
CHAPTER 2

Basis Set Superposition Errors: Theory and Practice

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INTRODUCTION

Intermolecular interaction energy is defined as the difference between the total energy of a combined system and that of its components. Compared to the total energies of a molecule or its individual atoms, the interaction energy is a small effect, being usually one part in a hundred thousand or less. There are essentially two ways to obtain that energy: by calculating it directly, or by obtaining the difference from calculations on all the pieces. The first approach involves perturbation theory.¹⁻³ At large intermolecular separations, it works well, but at small separations difficulties arise from the overlap of electron distributions, modified by the antisymmetry of the electron wavefunction. Because of antisymmetry, it is necessary to develop a non-Hermitian perturbation theory to include nonlocal effects and use nonorthogonal orbitals. In a non-Hermitian theory, the order of operations is critical and many standard quantum mechanical symmetries are not obeyed. A nonlocal operator like the exchange operator depends on the function on which it acts. If extreme care is not

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taken with these complicated operators, the results can become complex and nonsensical. Whereas those problems can be overcome, the theory is complicated and thus not widely used. The reader is referred to the work of Mayer et al.⁴⁻⁶ for a more detailed explanation of terms and methods.

The second way to obtain the interaction energy is the more traditional method that is sometimes called the supermolecular approach.⁷ In this method, the interaction energy of, say, a dimer AB (the supermolecule) is obtained by directly subtracting the energy of the isolated monomers, A and B, from the total energy of the dimer, as follows:

$$\Delta E_{\text{int}} = E(\text{dimer}) - E(\text{mon}_A) - E(\text{mon}_B) \quad [1]$$

where $E(\text{dimer})$ is the total energy of the dimer obtained using the dimer basis set {AB}, and $E(\text{mon}_A)$ and $E(\text{mon}_B)$ are the energies of the monomers using their respective basis sets {A} and {B}. Both the type and the size of the basis sets used to represent a system will determine the functional space in which all electronic properties of the system are evaluated. In practice, however, one is actually describing the dimer by means of functional space different from the functional space used to describe each of the separate monomers, because the energy for the monomers is obtained through the use of their own basis sets individually (A and B, respectively), whereas the energy for the dimer is obtained by means of a basis set for the dimer (AB), which could be the combined basis sets of the monomers.

The supermolecular approach may be visualized in a manner similar to that applied to the formation of a hydrogen molecule. At large internuclear distances, the monomers interact very weakly and thus are not really disturbed by the presence of each other. In a simplistic view, as the two monomers approach each other to form the dimer, the first monomer feels the presence of the second monomer through its orbitals; that is, the basis set of one monomer improves the basis set of the second (in essence providing more room for the electrons in that monomer to move about), thus producing an added stabilization to the electrons of the first monomer. And, likewise, similar stabilizations apply to the second monomer. The effect on the energies of the combined basis sets that now describe the monomers has been called *basis set extension* (BSE) effect.⁸ In short, the unbalancing of the basis sets creates an artificial lowering of the energy for each monomer as the dimer forms, and this phenomenon is known as *basis set superposition error* (BSSE). The artifact arises when the energy of the dimer is compared at separation distances where each partner's orbitals play an important role in stabilizing the electron distribution of the other partner. At infinite separations, of course, the partner orbitals do not affect each other.

Historically, this effect was discovered by Kestner⁹ while trying to explain the spurious minimum observed in the potential energy curve for a helium dimer. Later Liu and McLean¹⁰ gave it the name BSSE. "Basis set superposition

error” is an appropriate name because the issue is really how basis sets superimpose when atoms interact with each other.

BSSE is important because it arises whenever computational chemists try to model the interaction of two or more species. A literature survey indicates that over 300 papers using or calculating BSSE were published from 1991 through 1997. There have also been three especially relevant reviews. The first two were by van Lenthe, van Duijneveldt-van de Rijdt, and van Duijneveldt, who published a very careful analysis of weakly bound systems with special emphasis on BSSE corrections in 1987,¹¹ followed by a related one in 1994.¹² The third review, a more practical review by Scheiner,¹³ focused on calculating hydrogen bonds by *ab initio* methods and gave a long discussion of BSSE effects. In addition, Gutowski and Chalasinski wrote an excellent critical review, comparing various approaches to eliminating the error.¹⁴ While this chapter was being prepared, another review by van Duijneveldt¹⁵ appeared which emphasizes the practical issues of evaluating and eliminating BSSE.

To use a standard quantum chemistry program, one must choose a basis set or let the program make that decision based on the programmer’s knowledge and preferences. The selection of a basis set has many consequences.^{7,13,16} Not only does it limit the accuracy of the energy, but it can affect the accuracy of other predicted properties. Serious complications can arise when one takes the difference between two approximate *ab initio* calculations. Not only does the answer have errors due to the limitations of the finite basis set, but very often the two calculations may not have the same magnitude of error even if the same basis set is used. Using a finite basis set to represent a wavefunction always introduces errors, sometimes large and sometimes small.

The first part of this chapter defined the BSSE effect and explained why it occurs. The remainder of this chapter discusses the size, importance, and accuracy of BSSE corrections, and finally gives practical guides for making corrections for the effect within the standard computer packages now available.

ORIGIN AND MAGNITUDE OF BSSE

One of the earliest cases of an extreme BSSE error was found by Kestner⁹ in the calculation of the helium–helium interaction using Slater-type orbitals (STOs), all with the same exponent. Symmetry restriction at the Hartree–Fock level prevents the 2p and 2s orbitals from mixing in the atom, but they do mix in the molecule. Therefore when this basis set is used for the atom, the 2p functions do not contribute to the ground state energy. But, in the diatomic, where the symmetry is not spherical, the functions can contribute and thus lower the dimer energy rather significantly. Consequently, there is a large minimum in the interaction energy for the helium dimer even at the Hartree–Fock level, contrary to what is observed experimentally. This extreme example dramatically

illustrates the BSSE and the fact that, when one is using the supermolecule method of calculation, the space of the basis sets available to the dimer is always larger than those available to the atom.

Let us first review the theory of representation of arbitrary functions in terms of a generalized basis set. There are two general criteria for evaluating an approximate function: point-by-point determination and integral determination. With the former, the approximate and the correct functions are made to agree as closely as possible at a finite number of points in function space. With a large number of points and enough adjustable parameters and functions, the approximate solution can be fit arbitrarily close to the exact solution. This is the type of evaluation used in the simple least-squares fits where the square of the difference between the exact and approximate functions is made as small as possible. The other type of determination, which is more widely used, involves matching some integral of the approximate solution as closely as possible to that of the exact solution. This is essentially what is done in such applications as Fourier analysis or any expansion in terms of special functions. Both these evaluations work well, and the errors can be minimized to any limit if the exact answer is known and if we have a complete orthonormal set of functions to work with. When we try to solve for the wavefunction of an atom or orbital, however, we do not know the exact answer, nor do we have a complete set of functions to use in the expansion. In most calculations, we have a property (total energy) we want to minimize. It is important, then, to emphasize that the function used is the total energy of the system, not the interaction energy.

In any use of an integral minimization to fit or approximate some function, there are biases built into the system. Some of these are due to the nature of the basis set used, but some are due to the nature of the function being minimized. From the theory of special functions,¹⁷ we know that the normalization and orthogonalization integrals for every special function have their unique weighting factors; that is, they emphasize different regions of space. In quantum chemistry the *variational principle* states that wavefunctions can be determined by minimizing the energy of the system. So when we use energy as our “weighting factor” or minimization function, we are locked into emphasizing the portions of the wavefunction that a priori contribute most to the energy, namely, the areas that have the highest electron density, i.e., regions closest to the nuclei. Likewise, we are likely to have increasingly poor accuracy in the areas that contribute least, namely, the areas with lowest electron density. This condition plays an important role in deciding whether BSSE effects are large or small in typical problems.

Returning to the BSSE calculations themselves, let us consider what would happen if we were to calculate the energy of a simple but real system, such as H₂. Let us also start our modeling by using a simple basis set, namely, one function per atom. When we determine the energy of each atom, we use one function, but when we calculate the energy of a diatomic we use two functions, one centered on each nucleus. If the one function were the exact solution, the

atomic energy would be exact. That is, if one function is all that is needed for the exact calculation, the energy of the atom calculated with two functions would be identical to that calculated with one function no matter where the functions were located or what their functional form; the energy would not be changed. However, if the one function is only an approximate representation, as we know it usually is, then the second function could make up for some of the deficiencies of the first, i.e., the second function could fill in those regions of electron density poorly approximated by the first function. Thus when the energy is calculated with both functions, it is lower than that calculated with but one function. However, when we calculate the energy of the molecule, both functions are always used.

Consider now what happens if we try to determine the difference in energy of the atoms and the molecule. The answer will depend on how the atomic energy is determined, i.e., whether one or two functions were used for each atom in this case. Which way is correct? The answer is not obvious. Why would we use a basis set for an atom that contains functions from another center? The reason is that we would be using the same basis set for both the atomic and the molecular system, and consequently we would be consistent.

However, there is a problem. Recall that if we expand an arbitrary function in terms of orthogonal functions, those functions do not duplicate each other's effects. Considering spherical harmonics as an example of an orthogonal set of functions, expansion by means of the standard methods of any angular function in terms of s, p, and d functions assures that all spherical effects are in the s component. When one adds a p or d function to the basis set, one does not modify the spherical component of the function. Regardless of how many basis functions of higher angular momentum one uses, the spherically symmetric component is not modified. Returning to the diatomic problem, the two functions, one on each center, are not orthogonal, and in fact they overlap and duplicate some of each other's effects. If the two centers are widely separated, this duplication is small, so the effect on the interaction energy is less relevant. At separations of chemical interest where we need to correct for basis set effects, the two functions do overlap significantly. But another problem is associated with our use of two functions for both the atomic and the diatomic calculation, which we address later under the issue of overcorrection.

It should be clear already that the error will vary with the complexity of the system. The BSSE is usually small for H_2 because the hydrogen atom can be approximated by a few terms (one, if Slater-type orbitals are used), but if several Gaussian functions are used, as is common there can be substantial errors. A better example for this tutorial is the calculation of the binding energy of a larger diatomic such as F_2 . Substantial error can result from using a simple basis set of 1s, 2s, and 2p atomic orbitals, each represented by but a few functions when used to approximate the complicated molecular orbitals of this diatomic. The error in the energy of interaction between two F atoms can be very large if the basis set is not large enough.

The BSSE is difficult to calculate accurately. We know there will be a BSSE for any finite basis set, but most of the time we do not know its magnitude. Later in this chapter we will discuss the counterpoise method invented by Boys and Bernardi,^{18,19} a common method to estimate the error using basis sets from both centers to calculate both the atom and the diatomic. The method often works well, but it does have an inherent error. The error is the following: what we desire is really the energy of, say, the diatomic and the energy of the separate atoms calculated with the same functions as used by the diatomic. In our hydrogen molecule example, the occupancy of each atomic function from its own center is not exactly one because the functions overlap. So we should use only part of the atomic function from the other center in our calculations of the atomic energy to get an absolutely equivalent basis for both atom and molecule. That proves to be almost impossible to do except in certain cases that are explored later.

Magnitude of Error

The magnitude of the BSSE effect is affected by the size of the basis sets used, whether localized or bond orbitals are used, the type of system treated, and the level of calculation (Hartree–Fock or post-Hartree–Fock).

If the size of the basis set is small, the BSSE might be small as well, because the basis functions are fairly well localized on their respective centers and hence cannot contribute much to the atomic energy of other centers. Remember that a less-than-complete basis set attempts to explain the regions of higher electron density near the nuclei first, thus small basis sets underestimate the overlap density. This means that the BSSE at the Hartree–Fock level might be large. However, with small basis sets, the BSSE at the higher levels of theory could be small because there are probably insufficient functions to provide the flexibility needed to model the correlation energy (assuming either a perturbation approach like Møller–Plesset or a configuration interaction calculation using virtual orbitals²⁰). However, the absolute values of the total energies from such simple calculations are horrendously bad. At the other extreme, there is no BSSE with a basis set approaching completeness. But usually we cannot reach such limits even at the Hartree–Fock level. Obviously then, for intermediate-sized calculations just where we desire good, relatively accurate interaction energy numbers, the BSSE will be most important and must be evaluated.

One way to help a basis set have smaller BSSE is to use localized orbitals or bond orbitals. These functions should have inherently less overlap with adjacent atomic sites. We will explore this in more detail later, but the issue is often complicated by problems in generating these localized functions and calculating molecular properties.

From the preceding considerations, it is clear that some problems are inherently more sensitive to BSSE than others. One of the primary factors

leading to such errors is diffusiveness of the outer orbitals in the system. Any anionic state, which usually requires diffuse, extended basis functions, is very sensitive to basis set effects, and generally the more weakly bound the anion, the more serious the BSSE effect. Extreme cases also occur with the weakly bound states of polar neutral molecules and in studies of excess electrons in fluids or clusters. For these and related systems, the errors occur in two ways. First, the small-exponent basis functions (diffuse functions) one is forced to have in the basis set can overlap strongly with adjacent molecules or atoms and thus contribute to the other system's energy. Second, the anion's own basis set usually is not large enough, so the outer electrons often need to borrow electron density from orbitals on the adjacent atom. It is absolutely essential to correct for the BSSE, or one will find unusually large binding energies for the anion and strange effects of other sorts, such as unusual geometries for the anion. There are many calculations in the literature that have not corrected for these effects and have overly stable anionic species and often extremely distorted molecular geometries, which originate because the system tries to supply extra electron density by bringing atoms closer in an attempt to contribute the missing electron density necessary for the anionic state.

The magnitude of the error in an *ab initio* calculation also depends on the level of the calculation. There are serious BSSEs when electron correlation is included. In general, the errors at the Hartree–Fock level are less severe than those at higher levels of electron correlation. This is primarily due to the mixing of higher (virtual) orbitals into the wavefunction by either the perturbation or configuration interaction (CI) approach. Those virtual orbitals are required to be orthogonal to the occupied orbitals if they arise from a calculation such as Hartree–Fock. Because they are orthogonal, the virtual orbitals are forced to be larger, and larger orbitals have larger overlaps, with a concomitant increase in BSSE effects. In fact, even with very large basis sets it is difficult to remove the BSSE when one is using methods such as high order perturbation theory, CI, or coupled clusters to include electron correlation. It is expected that the BSSE effects would be smaller in post-Hartree–Fock methods when one is using localized orbitals or wavefunctions explicitly based on the interelectronic coordinate, the so-called r_{12} methods. Unfortunately, these are often hard to implement, but there has been some progress using localized orbital methods and localized basis sets.

BSSE exists for basis sets of all types and even for approximate or alternative Hamiltonians such as semiempirical forms or density functional methods. It is also not negligible if Slater-type functions are used; but the magnitude is often less in these circumstances because the outer regions of the wavefunction are usually better represented than with Gaussians.²¹ Likewise for various approximate Hamiltonians, the errors can be large or small. So, for example, since using exchange correlation functions in density functional calculations does not require an expansion in terms of virtual orbitals to obtain some electron correlation, there is a relatively small BSSE for the correlation effect in those calculations.

ATTEMPTS AT AN EXACT THEORY

There have been several attempts to develop methods that will eliminate the BSSE a priori and not a posteriori, as do most of the methods discussed later. In all a priori cases, operators are set up which eliminate the extraneous contributions of the atomic centers to the total wavefunction, consistent with the overall antisymmetry. Those operators are often quite complex and make calculations more lengthy.

Mayer, in a series of papers, developed a theory called the chemical Hamiltonian approach (CHA), which was based on observables, such as charge densities. Beginning with two 1983 papers,^{4,5} he developed a non-Hermitian perturbation theory that was able to separate out the energy components that comprise the BSSE. He was able to show that there are both over- and undercorrection effects, and later we demonstrate that overcorrection typically is small in most cases. Using a complete analysis of a four-orbital, two-electron model, Mayer and Turi²² were able to separate out and display all the BSSE terms. Their paper contains the most extensive discussion of the origins of BSSE and the most elaborate presentation of the theory.

Calculations have been performed by Mayer, Surjan, and their coworkers on small systems such as He_2 ,²²⁻²⁴ $(\text{LiH})_2$,²³ $(\text{H}_2\text{O})_2$,²³ and $(\text{HF})_2$.²⁴ Mayer and Vibo'k also developed a separate self-consistent field (SCF) theory that excluded BSSE effects,²⁵ and Mayer et al. recently applied the CHA approach to density functional theory.²⁶

In 1991 Sadlej²⁷ proposed another perturbation theory that is Hermitian but requires some major constraints on the wavefunctions. This method must be slightly modified in real problems to make sure that the wavefunctions of the subsystem descriptions are not made poorer by the process.^{28,29}

Another method, by Cullen,³⁰ uses the monomer's own basis set, which is a very localized valence bond description. This method is complicated in its implementation and also does not include the important charge transfer effects in its treatment.

There have been several critical analyses of these methods. Gutowski and Chalasinski¹⁴ compared the last three approaches described above to the standard counterpoise corrections, discussed next. They found that the simple counterpoise corrections were simpler to calculate and were generally more accurate. The review by van Duijneveldt et al.¹² discusses these various approaches and provides some numerical tests as well. In general, these authors strongly support the use of the counterpoise procedure.

At the post-Hartree-Fock level, Wind and Heully³¹ have projected out the BSSE effect in CI theory. In calculations on the interaction of a hydrogen molecule and a helium atom, the authors found that the results were similar to those of the counterpoise method. Muguet and Robinson³² more recently proposed a localized approach allowing not only energy calculations, but various molecular properties to be calculated with none of the BSSE complications,

again by modifying the operators used. The latter involves an iterative matrix procedure.

COUNTERPOISE CORRECTION METHOD

The most popular procedure of accounting for the BSSE effect,^{11–15} and possibly the most accurate one, was proposed almost three decades ago by Boys and Bernardi¹⁸ and first applied by Jansen and Ros.³³ The procedure, known as the counterpoise procedure (CP), is basically an a posteriori correction to the interaction energy aimed at improving this energy when BSE effects are considered for the monomers. In the CP, the interaction energy of a dimer is obtained as the difference between the dimer and monomer energies except that all these energies are evaluated using the same basis sets, i.e., the dimer basis sets are used for the dimer as well as for each monomer. Thus, the energy of an isolated monomer is calculated by means of a basis set composed of the monomer's basis set plus its partner's basis set. The additional basis functions are also known as ghost orbitals, because only the basis sets will be added but no electrons or nuclear particles for the second monomer are included in the calculation of the first monomer's energy.

The CP has been applied to the study of a wide variety of systems, including weak interacting systems such as van der Waals complexes,^{34–40} hydrogen bond complexes,^{13,41–43} and tight interactions (covalent bonds) such as molecular systems like N₂.^{44,45} In fact, it is now common practice to use some form of CP correction to account for BSSE whenever interaction energies are considered.

The use of the CP correction has generated some controversy related to the use of a full set of ghost orbitals (occupied and virtual) to obtain the BSE energy of the monomers [referred as full counterpoise procedure (FCP)]. Controversy also surrounds a slight variation of the CP in which only the virtual orbitals of the second monomer are used to evaluate the energy of the first monomer, and vice versa. This modification is known as the virtual counterpoise procedure (VCP).^{46,47} Some arguments supporting this modification are as follows:

1. Use of the FCP approach produces an overcorrection, and thus interaction energies are too repulsive. This argument was used extensively to explain some of the early results. One should stress that the vast majority of cases in which interaction energies were considered to be too repulsive due to the application of the FCP were carried out using small basis sets. Later it was realized that the overcorrection was mainly due to the improper description of the whole supersystem.

2. The Pauli exclusion principle should prevent one monomer from fully employing the full basis sets of the other monomer in the dimer.⁴⁸ If the FCP is applied, there seems to be a violation of the Pauli exclusion principle because the already occupied orbitals will not be able to accommodate more electrons.
3. The already occupied orbitals on one monomer will not contribute much to the energy lowering of the second monomer.

We will discuss in some detail a few of the approaches used to prove or disprove the validity of the FCP. It is important to note that in many studies, BSSE has been incorrectly blamed for not reproducing a value of the interaction energy close to the experimental value. As stated by Van Lenthe et al.,¹¹ the FCP does, in fact, eliminate the BSSE for the basis sets being used. It does not, however, correct for the inadequacy of the basis sets. Furthermore, one should not expect to obtain a particular value for the interaction energy such as the experimental value or some Hartree–Fock limit value, just because the energies are being corrected for the BSSE. The CP correction is supposed to correct for BSE effects, but it will not correct for the use of finite basis sets.

In general, it is agreed that the FCP approach is a good correction to the energy, but an overcorrection may be introduced when small basis sets are used.^{35–36} Nevertheless, the size of the overcorrection is small, and it is easily fixed by increasing the size of the basis set. In fact, it has been shown that this overcorrection decreases rapidly with basis sets size, even faster than other errors also introduced by small basis sets. Selection of the basis sets that properly describe the properties of the system being studied are perhaps more important than the size of the overcorrection. This topic is discussed later in the section about basis sets recommendations.

It has been widely accepted that the BSSE at the self-consistent field (SCF) level can be eliminated or reduced drastically if large enough basis sets with additional diffuse and diffuse polarization functions are added.^{49,50} Examples are presented below (see Case Studies section). It has also been shown that the BSSE is larger at correlated levels, and thus several studies^{12,14,34–41} have been conducted, mainly at the second-order Møller–Plesset level, to try to prove or disprove that the FCP does or does not produce an overcorrection to the interaction energy.

Energy Decomposition

Let us briefly describe a popular approach used to decompose the interaction energy into its components according to the type of interactions between monomers. In the theory of intermolecular forces, it is of interest to identify the physical forces that hold the two monomers together.⁵¹ First, each monomer has associated with itself an electronic distribution, which produces an electric field around the monomer. Therefore, when the two monomers approach each other, their electric fields interact via a Coulombic force that may be attractive

or repulsive according to the orientation of the two fields. This Coulombic interaction is usually denoted “electrostatic energy” (E_{el}).

A second component of the interaction energy arises from the quantum mechanical requirement that the wavefunction of any system be antisymmetric with respect to interchange of any of the electrons. The interchange of one electron from monomer A to monomer B produces the so-called exchange energy (E_x). The combination of E_{el} and E_x is also known as the Heitler–London energy.

Another aspect of intermolecular interactions is that as one monomer approaches the other one, the electric field of one perturbs the electron density, producing an electron redistribution in the other. This is a stabilizing effect, and it is known as the induction energy (E_{ind}). This term may be divided into two other terms if one considers dividing the electrons and space according to whether they belong to monomer A or monomer B. On one hand, the electrons belonging to monomer A can redistribute from their original location to some unoccupied space still defined as “A space.” This is known as polarization (P). On the other hand, electrons on monomer A can redistribute to space defined for monomer B, thus producing a charge transfer (CT) from A to B.

Finally, one or more electrons from monomer A can be excited to an unoccupied orbital coupled with a similar excitation for one or more electrons on monomer B. These multiple excitations are accounted for in correlated calculations and contribute a stabilization typically referred to as dispersion energy (E_{disp}). No matter what system is being studied, one has to properly represent these four major components of the interaction energy^{7,52} as summarized in Eq. [2].

$$\Delta E_{int} = E_{el} + E_x + E_{ind} + E_{disp} \quad [2]$$

Evaluation of Polarization and Charge Transfer Terms

We shall begin by considering an early study aimed at showing that the FCP indeed produced an overcorrection to the interaction energy. Collins and Gallup⁵³ compared the overcorrection results from FCP and VCP. In this study the CP-corrected (FCP and VCP) SCF energies for a series of van der Waals complexes involving He and H₂ were calculated. The idea was to examine the so-called P+CT (polarization + charge transfer) component of the interaction energy. This component normally arises from the changes in the subsystems as they approach one another. P+CT was defined in terms of the SCF energy for the dimer, the CP correction, and a Heitler–London type of dimer energy.⁵⁴ Collins and Gallup analyzed their results from the perspective that the P+CT term should be less than zero because, for this term to have any physical meaning, its contribution to the interaction energy (induction energy in Eq. [2]) should be negative (stabilizing). A positive value was taken as an indication that

the CP correction produced an overcorrection. It was found that the application of FCP approach to their calculation always produced a positive value, whereas the application of VCP correction did not. These results were taken as evidence that the VCP will produce better results than the FCP.

Gutowski et al.³⁸ subsequently questioned Gallup's approach; using a similar type of approach, they redefined the P+CT term into the monomer energies, the first-order exchange-repulsion and electrostatic interaction energies.⁵⁴ Using this P+CT term, Gutowski's group was able to show that when a small set of basis functions is used the VCP approach will also produce positive values for this P+CT term. It was concluded that with appropriate basis sets, none of the components of the interaction energy is better represented by the use of VCP or FCP.

Increased Functional Space

As we mentioned earlier, the BSSE depends on a variety of issues, one of which involves the number of basis functions used, and the kind. Tao and Pan^{35,36} used a simplistic approach in which the basis sets were increased by adding several sets of polarization functions (d and f). They tried polarization functions with tight (large) exponents and also the addition of both diffuse polarization functions and very diffuse functions. The idea behind this approach was to improve the description of the short-range region near the nuclei by adding diffuse functions and to also improve the long-range regions by adding polarization functions. They calculated ΔE and $\Delta E^{(CP)}$ at various levels of correlation (MP2, MP4) for a neon dimer system.

Tao and Pan wanted to obtain an interaction energy close to a preset value obtained previously by correcting the interaction energy with the FCP correction. They attempted to define an expression for the overcorrection based on an artificial basis set limit. This limit was to be given by an assumed saturated set of basis functions. The overcorrection was obtained by adding to a previously chosen set of basis functions either an sp function (s and p functions that share contraction coefficients for computational efficiency) or a diffuse d function and finding the difference between the energies. They found that only when large enough basis sets are used is FCP a valid approach to accounting for BSSE effects at correlated levels. Tao and Pan claimed that when small basis sets are used, an overcorrection is introduced, and this overcorrection seems to vanish as the size of the basis sets is increased. In fact, the overcorrection vanishes faster than other errors introduced by the inadequacy of the basis sets. They concluded that the addition of both diffuse polarization functions and additional diffuse functions is more important than the lone addition of tight polarization functions.

Localized Orbital Approach

Interaction energies are routinely obtained by means of a delocalized molecular orbital approach. That is, all the occupied and virtual orbitals that

form the two subsystems are mixed, to form a function that is not localized at one atomic center. However, to properly analyze and avoid any possible overestimation of BSSE in the CP method, it is desirable to maintain the local character of the monomers. In the localized orbital approach, the orbitals on each subsystem are primarily composed of the atomic orbitals of that center to facilitate the identification of virtual and occupied orbitals within each subsystem. Therefore, contributions of the occupied orbitals may be readily eliminated in the CP by using only virtual orbitals. It is also expected that BSSE errors might be smaller with these more localized orbitals.

Yang and Kestner^{34,41} used a variation of the localized orbital method to obtain the components of the interaction energy for a series of dimers. They wanted to be able to evaluate the BSSE explicitly. In their approach the localized pair correlation^{55,57} was used to decompose the second-order correlation energy into its components. There are several advantages of using localized orbitals to evaluate CP corrections. For instance, the localized orbital method uses only the best orbitals available for the dimer. The method can handle large orbital overlaps between monomers, and the localized orbitals of the dimer depend on internuclear separation. As shown by Yang and Kestner, the second-order correlation energy can be expressed in combinations of “inter” and “intra” contributions for occupied orbitals on the monomers and/or the dimer. In this way, the overcompensation—as named by the authors—due to a particular monomer was given by an expression defining the energy of this monomer using both its occupied and virtual orbitals in addition of the whole set of ghost orbitals (from the second monomer) subtracted from the energy for the same monomer obtained by means of its whole set of basis functions and only the virtual orbitals of the ghost atom, represented as follows:

$$\text{overcompensation} = [E_2^A\{AB_v\} - E_2^A\{AB\}] + [E_2^B\{A_vB\} - E_2^B\{AB\}] \quad [3]$$

where E_2^A is the second-order contribution from monomer A to the energy, $\{AB\}$ represents the full set of functions for monomer A or monomer B, and A_v and B_v represent only virtual orbitals for monomer A or B, respectively. The authors found that the FCP correction does overcorrect the interaction energy at the MP2 level, although it was claimed that this overcorrection is not large enough to affect most intermolecular potentials. This is an interesting result because, as far as we are aware, no one has refuted the applicability of the method to evaluate the BSSE effect.

Pulay^{58,59} developed a method aimed initially at reducing the computational cost of obtaining the complete correlation energy by means of modest basis sets based on localized orbitals. It was mentioned that, when correlation is included, BSSE effects remain significant even with the use of large, augmented basis sets. Pulay applied his local correlation method to investigate the size and effects of BSSE at correlated levels for the water dimer.⁶⁰ Pulay calculated intrapair correlation energies using localized orbitals. Weakly interacting electron pairs (at long distances) can be either neglected or treated at lower levels of

theory. On the other hand, strongly interacting pairs are given more weight in the calculations. Another feature in Pulay's method was the possibility of truncating the virtual space by means of a "local basis," which is basically a subspace of the virtual space, usually close in energy to the orbitals to be correlated. In his study of the water dimer,⁶⁰ Pulay was able to obtain accurate results that may be free of BSSE effects.

Many-Body Perturbation Theory Versus Symmetry-Adapted Perturbation Theory

In the two recent reviews on the applicability of the counterpoise correction,^{12,14} van Lenthe^{11,12,15} and Gutowski¹⁴ and their colleagues were strong defenders of the applicability and correctness of the full CP. These two groups showed that the methods that were used to demonstrate that the FCP method produced an overcorrection to the total interaction energy contained deficiencies in their implementation that give rise to serious errors. Both reviews covered in much detail several cases in which the FCP was shown to correctly account for BSSE. Symmetry-adapted perturbation theory (SAPT)⁶¹⁻⁶³ studies were performed to compare the contribution of the correlated (MP2) energies with similar results obtained using SAPT. From the argument that at the SCF level most of the BSSE effects can be taken care of by using large basis sets with added diffuse functions, one should then concentrate on the correlated energies, namely, the MP2 energies. Under SAPT, the MP2 energy can be expressed in terms of the uncoupled Hartree-Fock dispersion energy, the second-order correlation correction to the electrostatic interaction energy, and a term that covers both the exchange and correlation contributions to the interaction energy. The SAPT method worked well with nonpolar system such as the helium dimer.

In an attempt to settle the controversy about whether VCP or FCP is better, Gutowski and Chalasinski¹⁴ proposed the following scheme. From perturbation theory it has been proved that the dispersion term is the most sensitive to the basis set. Therefore, increasing the size of the basis sets should show a relationship between the correlated energy at the MP2 level and the dispersion term, provided the BSSE is properly accounted for in the MP2 value for the energy. The authors do indeed find a nice correlation between these two energies when the FCP was used. On the other hand, the MP2 energies obtained when the VCP correction was used did not produce any correlation at all. It was concluded that the FCP provided the proper correction to the interaction energy.

The results from the foregoing studies^{12,14} are in contradiction with the results of Yang and Kestner.^{34,41} However, the methodology used by the latter group has not been proven faulty; rather, the results differ because the later workers used smaller basis sets, partly on purpose, because they wanted to find some overcorrections. Moreover, the two studies were carried out with different sets of basis functions, so that a one-to-one comparison is unjustified. Gutowski and Chalasinski¹⁴ stress the fact that their results were obtained with large basis

sets, which have been called “extended interaction-energy-oriented basis sets.” One would question the applicability of basis set of the same kind for other large systems involving 20–30 electrons.

SECONDARY CORRECTIONS

Another aspect of BSSE is the distortion of the electron density on one of the monomers as the second monomer approaches. For a totally symmetric monomer such as a rare gas atom, an induced dipole will be created, thus adding an effect due to the induction energy⁶⁴ which is a component of the interaction energy. For polar molecules, their dipole moments could be highly distorted by the approaching monomer. Distortion of multipole moments is more important in the interaction of an ion with polar or nonpolar molecules as studied by Latajka and Scheiner.^{65,66} This effect has been called the secondary basis set superposition error⁶⁴ and is known to affect several one-electron properties such as dipole moments, higher moments, and polarizabilities. Secondary BSSE effects are more pronounced when small basis sets are used. However, it has been noted⁶⁷ that the use of well-tempered basis sets¹⁵ significantly reduces the change in the dipole moment and thus the secondary BSSE. In the case of ion–molecule interactions, Latajka and Scheiner^{65,66} found that secondary effects are as important as primary BSSE effects.

A likely source of secondary BSSE and even higher order BSSE effects is the current practice of adding bond functions (see next section). These bond functions should be used with care because they can alter the electronic distribution on a monomer. Beyond the cases of ion–molecule interactions and bond functions, secondary BSSE effects are ignored in practice because the basis sets employed for the study of interaction energies are both large enough and high enough in quality to ensure that little distortion of dipole moments on monomers is observed after the addition of the ghost orbitals. The effects of using small basis sets on the dipole moment is discussed in more detail later (see “Case Studies”).

BOND FUNCTIONS

The use of bond functions was an approach originally aimed at reducing the effects of BSSE,^{68–70} in addition to providing a mechanism to use what is known about a bond in small systems for creating a wavefunction of a larger system containing the same bonds. The traditional approach in applied quantum chemistry is to use basis functions centered on atoms and to add diffuse, high angular momentum polarization functions to account for effects taking

place far from the nuclei. The idea behind bond functions is to place ghost orbitals away from the nuclei in regions where possible electron interactions are poorly described by the atom-centered basis sets. Normally the location of a bond function is varied to improve performance.⁷ The addition of bond functions and their location was extensively studied by Tao,^{37,71,72} in particular for van der Waals complexes. He observed that bond functions are very helpful when correlation effects are included in the calculations. This can be simplistically described as follows. The interaction correlation energy of a system can be divided into intramonomer and intermonomer contributions, with the intermonomer correlation energy being the dominant term (induction energy). Consider an excited configuration of the dimer in which one electron from each monomer is excited. These two electrons may interact with each other in such a way that bonding and antibonding orbitals are formed, thus lowering the energy and contributing to the intermonomer energy. These newly formed orbitals are properly and easily represented by the addition of polarized, diffuse functions in the middle of the bond (or somewhere along the bond).

There are two important reasons for using bond functions. First, when two monomers approach each other, it is possible that at a location between the monomers electrons from each subsystem will interact thus forming diffuse bonding and antibonding orbitals. A limited basis set of atom-centered functions will not properly account for these “bonding” interactions. Second, the presence of bond functions at some point, such as at the centroid of the subsystems, will facilitate the formation of such “bonding” interactions; thus an energy lowering may occur which contributes to the intersystem correlation energy. These “bonding” interactions are expected to be highly diffuse and are thus properly represented by highly diffuse polarization functions.

A possible source of error is the selection of both the atom-centered basis sets and the bond function. Normally, one should optimize the bond functions subject to the constraint that the SCF energy is not significantly changed. This means that one should use saturated basis sets so that the distortion of the electron distribution is minimal. Usually the proper representation and rapid convergence of dispersion energies necessitates the use of high angular momentum polarization functions (f- and g-type functions). Tao⁷² found that the need for g-type and even f-type polarization functions could be eliminated if bond functions (diffuse spd functions) were used. Currently, bond functions are being used extensively in studies of molecular interactions to accelerate the convergence of dispersion energies.⁷³

BASIS SET RECOMMENDATIONS

As discussed in the Introduction, the selection of the best (yet practical) set of basis functions for describing a particular system (e.g., a chemical reaction) at all stages, with reactants, intermediates, transition states, and products, is not a

trivial task. In fact, it has been suggested that the selection of the basis sets that best describe a particular system is more an art than an exactly prescribed technique. It has been almost universally accepted that one must employ extended basis sets to obtain reasonable results when total energies, interaction energies, and molecular properties are being computed. Earlier studies^{49,50} found that the use of large basis sets as well as the use of additional diffuse functions would minimize the BSSE. By increasing the functional space of one monomer, the BSE effect of the second monomer can be better accommodated by the additional diffuse functions on the first monomer. Such reasoning may not work well for simple calculations at the post-Hartree–Fock level, however, because it has been found that when correlation is included, the BSSE cannot be reduced as effectively as with simple SCF calculations.^{74–76} We find, however, that with density functional theory (DFT) calculations the use of large basis sets, diffuse sp, and several sets of d- and f-type polarization functions also reduces and virtually eliminates BSSE.

Important guidelines for selecting basis sets for ab initio calculations are given by Feller and Davidson in the first volume of this review series.¹⁶ To select the appropriate basis sets that best describe a given system, one should always consider, as a starting point, the electronic properties or physical phenomena one wishes to study. Some of these computations may focus on geometrical studies, relative energies of isomers, or electronic properties such as the ionization potential, dipole or higher moments, polarizabilities, and interaction energies. If one is considering the dipole–dipole type of interactions, a good description of the electrostatic energy is required, whereas if interactions between nonpolar molecules are considered, dispersion effects are important, just to cite a couple of examples. The most important case is perhaps encountered when accurate interaction energies are wanted and thus BSSE corrections must be made. As stated by Chalasinski and Szczesniak in their review,⁷ to select the most adequate basis sets one should account for multiple moments, polarizabilities, and the electron density at long distances, among other things. In their review⁷ (see also Ref. 77), the contributions to the interaction energy in Eq. [2], as well as the effect of using basis sets of different sizes, are described in much detail. The chapter by Feller and Davidson¹⁶ is recommended reading for the novice computational chemist.

CASE STUDIES

Having defined the BSSE, its origins, and approximate magnitudes, and having discussed how to determine it and reduce it, we move on to several case studies in which BSSE has been the focus of study or deemed to be important in determining the results. We have selected two well-studied systems, the water dimer (H₂O)₂ and the hydrogen fluoride dimer (HF)₂, to illustrate the phenomena discussed above and to illustrate how the size of the basis sets, and the number and quality of polarization functions, affect properties such as dipole mo-

ment and interactions energies, as well as how BSSE affects some of these properties. In Tables 1–4 we present the variation of these properties at various levels of theory (SCF, MP2, and DFT) with respect to the basis sets used, their augmentation by means of additional diffuse functions, and the influence of several sets of polarization functions. We have chosen these two systems for several reasons:

1. The hydrogen fluoride dimer and the water dimer are small in size and thus large basis sets approaching saturation have been used to study their properties.
2. Several sophisticated correlation methods have been used to study interaction geometries and dipole moments, and there now exist many articles on these two systems describing most of their properties at different levels of accuracy.^{78–82}
3. Accurate experimental data are available^{83–88} for detailed comparisons with the calculated values.

The 6-311G family of basis functions,⁸⁹ which in many cases is known as “standard” by virtue of its availability on popular quantum chemistry packages such as Gaussian⁹⁰ and GAMESS,⁹¹ were selected for this study. This particular set of basis functions can be systematically enlarged by the addition of very diffuse functions and polarization functions on all atoms. The use of high angular momentum polarization functions has been advocated in the past^{7,71,72} as being necessary to reproduce accurately experimental results. Therefore, we want to study BSSE effects by adding the following sets of polarization functions: d on heavy atoms and p on hydrogen atoms (*nd, np* sets, *n* = 1–3), and the further addition of f functions (3df, 3pd). A second group of basis sets used in these sample calculations comprises the so-called correlation-consistent functions proposed by Dunning.^{92–95} These two general groups of basis sets are good representations for the medium to large basis sets typically employed by modern computational chemists.

Geometries

Geometry optimizations are now standard in computational quantum chemistry. Intramolecular geometrical features can be accurately obtained even at simple levels of theory. The addition of correlation effects does improve the results, in particular for bending interactions. On the other hand, accurate intermolecular geometrical parameters are somewhat more difficult to obtain. Correlation effects are needed, as a rule, but little improvement in agreement with respect to experimental results is obtained.

In Table 1 we present a summary of the variation of intermolecular distances, F–F in (HF)₂ and O–O in (H₂O)₂, with respect to the size of the basis sets. Van Duijneveldt et al.⁷⁹ averaged their results to determine a calculated internuclear O–O distance: 2.970 ± 0.006 Å for the water dimer and compared it to what the authors claim should be the correct experimental distance of 2.976 ± 0.004 Å. The distance has been measured experimentally with high

Table 1 Variation of Dimer Separation (Å) with Respect to the Size of the Basis Sets^a

Basis Set	$R_{F-F} (HF)_2$			$R_{O-O} (H_2O)_2$		
	HF	MP2	BLYP	HF	MP2	BLYP
6-311G	2.712	2.707	2.594	2.814	2.797	
6-311+G	2.738	2.769	2.726	2.833	2.816	
6-311++G	2.739	2.779	2.726	2.835	2.819	2.796
6-311++G(dp)	2.826	2.787	2.774	3.001	2.914	2.927
6-311++G(2d2p)	2.833	2.762	2.770	3.035	2.917	2.947
6-311++G(3d3p)	2.810	2.756	2.753	3.023	2.917	2.942
6-311++G(3df,3pd)	2.814	2.739	2.759	3.026	2.904	2.944
cc-PVTZ	2.809	2.717	2.714	3.029	2.907	2.935
aug-cc-PVTZ	2.826	2.753	2.756	3.039	2.907	2.948
Experiment	2.72–2.79 ^b			2.976 ± 0.004 ^c		

^aTheories compared are Hartree–Fock (HF), second-order Møller–Plesset (MP2), and the density functional theory of Becke and Lee, Yang, and Parr (BLYP).

^bFrom Refs. 83 and 84.

^cFrom Ref. 85.

accuracy.^{83–88} Dyke et al. reported an average distance of 2.78 Å for the F–F internuclear separation, but it is implied that this distance may vary between 2.72 and 2.79 Å.^{83,84}

Our results produced similar trends for both dimers. At the SCF level, small basis sets (6-311G) tend to underestimate the equilibrium intermolecular distance, but that distance rapidly increases with the addition of polarization functions to the basis sets, leading to an overestimation of the distance. This is, of course, expected because in both dimers dipole–dipole interactions are present, and thus correlation effects should be taken into consideration. As presented in Table 1 for the MP2 and DFT levels of theory, the intermolecular distances improve and grow closer to the experimental values without becoming overestimated. For the $(HF)_2$ system, the intermonomer distances obtained with most basis sets are within the experimental errors of the experimental distances, but the experimental error margin is too wide to make a precise comparison. The computed distances are only approximate values, and higher effects such as anharmonic effects were not considered. DFT methods are known to produce geometrical results that agree closely with MP2 results.^{96,97} We find that the DFT intermolecular geometrical parameters for the water dimer were slightly superior to those from the MP2 calculations by virtue of being closer to the experimental values. DFT methods include full correlation effects, thus accounting (possibly) for the improved results. In short, larger basis sets with several sets of polarization functions are needed at correlated levels to obtain intermolecular distances close to experimental results.

Dipole Moments

An accurate representation of multipole moments (in particular dipole moments) is important in systems for which long-range interactions are the

dominant forces. Many intermolecular potentials for the water molecule used in molecular dynamic simulations are based on ab initio studies of the water monomer or dimer. These intermolecular potentials need to describe all short-range interactions that are dominated by the dipole moment. Multipole moments affect mainly the induction term, which contributes to the interaction energy; thus proper representation is important to obtain accurate results. Similarly, as stated earlier, changes in the dipole moment of a monomer by the approaching second monomer's orbitals are responsible for secondary BSSE effects.

The dipole moments for the H₂O and HF dimers have been measured experimentally. Dyke et al.⁸⁸ reported an experimental dipole moment of 2.60 debye for the water dimer, and an experimental value of 2.987 ± 0.003 D has been reported for (HF)₂.⁸³ These experimental values can be compared to the computed values in Table 2. Excellent agreement is obtained for calculations in which the largest sets were used.

Next consider the changes to the dipole moments of the monomers after the addition of ghost orbitals at the optimum dimer distances. In Table 3 we present a representative sample of the results on the deformation of the dipole moment by the addition of ghost orbitals to each monomer. Small basis sets such as 6-311++G do not reproduce the experimental value⁹⁸ for the dipole moment, nor do they allow for the distortion of the dipole moment on each monomer. On the other hand, large basis sets with several sets of d- and f-type polarization functions (aug-cc-PVTZ) not only reproduce more closely the experimental parameters, but also appear to be saturated and capable of accommodating all effects that produce distortion of the electron density. Similar effects are observed at all levels of theory.

Table 2 Variation of the Dipole Moment (μ , debye) in (HF)₂ and (H₂O)₂ Dimers with Respect to the Size of the Basis Sets^a

Basis Set	(HF) ₂			(H ₂ O) ₂		
	HF	MP2	BLYP	HF	MP2	BLYP
6-311G	4.40	3.74	2.33	4.37	4.24	
6-311+G	4.76	4.59	4.24	4.40	4.39	
6-311++G	4.76	4.59	4.23	4.41	4.40	4.05
6-311++G(dp)	3.79	3.66	3.53	3.45	3.30	3.09
6-311++G(2d2p)	3.54	3.38	3.32	2.84	2.70	2.55
6-311++G(3d3p)	3.54	3.44	3.32	2.71	2.57	2.44
6-311++G(3df,3pd)	3.62	3.47	3.37	2.88	2.68	2.54
cc-PVTZ	3.47	3.17	2.95	2.92	2.55	2.30
aug-cc-PVTZ	3.51	3.33	3.30	2.95	2.62	2.53
Calculated ^b					2.60	
Experiment		2.987 ± 0.003^c			2.60^c	

^aFor theories compared, see note a, Table 1.

^bFrom Ref. 79.

^cFrom Ref. 83.

^dFrom Ref. 88.

Table 3 Dipole Moment (debye) of a Water Molecule in a Dimer: Effect of Adding Ghost Orbitals

	aug-cc-PVTZ			6-311G		
	A ^a	B ^b	C ^c	A ^a	B ^b	C ^c
SCF	1.939	1.940	1.933	2.550	2.519	2.385
MP2	1.860	1.856	1.853	2.555	2.498	2.333
BLYP	1.802	1.799	1.795	2.491	2.421	2.259
Experiment	1.84 ^d					

^aIsolated water molecule with no ghost orbitals

^bAcceptor water monomer in water dimer with ghost orbitals.

^cDonor water monomer in water dimer with ghost orbitals.

^dFrom Ref. 101.

Interaction Energies

All computed electronic properties are dependent upon the size and quality of the basis sets and to the extent of inclusion of correlation effects. For example, in Table 4 we present the variation of the interaction energy (Eq. [1]) for the water and hydrogen fluoride dimers with respect to the size of the basis sets at three levels of theory: SCF (HF), MP2, and DFT (BLYP). The small basis sets (in our case, 6-311G) highly overestimate these energies. The addition of extradiffuse functions barely improves the results. The addition of (the more important) polarization functions produces several effects depending on the method used. At the SCF level, the interaction energies are underestimated, and the addition of several sets of polarization functions further underestimates these results. Also, at the SCF level, we find the intersystem distances (O–O and

Table 4 Variation of Interaction Energies (D_e , kcal/mol) with Respect to the Size of the Basis Sets with Hartree–Fock (HF), Møller–Plesset Second Order, and Density Functional Theory Methods

Basis Set	(HF) ₂			(H ₂ O) ₂		
	HF	MP2	BLYP	HF	MP2	BLYP
6-311G	6.91	7.33		8.17	9.12	
6-311+G	6.48	6.49		8.04	9.05	
6-311++G	6.52	6.54	6.60	8.03	9.12	8.81
6-311++G(dp)	4.33	4.74	4.73	4.80	6.08	5.44
6-311++G(2d2p)	4.06	4.87	4.48	4.07	5.36	4.60
6-311++G(3d3p)	4.12	4.98	4.57	4.05	5.39	4.56
6-311++G(3df,3pd)	4.11	4.95	4.49	4.00	5.31	4.46
cc-PVTZ	4.32	5.50	6.08	4.45	6.08	6.11
aug-cc-PVTZ	3.73	4.71	4.16	3.74	5.18	4.18
Experiment	4.81 ± 0.2 ^a			5.4 ± 0.2 ^b		

^aFrom Ref. 82 and 86.

^bFrom Ref. 87.

F–F) to be overestimated as discussed earlier. The overestimation in separation is caused by several terms that contribute to the interaction energy and are either underestimated or absent. For example, some of the terms in Eq. [2] (e.g., the dispersion term) are known to be underestimated or not accounted for at the SCF level.

The inclusion of correlation effects improves the contributions of these terms to the total interaction energy, as seen in Table 4 for the MP2 and DFT results. One should be careful in attaching too much meaning to the interaction energies calculated using Eq. [1]; those results should be corrected for the use of incomplete basis sets first. The interaction energy obtained at the DFT level is not improved by the addition of f-type polarization functions; the 6-311++G(3df,3pd) and aug-cc-PVTZ DFT values are underestimated, in contrast to the effects of adding f functions at the MP2 level.

A final point to be made in this section is that BSSE also affects the calculation of potential energy surfaces, which in turn are used extensively in calculations of interaction energies. These effects may produce drastic shifting of equilibrium distances between monomers, the depth of energy wells, and dissociation energies. As an example, we present in Figure 1 the potential energy surface for the interaction of two fluorine atoms to produce a fluorine molecule (F_2). The BSSE effect is shown for the STO-3G basis set, a very small basis set. The equilibrium distance is shifted from 1.68 Å at the uncorrected level to 1.806 Å when BSSE corrected. The change in the depth of the energy well is also affected by the addition of a counterpoise correction. This example illustrates a case of a strong interaction (covalent bond). One should expect these effects to be proportionately more pronounced in weakly interacting systems such as van der Waals complexes. Newton and Kestner⁷⁴ reported differences in the equilibrium distance of the water dimer of 2.99 and 2.90 Å (no-CP) at the MP2 level.

BSSE Corrected Interaction Energies

As emphasized several times, interaction energies need to be corrected for the effect of using incomplete basis sets. When the full CP correction is used, the corrected interaction energy is defined as follows:

$$\Delta E_{\text{int}}^{\text{CP}} = E(\text{dimer}\{AB\}) - E(\text{mon}_A\{AB\}) - E(\text{mon}_B\{AB\}) \quad [4]$$

where all energies, including the monomer energies, were obtained using basis sets {AB} for the dimer. The reader is reminded that correcting for BSSE effects does not necessarily mean that interaction energies are closer to the experimental values. Rather, one is correcting for the incomplete basis set that was used. In Table 5 we present examples of corrected interaction energies. The general trend is that all interaction energies are reduced by BSSE effects. The magnitude

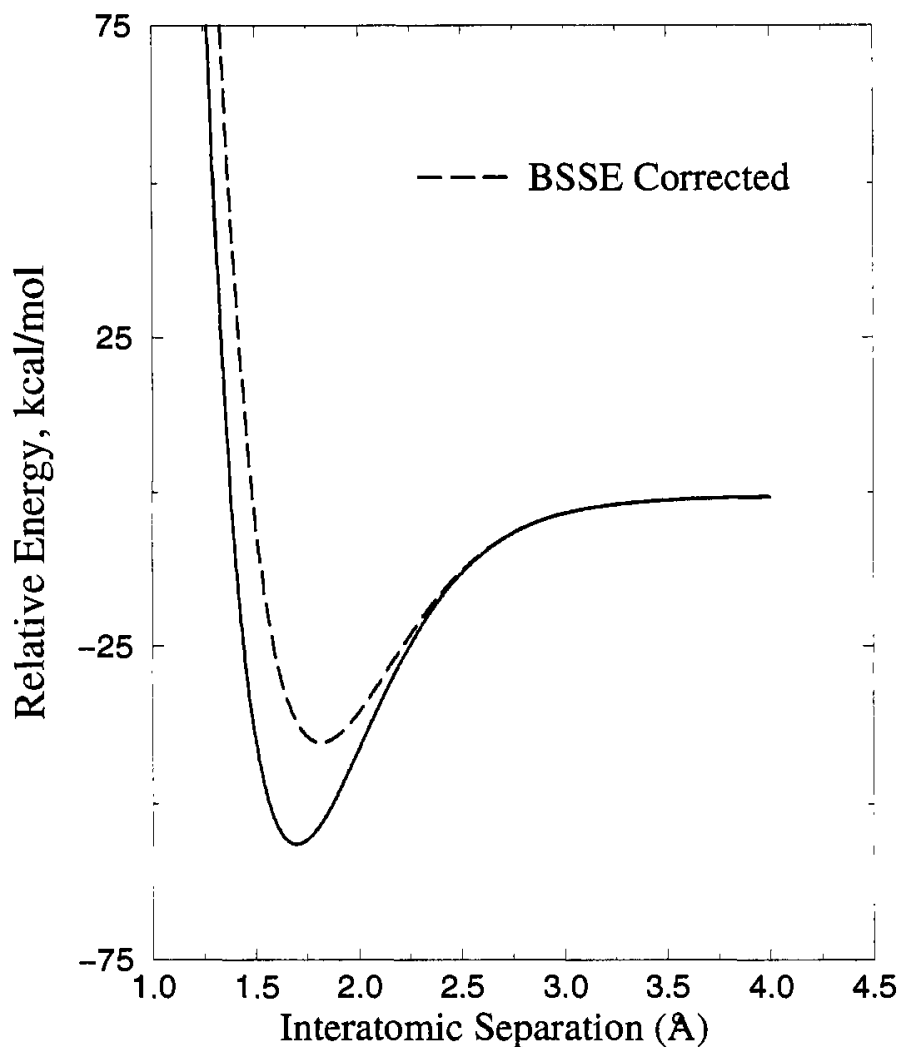


Figure 1 Typical potential energy surface (interatomic potential) for a poor basis set. The curves compare the uncorrected and the corrected (by counterpoise method) energies of the F_2 molecule as obtained with a STO-3G basis set. With better basis sets, the effect is much less, but the correction generally improves the results.

Table 5 Variation of the BSSE Corrected Interaction Energies ($\Delta E_{\text{int}}^{\text{CP}}$, kcal/mol) with Respect to the Size of the Basis Sets

Basis Sets	$(HF)_2$			$(H_2O)_2$		
	HF	MP2	BLYP	HF	MP2	BLYP
6-311G	5.80	5.09		6.62	6.15	
6-311+G	5.64	5.08		6.42	6.19	
6-311++G	5.64	5.08	5.60	6.40	6.17	6.80
6-311++G(dp)	3.96	3.80	4.26	4.27	4.48	4.65
6-311++G(2d2p)	3.67	3.90	4.11	3.77	4.48	3.75
6-311++G(3d3p)	3.70	4.08	4.21	3.74	4.57	4.25
6-311++G(3df,3pd)	3.68	4.09	4.15	3.72	4.61	4.18
cc-PVTZ	3.76	4.12	4.35	3.73	4.40	4.10
aug-cc-PVTZ	3.64	4.26	4.15	3.69	4.74	4.18
Experiment		4.81 ± 0.2^a			5.4 ± 0.2^b	

^aFrom Ref. 82 and 86.

^bFrom Ref. 87.

Table 6 BSSE Values (kcal/mol) Calculated Using Eq. [5], Counterpoise Method

Basis Sets	(HF) ₂			(H ₂ O) ₂		
	HF	MP2	BLYP	HF	MP2	BLYP
6-311G	1.11	2.24		1.56	2.97	
6-311+G	0.84	1.41		1.62	2.86	
6-311++G	0.88	1.46	1.0	1.63	2.93	2.01
6-311++G(dp)	0.37	0.94	0.47	0.53	1.60	0.79
6-311++G(2d2p)	0.39	0.97	0.37	0.30	0.88	0.85
6-311++G(3d3p)	0.42	0.90	0.36	0.31	0.82	0.31
6-311++G(3df,3pd)	0.43	0.86	0.34	0.28	0.70	0.68
cc-PVTZ	0.56	1.38	1.73	0.72	1.68	2.01
aug-cc-PVTZ	0.09	0.45	0.01	0.05	0.44	0.00

of this reduction can be seen in Table 6 and depends on the method employed. Equation [5], which is a combination of Eqs. [1] and [4], was used to obtain the value of the “BSSE energy” presented in the table.

$$\text{BSSE} = E(\text{mon}_A\{A\}) + E(\text{mon}_B\{B\}) - E(\text{mon}_A\{AB\}) - E(\text{mon}_B\{AB\}) \quad [5]$$

From the data in Table 6, we can make several observations. Clearly at the SCF (HF) and DFT (BLYP) levels, the BSSE can be reduced by the use of large basis sets with several sets of diffuse basis functions. For the largest basis sets used, BSSE is practically eliminated. At the MP2 level, the BSSE is not reduced as easily as in the SCF cases, but in all cases it is still a significant contribution to the total interaction energy. At the DFT level, the magnitude of the BSSE is small, even smaller than at the SCF level. The results for the largest basis sets employed (aug-cc-PVTZ) seem to be free of BSSE effects, although the interaction energies are not as good as the MP2 values.

To help provide the reader with a feeling for what is required to carry out such calculations, we provide in the Appendix sample files for the programs (Gaussian 94 and GAMESS) to calculate BSSE of simple dimers. The Gaussian sample file contains first an input deck to perform the full optimization of the dimer. Then the geometry is read from the checkpoint file and a subsequent calculation is to be carried out on the optimized geometry using the keyword “massage” to eliminate the nuclei and the electrons on one of the monomers. An additional calculation is then run to obtain the BSE energy for the second monomer using the optimized geometry, again, by changing the atomic centers that have zero nuclear charges.

The input file for GAMESS is not as simple. One has to prepare and carry out three calculations. First, one performs the full optimization using the chosen basis sets. Then one must prepare an input file with the optimized geometry and use a nuclear charge of zero to eliminate nuclei and electrons on one of the monomers. Similarly, another input file must be prepared for the second mono-

mer. There is no equivalent to the “massage” keyword in the Gaussian programs. Of course, the GAMESS procedure is general, and any program, including the Gaussian programs, can be run similarly using explicitly defined basis sets followed by repeating the calculation again while defining the ghost atoms. In Gaussian the ghost atoms could be defined as Bq rather than by means of their atomic symbol (H, O, N, etc.), but the method using “massage” is simpler. Clearly, though, the idea of describing and using ghost orbitals for CP is straightforward, and most scientists should take it into account in their calculations.

MANY-BODY COUNTERPOISE CORRECTION

So far we have described the CP correction for dimers that were well defined. When we have many monomers present, how best to do the CP is not so obvious because the BSSE is not additive, and thus ambiguities can result. Earlier workers such as Turi and Dannenberg⁹⁹ addressed this problem, but their solution:

$$\text{CP} = \sum_i (E_i - E_i^*) \quad [6]$$

and the CP corrected energy:

$$\Delta E_{ABC} = E_{ABC(\{AB\})} - E_A(\{ABC\}) - E_B(\{ABC\}) - E_C(\{ABC\}) \quad [7]$$

are adequate. In Eq. [6] the sum is over all monomers, and the asterisk means that the monomer is calculated with the full basis set, including all functions of the n -mer. In Eq. [7] the notation is as follows: the symbols in parentheses are the basis sets used; so $\{ABC\}$ means that the calculation is performed using the same bases on all three centers in each calculation. This was tested on hydrogen fluoride clusters with good success.⁹⁹ However, Valiron and Mayer¹⁰⁰ encountered some difficulties in treating the helium trimer. They proposed a new scheme, which behaves like a perturbation scheme, based on ideas similar to those of White and Davidson.¹⁰¹ Valiron and Mayer suggested that the CP-corrected form for a trimer should be:

$$\begin{aligned} \Delta E_{ABC} = & E_{ABC(\{ABC\})} - E_{AB(\{ABC\})} + E_{AB(\{AB\})} - E_{AC(\{ABC\})} + E_{AC(\{AC\})} \\ & - E_{BC(\{ABC\})} + E_{BC(\{BC\})} - E_A(\{AB\}) - E_A(\{AC\}) + E_A(\{ABC\}) \quad [8] \\ & - E_B(\{AB\}) - E_B(\{BC\}) + E_B(\{ABC\}) - E_C(\{AC\}) - E_C(\{BC\}) + E_C(\{ABC\}) \end{aligned}$$

The expressions for a general n -mer are also in their paper.¹⁰⁰ Results for the helium trimer and preliminary results for the tetramer appear to be well be-

haved, but this does not completely resolve the problems of many-body correlations. Fortunately the CP corrections reach a limit for fairly small clusters because orbitals are reasonably localized, thus large n -mers should not have BSSE much larger than small clusters.

SUMMARY

The basis set superposition error is a major impediment to obtaining accurate interaction energies and other properties of molecules when "small" basis sets are used. The larger the system being studied, the more one is forced to use smaller basis sets and the larger the BSSE. The errors are largest at levels of electronic structure theory that include electron correlation. It is often possible with small molecules to use basis sets large enough to remove the BSSE at the SCF level, but usually not at the correlated level. The simple counterpoise (CP) correction method works amazingly well, although in theory it could overcorrect. Overcorrection does not appear to be a serious problem.

We have presented the situation as it exists now based on many studies, but what can we expect in the future? It seems clear that for routine work, even at the correlated level, one must correct for BSSE, and the simplest and quite accurate way to do that is via the full counterpoise (FCP) correction. When one needs very accurate calculations including electron correlation, or to study large systems with many atoms (where bond functions and other techniques might work), FCP may not be sufficient. Better methods may be necessary. Right now those newer methods have their bottlenecks in the form of more complex computer programs for very little gain. Also disturbing is the need to calculate the interaction energy between large systems by taking the difference between very large numbers, but that need exists because methods like symmetry-adapted perturbation theory and the chemical Hamiltonian approach are difficult to implement in the general case or at least are not readily available. The hope is that new, easier-to-use methods will be found and incorporated into standard quantum chemistry packages.

When we begin to calculate the interaction of systems in excited states, the problems will get much, much worse because present approaches are not up to the task. In addition, when geometries are sensitive to the BSSE, we need much better methods than are currently available, since geometry optimization must be done concurrently with the energy minimization (requiring better coupling of statistical mechanics and quantum mechanics, a problem many researchers are now exploring).

We end by encouraging more research into cases where the BSSE is large. For small systems the FCP usually works well, but not always.

APPENDIX. SAMPLE INPUT DECKS FOR COUNTERPOISE CORRECTIONS

Sample Input Deck for Counterpoise Corrections Using Gaussian 92 or 94

The first part below calculates the optimum geometry of the water dimer and saves necessary information in a checkpoint file (bsse.chk). The second part, beginning with "Link 1" repeats the calculation, but the keyword "message" sets the nuclear charge on all atoms in one water molecule equal to zero (atoms 1,3,4). This step should be followed by another calculation that sets the nuclear charge on centers 2, 5, and 6 equal to zero, to obtain the second monomer-corrected term.

```
%Chk=bsse.chk
#n hf/6-311++G(d,p) test scf=(direct,tight) opt=tight

water dimer at 6-311++G(d,p) diffuse and polarization
functions, optimization

0 1
  O
  O 1 r2
  H 2 r3  1 a3
  H 2 r4  1 a4  3 d4
  H 1 r5  2 a5  3 d5
  H 1 r6  2 a6  3 d6

r2= 2.7398
r3= 0.9871
a3= 110.83
r4= 0.9871
a4= 110.83
d4= 111.20
r5= 0.9895
a5=  0.19
d5= 124.40
r6= 0.9881
a6= 100.58
d6= 124.40

--Link1--
%Chk=bsse.chk
#n hf/6-311++G(d,p) test MESSAGE GEOM(check)
```

BSE energy, monomer 1

0 1

1 Nuc 0.0

3 Nuc 0.0

4 Nuc 0.0

Sample Input Deck for Counterpoise Corrections Using GAMESS

This calculation assumes that the optimum geometry has been determined in a previous run. Note that the second oxygen and the first two hydrogens have their nuclear charges set to zero. To get the other corrected monomer energy, a third run is necessary, with the first oxygen and last two hydrogens having their nuclear charges set to zero.

+++++

! Sample input file (H2O) 2 at STO-3G

!

\$CONTRL SCFTYP=RHF RUNTYP=ENERGY \$END

\$SYSTEM TIMLIM=99999 MEMORY=5000000 \$END

\$GUESS GUESS=HCORE \ \$END

\$DATA

water dimer Ghost functions

C1

OXYGEN 8. .000000 .000000 .000000

S 3

1 130.70932000 0.15432897

2 23.80886100 0.53532814

3 6.44360830 0.44463454

L 3

1 5.03315130 -0.09996723 0.15591627

2 1.16959610 0.39951283 0.60768372

3 0.38038900 0.70011547 0.39195739

OXYGEN 0.0 .000000 .000000 2.739800

S 3

1 130.70932000 0.15432897

2 23.80886100 0.53532814

3 6.44360830 0.44463454

L 3

1 5.03315130 -0.09996723 0.15591627

2 1.16959610 0.39951283 0.60768372

3 0.38038900 0.70011547 0.39195739

HYDROGEN	0.0	.922583	.000000	3.090809
S	3			
1	3.42525091	0.15432897		
2	0.62391373	0.53532814		
3	0.16885540	0.44463454		
HYDROGEN	0.0	-.333629	.860146	3.090809
S	3			
1	3.42525091	0.15432897		
2	0.62391373	0.53532814		
3	0.16885540	0.44463454		
HYDROGEN	1.0	-.001854	-.002707	.989495
S	3			
1	3.42525091	0.15432897		
2	0.62391373	0.53532814		
3	0.16885540	0.44463454		
HYDROGEN	1.0	-.548753	-.801434	-.181423
S	3			
1	3.42525091	0.15432897		
2	0.62391373	0.53532814		
3	0.16885540	0.44463454		

\$END

REFERENCES

1. C. Møller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934). Note on the Approximation Treatment for Many-Electron Systems.
2. J. A. Pople, R. Seeger, and R. Krishnan, *Int. J. Quantum. Chem., Quantum Chem. Symp.*, **11**, 149 (1977). Variational Configuration Interaction Methods and Comparison with Perturbation Theory.
3. R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.*, **14**, 91 (1978). Approximate Fourth-Order Perturbation Theory of Electron Correlation Energy.
4. P. R. Surjan, I. Mayer, and I. Lukovitz, *Chem. Phys. Lett.*, **119**, 538 (1983). Second Quantization-Based Perturbation Theory for Intermolecular Interactions Without Basis Set Superposition Error.
5. I. Mayer, *Int. J. Quantum Chem.*, **23**, 341 (1983). Towards a Chemical Hamiltonian.
6. I. Mayer, *Mol. Phys.*, **89**, 515 (1996). On the Hylleraas Functional for a Non-Hermitian Unperturbed Hamiltonian.
7. G. Chalasinski and M. M. Szczesniak, *Chem. Rev.*, **94**, 1723 (1994). Origins of Structure and Energetics of van der Waals Clusters from Ab Initio Calculations.
8. G. Chalasinski and M. Gutowski, *Chem. Rev.*, **88**, 943 (1988). Weak Interactions Between Small Systems. Models for Studying the Nature of Intermolecular Forces and Challenging Problems for Ab Initio Calculations.
9. N. R. Kestner, *J. Chem. Phys.*, **48**, 252 (1968). He-He Interaction in the SCF-MO Approximation.

10. B. Liu and A. D. McLean, *J. Chem. Phys.*, **59**, 4557 (1973). Accurate Calculations of the Attractive Interactions of Two Ground State Helium Atoms.
11. J. H. van Lenthe, J. G. C. M. van Duijneveldt-van de Rijdt, and F. B. van Duijneveldt, in *Ab Initio Methods in Quantum Chemistry*, Part 2, K. P. Lawley, Ed., Wiley, New York, 1987, pp. 521–566. Weakly Bonded Systems.
12. F. B. van Duijneveldt, J. G. C. M. van Duijneveldt, and J. H. van Lenthe, *Chem. Rev.*, **94**, 1873 (1994). State of the Art in Counterpoise Theory.
13. S. Scheiner, in *Reviews in Computational Chemistry*, K. B. Lipkowitz and D. B. Boyd, Eds., VCH Publishers, New York, 1991, Vol. 2, pp. 165–217. Calculating the Properties of Hydrogen Bonds by Ab Initio Methods.
14. M. Gutowski and G. Chalasinski, *J. Chem. Phys.*, **98**, 5540 (1993). Critical Evaluation of Some Computational Approaches to the Problem of Basis Set Superposition Error.
15. F. B. van Duijneveldt, in *Molecular Interactions. From van der Waals to Strongly Bound Complexes*, S. Scheiner, Ed., Wiley, New York, 1997, pp. 81–104. Basis Set Superposition Error.
16. D. Feller and E. R. Davidson, in *Reviews in Computational Chemistry*, K. B. Lipkowitz and D. B. Boyd, Eds., VCH Publishers, New York, 1990, Vol 1, pp. 1–43. Basis Sets for Ab Initio Molecular Orbital Calculations and Intermolecular Interactions.
17. P. Dennery and A. Krzywicki, *Mathematics for Physicists* (Dover Books on Mathematics), Dover, New York, 1996.
18. S. F. Boys and F. Bernardi, *Mol. Phys.*, **19**, 553 (1970). The Calculation of Small Molecular Interaction by the Differences of Separate Total Energies: Some Procedures with Reduced Errors.
19. N. C. Handy, J. A. Pople, and I. Shavitt *J. Phys. Chem.*, **100**, 6007 (1996). Samuel Francis Boys. (This paper gives a biographical synopsis on Boys's work.)
20. R. J. Bartlett and J. F. Stanton, in *Reviews in Computational Chemistry*, K. B. Lipkowitz and D. B. Boyd, Eds., VCH Publishers, New York, 1993, Vol. 5, pp. 65–169. Applications of Post-Hartree–Fock Methods: A Tutorial.
21. G. Alagona and C. Ghio, *J. Mol. Struct. (THEOCHEM)*, **330**, 77 (1995). Basis-Set Superposition Errors for Slater vs. Gaussian Basis Functions in H-Bond Interactions.
22. I. Mayer and L. Turi, *J. Mol. Struct. (THEOCHEM)*, **227**, 43 (1991). An Analytical Investigation into the BSSE Problem.
23. P. R. Surjan and R. A. Poirier, *Chem. Phys. Lett.*, **128**, 358 (1986). Intermolecular Interactions Using Small Basis Sets: Perturbation Theory Calculations Avoiding Basis Set Superposition Error.
24. J. Noga and A. Vibo'k, *Chem. Phys. Lett.*, **180**, 114 (1991). Second-Order BSSE-Free Perturbation Theory: Intermolecular Interactions Within the Supermolecular Approach.
25. I. Mayer and A. Vibo'k, *Chem. Phys. Lett.*, **136**, 115 (1987). SCF Theory of Intermolecular Interactions Without Basis Set Superposition Error.
26. M. Kieninger, S. Suhai, and I. Mayer, *Chem. Phys. Lett.*, **230**, 483 (1994). The Chemical Hamiltonian Approach in Density Functional Theory.
27. A. Sadlej, *J. Chem. Phys.*, **95**, 6705 (1991). Exact Perturbation Treatment of the Basis Set Superposition Correction Based on the Constrained Dimer Function.
28. I. Mayer, *J. Chem. Phys.*, **97**, 5257 (1992). Comment on: Exact Perturbation Treatment of the Basis Set Superposition Correction.
29. A. Sadlej, *J. Chem. Phys.*, **97**, 5259 (1992). Reply to Comment on: Exact Perturbation Treatment of the Basis Set Superposition Correction.
30. J. M. Cullen, *Int. J. Quantum Chem., Quantum Chem. Symp.*, **25**, 193 (1991). An Examination of the Effects of Basis Set and Charge Transfer in Hydrogen-Bonded Dimers with a Constrained Hartree–Fock Method.
31. P. Wind and J.-L. Heully, *Chem. Phys. Lett.*, **230**, 35 (1994). Reduction of the Basis Set Superposition Error at the Correlation Level.
32. F. F. Muguet and G. W. Robinson, *J. Chem. Phys.*, **102**, 3648 (1995). Towards a New Correction Method for the Basis Set Superposition Error: Application to the Ammonia Dimer.
33. H. B. Jansen and P. Ros, *Chem. Phys. Lett.*, **3**, 140 (1969). Non-empirical Molecular Orbital Calculations on the Protonation of Carbon Monoxide.

34. J. Yang and N. R. Kestner, *J. Phys. Chem.*, **95**, 9214, (1991). Accuracy of Counterpoise Corrections in 2nd-Order Intermolecular Potential Calculations. 1. Helium Dimer.
35. F.-M. Tao and Y. K. Pan, *J. Phys. Chem.*, **95**, 3582, (1991). Validity of the Function Counterpoise Method and Ab Initio Calculations of van der Waals Interaction Energy.
36. F.-M. Tao and Y. K. Pan, *J. Phys. Chem.*, **96**, 5815 (1992). Validity of the Function Counterpoise Method. Results from the Complete 4th-Order MBPT Calculations.
37. F. M. Tao, *Chem. Phys. Lett.*, **206**, 560, (1993). The Counterpoise Method and Bond Functions in Molecular Dissociation-Energy Calculations.
38. M. Gutowski, F. B. van Duijneveldt, G. Chalasinski, and L. Piela, *Chem. Phys. Lett.*, **129**, 325 (1986). Does the Boys and Bernardi Function Counterpoise Method Actually Overcorrect the Basis Set Superposition Error?
39. M. Gutowski, J. H. van Lenthe, J. Verbeek, F. B. van Duijneveldt, and G. Chalasinski, *Chem. Phys. Lett.*, **124**, 370 (1986). The Basis Set Superposition Error in Correlated Electronic Structure Calculations.
40. R. Bukowski, B. Jeziorski, and K. Szalewicz, *J. Chem. Phys.*, **104**, 3306 (1996). Basis Set Superposition Problem in Interaction Energy Calculations with Explicitly Correlated Bases: Saturated Second- and Third-Order Energies for He₂.
41. J. Yang and N. R. Kestner, *J. Phys. Chem.*, **95**, 9221 (1991). Accuracy of Counterpoise Corrections in Second-Order Intermolecular Potential Calculations. 2. Various Molecular Dimers.
42. S. Simon, M. Duran, and J. J. Dannenberg, *J. Chem. Phys.*, **105**, 11024 (1996). How Does Basis Set Superposition Error Change the Potential Surfaces for Hydrogen Bonded Dimers?
43. S. Scheiner, *Annu. Rev. Phys. Chem.*, **45**, 23 (1994). Ab-Initio Studies of Hydrogen-Bonds—The Water Dimer Paradigm.
44. J. Almlöf, B. J. DeLeeuw, P. R. Taylor, C. W. Bauschlicher, and P. Siegbahn, *Int. J. Quantum Chem., Quantum Chem. Symp.*, **23**, 345 (1989). The Dissociation Energy of N₂.
45. V. Parasuk, J. Almlöf, and B. DeLeeuw, *Chem. Phys. Lett.*, **176**, 1 (1991). Basis-Set Superposition Errors in Tightly Bound Systems.
46. A. Johansson, P. Kollman, and S. Rothenberg, *Theor. Chim. Acta*, **29**, 167 (1973). An Application of the Functional Boys–Bernardi Counterpoise Method to Molecular Potential Surfaces.
47. J. P. Daudaey, P. Claverie, and J. P. Malrieu, *Int. J. Quantum Chem.*, **1**, 8 (1974). Perturbative Ab Initio Calculations of Intermolecular Energies. I. Method.
48. B. Jönsson and B. Nelander, *Chem. Phys.*, **25**, 263, (1977). Infrared Spectrum and Structure of an Ammonia–Carbon Dioxide Complex. A Comparison Between MO Calculations and Matrix Isolation Results.
49. D. W. Schwenke and D. G. Truhlar, *J. Chem. Phys.*, **82**, 2418 (1985). Systematic Study of Basis Set Superposition Errors in the Calculated Interaction Energy of Two HF Molecules.
50. M. J. Frisch, J. E. Del Bene, J. S. Binkley, and H. F. Schaefer III, *J. Chem. Phys.*, **84**, 2279 (1986). Extensive Theoretical Studies of the Hydrogen-Bonded Complexes (H₂O)₂, (H₂O)₂H⁺, (HF)₂, (HF)₂H⁺, F₂H⁻, and (NH₃)₂.
51. H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces*, Pergamon Press, Oxford, 1969.
52. S. Scheiner, *Hydrogen Bonding. A Theoretical Perspective*, Oxford University Press, Oxford, 1997.
53. J. R. Collins and G. A. Gallup, *Chem. Phys. Lett.*, **123**, 56 (1986). The Full Versus the Virtual Counterpoise Correction for Basis Set Superposition Errors in Self-Consistent Field Calculations.
54. P. Claverie, in *Intermolecular Interactions from Diatomics to Biopolymers*, B. Pullman, Ed., Wiley, New York, 1978, pp. 69–306. Elaboration of Approximate Formulas for the Interaction Between Large Molecules: Applications in Organic Chemistry.
55. O. Sinanoglu, in *Modern Quantum Chemistry—Istanbul Lectures*, Part II, *Interactions*, O. Sinanoglu, Ed., Academic Press, New York, 1965, pp. 221–238. Intermolecular Forces in Gases and Dense Media.
56. O. Sinanoglu, *J. Chem. Phys.*, **37**, 191 (1962). Bonds and Intermolecular Forces.

57. O. Sinanoglu, *J. Phys. Chem.*, **66**, 2283 (1962). Some Aspects of the Quantum Theory of Atoms, Molecules and Their Interactions.
58. P. Pulay, *Chem. Phys. Lett.*, **100**, 151 (1983). Localizability of Dynamic Electron Correlation.
59. S. Saebo and P. Pulay, *Chem. Phys. Lett.*, **113**, 13 (1985). Local Configuration Interaction: An Efficient Approach for Large Molecules.
60. S. Saebo, W. Ton, and P. Pulay, *J. Chem. Phys.*, **98**, 2170 (1992). Efficient Elimination of Basis Set Superposition Errors by the Local Correlation Method: Accurate Ab Initio Studies of Water Dimer.
61. B. Jeziorski and W. Kolos, in *Molecular Interactions*, H. Ratajczak and W. J. Orville-Thomas, Eds., Wiley, New York, 1982, Vol. 3, pp. 1–46. Perturbation Approach to the Study of Weak Intermolecular Interactions.
62. B. Jeziorski, R. Moszynski, S. Rybak and K. Szalewicz, in *Lecture Notes in Chemistry*, U. Kaldor, Ed. Springer-Verlag, New York, 1989, Vol. 52, pp. 65–94. Many-Body Theory of van der Waals Interactions.
63. S. Rybak, B. Jeziorski, and K. Szalewicz, *J. Chem. Phys.*, **95**, 6576 (1991). Many-Body Symmetry-Adapted Perturbation Theory of Intermolecular Interactions. H₂O and HF Dimers.
64. G. Karlström and A. J. Sadlej, *Theor. Chim. Acta*, **61**, 1 (1982). Basis Set Superposition Effects on Properties of Interacting Systems. Dipole Moments and Polarizabilities.
65. Z. Latajka and S. Scheiner, *J. Chem. Phys.*, **87**, 1194 (1987). Primary and Secondary Basis Set Superposition Error at the SCF and MP2 Levels: H₃N-Li⁺ and H₂O-Li⁺.
66. Z. Latajka and S. Scheiner, *Chem. Phys. Lett.*, **140**, 338 (1987). Three-Dimensional Spatial Characteristics of Primary and Secondary Basis Set Superposition Error.
67. M. M. Szczesniak and S. Scheiner, *Collect. Czech. Chem. Commun.*, **53**, 2214 (1988). Accurate Evaluation of SCF and MP2 Components of Interactions Energies. Complexes of HF, OH₂ and NH₃ with Li⁺.
68. P. G. Burton, *J. Chem. Phys.*, **67**, 4696 (1977). The Computation of Intermolecular Forces with Gaussian Basis Functions. Illustrated with He₂.
69. U. E. Senff and P. G. Burton, *J. Phys. Chem.*, **89**, 797 (1985). An Ab Initio Study of the Isotropic and Anisotropic Potential Energy Surfaces of the He–H₂ Interaction.
70. M. Gutowski, J. Verbeek, J. H. van Lenthe and G. Chalasinski, *Chem. Phys.*, **111**, 271 (1987). The Impact of Higher Polarization Functions on Second-Order Dispersion Energy. Partial Wave Expansion and Damping Phenomenon for He₂.
71. F.-M. Tao and Y. K. Pan, *J. Chem. Phys.*, **97**, 4989 (1992). Møller–Plesset Perturbation Investigation of the He₂ Potential and the Role of Midbond Functions.
72. F.-M. Tao, *J. Chem. Phys.*, **98**, 3049 (1993). The Use of Midbond Functions for Ab Initio Calculations of the Asymmetric Potentials of He–Ne and He–Ar.
73. R. Burcl, G. Chalasinski, R. Bukowski, and M. Szczesniak, *J. Chem. Phys.*, **103**, 1498 (1995). On the Role of Bond Functions in Interaction Energy Calculations: Ar ··· HCl, Ar ··· H₂O, (HF)₂.
74. M. D. Newton and N. R. Kestner, *Chem. Phys. Lett.*, **94**, 198 (1983). The Water Dimer: Theory and Experiment.
75. H. J. Böhm and R. Ahlrichs, *Mol. Phys.*, **55**, 1159 (1985). The N₀retical Investigation.
76. P. Wind and J.-L. Heully, *Chem. Phys. Lett.*, **230**, 35 (1994). Reduction of the Basis-Set Superposition Error at the Correlation Level.
77. S. M. Cybulski, G. Chalasinski, and R. Moszynski, *J. Chem. Phys.*, **92**, 4357 (1990). On Decomposition of Second-Order Møller–Plesset Supermolecular Interaction Energies and Basis Sets Effects.
78. D. Feller, *J. Chem. Phys.*, **96**, 6104 (1992). Application of Systematic Sequences of Wave Functions to the Water Dimer.
79. J. G. C. M. van Duijneveldt-van der Rijdt and F. B. van Duijneveldt, *J. Chem. Phys.*, **97**, 5019 (1992). Convergence to the Basis Set Limit in Ab Initio Calculations at the Correlated Level on the Water Dimer.
80. S. J. Chakravorty and E. R. Davidson, *J. Phys. Chem.*, **97**, 6373 (1993). The Water Dimer. Correlation Energy Calculations.

81. W. Chen and M. S. Gordon, *J. Phys. Chem.*, **100**, 14316 (1996). Energy Decomposition Analyses for Many-Body Interaction and Applications to Water Complexes.
82. Z. Latajka and Y. Bouteiller, *J. Chem. Phys.*, **101**, 9793 (1994). Application of Density Functional Methods for the Study of Hydrogen Bonded Systems. The Hydrogen Fluoride Dimer.
83. T. R. Dyke, B. J. Howard, and W. Klemperer, *J. Chem. Phys.*, **56**, 2442 (1972). Radiofrequency and Microwave Spectrum of the Hydrogen Fluoride Dimer: A Nonrigid Molecule.
84. B. J. Howard, T. R. Dyke, and W. Klemperer, *J. Chem. Phys.*, **81**, 5417 (1984). The Molecular Beam Spectrum and the Structure of the Hydrogen Fluoride Dimer.
85. J. A. Odutola and T. R. Dyke, *J. Chem. Phys.*, **72**, 5062 (1980). Partially Deuterated Water Dimers: Microwave Spectra and Structure.
86. D. C. Dayton, K. W. Jucks, and R. E. Miller, *J. Chem. Phys.*, **90**, 2631 (1989). Photofragment Angular Distributions for HF Dimer. Scalar J-J Correlations in State-to-State Photodissociation.
87. L. A. Curtis, D. J. Frurip, and M. Blander, *J. Chem. Phys.*, **71**, 2703 (1979). Studies of Molecular Association in H₂O and D₂O Vapors by Measurements of Thermal Conductivity.
88. T. R. Dyke, K. M. Mack, and J. S. Muenter, *J. Chem. Phys.*, **66**, 498 (1977). The Structure of Water Dimer from Molecular Beam Electric Resonance Spectroscopy.
89. R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.*, **72**, 650 (1980). Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions.
90. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian 94, Revision E.2, Gaussian, Inc., Pittsburgh, PA, 1995.
91. The original program of GAMESS was assembled and distributed by the staff of the NRCC: M. Dupuis, D. Spangler, and J. J. Wendoloski, *National Resource for Computations in Chemistry Software Catalog*, University of California, Berkeley, CA, 1980, Program QG01. A more recent version of GAMESS is described in M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, **14**, 1347 (1993). General Atomic and Molecular Electronic Structure System.
92. T. H. Dunning, Jr., *J. Chem. Phys.*, **90**, 1007 (1989). Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron Through Neon and Hydrogen.
93. R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *J. Chem. Phys.*, **96**, 6796 (1992). Electron Affinity of the First-Row Atoms Revisited. Systematic Basis Sets and Wave Functions.
94. D. Woon and T. H. Dunning, Jr., *J. Chem. Phys.*, **103**, 4572 (1995). Gaussian Basis Sets for Use in Correlated Molecular Calculations. V. Core-Valence Basis Sets for Boron Through Neon.
95. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The PNNL is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.
96. B. G. Johnson, P. M. W. Gill, and J. A. Pople, *J. Chem. Phys.*, **98**, 5612 (1993). The Performance of a Family of Density Functional Methods.
97. J. E. Combariza and N. R. Kestner, *J. Phys. Chem.*, **99**, 2717 (1995). Density Functional Study of Short-Range Interaction Forces Between Ions and Water Molecules.
98. S. A. Clough, Y. Beers, G. P. Klein, and L. S. Rothman, *J. Chem. Phys.*, **59**, 2254 (1973). Dipole Moment of Water from Stark Measurements of H₂O, HDO, and D₂O.

99. L. Turi and J. J. Dannenberg, *J. Phys. Chem.*, **97**, 2488 (1993). Correcting for Basis Set Superposition Error in Aggregates Containing More Than Two Molecules: Ambiguities in the Calculation of the Counterpoise Correction.
100. P. Valiron and I. Mayer, *Chem. Phys. Lett.*, **275**, 46 (1997). Hierarchy of Counterpoise Corrections for *N*-Body Clusters: Generalization of the Boys–Bernardi Scheme.
101. J. C. White and E. R. Davidson, *J. Chem. Phys.*, **93**, 8029 (1994). An Analysis of the Hydrogen Bond in Ice.