recipe is in a strict manner, it has to be calculated in the case that all calculations$^{172,203,204}$ have been applied to trimer interactions. Using the counterpoise function method and assuming additivity, the monomer calculations are$^{196}$

Extra complications of distortions of the internal geometries can be handled with respect to the undistorted geometry of both the monomer and the dimer.
calculated once with its own basis set (this energy contains the small energy lowering $-\delta_{\text{sec}}$), and once with the total dimer basis set, where the occupied orbitals of B are already used. The difference is the extra energy gained by monomer A if it is offered the orbitals of B in the dimer situation. Since it is impossible to avoid charge transfer in this extra energy, the BSSE so defined will contain some charge-transfer energy and is therefore named $\delta_{\text{CT}}$. Even allowing for some charge transfer, which for He$_2$ is estimated as $0.16K^{138}$, it seems from Table VIII that the total $\delta_{\text{vir}} + \delta_{\text{sec-vir}}$ is reproduced by the $\delta_{\text{CT}}$ estimate, rather than $\delta_{\text{vir}}$ alone.

C. Practical Considerations

A few practical points remain to be discussed. Acceptance of the counterpoise principle implies that all energy terms contained in the final $\Delta E$ must be interpreted in terms of monomer wavefunctions and properties calculated in the full dimer basis set. As mentioned before, the final representation of $E_{\text{exch}}$ may in fact be better than would be expected from an estimate of $E_{\text{exch}}$ in terms of the $\psi_A(\chi_A)$ monomer wavefunctions. On the other hand, the final representation of $E_{\text{Coul}}$ and $E_{\text{Ind}}$ may contain undesirable artefacts$^{139,198}$, such as an unphysical dipole–dipole contribution to $E_{\text{Coul}}$ of He$_2$. These effects have been termed higher-order BSSE$^{139}$, and they will not be removed by applying the $\delta_{\text{CT}}$ correction. In certain applications it may be desirable to remove these artefacts$^{178,198}$ for example by adding a correction $E_{\text{Coul}}(\psi_A(\chi_A),\psi_B(\chi_B)) - E_{\text{Coul}}(\psi_A(\chi_A \oplus \chi_B),\psi_B(\chi_A \oplus \chi_B))$ to the final $\Delta E$. Likewise, if in polar complexes the multipole energy is corrected by inserting better values of the multipole moments$^{78,104,105,107}$, then the dimer–basis multipole energy is the proper reference. The same applies to the calculation of differential properties of van der Waals molecules. Counterpoise corrections have been applied to electron densities$^{198,251}$, multipole moments$^{139,198,201,205}$ and polarizabilities$^{139,252}$.

If, instead of dimer interactions, many-body effects are calculated, the Boys–Bernardi recipe is in a straightforward way extended to read ‘each subsystem is to be calculated in the complete basis of the supersystem’, a recipe that has been applied to trimer interactions$^{262,263}$ and, albeit approximately, to cluster calculations$^{197,203,204}$. Wells and Wilson$^{196}$ call this the site–site counterpoise function method and formulate it nicely for two-body, three-body, etc., interactions. Computing only a counterpoise correction for pairs of monomers and assuming additivity proved to overestimate the BSSE even for small systems$^{196}$.

Extra complications occur if a full geometry optimization is performed, distorting the internal geometrical parameters of the monomers. Two monomer calculations are now needed to calculate an interaction energy with respect to the undistorted monomers. A counterpoise calculation with both the monomer and the ghost at their distorted geometry $R'$ yields the
reference energy for the interaction between the distorted monomers

\[ \Delta E' = E_{A\text{int}}(\chi_A \oplus \chi_B; R_A R_B') - E_A(\chi_A \oplus \chi_B; R_A R_B') - E_B(\chi_A \oplus \chi_B; R_A R_B') \]  

(31)

Then the deformation energy, needed to distort each monomer from its original geometry \( R \) to its dimer geometry \( R' \), must be calculated, e.g. according to

\[ E_{\text{def}} = E_A(\chi_A, R_A) - E_A(\chi_A, R_A') \]  

(32)

Since the basis \( \chi_A \) will usually be designed for describing interactions rather than monomer deformations, there may be a need to use a different basis in this step. One might even use a different calculational method than in the dimer calculation, or one could use experimental force constant and geometry information for the monomer. The total interaction energy is now given by

\[ \Delta E = \Delta E' + E_{\text{def}}^A + E_{\text{def}}^B \]  

(33)

and the optimized geometry is that which minimizes \( \Delta E \). This recipe has been applied rarely yet and only as far as we are aware using the monomer basis to calculate the deformation energy. Since analytical gradient techniques have become widely available, the simultaneous optimization of many geometrical parameters has become feasible, so formulae (31)--(33) should find widespread use.

VII. CONCLUSIONS

Although the calculation of a potential energy surface for a van der Waals molecule is fraught with difficulties, a reliable ab initio surface should not be out of reach.

The basis set employed should be geared towards a proper description of all components of the interaction energy, suggesting a basis of triple-zeta quality augmented with polarization functions allowing a proper description of electrical moments, intra-correlation and inter-correlation (dispersion) effects. If the dispersion energy is not the major component of the interaction energy, a single moment-optimized \((1s^1p^4)\) set or an energy/polarizability-optimized \((2d^8 \text{p}^{11})\) set of polarization functions, possibly augmented by \((1f^8 \text{d}^{11})\), may suffice. SCF and MP2 may then be used as a cost-effective method to obtain a reasonable potential energy surface. For better results one could turn to a size-consistent CI method, like CEPA. If the dispersion energy is the major factor in the van der Waals interaction, like in He2, the basis set should be quite extended and an approach better than single-reference CEPA is called for. A simple recipe is not available as yet in these cases.

The counterpoise procedure must be applied in order to avoid the basis-set superposition error.

We recommend that the components of the interaction energy be monitored routinely in order to avoid basis-set superposition error.

The debate on the BSSE has of late been refueled. A recent letter to the editor (J. Chem. Phys. 1988, 89, 5900) proposed a new definition of the BSSE.

Perhaps the most direct way is to perform SCF calculations with both virtual and occupied shells for each molecule in the dimer. The resulting correction \( \Delta E' \) is performed in a complete basis set, and the correlation energy in the correction \( \Delta E' \) is performed in a complete basis set as well.

The exact interaction energy would then be obtained by summing \( \Delta E' \) and \( \Delta E' \) with the same complete basis set for both monomers.

We thank R. N. Zare for help in preparing the manuscript, and many insights into the nature of the BSSE. We thank V. Bumbu for discussions. We thank J. Veith for reading the manuscript.
WEAKLY BONDED SYSTEMS

the distorted monomers
\[ R_A(R_a) - E_{H}(R_A \oplus X_H R_A R_B) \] (31)
distort each monomer from its
etry \( R' \), must be calculated, e.g.
\[ E_{g}(X_A, R_A) \] (32)
for describing interactions rather
need to use a different basis in this
ional method than in the dimer
ic force constant and geometry
raction energy is now given by
\[ E_{d}^{n} + E_{d}^{n} \] (33)
minimizes \( \Delta E \). This recipe has been
are using the monomer basis to
Since analytical gradient techni-
 simultaneouse optimization of feasible, so formulae (31)–(33)

IONS

t energy surface for a van der Waals
ce \( ab \) initio surface should not be
owards a proper description of all-
ning a basis of triple-zeta quality
ving a proper description of the-
ation (dispersion) effects.
onment of the interaction energy, an
energy/polarizability-optimized
by \( 11s1d4p \), may
pe-effectiveness to obtain a
result one could turn to a size-
ion energy is the major factor
8, the basis set should be quite
reference CEPA is called for. A
es.
order to avoid the basis-set
interaction energy be monitored

Note Added in Proof

The debate on the BSSE problem (section VI) has continued since we completed our manuscript.

Szczesiak and Scheiner have applied the ideas developed in Refs. 134 and 178 to an MP2 study on \( (HF)_{2}^{2+} \). The full \( \delta_{CP} \) correction scheme was shown to produce interaction energies that behave as one should expect for the given basis, thus confirming the validity of the function counterpoise method at the correlated level of theory.

Perhaps the most direct theoretical argument in favour of including all (virtual and occupied) ghost orbitals in the monomer + ghost calculation and hence in the correction \( \delta_{CP} \) is the following\(^{178}\). Suppose the dimer calculation is performed in a complete set of (one-electron) basis functions, composed of two incomplete sets, one centered at monomer A and one at monomer B. The exact interaction energy (for the given method) will then only be recovered if the same complete basis is used in calculating the monomer energies. Nobody would argue that the 'to be occupied' orbitals of the ghost at B should be removed when calculating the energy of A, since this would render the A-basis incomplete.

Alternative counterpoise correction schemes were proposed by Olivares \( et al^{265} \) and by Dykstra \( et al^{266} \). Neither of these schemes produces the exact correction in the hypothetical case of a complete dimer basis, as sketched above, and so they must be rejected.

A rather novel objection\(^{143,266,267}\) against the function counterpoise method is that it does not increase reliability, since \( \delta_{CP} \) does not remove the remaining errors in \( \Delta E \). Thus 'the extra expense of performing counterpoise calculations is not warranted and it is better to increase the basis-set to the maximum affordable'\(^{143} \). This argument tacitly assumes that increasing the basis will simultaneously reduce both the BSSE and the remaining errors in \( \Delta E \). While this may be true in some special cases (e.g. see Refs. 266 and 178), there are now several well-documented examples where increases in the basis set lead to increased BSSE\(^{134,202,264,268} \).

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References

WEAKLY BONDED SYSTEMS

110. Chalafinski, G., private communication.
WEAKLY BONDED SYSTEMS


250. Saunders, V. R., private communication.


258. Vos, R. J., unpublished results using a [5s, 3p, 2d] gaussian basis for He and a [9s, 7p, 2d, (4d) 7] basis for Ar.


