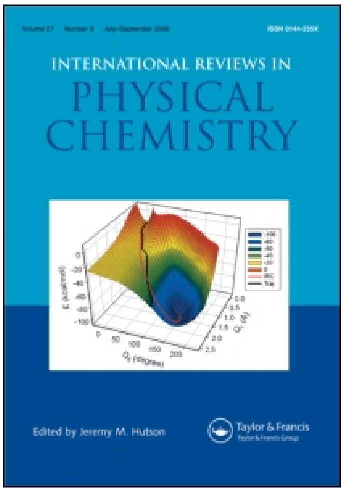

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Bond functions, basis set superposition errors and other practical issues with ab initio calculations of intermolecular potentials

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Intermolecular potentials determine the physical and chemical properties of matter. Quantum mechanical calculation based on *ab initio* molecular orbital theory has overcome many challenging problems for the past decade and become a leading tool for the study of intermolecular potentials. Bond functions, supplementing traditional atomic basis sets, have been proven highly effective in offsetting major deficiencies in atomic basis sets and are increasingly popularly employed in *ab initio* calculations of intermolecular potentials, particularly for weakly bound systems. This review revisits the present author's own work that has contributed to the eventual development of the bond function method, followed by highlighting recent applications of the method to a range of weakly bound systems. Emphases are placed on the present author's unique logic and viewpoints about a range of related issues, such as the efficiency of basis set, the basis set superposition error and the counterpoise method, which have played an important role in the conceptual development of the bond function method.

Contents

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1. Introduction

Determination of intermolecular potentials is essential in our understanding of the physical and chemical properties of matter. For the past decade, considerable progress has been achieved in the fundamental understanding of intermolecular interactions as well as in the determination of accurate intermolecular potentials, particularly for weakly interacting systems (Brutschy and Hobza 2000). Quantum-mechanical calculation based on *ab initio* molecular orbital theory has played a central role that it never did before in leading the progress in the study of intermolecular potentials.

Many factors have contributed to the recent advances in *ab initio* study of intermolecular potentials. These include the development and improvement of new computer technologies and computational software, allowing the use of highly correlated methods and large basis sets. Various computational strategies and special techniques have also been proposed and developed in the attempt to improve the efficiency and accuracy of *ab initio* intermolecular potentials. Among the various strategies and techniques, one method has achieved a great impact on improving the efficiency and accuracy and become an increasingly popular technique for *ab initio* calculation of intermolecular potentials. This new method supplements a traditional atomic basis set with a small set of bond functions, together with the full counterpoise correction (Tao and Pan 1991a,b, 1992a,b,c,d,e,f). The bond function method is convenient to apply and has proven unusually efficient in recovering the dispersion energy, leading to a significant improvement in the *ab initio* intermolecular potentials (Hobza 1994, William *et al.* 1995, Bauschlicher and Partridge 1998, Partridge and Bauschlicher 1999, Taylor and Hinde 1999).

The use of bond functions has remained effective and important even with the latest development of large systematic basis sets, such as the Dunning (1989) correlation-consistent basis sets (Kendall *et al.* 1992, Woon and Dunning 1993, Xantheas and Dunning 1993). Koch *et al.* (1998) have shown that the performance of a moderate basis set with bond functions can be superior to that of the aug-cc-pVQZ basis set. On the other hand, the widely available Dunning correlation-consistent basis sets in most *ab initio* programs have in fact enabled bond functions to be employed conveniently (Tao 1993c), promoting the popular use of bond function basis sets. For the past 3 years, there has been a dramatic increase in the literature reporting the applications of bond function basis sets for accurate *ab initio* intermolecular potentials of a wide variety of systems, from simple rare gas dimers to the interaction systems involving aromatic hydrocarbons and open-shell radicals.

This article reviews the development of the bond function method and some of the recent applications to various systems. The present author has contributed critically in the development of the method, particularly at the early stage when controversial opinions persisted about the basis set superposition error (BSSE) and other related problems. Some of the present author's initial thoughts and conceptual arguments will be detailed in this review. Several related issues, including BSSE and the counterpoise method, will also be discussed with unique opinions. Three past reviews (van Lenthe *et al.* 1987, Hobza and Zahradnik 1988, van Duijneveldt *et al.* 1994), which discuss the challenges and controversial problems for *ab initio* determination of intermolecular potentials and have benefited the present author, are recommended to interested readers and the major viewpoints there still stand today.

The article is organized as follows. Section 2 introduces the *ab initio* supermolecular calculation of intermolecular potentials and the challenging problems in the area. Section 3 describes the thoughts and intuition that guided the early work on the use of bond functions. Section 4 discusses the nature of BSSE and the logical justification for the counterpoise method. Section 5 highlights recent applications of bond function basis sets for accurate *ab initio* intermolecular potentials of various weakly bound systems. Section 6 presents the conclusion and final remarks on the use of bond function basis sets.

2. Background

About a decade ago, *ab initio* calculation of intermolecular potentials was confronted with three major problems or challenges in practice (van Lenthe *et al.* 1987, Hobza and Zahradnik 1988): the demand for large flexible basis sets, the demand for the highly correlated theoretical method, and the correction for the BSSE. These three problems seriously limited the accuracy of calculated intermolecular potentials at the time and prevented the full acceptance of *ab initio* results among experimental physical chemists, particularly among those using high-resolution spectroscopy. Experimental methods such as microwave and infrared spectroscopy, recognized as being more accurate and reliable, were widely used in the study of intermolecular structure and potentials (Dyke 1984, Janda 1985, Legon and Millen 1986, Novick *et al.* 1990, Leopold *et al.* 1994, Zwier 1998).

Ab initio calculation of intermolecular potentials can be carried out by either the supermolecular approach or the perturbation approach. Both approaches, however, suffer from similar limitations, particularly in terms of basis set. The supermolecular approach can be applied equally to van der Waals (weak) and covalent bond (strong) interactions and is more straightforward and more commonly used. In this approach, the interaction energy (or potential) ΔE^{INT} between two molecules A and B is given as an energy difference between the dimer (or supermolecule) AB and the two constituent molecules (submolecules) A and B, that is

$$\Delta E^{\mathrm{INT}} = E_{\mathrm{AB}} - (E_{\mathrm{A}} + E_{\mathrm{B}}). \tag{1}$$

The total electronic energies E_{A}, E_{B} and E_{AB} of molecules are typically of the orders of 10–10^3 au (Hartree) while the intermolecular energy ΔE^{INT} is around 10^{-3} au or smaller. Challenges and controversies arise on how to calculate accurately and consistently the molecular energies E_{A}, E_{B} and E_{AB}, such that sufficiently reliable ΔE^{INT} values are resulted.

Electron correlation plays a critical role in the intermolecular interactions between the two stable closed-shell molecules A and B. The intermolecular energy ΔE^{INT} can formally be partitioned into two components, namely ΔE^{HF} and ΔE^{COR}, the Hartree–Fock and correlation contributions respectively:

$$\Delta E^{\mathrm{INT}} = \Delta E^{\mathrm{HF}} + \Delta E^{\mathrm{COR}}. \tag{2}$$

Approximately, ΔE^{HF} recovers contributions from the exchange repulsion and electrostatic interactions between the two molecules while ΔE^{COR} recovers the dispersion energy. The electrostatic interaction can be repulsive or attractive, depending upon the mutual orientations of the molecules, but the dispersion interaction is always attractive. The calculation of ΔE^{HF} is relatively simple and straightforward. However, the calculation of ΔE^{COR} requires a post-Hartree–Fock method for the treatment of electron correlation. For interactions involving non-polar or slightly polar molecules, ΔE^{HF} is repulsive everywhere in the potential surface except for the long-range tail region while the attractive contribution in ΔE^{INT} is dominated by ΔE^{COR}. As a result, the accurate treatment of electron correlation is critically important in recovering the well depth and the attractive region of an intermolecular potential.

The accurate calculation of ΔE^{INT} also relies on the large flexible basis set for the expansion of one-particle electronic wavefunction. It is found that ΔE^{HF} converges fairly rapidly with the basis set. However, ΔE^{COR} converges much more slowly, which is consistent with the fact that ΔE^{COR} recovers primarily the dispersion energy. The basis set must typically include a large set of polarization functions, up to g or h type, as well as a consistently large set of core and valence-shell basis functions. Not only were these high polarization functions generally unavailable a decade ago, but also computers at the time were too slow or too small to handle such a large basis set except for very small intermolecular systems such as He_2. This is particularly true considering that a high-level treatment of electron correlation is also required.

Further complication to the basis set problem is the interference of the basis set superposition error (BSSE). In the supermolecular calculation (equation (1)), the energies E_{A} and E_{B} of the submolecules are calculated with the respective basis sets (say, χ_{A} and χ_{B}) for the submolecules while the energy E_{AB} of the supermolecule is calculated with the basis set χ_{AB} for the supermolecule formed by union of the submolecule basis sets $(\chi_{\mathrm{AB}} = \chi_{\mathrm{A}} + \chi_{\mathrm{B}})$. In practice, the basis sets are never complete. The extension of basis set in the supermolecule AB from the submolecule basis sets gives arise to a favoured description of the supermolecule over the submolecules. The energy lowering in E_{AB} due to such an extension of basis set is commonly known as the BSSE. The BSSE effect is significant compared with ΔE^{INT}, although it is difficult to be quantified unambiguously. As a result, the ΔE^{INT} tends to be overestimated or even completely overshadowed by the BSSE if it goes uncorrected. Worse still is the fact that, if a deficient basis set is used, the BSSE may very likely lead to apparently better ΔE^{INT} values without corrections than with corrections, in comparison with the experiment values. This is because the major deficiency in a basis set is typically a lack of adequate polarization functions that are necessary to recover the attractive dispersion energy contribution in ΔE^{INT}. The presence of the BSSE may not only severely interfere with ΔE^{INT} but also compensate by chance the major deficiency in the basis set, leading to a highly unpredictable performance of a basis set on ΔE^{INT}.

3. Bond functions

3.1. *From Rydberg molecule to van der Waals molecule*

Rydberg molecules, such as H_3, H_3O and NH_4, are a class of molecules for which the ground electronic state is dissociative but excited states enjoy lifetimes quite long compared with vibrational and rotational periods (Herzberg 1979, 1987, Raynor and Herschbach 1982, Olah *et al.* 1986). To calculate the potential energy surface of a Rydberg molecule, diffuse functions of the s and p types, centred at the centre of the molecule, must be included in the basis set for the appropriate description of the Rydberg states (McMaster *et al.* 1982). For H_3O or NH_4, such diffuse functions are centred on the oxygen or nitrogen atom. For the equilateral triangular H_3 molecule, however, the diffuse functions may be most effectively centred at the geometric centre of H_3, where no atom exists.

The above thoughts, together with a study of H_4O^+ as a potential Rydberg molecule (Tao and Pan 1989), prompted the present author's first attention to the unique role played by basis functions centred off atom, or non-atomic basis functions. They thought, for the reasons given below, that the usefulness of such basis functions might be general for all molecules and not limited to Rydberg molecules. All molecules have excited Rydberg states, although they may not necessarily be Rydberg molecules. These Rydberg states contribute significantly to electron correlation and, therefore, to the stability of a molecule. This is particularly true for tight molecules of high symmetry where Rydberg states occur in quite low excited states. Benzene might be a good example of such molecules (Tao and Pan 1992f). As a result, one could suspect that the effect of electron correlation might be underestimated if the Rydberg states were poorly described. Such a problem would be effectively resolved by use of basis functions centred at the centre of the benzene molecule.

The covalent-bonded molecules such as benzene turned out to be not an ideal case to demonstrate the effect of non-atomic basis functions. This is because electron correlation does not play a decisive role in the stability of benzene. A better case would be a molecule that is bound purely by the electron correlation effect. Thoughts in this direction eventually led to the present author's full attention to the use of bond functions for *ab initio* study of van der Waals molecules.

3.2. *Practice with bond functions*

Around 1990, the literature on *ab initio* study of van der Waals molecules was already enormous and several informative reviews on the topics were available for a beginner in the area. As expected, the area was directly challenged by problems associated with basis set. The traditional atomic basis set at the time was far from adequate for the accurate calculation of interaction energy of weakly bound systems, particularly of van der Waals molecules. Such a basis set problem was further complicated by another unresolved problem: how to correct for the BSSE. As a result, the attention to the BSSE problem became unavoidable, and the two problems must be considered together.

Convincing evidence was obtained to show (Tao and Pan 1991a,b, 1992c, Yang and Kestner 1991a,b) that the counterpoise method of Boys and Bernardi (1970) was a reliable approach to the BSSE problem. With the counterpoise method, bond functions were tested for the calculation of the neon dimer potential (Tao and Pan 1992a,d,e). A well depth of 130 μHartree was obtained at the fourth-order Møller–Plesset (MP4) level with the 6-311+G(3d2f) atomic basis set augmented with two sets of s- and p-type bond functions, 2s2p in contrast with a value of 115 μHartree without bond functions (Tao and Pan 1992a). The well depth from the empirical potentials for Ne_2 ranges from 131 to 136 μHartree (Aziz 1976, 1980, Aziz *et al.* 1983). The 2s2p bond functions were located at the midpoint of the Ne–Ne van der

Waals bond and the exponents used were $\alpha_s = \alpha_p = 0.3$, 0.075. The use of bond functions resulted in 15 μHartree, or 13%, of net improvement in the calculation well depth for Ne_2. Similar improvements were also found in the other regions of the interaction potential. However, a subtle but rather serious problem was noticed as the study was carried out. The bond functions were found to change the Hartree–Fock interaction energy ΔE^{HF}. Such an effect was expected to be rather small for weak interactions since the bond functions were primarily intended to recover the correlation contribution ΔE^{COR}. However, the effect was found to be larger than expected if multiple bond functions with large exponent values were used, indicating a possible severe distortion in molecular electronic distribution caused by the introduction of bond functions. To minimize such a distortion, a small set of bond functions were used with the exponent values so adjusted that the ΔE^{HF} would remain approximately the same as that without bond functions (Tao and Pan 1992a).

It was not completely clear at this point that the effect of bond functions was genuine or simply an artefact resulting from the possible unnatural alternation of electronic distribution. The electronic distribution distortion was probably attributed to the inadequacy of the atomic basis set used, such as 6-311+G(3d2f) in the Ne_2 study (Tao and Pan 1992a). A possible solution would be to use a sufficiently large basis set to improve the core and valence electron wave functions. Such an idea was first tested in a study on the He_2 interaction potential (Tao and Pan 1992b). The helium dimer is small enough that the basis functions for the valence shell (1s) could be easily saturated. A series of relatively large basis sets was employed to examine the effects from the bond function basis sets with respect to the corresponding purely atomic basis sets. The study convincingly showed that the bond functions were highly efficient in reproducing ΔE^{COR} while maintaining ΔE^{HF} unchanged from that for the purely atomic basis sets. The use of bond functions drastically improved the systematic convergence of ΔE^{INT} at different regions of the interaction potential for He_2 (table 1).

In the He_2 study (Tao and Pan 1992b), a fixed set of the bond functions, {3s3p2d}, with the s and p exponents 0.9, 0.3 and 0.1 and the d exponents 0.6 and 0.2, was suggested to be generally applicable to other van der Waals systems. These Gaussian functions are flexible enough to span the entire region of practical interest for any van der Waals bond. This set of bond functions, or an expanded version of this set, has indeed received wide popularity in later studies on different systems. One might wish to optimize the exponents for the best effect from the bond functions. One might also expect the optimal exponents for the bond functions to depend on the intermolecular distance and to differ from one system to another. However, it turns out that the dependence or difference is rather weak, and is further minimized by the use of multiple functions. The bond functions {3s3p2d} with the given exponents are well balanced and effective in a wide range of intermolecular distance, and are appropriate for different intermolecular systems. This has been verified independently and repeatedly by many researchers in studies of different systems, including the latest study of the water dimer by van Duijneveldt-van de Rijdt and van Duijneveldt (1999).

Basis sets supplemented with the {3s3p2d} bond functions were immediately applied in the calculations of the He–Ne and He–Ar potentials (Tao 1993c). Large well-tempered atomic basis sets of the s and p types (Huzinaga 1965, Huzinaga and Klobukowski 1988, Dingle *et al.* 1989) were used to ensure near saturation of the basis functions for core and valence electron orbitals. More importantly, the

Table 1. Values of ΔE^{HF}, ΔE^{COR} and ΔE^{INT} for He_2 at the three internuclear distances from MP4 calculations using various basis sets (Tao and Pan 1992b).

	$R = 5.6a_0$			$R = 5.0a_0$			$R = 8.0a_0$		
Basis set [atomic]–bond functions	ΔE^{HF} (μHartree)	ΔE^{COR} (μHartree)	ΔE^{INT} (μHartree)	ΔE^{HF} (μHartree)	ΔE^{COR} (μHartree)	ΔE^{INT} (μHartree)	ΔE^{HF} (μHartree)	ΔE^{COR} (μHartree)	ΔE^{INT} (μHartree)
[5s4p2d][a] (54)[b]	29.4	−56.6	−27.2	126.4	−108.0	8.5	0.07	−6.3	−6.2
[5s4p3d2f][a] (92)	29.4	−60.0	−30.6	126.4	−116.7	9.8	0.07	−6.4	−6.3
[8s5p3d2f][c] (104)	29.2	−57.2	−28.0						
[5s4p2d]–{3s3p} (66)	29.4	−60.6	−31.2						
[5s4p2d]–{3s3p2d} (76)	29.4	−61.2	−31.8						
[5s4p2d]–{3s3p2d1f} (83)	29.4	−61.5	−32.0	126.4	−120.7	5.7	0.07	−6.4	−6.3
[5s4p3d2f]–{3s3p2d1f} (121)	29.4	−61.6	−32.1	126.4	−120.9	5.6	0.07	−6.4	−6.4
[8s5p3d2f]–{3s3p2d} (126)	29.2	−61.4	−32.2						

[a] Atomic basis set from Chalasinski and Jeriorski (1976).
[b] The total number of basis functions.
[c] Atomic basis set from Huzinaga (1965).

Table 2. Dependence of ΔE^{HF}, ΔE^{COR} and ΔE^{INT} on the position of the bond functions {3s3p2d} for He–Ne at the internuclear distance $R = 5.8a_0$ from MP4 calculations (Tao 1993c).[a]

$R_{\mathrm{Ne\text{-}G}}$[b] (units of a_0)	ΔE^{HF} (μHartree)	ΔE^{COR} (μHartree)	ΔE^{INT} (μHartree)
2.6	42.2	−103.3	−61.1
2.8	42.2	−103.5	−61.3
2.9	42.2	−103.6	−61.4
3.0	42.2	−103.7	−61.5
3.2	42.2	−103.7	−61.5
3.4	42.2	−103.6	−61.5
Without bond functions	42.2	−72.5	−30.3

[a] The atomic basis set for helium is [5s2p1d] from Huzinaga (1965) and for neon is [8s5p2d1f] from Huzinaga and Klobukowski (1988) and Dingle *et al.* (1989).
[b] R is the distance between the neon nucleus and the centre of the bond functions along the He—Ne bond.

dependence of ΔE^{HF}, ΔE^{COR} and ΔE^{INT} on the position of the bond functions was studied (table 2). The study showed that ΔE^{COR} or ΔE^{INT} was highly stable with respect to the shift of the bond functions in a wide range along the van der Waals bond, which further established the stable effective role of the bond functions. Similar studies were also carried out for the main geometric configurations of the He–H_2 system (linear and T shaped) (Tao 1994c) and the Ar–HF system (linear Ar–H–F, T shaped and linear Ar–F–H) (Tao and Klemperer 1994). For the He–H_2 system, test calculations were also conducted by shifting the bond functions away from the van der Waals bond (the line connecting the helium atom and the H_2 centre of mass). The bond functions were used to calculate three-body intermolecular forces for the helium trimer (Tao 1994a). All these studies showed that the bond functions are effective and reliable, and stable with the position of the functions. This sufficiently validates applications of bond functions to intermolecular systems consisting of diatomic or polyatomic molecules.

3.3. *An interesting case: ammonia dimer* $(NH_3)_2$

Following the establishment of the effective role of bond functions, bond function basis sets were used in *ab initio* studies of a number of weakly bound systems. One of the most interesting applications was a study of the equilibrium structure for the ammonia dimer (Tao and Klemperer 1993). The molecular structure for $(NH_3)_2$ was the subject of a considerable body of experimental and theoretical studies during the 1980s and the early 1990s. The central question was whether or not the dimer could be recognized as a prototypical hydrogen-bonded complex similar to the water dimer and the hydrogen fluoride dimer, where one NH_3 unit acts as a hydrogen bond donor to the other unit. Gas-phase rotational spectra of $(NH_3)_2$ indicated inconsistency with a hydrogen-bonded structure for $(NH_3)_2$ and suggested an asymmetric cyclic structure (Fraser *et al.* 1985, Nelson *et al.* 1985, 1987a,b). However, most theoretical calculations (Sagarik *et al.* 1986, Frisch *et al.* 1986, Latajka and Scheiner 1986, Hassett *et al.* 1991) concluded at the time that the stable structure for $(NH_3)_2$ would contain a traditional hydrogen bond. A new infrared spectroscopy study (Loeser *et al.* 1992) also supported the hydrogen-bonded structure for $(NH_3)_2$, while it also recognized that the hydrogen bond might not be as rigid as previously thought. The debate about the structure for $(NH_3)_2$ was featured in *The Chemical & Engineering News* (Baum 1992), partly because of its wide implications in biological systems.

Bond function basis sets were applied in the *ab initio* study of the equilibrium structure for the ammonia dimer (Tao and Klemperer 1993). Although ammonia is a polar molecule, the interaction energy ΔE^{INT} of $(NH_3)_2$ in the attraction region was found to be contributed nearly equally from ΔE^{HF} and ΔE^{COR}. This is in contrast with the case of the water dimer or the hydrogen fluoride dimer, where ΔE^{INT} is dominated by ΔE^{HF}. As a result, the recovery of a converged ΔE^{COR} is critical for the accurate location of the potential minimum for $(NH_3)_2$. More significantly, Tao and Klemperer maintained that the hydrogen-bonded structure for $(NH_3)_2$ would be favoured over other structures in a calculation using an inadequate atomic basis set. The reason for this is that the basis functions on the hydrogen atom of the hydrogen bond donor would inevitably play the role as bond functions to recover ΔE^{COR}. The other structures without a hydrogen bond, on the other hand, are lack of such basis functions and therefore would be unfavorable in the calculations. In other words, calculations using a purely atomic basis set would be biased and favour the hydrogen-bonded structure for $(NH_3)_2$.

Tao and Klemperer (1993) further proposed that the use of bond functions could strategically minimize such a bias and give a more accurate account for the equilibrium structure of $(NH_3)_2$. Two distinct structures of $(NH_3)_2$ were compared to show the effect of bond functions. One was the traditional hydrogen-bonded structure with C_s symmetry and the other was the cyclic structure with C_{2h} symmetry. Table 3 compares the ΔE^{HF}, ΔE^{COR} and ΔE^{INT} values between the two structures calculated at the second-order Møller–Plesset (MP2) level using a basis set with various bond functions. Consistent with early *ab initio* results, the C_s structure was more stable than the C_{2h} structure from calculations without bond functions. With the bond functions, however, the C_{2h} structure became more stable

Table 3. Comparisons of ΔE^{HF}, ΔE^{COR} and ΔE^{INT} for $(NH_3)_2$ between the hydrogen-bonded structure (C_s) and the cyclic structure (C_{2h}) from MP2 calculations (Tao and Klemperer 1993).

	C_s structure[b]			C_{2h} structure[b]		
Basis[a]–{bond functions}	ΔE^{HF} (μHartree)	ΔE^{COR} (μHartree)	ΔE^{INT} (μHartree)	ΔE^{HF} (μHartree)	ΔE^{COR} (μHartree)	ΔE^{INT} (μHartree)
Without bond functions	−2.832	−1.619	−4.451	−2.512	−1.809	−4.321
-{3s}	−2.804	−1.723	−4.527	−2.505	−1.964	−4.469
-{1s1p}	−2.776	−1.860	−4.636	−2.510	−2.071	−4.581
-{2s2p}	−2.714	−1.911	−4.625	−2.523	−2.115	−4.638
-{3s3p}	−2.723	−1.916	−4.639	−2.524	−2.136	−4.660
-{3s3p2d}	−2.685	−2.014	−4.699	−2.489	−2.264	−4.753

[a] The atomic basis set for hydrogen is [4s1p] contracted from (9s1p) of Huzinaga (1965) and for nitrogen is [7s5p3d] contracted from (15s10p3d) of Huzinaga and Klobukowski (1988) and Dingle *et al.* (1989).

[b] The C_s structure is from Hasset *et al.* (1991) and the C_{2h} structure is from Latajka and Scheiner (1986).

than the C_{2h} structure. It is interesting to note from table 3 that the hydrogen-bonded structure is always favoured at the Hartree–Fock level while the cyclic structure is favoured by electron correlation.

To find the equilibrium structure for $(NH_3)_2$, Tao and Klemperer (1993) also calculated the minimum energy pathway for the hydrogen donor–acceptor interchange between two equivalent C_s structures. It was found that the minimum energy pathway was extraordinarily flat in an extended region around the C_{2h} structure. This suggested that a potential minimum would be possible at any point in the broad region and it would be difficult in claiming the equilibrium structure for $(NH_3)_2$ with a certainty. The study clearly ruled out the traditional hydrogen bonded structure as the equilibrium structure for $(NH_3)_2$, because a traditional hydrogen bond would be much more rigid and directional. A Stark effect measurement (Linnartz *et al.* 1993) supported the highly non-rigid structure for $(NH_3)_2$ with a very flat potential surface near its equilibrium structure.

The most recent theoretical studies (Olthof *et al.* 1994, Lee and Park 2000) have agreed on an equilibrium structure for $(NH_3)_2$ that is asymmetric, cyclic and close to the C_{2h} structure. These studies also show that the potential along the asymmetric and the symmetric C_{2h} structures is extraordinarily flat, with a small barrier of about $7\,\mathrm{cm}^{-1}$ at the C_{2h} structure from the potential minimum. This result is in good agreement with the early *ab initio* study using bond functions (Tao and Klemperer 1993).

3.4. *Historic debate on the use of bond functions*

The attempt to use non-traditional functions existed for decades to improve the convergence of a basis set (Ahlrichs and Kutzelnigg 1968, Rothenberg and Schaefer 1971). Many researchers tested the idea for the calculation of covalent bond energies such as for N_2 but obtained rather controversial results (Hirsch *et al.* 1977, Bauschlicher 1980, 1985, Wright and Williams 1983, Wright and Buenker 1985, Martin *et al.* 1989a). One of the most serious problems was that the calculated bond energy would sensitively depend on the parameters of bond functions, as pointed out by Bauschlicher (1980, 1985). In most cases, bond energies could be easily overestimated by the use of bond functions. Wright and co-workers (Wright and Buenker 1985, Barclay and Wright 1991, Wright and Barclay 1991) resorted to the use of optimized bond functions in terms of both the exponents and the locations of the functions, but this would severely limit the predictive value of *ab initio* theory.

The principal problem in the early use of bond functions was the neglect of the basis set superposition error (BSSE). The effect of counterpoise corrections was explored in several studies (Martin *et al.* 1989b, Wright and Barclay 1991), but such corrections were strongly rejected by these studies on the ground that the corrections made the results appear worse. On the other hand, Bauschlicher (1980, 1985) recognized the serious BSSE problem with bond functions and strongly discouraged the use of bond functions. He concluded that the effect of bond functions was completely an artefact due to the BSSE and that there were no benefits from bond functions. At that time, the way in which the BSSE could be correctly removed was a highly controversial topic and, as a result, there was widespread hesitance in using bond functions.

A systematic study (Tao 1993a) clearly shows that the Boys–Bernardi full counterpoise method plays a key role in taking proper advantage of bond functions. Table 4 compares the values for the bond dissociation energy D_e of F_2 with and

Table 4. Values of the dissociation energy D_e for F_2 calculated at the MP4 level with and without counterpoise corrections (Tao 1993a).

Bond functions	D_e (eV) for the following polarization functions[a]							
	None		*d*		2d1f		3d2f	
	NCP[b]	CP[b]	NCP[b]	CP[b]	NCP[b]	CP[b]	NCP[b]	CP[b]
None	0.689[c]	0.559	1.169	0.995	1.573	1.435	1.778	1.556
3s	1.451	1.091	1.566	1.226	1.747	1.500	1.871	1.562
3s3p	2.554	1.445	1.904	1.456	2.054	1.549	2.145	1.577
3s3p2d	3.566	1.490	2.819	1.512	2.263	1.586	2.284	1.593

[a] The atomic basis set used for core and valence shells is 6-311G.
[b] NCP, without counterpoise corrections; CP, with counterpoise corrections.
[c] The experimental D_e value is 1.6585 eV.

without counterpoise corrections, calculated at the MP4 level using a series of basis sets, formed by adding different sets of polarization functions and bond functions to the 6-311G basis set. It is clear that the D_e values without counterpoise corrections easily become overestimated, even without the use of bond functions. The use of bond functions drastically enhances the overestimates of D_e. In contrast, the D_e values with counterpoise corrections are all underestimated compared with the experimental value (1.6585 eV) but they converge systematically to the experimental value. The bond functions appear to produce effects on D_e complementary to atomic polarization functions, indicating that bond functions assume the role of polarization functions. Since the total number of functions is much smaller with the bond functions than with the polarization functions, the bond functions are more efficient than the polarization functions. Similar tests and results were obtained for other diatomic molecules and for other molecular properties such as equilibrium bond lengths and harmonic frequencies (Tao 1993b, 1994b).

4. Basis set superposition errors and the counterpoise method

4.1. *Definition of the basis set superposition error problem*

As introduced earlier, it is generally interpreted that the BSSE originates from the extension of the basis set in the supermolecule from the submolecule basis sets and, as a result, the BSSE effect may be quantified as an energy lowering in E_{AB} due to such an extension of the basis set. However, the way in which such an effect is quantitatively calculated and accurate correction for BSSE is made has turned out to be a great controversy for decades.

Boys and Bernardi (1970) proposed that the full set of basis functions χ_{AB} used in the calculation of the supermolecule energy E_{AB} should also be used in the calculations of the submolecule energies E_A and E_B. The intermolecular energy should, therefore, be given as

$$\Delta E^{\mathrm{INT,CP}} = E_{AB}(\chi_{AB}) - [E_A(\chi_{AB}) + E^B(\chi_{AB})], \qquad (3)$$

rather than

$$\Delta E^{\mathrm{INT,NCP}} = E_{AB}(\chi_{AB}) - [E_A(\chi_A) + E^B(\chi_B)], \qquad (4)$$

where $E_A(\chi_A)$ and $E_B(\chi_B)$ are the energies of the submolecules A and B respectively, calculated using the respective basis sets for the submolecules. Equation (3) gives the intermolecular energy by the counterpoise method while equation (4) gives the value without a counterpoise correction. The difference between the two equations is a quantity commonly recognized as the BSSE by the counterpoise method:

$$\delta^{CP} = [E_A(\chi_A) + E_B(\chi_B)] - [E_A(\chi A_B) + E_B(\chi_{AB})]. \quad (5)$$

Clearly, such a correction is consistent with what is believed to be the origin of BSSE.

Until very recently, the counterpoise method did not appear to produce better results than the non-counterpoise method, equation (4). The values of $\Delta E^{INT,CP}$ in most cases were severely underestimated while those of $\Delta E^{INT,NCP}$ were overestimated. This led many to believe that the counterpoise method would give overcorrections for BSSE (Olivares del Valle *et al.* 1986, Loushin *et al.* 1986, de Oliveira and Dykstra 1995). The argument of overcorrection was based on the Pauli principle which would prevent one submolecule to fully occupy the basis functions of the other submolecule in the calculation of E_{AB}.

Alternative counterpoise methods (Johansson *et al.* 1973, Daudey *et al.* 1974, Spiegelmann and Malrieu 1980) were proposed for the BSSE correction, most of which suggested to scale down the counterpoise correlation using different schemes based on various interpretations of BSSE, but none of them became successful and accepted (Gutowski *et al.* 1986, 1987). A general consensus thus prevailed until quite recently was to avoid the counterpoise method by using extraordinarily large, systematically saturated basis sets so that the BSSE would be practically insignificant (Schwenka and Truhlar 1985, Frisch *et al.* 1986). This idea was encouraged by the latest development of the correlation-consistent basis sets of Dunning and coworkers (Dunning 1989, Kendall *et al.* 1992, Woon and Dunning 1993, Xantheas and Dunning 1993).

4.2. *Validity of the counterpoise method*

Most of the arguments against the counterpoise method are based on the fact that the counterpoise method does not produce results in better agreement with experiment than the non-counterpoise method. These arguments appear to overlook the inherited deficiencies in the basis set and theory used for such comparisons. In most situations, the BSSE seems to compensate for the errors caused by the deficiencies in the basis set and theory. In some special cases, the BSSE could happen to compensate exactly for the other errors, prematurely giving a sense of security about the quality of the basis set and theory used. In such cases, the balance in cancelling of errors would be destroyed if the BSSE were removed, causing the BSSE correction to appear unfavourable. A good example is the calculation of the binding energy for the water dimer. At the MP2 level without counterpoise corrections, Frisch *et al.* (1986) obtained a value of 5.35 kcal mol^{-1} using the 6-311+G** basis set, in contrast with a value of 4.95 kcal mol^{-1} by Feller (1992) using a much larger basis set (aug-cc-pVTZ). Compared with the experimental value of 5.4 ± 0.7 kcal mol^{-1}, the former appears to be favoured over the latter, despite an apparently inferior basis set used in the former calculation. With counterpoise corrections, however, the respective values of the binding energy from the two basis sets are 4.05 and 4.64 kcal mol^{-1}, leading to the conclusion that the 6-311 + G** basis set is inferior to aug-cc-pVTZ.

In contrast, proponents of the counterpoise method insist that one should focus on the genuine result expected for the quality of the basis set and theory used. In recovering the dispersion energy, the quality of a basis set is measured by the size of the polarization functions in the basis set and the level of electron correlation in the theory. One would not expect to recover the dispersion energy in a calculation without the use of sufficient polarization functions and a highly correlated method. In the case of the water dimer discussed above, the dispersion energy contributes about 40% to the binding energy at the equilibrium geometry. As a result, one would expect an inferior result from the 6-311+G** basis set compared with that from aug-cc-pVTZ. The counterpoise method makes it possible to give a result consistent with the quality of the basis set.

There is still no formal proof to date to validate rigorously the counterpoise method. However, various schemes and arguments have been proposed in an attempt to prove numerically the validity of the counterpoise method (Meyer *et al.* 1980, Szczesniak and Scheiner 1986, Yang and Kestner 1991a,b, Tao and Pan 1991a, 1992c). The fundamental philosophy followed in these schemes is that the calculated interaction energy $\Delta E^{\mathrm{INT,CP}}$ is expected for the quality of the basis set and theory or that the improvement in $\Delta E^{\mathrm{INT,CP}}$ is consistent with the improvement in the basis set and theory. A major problem in these studies is the fact that the quality of a basis set is hardly quantifiable in a rigorous manner (van Duijneveldt-van de Rijdt and van Duijneveldt 1992). As a result, the validity of the counterpoise method is not formally or rigorously confirmed.

A rigorous and ultimate confirmation of the validity of the counterpoise method may even not exist. However, the application of the counterpoise method has become widespread, providing strong evidence in support of the method itself. A general consensus has apparently been reached as of today that the counterpoise method is valid.

4.3. *Consistency in the basis set and theory*

As discussed above, the counterpoise method is now widely accepted by the majority of researchers in the area in spite of the lack of a formal proof for the validity of the method. The following discussions (Tao 1993a,c, 1996, 1999) might offer a logical justification for the counterpoise method.

The BSSE, as it is named, is commonly regarded as an error introduced in the calculation of an energy difference from one state (two separate submolecules A and B) to another (the supermolecule AB). Such an error is simply an inconsistency in energy between the two calculations using two different sets of basis functions. In order to calculate the energy difference accurately, the two calculations must be carried out in the most consistent manner. This requires the use of the same theory and the same basis set for both calculations. Practically and conceptually it is easier to follow the use of the same theory, with special attention to the size consistency of the theory. However, it is not so obvious to understand the consistency in the basis set and to follow it rigorously in practice.

The consistency in the basis set has traditionally been mistaken as the same set of basis functions for each atom to be used in the calculations. This conceptual mistake subtly assumes the basis functions or a set of basis functions to be associated with a specific atom or a group of atoms in a calculation. However, atoms and basis functions are two fundamentally separate concepts that do not have any necessary associations in the construction of molecular wavefunctions. An atom in a

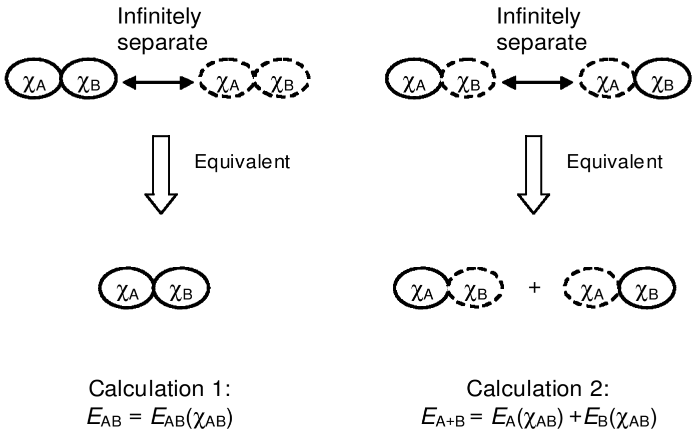

Figure 1. Schematic illustration of how the basis set consistency leads to the counterpoise method. Two calculations are defined: calculation 1 for the energy of AB and calculation 2 for the sum of the energies of A and B. Both calculations would use the consistent basis set, a schematic basis set consists of two infinitely separate unions of the basis functions, $\chi_{AB} = \chi_A + \chi_B$ (shown by the double cycles). In calculation 1, one of the two unions is set to be a ghost (broken double cycles). In calculation 2, one portion of the first union and another portion of the second union are set to be ghosts (broken single cycles). Since the two unions of basis functions are infinitely separate, calculation 1 equivalently gives $E_{AB} = E_{AB}(\chi_{AB})$ and calculation 2 gives $E_{A+B} = E_A(\chi_{AB}) + E_B(\chi_{AB})$. The energy difference is $\Delta E^{INT} = E_{AB}(\chi_{AB}) - [E_A(\chi_{AB}) + E_B(\chi_{AB})]$ as given by the counterpoise method.

calculation is distinguished by its nucleus where some basis functions happen to have certain mathematically characteristic values or properties, such as a maximum or a value of zero (node). However, these basis functions do not have any other unique, physically significant connection to the particular nucleus. They are equivalent to all other basis functions, located at other nuclei. This argument can further be extended to the fact that all basis functions in a calculation are intrinsically equivalent with respect to a specific group of nuclei or atoms. In other words, the basis functions in a calculation cannot be designated by a specific atom or a group of atoms and cannot be subdivided into two or more groups just based on where they are centred. In fact, the molecular wavefunction is always expanded by the entire set of (symmetry-adapted) basis functions used in a calculation, regardless of where the basis functions are located. Therefore, the consistency in the basis set means the exactly same set of basis functions located at the exactly same positions.

The intermolecular energy between two molecules A and B can be treated as the relative energy of the supermolecule AB with respect to the state where A and B are infinitely separate. Two different calculations should be performed: one for AB at a given intermolecular separation (and mutual orientations of A and B) and the other for AB at the infinite separation (A + B). The corresponding energies are E_{AB} and $E_{A+B} = E_A + E_B$. In order to maintain the consistency in the basis set between the two calculations, exactly the same set of basis functions should be used. Figure 1 shows how a schematic basis set is constructed to retain the consistency and how the basis set consistency leads to the counterpoise method. The schematic basis set consists of two infinitely separate unions of the basis functions: $\chi_{AB} = \chi_A + \chi_B$. In calculation 1, one of the two unions is set to be the ghost. In calculation 2, one portion of the first union, corresponding to χ_A, and another portion of the second union, corresponding to χ_B, are set to be ghosts. Since the two unions are infinitely separate, calculation 1 gives $E_{AB} = E_{AB}(\chi_{AB})$ and calculation 2 gives $E_{A+B} = E_A(\chi_{AB}) + E_B(\chi_{AB})$. As a result, the energy difference between the two calculations is the intermolecular energy given by the counterpoise method, (equation (3)).

The above illustration shows how the consistency in the basis set directly leads to the counterpoise method. As a contrast, one can also easily find how inconsistent is the basis set without the use of the counterpoise method, equation (4). The major problem with equation (4) is the ambiguity in choosing the basis sets χ_A and χ_B for the calculations of the corresponding submolecular energies $E_A(\chi_A)$ and $E_B(\chi_B)$. Once a basis set is chosen for the supermolecule, such as $\chi_{AB} = \chi_A + \chi_B$, one can no longer logically separate it out to form χ_A or χ_B. A basis function may have larger function values near a nucleus of A but the function is probably centred on a nucleus of B, or vice versa. As a result, to truncate χ_{AB} into χ_A or χ_B is just as arbitrary as to pick up any subset out of χ_{AB}. For example, one, of course, would not accept the interaction energy from the following calculations: E_{AB} is calculated using the 6-31+G(d) basis set for the supermolecule while E_A and E_B are calculated using the 6-31G basis set for the submolecules. However, the nature of the problem remains essentially the same even if the 6-31+G(d) basis set for a submolecule were used for the calculation of E_A or E_B. This is because all basis functions, including the diffuse functions or polarization functions, have function values everywhere around the nuclei of AB and the inclusion or exclusion of any functions from χ_{AB} to form a subset for the calculation of E_A or E_B is arbitrary.

The basis set inconsistency with the non-counterpoise method, equation (4), becomes even more apparent when bond functions are included in χ_{AB}. Bond functions are centred off the nucleus in the region between the submolecules A and B. It would be completely uncertain whether or not to include the bond functions in a subset for the calculation of E_A or E_B. Furthermore, the locations for the bond functions are not unique and could in principle be anywhere within and around the supermolecule AB, which would also naturally include the nuclear positions of AB. The bond functions should not be treated as unique and different from any other basis functions in χ_{AB}. The exclusion of either bond functions or any other basis functions to form a subset from χ_{AB} for the calculation of E_A or E_B would unavoidably be arbitrary and create inconsistency. The only consistent approach would be to include all basis functions from χ_{AB} for the calculation of E_A or E_B. This is exactly the counterpoise method, given by equation (3).

4.4. *The nature of the basis set superposition error*

The above discussions may provide insight into the nature of the BSSE. The BSSE, given by equation (5), can be partitioned as

$$\delta^{CP} = \delta^A + \delta^B, \tag{6}$$

where $\delta^A = E_A(\chi_A) - E_A(\chi_{AB})$ and $\delta^B = E_B(\chi_B) - E_B(\chi_{AB})$ are the contributions for the submolecules A and B respectively. It is clear that the BSSE is simply an energy difference of a molecule from two different calculations, one with χ_{AB} and the other with χ_A or χ_B. The calculation of a molecule with two different basis sets would naturally lead to a difference in the two resulting energy values. Such a difference does not represent any usual physical significance and is purely due to the difference in the two basis sets used. It would be deceiving to interpret the difference as an error attributed to the deficiency in any of the basis sets or as a correction for the deficiency in a basis set. When inconsistency is present in the basis set in a calculation as in the case of equation (4), δ^{CP} is just to remove the *specific* inconsistency in the basis set in order to retain the physically meaningful quantity (namely the intermolecular energy). When consistency is already present, on the other hand, it is unnecessary to consider the BSSE problem in a calculation.

The size of δ^{CP} was thought to reflect the quality of the atomic basis set used in a calculation. It was believed that a smaller δ^{CP} corresponds to a better basis set. Such an idea turned out to be contradictory to the results of many studies (Tao and Pan 1991a, Tao and Klemperer 1992) in which an inferior basis set resulted in small δ^{CP} while a superior basis resulted in relatively large δ^{CP}. As discussed before, it is highly arbitrary and uncertain to include or exclude basis functions from χ_{AB} to form χ_{A} or χ_{B}. The resulting δ^{CP} is thus arbitrary and does not reflect the quality of the basis set.

5. Applications of the bond function basis set

5.1. *Rare-gas dimers*

The interaction potential for He_2 has drawn the most attention in recent high-level *ab initio* calculations. van Mourik and van Lenthe (1995) performed benchmark full configuration interaction (CI) calculations on He_2 in the internuclear distances from 4.0 to 12.0 Bohr. Two different basis sets were used. One, labelled LARSAT155, consists of 122 atomic basis functions (up to the h type) and 39 bond functions {2s2p1d} distributed evenly at three positions along the He—He bond. The other basis set, STAND 159, consists of 130 atomic basis functions (up to the f type) and 29 bond functions {3s3p2d1f} located at the midpoint of the He—He bond. The full CI calculations give a minimum potential of -10.947 K at the internuclear distance of 5.6 Bohr from the LARSAT155 basis set and -10.903 K from the STAND 159 basis set. The calculated potentials are in good agreement with an empirical potential (Aziz and Slaman 1991) except that the empirical potential appears too attractive at 4.0 Bohr. van de Bovenkamp and van Duijneveldt (1999) later performed multireference CI calculations on He_2 at 4.0 and 5.6 Bohr. The basis set used consists of a [8s]6p5d4f3g2h atomic set and a set of the {3s3p2d2f1g} midbond functions (a total of 301 basis functions). The calculations resulted in a minimum potential of -10.95 K. Hattig *et al.* (1999) performed coupled cluster singles plus doubles with perturbative triples (CCSD(T)) and full CI calculations on He_2 from 3.0 to 13.0 Bohr. A series of large basis sets were used, consisting of a *d*-aug-cc-pV*n*Z atomic basis set ($n =$ D, T, Q, 5 or 6) and a set of the {3s3p2d1f1g} bond functions, labelled 3211. The results are comparable with those of the other studies. For example, the full CI calculation with the *d*-aug-cc-pVQZ–33211 basis set gave a minimum potential of -10.93 K. In addition to the interaction potential, the frequency-dependent interaction-induced polarizabilities and second hyperpolarizabilities of He_2 were also calculated by Hattig *et al.* (1999). Finally, Cybulski and Toczylowski (1999) calculated the He_2 potential from 1.75 to 5.00 Å using a series of basis sets consisting of aug-cc-pV*n*Z ($n =$ T, Q or 5) and the bond functions {3s3p2d} (labelled as 332) and {3s3p2d2f1g} (labelled 33221). The results are better than those from the larger *d*-aug-cc-pV6Z and *t*-aug-cc-pV6Z basis sets without bond functions.

Fewer *ab initio* calculations have been reported for other rare-gas dimers. In the same study of He_2, Cybulski and Toczylowski (1999) also calculated the interaction potentials for all other rare-gas dimers consisting of He_2, Ne_2, and Ar_2. The CCSD(T) calculations with the largest basis set aug-cc-pV5Z–33221 give the following potential well depths D_e and minimum distances R_e: for Ne_2, $D_e = 130.33\,\mu$Hartree and $R_e = 5.8559$ Bohr; for Ar_2, $D_e = 441.90\,\mu$Hartree and $R_e = 7.1403$ Bohr; for HeNe, $D_e = 66.57\,\mu$Hartree and $R_e = 5.7224$ Bohr; for HeAr, $D_e = 94.15\,\mu$Hartree and $R_e = 6.5998$ Bohr; for NeAr, $D_e = 205.87\,\mu$Hartree and $R_e = 6.6015$ Bohr. The corresponding experimental values for comparison are as follows: for Ne_2, $D_e = 133.8\,\mu$Hartree and $R_e = 5.841$ Bohr; for Ar_2, $D_e = 452.0\,\mu$Hartree and $R_e = 7.107$ Bohr; for HeNe, $D_e = 66.15\,\mu$Hartree and $R_e = 5.7362$ Bohr; for HeAr, $D_e = 93.89\,\mu$Hartree and $R_e = 6.5718$ Bohr; for NeAr, $D_e = 208.62\,\mu$Hartree and $R_e = 6.5453$ Bohr. Other molecular properties at the ground vibrational state, such as the rotational constants B_0, dissociation energies D_0 and vibrationally averaged bond distances $\langle R \rangle_0$, were also calculated using the *ab initio* potentials. The MP4 calculations of Ne_2 by Tao and Pan (1992a) and of Ar_2 by Tao and Pan (1994) were reported in their early applications of bond functions. The D_e and R_e values for Ne_2 from the 6-311+G(3d2f)–{2s2p} basis set, namely 130.07 μHartree and 5.896 Bohr respectively, are better than expected for the basis set and MP4 method. This was later attributed to the second-order BSSE, prompting the use of bond functions with sufficient large atomic basis sets in later studies (Tao and Pan 1992b, Tao 1993c, 1994c). The D_e and R_e values for Ar_2 from the [9s7p2d1f]–{3s3p2d} basis set, namely 421.4 μHartree and 7.22 Bohr respectively, are reasonable for the basis set and theory and are in contrast with the corresponding values of 339.9 μHartree and 7.30 Bohr from the purely atomic basis set [9s7p2d1f]. The [9s7p] atomic basis set was contracted from the well-tempered set (14s10p) of Huzinaga and Klobukowski (1988). MP4 calculations were also carried out for HeNe and HeAr using bond function basis sets extended from the large well-tempered atomic basis sets (Tao 1993c). The D_e and R_e values for HeNe are 62.58 μHartree and 5.8 Bohr respectively and for HeAr are 89.81 μHartree and 6.65 Bohr respectively, and are reasonable compared with the latest CCSD(T) calculations (Cybulski and Toczylowski 1999). In a recent study of bond functions (Tao 1999), MP4 and CCSD(T) calculations were performed for the Kr_2 interaction potential. The CCSD(T) calculations with the bond function basis set [9s7p4d3f]–{3s3p2d1f} produced a well depth $D_e = 617\,\mu$Hartree at $R_e = 4.058$ Å, recovered over 99% of the experimental depth (Aziz 1979, Aziz and Slaman 1986). The MP4 calculations with the same bond function basis set gave $D_e = 613\,\mu$Hartree (at $R = 4.0$ Å), which was compared with the values of 354 and 461 μHartree from the purely atomic basis sets [9s7p4d3f] and [9s7p4d3f2g] respectively.

5.2. *Rare-gas–molecule complexes*

The systems of a rare-gas atom and a closed-shell stable molecule have long been studied for the fundamental understanding of intermolecular forces and dynamics. With the development of bond function basis sets, *ab initio* calculation has become the most powerful tool for the intermolecular potential surfaces of rare-gas–molecule complexes. Applications of the bond function method to these van der Waals systems are systematic, routine and yet crucially important for accurate potential surfaces. In fact, a vast majority of *ab initio* calculations of accurate potential surfaces using bond functions have been for this class of complexes, which involve a wide variety of molecules, including hydrogen halides, molecular halogens, non-hydrogen diatomics, polyatomic molecules, organic molecules and aromatic compounds.

Tao and Klemperer (1994) used bond function basis sets to investigate the potential surfaces of Ar–HF, Ar–H_2O and Ar–NH_3. The study first tested the effectiveness of bond functions for the Ar–HF system at various geometries and then applied bond function basis sets for the calculations of the potential surfaces for Ar–HF, Ar–H_2O, and Ar–NH_3 at the MP2 and MP4 levels. The basis sets consisted of large atomic basis sets and a set of bond functions {3s3p2d} located at the midpoint between the rare-gas atom and the centre of mass of the halide. For Ar–HF, the MP4 calculations found a global potential minimum (with a potential energy of $-200.0\,\mathrm{cm}^{-1}$) at the linear Ar–H–F configuration, a second minimum ($-88.1\,\mathrm{cm}^{-1}$) at the linear Ar–F–H configuration, and a potential barrier ($-71.7\,\mathrm{cm}^{-1}$). For Ar–H_2O, a single potential minimum ($-130.2\,\mathrm{cm}^{-1}$) was found at a nearly linear hydrogen-bonded configuration, together with the barriers of 22.6 and $26.6\,\mathrm{cm}^{-1}$ for in-plane and out-of-plane rotations respectively. For Ar–NH_3, a single potential minimum ($-130.1\,\mathrm{cm}^{-1}$) was found at a nearly linear hydrogen-bonded configuration, together with the barriers of 26.6 and $38.0\,\mathrm{cm}^{-1}$ for rotation about the NH_3 symmetry axis and end-over-end rotation respectively. All these were in good agreement with the newly available experimental potentials (Hutson 1992a,b, Cohen and Saykally 1993, Schmuttenmaer *et al.* 1993). The dependence of the Ar–HF potential surface on the HF valence bond length *r*(HF) was also studied in several calculations using bond function basis sets (Chang *et al.* 1993, 1995, Chuang *et al.* 2000). Such a dependence was found to be highly anisotropic, being maximal for linear Ar–H–F and becoming essentially independent of *r*(HF) for an angle of 45° or greater from linearity. These calculations were used to study the infrared transitions corresponding to the vibrational states of HF in the Ar–HF complex. Excellent agreement was found between new experiments and the predictions (Chang and Klemperer 1993, Chuang and Klemperer 2000).

Tao *et al.* (1996b) calculated the potential surface for He–H_2O at the MP4 level using large atomic basis sets and the {3s3p2d} bond functions. The He–H_2O potential surface is characterized by a single potential minimum ($-31.8\,\mathrm{cm}^{-1}$) at a T-shaped He–H–O configuration ($\theta = 105°$), together with the barriers of 13.4 and $12.6\,\mathrm{cm}^{-1}$ for in-plane rotation at $\theta = 0°$ and 180° respectively, and $20.0\,\mathrm{cm}^{-1}$ for out-of-plane rotation. Li *et al.* (1999) calculated the potential surface for He–NH_3 using a similar approach. The He–NH_3 potential surface is characterized by a global minimum ($-33.0\,\mathrm{cm}^{-1}$) at $R = 3.26\,\mathrm{\AA}$, $\theta = 90°$ and $\phi = 60°$, together with the barriers of 23.1 and $20.9\,\mathrm{cm}^{-1}$ for in-plane rotation at $\theta = 0°$ and 180° respectively, and $10.5\,\mathrm{cm}^{-1}$ for out-of-plane rotation. Also similarly, Gao *et al.* (1997) calculated the potential surfaces for He–CH_4 and Ne–CH_4. The potential minima correspond to the face configuration (hydrogen-bonded) with well depths of $26.2\,\mathrm{cm}^{-1}$ for He–CH_4 and $59.0\,\mathrm{cm}^{-1}$ for Ne–CH_4.

Slavíek *et al.* (2001) calculated the potential surfaces for the Ne–HBr and Ne–HI complexes at the CCSD(T) level using the aug-cc-pVDZ basis set extended with additional polarization functions and the {3s3p2d} bond functions. For Ne–HBr, they obtained the global minimum potential of $-58.6\,\mathrm{cm}^{-1}$ and a secondary minimum potential of $-55.7\,\mathrm{cm}^{-1}$ at the linear Ne–H–Br and Ne–Br–H configurations respectively. For Ne–HI, in contrast, they obtained the global minimum potential of $-55.7\,\mathrm{cm}^{-1}$ and a second minimum potential of $-48.1\,\mathrm{cm}^{-1}$ at the linear Ne–I–H and Ne–H–I configurations, respectively. In the same study, MP2 and CCSD(T) calculations using similar bond function basis sets were also performed for the global and secondary minima of the potential surfaces for Ar–HCl, Ar–HBr, Ne–HCl and Ar–HI. These calculations produced potential values in good agreement with those from the known empirical potential surfaces (Hutson 1988, 1989, 1992a,b).

Taylor and Hinde (1999) reported CCSD(T) calculations of the potential energy surface for He–LiH. The {3s3p2d} bond functions (Tao and Pan 1992b) were used to augment the atomic basis set which consisted of aug-cc-pVTZ for hydrogen and helium and truncated cc-pVQZ (which omits g-type functions) for lithium. Before calculating the intermolecular potential surface for He–LiH, a series of test calculations was carefully carried out to validate the reliability of the basis set in reproducing monomer properties as well as in saturating the intermolecular energies. The calculations produced a binding energy of $D_e = 176.7\,\mathrm{cm}^{-1}$ for He–LiH at the linear He–Li–H configuration, more than twice that of an early *ab initio* study without use of bond functions (Gianturco *et al.* 1997).

All complexes of rare-gas–halogen molecules appear to share similar shapes of the intermolecular potential surface: two minima at the linear configurations and a third minimum at the T-shaped configuration. Tao and Klemperer (1992) surprisingly discovered the linear minima in the *ab initio* study of ArClF and $ArCl_2$ complexes by MP2 and MP4 calculations with the modest basis set 6-31+G(2df) without bond functions. The linear and T-shaped minima were found to have nearly the same well depths, generating strong interest in these complexes in a series of later studies. Huang *et al.* (1995) reported an accurate *ab initio* potential surface for He–Cl_2 from MP4 calculations with a large basis set consisting of a well-tempered atomic set [8s6p3d,5s3p] and the {3s3p2d} bond functions. The calculations produced a linear global minimum ($-40.5\,\mathrm{cm}^{-1}$) and a T-shaped secondary minimum ($-36.6\,\mathrm{cm}^{-1}$). Bound state calculations were performed on the *ab initio* potential surface. Despite the deeper minimum at the linear configuration, the probability distribution of the ground vibrational state still maximizes in the T-shaped configuration, in agreement with the observed microwave spectra for the similar complexes (Harris *et al.* 1974, Xu *et al.* 1993). Williams *et al.* (1997) obtained similar *ab initio* potential surfaces for He–Cl_2, Ne–Cl_2 and Ar–Cl_2 from MP4 and CCSD(T) calculations using bond function basis sets. Higgins *et al.* (1998) calculated the intermolecular potential surface for HeClF and used it for the calculations of the rotation–vibration levels of HeClF. The T-shaped secondary minimum for HeClF was confirmed by comparing the predicted transitions with the observed transitions.

Chan *et al.* (1999) reported potential surfaces for He–F_2, Ne–F_2 and Ar–F_2 from CCSD(T) calculations using large triple and quadruple zeta basis sets (Dunning 1989, Kendall *et al.* 1992, Woon and Dunning 1993) supplemented with the {3s3p2d} bond functions (Tao and Pan 1992b). The linear well depths obtained are 35.9, 61.5 and $122.8\,\mathrm{cm}^{-1}$ for He–F_2, Ne–F_2 and Ar–F_2, respectively, and the T-shaped well depths are 31.9, 61.4 and $110.0\,\mathrm{cm}^{-1}$ respectively. Cybulski and Holt (1999) reported the same calculations for He–Cl_2, Ne–Cl_2 and Ar–Cl_2; they obtained linear well depths of 44.3, 80.1 and $211.4\,\mathrm{cm}^{-1}$ respectively, and T-shaped well depths of 41.9, 83.6 and $204.5\,\mathrm{cm}^{-1}$ respectively. Consistent with the earlier studies of Huang *et al.* (1995), Cybulski and Holt (1999) also found that large zero-point energy at the linear configuration contributed to the T-shaped configuration of the ground vibrational state for these complexes.

Tao (1994c) reported a potential surface for He–H_2 from MP4 calculations using a large bond function basis set consisting of the atomic set [6s4p2d] and the bond functions {3s3p2d}. The calculated well depth of 47.2 μHartree at the linear configuration agrees well with the experimental value of 48 μHartree. Groenenboom and Struniewicz (2000) presented a potential surface for He–O_2 from CCSD(T) calculations using the aug-cc-pVTZ atomic basis set and the {3s3p2d1f} bond functions. The potential surface has a T-shaped global minimum with a well depth of 127.1 μHartree and a linear secondary minimum with a well depth of 116.7 μHartree. Fernandez *et al.* (1999) studied the potential surface for Ar–N_2 by CCSD(T) calculations using the aug-cc-pVXZ (X = D, T or Q) atomic basis sets and the {3s3p2d1f1g} bond functions. The CCSD(T) aug-cc-pVTZ–33211 surface was characterized by two energy minima, the T-shaped global minimum with a well depth of 451.5 μHartree and the linear secondary minimum with a well depth of 343.1 μHartree.

Tao *et al.* (1994) calculated the MP4 potential surface for He–CO using a large bond function basis set and the corresponding rotation–vibration levels. A single near-T-shaped minimum was found with a well depth of 20.3 cm^{-1}, in good agreement with the well depth of 22.9 cm^{-1} from a new empirical potential surface of Le Roy *et al.* (1994). Kukawska-Tarnawska *et al.* (1994) calculated the potential surfaces for He–CO and Ar–CO at the MP4 level using large basis sets with the {3s3p2d} bond functions. Single potential minima were found for both systems at the near-T-shaped configuration with well depths of 21.9 and 108.9 cm^{-1} respectively. Shin *et al.* (1996) also reported a potential surface and rotation–vibration energies for Ar–CO. The potential surface was from MP4 calculations with a large basis set with the {3s3p2d} bond functions. A single near-T-shaped potential minimum was found with a well depth of 96.3 cm^{-1}. Most recently, Toczylowski and Cybulski (2000) reported a CCSD(T) potential surface for Ar–CO using a large basis set consisting of the aug-cc-pVTZ atomic set and the bond functions {3s3p2d2f1f}. The near T-shaped minimum was confirmed with a well depth of 104.7 cm^{-1}.

The complexes of Rg–HCN (Rg ≡ rare gas) have been the subject of many experimental and theoretical studies. Drucker *et al.* (1995) calculated a potential surface for He–HCN at the MP4 level with a bond function basis set. The MP4 surface was characterized by a single linear minimum with a well depth of 25 cm^{-1}. Bound state calculations using the surface were carried out for the rotation–vibration level of He–HCN. Some of the predicted rotational transitions, $J = 1$ 0 and $J = 2$ 1, were successfully observed in the supersonic molecular beam by millimetre wave–microwave double-resonance techniques. The He–HCN system is floppy without a rigid geometry and the potential surface is shallow and flat. As a result, the *ab initio* calculations proved to be especially valuable in assisting the search of spectral transitions. Tao *et al.* (1995) studied the potential surfaces for Ar–HCN and Ar–HCCH. The MP4 surface for Ar–HCN was characterized by a single linear minimum with a well depth of 135.9 cm^{-1}. In contrast, the MP4 surface for Ar–HCCH was characterized by a single near-T-shaped minimum with a well depth of 110.9 cm^{-1}. Bound state calculations were also carried out using the MP4 surfaces and the predicted transitions were compared with the experimental frequencies (Cooksy *et al.* 1991, Bemish *et al.* 1993, Drucker *et al.* 1993). Cybulski *et al.* (1999) calculated a CCSD(T) potential surface for Ar–HCN using a large bond function basis set (aug-cc-pVTZ+bf). The CCSD(T) surface gave a linear global minimum with a well depth of 141 cm^{-1} and a barely noticeable secondary minimum near the T-shaped configuration. Bound-state calculations were also performed using the CCSD(T) surface and the comparisons with experiment were made. Toczylowski *et al.* (2001) recently determined the CCSD(T) potential surfaces for Rg–HCN (Rg = He, Ne, Ar or Kr) using large basis sets including the {3s3p2d2f1g} bond functions. The vibration–rotation levels were calculated using the CCSD(T) surfaces for the four complexes and their deuterated analogues. The predicted rovibrational transitions were in good agreement with available experimental measurements. The study suggested that the agreement with experiment could be further improved by using even larger basis sets.

The complexes of Rg–CO_2 and Rg–OCS have also attracted attention in several recent *ab initio* studies. Yan *et al.* (1998) presented a potential surface for He–CO_2 from MP4 calculations using a large basis set with the {3s3p2d} bond functions. They found a T-shaped global minimum with a well depth of 44.4 cm^{-1} and a linear secondary minimum with a well depth of 27.7 cm^{-1}. The rotation–vibration levels were calculated using the MP4 potential surface and the results were in good agreement with available experiments. Negri *et al.* (1999) presented MP4 potential surfaces for He–CO_2 and Ne–CO_2 using large basis sets with the {3s3p2d} bond functions. The He–CO_2 surface was essentially the same as that found by Yan *et al.* (1998) while the Ne–CO_2 surface was similar to the He–CO_2 surface except for the greater well depths, 91.6 and 54.3 cm^{-1}, for T-shaped and linear Ne–CO_2 respectively. Higgins and Klemperer (1999) reported a potential surface for He–OCS from MP4 calculations using a large basis set with the {3s3p2d} bond functions. The potential surface has a T-shaped global minimum of -45.4 cm^{-1}, a linear He–S–C secondary minimum of -28.7 cm^{-1} and a third minimum of -26.3 cm^{-1} at the linear He–O–C configuration. The rotation–vibration states were calculated using the potential surface and were used to aid the experimental search for the spectral transitions.

Koch *et al.* (1998) calculated the intermolecular energy of Ar–benzene at the CCSD(T) level with a series of large basis sets (aug-cc-pVXZ; X = D, T or Q) supplemented with the {3s3p2d1f1g} bond functions. They obtained a dissociation energy $D_e = 386\,cm^{-1}$ from the bond function basis set aug-cc-pVDZ–{3s3p2d1f1g}, better than the value of 385 cm^{-1} estimated for the large atomic basis set aug-cc-pVQZ. In a later study (Koch *et al.* 1999), they determined a three-dimensional potential surface for Ar–benzene from CCSD(T) calculations with the aug-cc-pVDZ–{3s3p2d1f1g} basis set. The vibrational levels obtained from dynamical calculations using the three dimensional surface were in excellent agreement with the available experimental data.

5.3. *Molecule–molecule complexes*

Wang *et al.* (1994a) calculated the binding energy D_e of the water dimer $(H_2O)_2$ at the MP2 level using several large atomic basis sets extended with bond functions. The values of D_e were shown to converge systematically to 4.75 kcal mol^{-1}. van Duijneveldt-van de Rijdt and van Duijneveldt (1999) calculated the binding energy of $(H_2O)_2$ at the MP2 level using a very large basis set consisting of the atomic set of 249 functions and a set of bond functions {3s3p2d1f}. The calculations gave $D_e = 4.87$ kcal mol^{-1} for the Feller–Frisch geometry (Feller 1992). Wang *et al.* (1994b) studied the relative stabilities of the two hydrogen-bonded structures of H_2O–H_2S by *ab initio* calculations at the self-consistent field (SCF), MP2, MP4, coupled cluster singles plus doubles (CCSD) and CCSD(T) levels using basis sets consisting of the 6-311++G(3df,3pd) atomic basis set and a varying set of bond functions from {3s}, {3s3p}, {3s3p2d}, to {3s3p2d1f}. The calculations showed that the structure where H_2O donated a hydrogen bond to H_2S was more stable than the other structure where H_2S donated a hydrogen bond to H_2O. The calculated binding energies were 12.1 kJ mol^{-1} for the former and 10.9 kJ mol^{-1} for the latter. Wang *et al.* (1995) calculated the binding energy D_e for the complexes HOH...NH_3, FH...NH_3, and H_2O...HF at the MP2, MP4 and quadratic configuration interaction singles plus doubles with perturbative triples QCISD(T) levels using several large atomic basis sets extended with bond functions. The respective values of D_e for the three complexes were shown to converge systematically to 6.15, 11.64 and 8.16 kcal mol^{-1}.

Tao and Klemperer (1995) reported MP2 and MP4 potential surfaces for the HCl dimer. The basis set consisted of a large atomic basis set (Huzinaga and Klobukowski 1988) and the {3s3p2d} bond functions (Tao and Pan 1992b). The well depth at the global minimum, corresponding to a hydrogen-bonded geometry, was calculated to be 710.9 cm^{-1} at the MP2 level and 643.9 cm^{-1} at the MP4 level. The potential surface was in good agreement with a new empirical potential of Elrod and Saykally (1995). Chen *et al.* (1997) reported MP2 calculations on the HBr dimer using a basis set similar to that for $(HCl)_2$ (Tao and Klemperer 1995). A hydrogen-bonded global minimum was found for the HBr dimer with a well depth of 630 cm^{-1}, in good agreement with their own experimental results from pulsed-jet Fourier transform microwave spectroscopy.

Tao and Klemperer (1993) studied the equilibrium structure of the ammonia dimer $(NH_3)_2$ by MP2 and MP4 calculations using large bond function basis sets. They found that the potential minimum for $(NH_3)_2$ probably corresponded to a cyclic configuration rather than to a configuration containing a nearly linear hydrogen bond. Their MP2–[7s5p3d, 4s1p]–{3s3p2d} calculations gave a well depth of 12.5 kJ mol^{-1}. Lee and Park (2000) repeated the study of $(NH_3)_2$ using a series of correlation-consistent basis sets without bond functions. Their study essentially confirmed the flatness of the potential pathway along a wide region from the symmetric cyclic configuration to the asymmetric hydrogen-bonded configuration, consistent with the study of Tao and Klemperer (1993). Tao *et al.* (1996a) studied the equilibrium structure for the nitric acid–water complex and obtained a binding energy of 9.8 kcal mol^{-1} by MP2 calculations using large bond function basis sets.

5.4. *Open-shell and ionic complexes*

Partridge and Bauschlicher (1999) compared the bond energies and bond lengths of He·H and Ar·H calculated at the CCSD(T) level using bond function basis sets with those calculated using atomic basis sets. Using the aug-cc-pVTZ–{3s3p2d} basis set, they found that the D_e and R_e values for He·H are 22.26 μHartree and 6.673 Bohr respectively and for Ar·H they are 149.90 μHartree and 6.815 Bohr respectively, essentially identical with those from the aug-cc-pV5Z basis set. Their best CCSD(T) values of 22.55 μHartree and 6.665 Bohr and of 150.77 μHartree and 6.802 Bohr respectively are obtained from the aug-cc-pV5Z–{3s3p2d} basis set. The study concluded that employing bond functions is an extremely effective approach for studying weakly bound systems.

Lee *et al.* (2000) calculated the potential surfaces for the ground and first excited states ($\tilde{X}\,^2\Pi$ and $\tilde{A}\,^2\Sigma^+$) of the He·OH and Ne·OH complexes and further calculated the rotation–vibration energies using the potential surfaces. The potential surfaces were calculated at the CCSD(T) level using the aug-cc-pVTZ–{3s3p2d2f1g} basis set. The calculated rotation–vibration energies are in good agreement with available results. Similarly, Klos *et al.* (2000b) calculated the potential surface for the ground state of the Ar·OH complex and further determined the rotation–vibration states. The global minimum was found at the linear Ar–H–O geometry with a centre-of-mass distance $R_e = 7.0$ Bohr and a well depth $D_e = 141.2\,\text{cm}^{-1}$.

Cybulski *et al.* (1996) calculated the potential surface for the ground state of the He·CH complex at the MP4 level using a large well-tempered basis set extended with the {3s3p2d} bond functions. A relatively deep minimum of $D_e = 335$ μHartree was obtained for the A$''$ state at the T-shaped geometry with $R_e = 5.0$ Bohr and $\theta = 100°$. Kendall *et al.* (1998) calculated the potential surface for the ground state of the Ar·NH complex at the MP4 level using a similar bond function basis set. A global minimum of $D_e = 100.3\,\text{cm}^{-1}$ was obtained at the T-shaped geometry with $R_e = 6.75$ Bohr and $\theta = 67°$. Cybulski *et al.* (2000) also calculated the potential surfaces for the ground state ($\tilde{X}\,^2\Pi$) and the first excited state ($\tilde{A}\,^2\Sigma^+$) of the He·SH and Ne·SH complexes at the CCSD(T) level using the aug-cc-pVTZ–{3s3p2d2f1g} basis set. They further calculated the rotation–vibration states of the systems, which were in good agreement with available experimental results. Similarly, Klos *et al.* (2000a) calculated the potential surface for the ground state of the He·NO complex and further calculated the rotation–vibration energies of the system.

Buchachenko *et al.* (2000) calculated the interaction potentials for the lowest adiabatic states of Σ and Π symmetry of Ar·O and Ar·O$^-$ at the CCSD(T) level using the aug-cc-pVTZ–{3s3p2d} basis set. The study shows that, for the Ar·O neutral complex, the Π state potential (with a well depth $D_e = 380$ μHartree at $R_e = 3.4$ Å) is deeper than the Σ state potential ($D_e = 220$ μHartree at $R_e = 3.8$ Å) but, for the Ar·O$^-$ anion complex, the Π state potential ($D_e = 2400$ μHartree at $R_e = 3.35$ Å) is shallower than the Σ state potential ($D_e = 3600$ μHartree at $R_e = 3.02$ Å).

6. Conclusion

It is clear from this review that bond functions, supplementing traditional atomic basis sets, are highly effective in offsetting major deficiencies in atomic basis sets and are becoming an increasingly popular approach for accurate *ab initio* calculations of intermolecular potentials. The main intuition and expectations that guided the early use of bond functions have been confirmed. The understanding of the nature of BSSE not only has provided a logical justification for the counterpoise method but also has contributed to the ultimate successful use of bond functions.

Bond function basis sets will continue to serve as a popular approach for high-level *ab initio* calculations of intermolecular potentials and will play a major role in the fundamental understanding of intermolecular forces.

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References

AHLRICHS, R., and KUTZELNIGG, W., 1968, *Chem. Phys. Lett.*, **1**, 651.

AZIZ, R. A., 1976, *Chem. Phys. Lett.*, **40**, 57; 1979, *Molec. Phys.*, **38**, 177; 1980, *High Temp. Pressures*, **12**, 565.

AZIZ, R. A., MEATH, W. J., and ALLNATT, A. R., 1983, *Chem. Phys.*, **78**, 295.

AZIZ, R. A., and SLAMAN, M. J., 1986, *Molec. Phys.*, **58**, 679; 1991, *J. Chem. Phys.*, **94**, 8047.

BARCLAY, V. J., and WRIGHT, J. S., 1991, *J. Comput. Chem.*, **12**, 690.

BAUM, R. M., 1992, *Chem. Engng News.*, October 19, 20–23.

BAUSCHLICHER, C. W., JR, 1980, *Chem. Phys. Lett.*, **74**, 277; 1985, *ibid.*, **122**, 572.

BAUSCHLICHER, C. W., JR, and PARTRIDGE, H., 1998, *J. Chem. Phys.*, **109**, 4707.

BEMISH, R. J., BLOCK, P. A., PEDERSEN, L. G., YANG, W., and MILLER, R. E., 1993, *J. chem. Phys.*, **99**, 8585.

BOYS, S. F., and BERNARDI, F., 1970, *Molec. Phys.*, **19**, 553.

BRUTSCHY, B., and HOBZA, P., 2000, *Chem. Rev.*, **100**, 3186.

BUCHACHENKO, A. A., JAKOWSKI, J., CHALASINSKI, G., SZCZESNIAK, M. M., and CYBULSKI, S. M., 2000, *J. Chem. Phys.*, **112**, 5852.

CHALASINSKI, G., and JERIORSKI, B., 1976, *Molec. Phys.*, **32**, 81.

CHAN, K. H., POWER, T. D., JAI-NHUKNAN, J., and CYBULSKI, S. M., 1999, *J. Chem. Phys.*, **110**, 860.

CHANG, H.-C., and KLEMPERER, W., 1993, *J. Chem. Phys.*, **98**, 2497.

CHANG, H.-C., TAO, F.-M., KLEMPERER, W., HEALEY, C., and HUTSON, J. M., 1993, *J. chem. Phys.*, **99**, 9337.

CHANG, H.-C., TAO, F.-M., TSANG, S. N., and KLEMPERER, W., 1995, *Chin. J. chem. Soc.*, **42**, 8.

CHEN, W., WALKER, A. R. H., NOVICK, S. E., and TAO, F.-M., 1997, *J. chem. Phys.*, **106**, 6240.

CHUANG, C. C., HIGGINS, K. J., FU, H. C., and KLEMPERER, W., 2000, *J. phys. Chem.*, **112**, 7022.

CHUANG, C. C., and KLEMPERER, W., 2000, *J. phys. Chem.*, **113**, 4116.

COHEN, R. C., and SAYKALLY, R. J., 1993, *J. chem. Phys.*, **98**, 1007.

COOKSY, A. L., DRUCKER, S., FAEDER, J., GOTTLIEB, C. A., and KLEMPERER, W., 1991, *J. chem. Phys.*, **95**, 3017.

CYBULSKI, S. M., CHALASINSKI, G., and SZCZESNIAK, M. M., 1996, *J. chem. Phys.*, **105**, 9525.

CYBULSKI, S. M., COUVILLION, J., KLOS, J., and CHALASINSKI, G., 1999, *J. chem. Phys.*, **110**, 1416.

CYBULSKI, S. M., and HOLT, J. S., 1999, *J. chem. Phys.*, **110**, 7745.

CYBULSKI, S. M., and TOCZYLOWSKI, R. R., 1999, *J. chem. Phys.*, **111**, 10 520.

CYBULSKI, S. M., TOCZYLOWSKI, R. R., LEE, H. S., and MCCOY, A. B., 2000, *J. chem. Phys.*, **113**, 9549.

DAUDEY, J. P., CLAVERIE, P., and MALRIEU, J. P., 1974, *Int. J. quant. Chem.*, **8**, 1.

DE OLIVEIRA, G., and DYKSTRA, C. E., 1995, *J. Mol. Struct.* (*Theochem.*), **337**, 1.

DINGLE, T. W., HUZINAGA, S., and KLOBUKOWSKI, M., 1989, *J. comput. Chem.*, **10**, 753.

DRUCKER, S., COOKSY, A. L., and KLEMPERER, W., 1993, *J. chem. Phys.*, **98**, 5158.

DRUCKER, S., TAO, F.-M., and KLEMPERER, W., 1995, *J. phys. Chem.*, **99**, 2646.

DUNNING, T. H. JR, 1989, *J. chem. Phys.*, **90**, 1007.

DYKE, T. R., 1984, *Top. Curr. Chem.*, **120**, 85.

ELROD, M. J., and SAYKALLY, R. J., 1995, *J. chem. Phys.*, **103**, 933.

FELLER, D., 1992, *J. chem. Phys.*, **96**, 6104.

FERNANDEZ, B., KOCH, H., and MAKAREWICZ, J., 1999, *J. chem. Phys.*, **110**, 8525.

FRASER, G. T., NELSON, D. D., JR, CHARO, A. C., and KLEMPERER, W., 1985, *J. chem. Phys.*, **82**, 2535.

FRISCH, M. J., DEL BENE, J. E., BINKLEY, J. S., and SCHAEFER, H. F., III, 1986, *J. chem. Phys.*, **84**, 2279.

GAO, D., CHEN, L., LI, Z., TAO, F.-M., and PAN, Y.-K., 1997, *Chem. Phys. Lett.*, **277**, 483.

GIANTURCO, F. A., KUMAR, S., PATHAK, S. K., RAIMONDI, M., SIRONI, M., GERRATT, J., and COOPER, D. L., 1997, *Chem. Phys.*, **215**, 227.

Groenenboom, G. C., and Struniewicz, I. B., 2000, *J. chem. Phys.*, **113**, 9562.

Gutowski, M., van Duijneveldt, F. B., Chalasinski, G., and Piela, L., 1987, *Mol. Phys.*, **61**, 233.

Gutowski, M., van Lenthe, J. H., Verbeek, J., van Duijneveldt, F. B., and Chalasinski, G., 1986, *Chem. Phys. Lett.*, **124**, 370.

Harris, S. J., Novick, S. E., Klemperer, W., and Falconer, W. E., 1974, *J. chem. Phys.*, **61**, 193.

Hassett, D. M., Marsden, C. J., and Smith, B. J., 1991, *Chem. Phys. Lett.*, **183**, 449.

Hattig, C., Larsen, H., Olsen, J., Jorgensen, P., Koch, H., Fernandez, B., and Rizzo, A., 1999, *J. chem. Phys.*, **111**, 10 099.

Herzberg, G., 1979, *J. chem. Phys.*, **70**, 4806; 1987, *A. Rev. phys. Chem.*, **38**, 27.

Higgins, K., Tao, F.-M., and Klemperer, W., 1998, *J. chem. Phys.*, **109**, 3048.

Hirsch, G., Bruna, P. J., Peyerimhoff, S. D., and Buenker, R. J., 1977, *Chem. Phys. Lett.*, **52**, 442.

Hobza, P., 1994, *Chem. Rev.*, **94**, 871.

Hobza, P., and Zahradnik, R., 1988, *Chem. Rev.*, **88**, 871.

Huang, S. S., Bieler, C. R., Janda, K. C., Tao, F.-M., Klemperer, W., Casavecchia, P., Volpi, G. G., and Halberstadt, N., 1995, *J. chem. Phys.*, **102**, 8846.

Hutson, J. M., 1988, *J. chem. Phys.*, **89**, 4550; 1989, *ibid.*, **91**, 4455; 1992a, *J. phys. Chem.*, **96**, 4237; 1992b, *J. chem. Phys.*, **96**, 6752

Huzinaga, S., 1965, *J. chem. Phys.*, **42**, 1293.

Huzinaga, S., and Klobukowski, M., 1988, *J. mol. Struct.*, **167**, 1.

Janda, K. C., 1985, *Adv. chem. Phys.*, **60**, 201.

Johansson, A., Kollman, P., and Rothenberg, S., 1973, *Theor. chim. Acta*, **29**, 167.

Kendall, R. A., Chalasinski, G., Klos, J., Bukowski, R., Severson, M. W., Szczesniak, M. M., and Cybulski, S. M., 1998, *J. chem. Phys.*, **108**, 3235.

Kendall, R. A., Dunning, T. H., Jr, and Harrison, R. J., 1992, *J. chem. Phys.*, **96**, 6796.

Klos, J., Chalasinski, G., Berry, M. T., Bukowski, R., and Cybulski, S. M., 2000a, *J. chem. Phys.*, **112**, 2195.

Klos, J., Chalasinski, G., Berry, M. T., Kendall, R. A., Burcl, R., Szczesniak, M. M., and Cybulski, S. M., 2000b, *J. chem. Phys.*, **112**, 4592.

Koch, H., Fernandez, B., and Christiansen, O., 1998, *J. chem. Phys.*, **108**, 2784.

Koch, H., Fernandez, B., and Makarewicz., 1999, *J. chem. Phys.*, **111**, 198.

Kukawska-Tarnawska, B., Chalasinski, G., and Olszewski, K., 1994, *J. chem. Phys.*, **101**, 4964.

Latajka, Z., and Scheiner, S., 1986, *J. chem. Phys.*, **84**, 341.

Lee, H. S., McCoy, A. B., Toczylowski, R. R., and Cybulski, S. M., 2000, *J. chem. Phys.*, **113**, 5736.

Lee, J. S., and Park, S. Y., 2000, *J. chem. Phys.*, **112**, 230.

Legon, A. C., and Millen, D. J., 1986, *Chem. Rev.*, **86**, 635.

Leopold, K. R., Fraser, G. T., Novick, S. E., and Klemperer, W., 1994, *Chem. Rev.*, **94**, 1807.

Le Roy, R. J., Bissonnette, C., Wu, T. H., Dham, A. K., and Meath, W. J., 1994, *Discuss. Faraday Soc.*, **97**, 81.

Li, Z., Chou, A., and Tao, F.-M., 1999, *Chem. Phys. Lett.*, **313**, 313.

Li, Z., Tao, F.-M., and Pan, Y.-K., 1996, *Int. J. quant. Chem.*, **57**, 207.

Linnartz, H., Kips, A., Meerts, W. L., and Havenith, M., 1993, *J. chem. Phys.*, **99**, 2449.

Loeser, J. G., Schmuttenmaer, C. A., Cohen, R. C., Elrod, M. J., Steyert, D. W., Saykally, R. J., Bumgarner, R. E., and Blake, G. A., 1992, *J. chem. Phys.*, **97**, 4727.

Loushin, S. K., Liu, S.-Y., and Dykstra, C. E., 1986, *J. chem. Phys.*, **84**, 2720.

Martin, J. M. L., Francois, J. P., and Gijbels, R., 1989a, *J. comput. Chem.*, **10**, 152; 1989b, *Theor. chim. Acta*, **76**, 195.

McMaster, B. N., Mrozek, J., and Smith, V. H., Jr, 1982, *Chem. Phys.*, **73**, 131.

Meyer, W., Hariharan, P. C., and Kutzelnigg, W., 1980, *J. chem. Phys.*, **73**, 1880.

Negri, F., Ancilotto, F., Mistura, G., and Toigo, F., 1999, *J. chem. Phys.*, **111**, 6439.

Nelson, D. D., Jr, Fraser, G. T., and Klemperer, W., 1985, *J. chem. Phys.*, **83**, 6201; 1987a, *Science*, **238**, 1670.

Nelson, D. D., Jr, Klemperer, W., Fraser, G. T., Lovas, F. J., and Suenram, R. D., 1987b, *J. chem. Phys.*, **87**, 6364.

Novick, S. E., Leopold, K. R., and Klemperer, W., 1990, *Atomic and Molecular Clusters*, edited by E. R. Bernstein (Amsterdam: Elsevier), p. 359.

Olah, G. A., Prakash, G. K. S., Barzaghi, M., Lammertsma, K., Schleyer, P. von R., and Pople, J. A., 1986, *J. Am. chem. Soc.*, **108**, 1032.

Olivares del Valle, F. J., Tolosa, F., Esperilla, J. J., Ojalvo, E. A., and Requena, A., 1986, *J. chem. Phys.*, **84**, 5077.

Olthof, E. H. T., van der Avoird, A., and Wormer, P. E. S., 1994, *J. chem. Phys.*, **101**, 8430.

Partridge, H., and Bauschlicher, C. W., 1999, *Molec. Phys.*, **96**, 705.

Raynor, S., and Herschbach, D. R., 1982, *J. phys. Chem.*, **86**, 3592.

Rothenberg, S., and Schaefer, H. F., III, 1971, *J. chem. Phys.*, **54**, 2764.

Sagarik, K. P., Ahlrichs, R., and Brode, S., 1986, *Molec. Phys.*, **57**, 1247.

Schmuttenmaer, C. A., Cohen, R. C., and Saykally, R. J., 1993, *J. chem. Phys.*, **101**, 146.

Shin, S., Shin, S. K., and Tao, F.-M., 1996, *J. chem. Phys.*, **104**, 183.

Slavíek, P., Roeselová, M., Jungwirth, P., and Schmidt, B., 2001, *J. chem. Phys.*, **114**, 1539.

Spiegelmann, F., and Malrieu, J. P., 1980, *Molec. Phys.*, **40**, 127.

Schwenka, D. W., and Truhlar, D. G., 1985, *J. chem. Phys.*, **82**, 2418.

Szczesniak, M. M., and Scheiner, S., 1986, *J. chem. Phys.*, **84**, 6328.

Tao, F.-M., 1993a, *J. chem. Phys.*, **98**, 2481; 1993b, *Chem. Phys. Lett.*, **206**, 560; 1993c, *J. chem. Phys.*, **98**, 3049; 1994a, *Chem. Phys. Lett.*, **227**, 401; 1994b, *J. chem. Phys.*, **100**, 3645; 1994c, *ibid.*, **100**, 4947; 1996, *J. molec. Struct. (Theochem.)*, **367**, 55; 1999, *J. chem. Phys.*, **111**, 2407.

Tao, F.-M., Drucker, S., Cohen, R., and Klemperer, W., 1994, *J. chem. Phys.*, **101**, 8680.

Tao, F.-M., Drucker, S., and Klemperer, W., 1995, *J. chem. Phys.*, **102**, 7289.

Tao, F.-M., Higgins, K., Klemperer, W., and Nelson, D. D., 1996a, *Geophys. Res. Lett.*, **23**, 1797.

Tao, F.-M., and Klempener, W., 1992, *J. chem. Phys.*, **97**, 440; 1993, *ibid.*, **99**, 5976; 1994, *ibid.*, **101**, 1129; 1995, *ibid.*, **103**, 950.

Tao, F.-M., Li, Z., and Pan, Y.-K., 1996b, *Chem. Phys. Lett.*, **255**, 179.

Tao, F.-M., and Pan, Y.-K., 1989, *Chem Phys.*, **136**, 95; 1991a, *J. phys. Chem.*, **95**, 3582; 1991b, *ibid.*, **95**, 9811; 1992a, *Chem. Phys. Lett.*, **194**, 162; 1992b, *J. chem. Phys.*, **98**, 4989; 1992c, *J. Phys. Chem.*, **96**, 5815; 1992d, *ibid.*, **96**, 6104; 1992e, *ibid.*, **96**, 7145; 1992f, *Theor. chim. Acta*, **83**, 377; 1994, *Molec. Phys.*, **81**, 507.

Taylor, B. K., and Hinde, R. J., 1999, *J. chem. Phys.*, **111**, 973.

Toczylowski, R. R., and Cybulski, S. M., 2000, *J. chem. Phys.*, **112**, 4604.

Toczylowski, R. R., Doloresco, F., and Cybulski, S. M., 2001, *J. chem. Phys.*, **114**, 851.

van de Bovenkamp, J., and van Duijneveldt, F. B., 1999, *J. chem. Phys.*, **110**, 11 141.

van Duijneveldt, F. B., van Duijneveldt-van de Rijdt, J. G. C. M., and van Lenthe, J. H., 1994, *Chem. Rev.*, **94**, 1873.

van Duijneveldt-van de Rijdt, J. G. C. M., and van Duijneveldt, F. B., 1992, *J. chem. Phys.*, **97**, 5019; 1999, *ibid.*, **111**, 3812.

van Lenthe, J. H., van Duijneveldt-van de Rijdt, J. G. C. M., and van Duijneveldt, F. B., 1987, *Adv. chem. Phys.*, **69**, 521.

van Mourik, T., and van Lenthe, J. H., 1995, *J. chem. Phys.*, **102**, 7479.

Wang, Y.-B., Tao, F.-M., and Pan, Y.-K., 1994a, *J. Mol. Struct. (Theochem.)*, **309**, 235; 1994b, *Chem. Phys. Lett.*, **230**, 480; 1995, *Sci. China.*, **25**, 1016.

Williams, H. L., Mas, E. M., Szalewicz, K., and Jeziorski, B., 1995, *J. chem. Phys.*, **103**, 7374.

Williams, J., Rohrbacher, A., Djahandideh, D., Janda, K.C., Jamka, A., Tao, F.-M., and Halberstadt, N., 1997, *Molec. Phys.*, **91**, 573.

Woon, D. E., and Dunning, T. H., Jr, 1993, *J. chem. Phys.*, **98**, 1358.

WRIGHT, J. S., and BARCLAY, V. J., 1991, *J. comput. Chem.*, **12**, 697.
WRIGHT, J. S., and BUENKER, R. J., 1985, *J. chem. Phys.*, **83**, 4059.
WRIGHT, J. S., and WILLIAMS, R. J., 1983, *J. chem. Phys.*, **78**, 5264.
XANTHEAS, S. S., and DUNNING T. H., JR, 1993, *J. chem. Phys.*, **99**, 8774.
XU, Y. J., JAGER, W., OZIER, I., and GERRY, M. C. L., 1993, *J. chem. Phys.*, **98**, 3726.
YAN, G., YANG, M., and XIE, D., 1998, *J. chem. Phys.*, **109**, 10 284.
YANG, J., and KESTNER, N. R., 1991a, *J. phys. Chem.*, **95**, 9214; 1991b, *ibid.*, **95**, 9221.
ZWIER, T. S., 1998, *Adv. Molec. Vibr. Colloid Dynam.*, **3**, 249.