Comparative Study of BSSE Correction Methods at DFT and MP2 Levels of Theory

BÉLA PAIZS, SÁNDOR SUHAI

Department of Molecular Biophysics, German Cancer Research Center, Im Neuenheimer Feld 280, D-69120 Heidelberg, Germany

ABSTRACT: A comparative study of intermolecular potential energy curves is performed on the complexes H_2O—HF, H_2O—H_2O, H_2O—H_2S, and H_2S—H_2S using nine different basis sets at the MP2 and DFT (BLYP and B3LYP) levels of theory. The basis set superposition error is corrected by means of the counterpoise scheme and based on the ''chemical Hamiltonian approach.'' The counterpoise and CHA-corrected DFT curves are generally close to each other. Using small basis sets, the B3LYP functional cannot be favored against the BLYP one because the BLYP results sometimes get closer to the MP2 values than those of B3LYP. From the results—including the available literature data—we suggest that one has to use at least polarized-valence triple-zeta-quality basis sets (TZV, 6-311G) for the investigation of hydrogen-bonded complexes. Special attention must be paid to the physical nature of the binding. If the dispersion forces become significant DFT methods are not able to describe the interaction. Proper correction for the basis set superposition error is found to be mandatory in all cases.   © 1998 John Wiley & Sons, Inc.   J Comput Chem 19: 575–584, 1998

Keywords: Boys–Bernardi scheme; chemical Hamiltonian approach; hydrogen bond

Introduction

Density functional theory[1] (DFT) has become one of the most popular quantum chemical models in the last few years. For the investigation

Correspondence to: B. Paizs (permanent address), Central Research Institute of Chemistry, Hungarian Academy of Sciences, P.O. Box 17, 1525 Budapest, Hungary

of the electronic structure of ground state molecules DFT offers a less expensive alternative than the conventional correlation methods (MPn, CC). The accuracy of DFT applying gradient-corrected functionals is about the same as that of MP2.[1] There are some cases in which DFT works well, whereas the standard wave-function-based quantum chemistry can predict meaningful results only by using the most sophisticated methods available.[1b,2] However, in some cases (reactions

involving hydrogen atoms[3]), DFT fails to predict reaction barriers. Considering these facts, one should handle DFT as a method that ought to be applied by paying special attention to the problem under investigation, keeping in mind the limits of the model. These limits are now well known for intramolecular problems.[1] This is not the case, however, if one deals with intermolecular complexes.

By investigating molecular complexes we have to face the problem of basis set superposition error (BSSE). Because one cannot use saturated basis sets in practical computations, the description of internal monomer properties depends on the quality and location of the basis functions of the partner molecule(s). Due to BSSE, the computed interaction energies become too high and the predicted potential energy surfaces are distorted.

The most popular method for correction of BSSE is the *a posteriori* Boys−Bernardi[4] (BB) scheme. Using the BB scheme one must recalculate the monomers in the basis of the whole complex for every geometrical arrangement. The change of internal monomer geometry (''geometry relaxation'') constitutes a special difficulty.[5] There has been a continuous debate about this method in the literature during the last decades.[6] It is now widely accepted that one must correct for BSSE and *adequate*[7] basis sets have to be applied to avoid the overcompensation nature of the BB method.

A conceptually different way to handle BSSE is the application of the ''chemical Hamiltonian approach'' (CHA)[8] for the case of intermolecular complexes.[9−14, 19] CHA eliminates the nonphysical terms of the Hamiltonian that cause BSSE, thus representing an *a priori* BSSE correction method. In contrast to the BB scheme, in the CHA framework it is possible:

- to determine relaxed molecular geometries[15, 16] using gradient techniques; and
- to calculate BSSE-free one-electron properties (dipole moments, Mulliken population analyses, intermolecular bond orders).[17] (BSSE-free calculation of the one-electron properties can be very important; e.g., in the case of the ammonia dimer where the energetic order of the possible conformers and the calculated dipole moments are dependent on how the BSSE is handled.[18])

The CHA is now available at the SCF,[11, 12, 19] DFT,[13, 19] and full CI[14] levels of theory. Our present SCF and DFT implementation[19] is suitable for

investigation of complexes consisting of an arbitrary number of monomers. Because we have built our CHA code into the GAUSSIAN-92/DFT[32] program system without destroying its overall structure, one can easily obtain BSSE-free one-electron properties for intermolecular complexes.

In the last few years, a few attempts have been made[20−31] to explore the limits of DFT in the intermolecular framework. The most important observations were made by Kristyán and Pulay[23] and Pérez-Jordá and Becke[24] who demonstrated that available DFT functionals cannot describe true correlation effects like the London dispersion forces. Moreover, because one has to apply numerical integration in the DFT methods, the inadequate grid assignment in the ghost calculations can lead to a grid superposition error, which was shown to be significant in the case of rare gas complexes.[23] Other studies have been devoted to investigate charge-transfer[26] and hydrogen-bonded complexes[20−22, 25, 27, 28, 30] and hydrogen-bonded crystals.[29, 31] Although it is clear that available exchange and correlation functionals are not able to describe charge-transfer interactions in an appropriate manner,[26] there are contradictory opinions concerning the hydrogen-bonded systems.[25, 27] The most important conclusions adopted by almost all investigators include: that there is a need for at least triple-zeta-quality basis sets and BSSE correction, and also that BSSE correction can get rather large for MP2 calculations when flexible but still unsaturated basis sets are used.

In the present article, we extend the systematic BSSE investigations of ref. 12 to the case of correlation methods. In ref. 12, the potential energy curves for four hydrogen-bonded complexes (H_2O—HF, H_2O—H_2O, H_2O—H_2S, H_2S—H_2S) were determined using nine different basis sets at the SCF level of theory. In the present study we use the same systems, geometries, and basis sets, and calculate the potential energy curves at the MP2, MP2-BB, DFT(BLYP), DFT(B3LYP), DFT(BLYP)-BB, DFT(B3LYP)-BB, CHA/F-DFT(BLYP), and CHA/F-DFT(B3LYP) (CHA applied to the Kohn−Sham Fockian) levels of theory to compare the behavior of the uncorrected and (*a posteriori* and *a priori*) corrected models, respectively. [The notation DFT(BLYP) and DFT(B3LYP) is used throughout the article to make the applied particular approximation of the exact exchange-correlation functional unambiguous.] Beyond the comparison of the BB and CHA correction methods, the aim of this study is to check the generally adopted conclusions listed above from a CHA point of

view. Because there are strong (H_2O—HF) and weak (H_2S—H_2S) hydrogen-bonded complexes among our investigated systems, it is possible to draw some conclusions about the behavior of DFT and MP2 methods in the framework of hydrogen-bonded complexes.

Computational Details

All computations were carried out using the GAUSSIAN-92[32] and GAUSSIAN-94[33] program systems. For the CHA/F calculations we used our modified version of GAUSSIAN-92. (Details of the implementation are described in ref. 19.) The geometries are the same as those used in ref. 12. (We did not attempt to find the most recent experimental values. Our aim was only to examine the behavior of the corrected and uncorrected MP2 and DFT methods.) The intermolecular distances (e.g., the oxygen–hydrogen distance in the case of the H_2O—HF complex) have been varied over a wide range using a grid that was more dense around the minimum. The internal structures of the monomers have been kept fixed. (The actual atomic coordinates are given in the captions of the respective figures.)

In the calculations we used Pople's 6-31G and Dunning's valence-double-zeta (DZV) and valence-triple-zeta (TZV) basis sets. The 6-31G basis for all atoms and the DZV basis for the hydrogen, oxygen, and fluorine atoms are internally stored in the GAUSSIAN program systems. The TZV basis for all atoms and the DZV basis for sulfur were taken from the HONDO program system.[34] [The exponents of the polarization functions were: H: 6-31G—1.1(p-orbitals), DZV—1.0(p), TZV—1.0(p); O: 6-31G—0.8(6d-orbitals), DZV—0.85(6d), TZV—1.28(6d); F: 6-31G—0.8(6d), DZV—0.9(6d), TZV—1.62(6d); S: 6-31G—0.65(6d), DZV—0.6(6d), TZV—0.542(6d). The diffuse functions had the following exponents: H: 0.036(s-orbitals); O: 0.0845 (sp-orbitals); F:0.1046(sp); S:0.0405(sp).]

In the DFT calculations we restricted ourselves to the use of the BLYP (Becke exchange[35] and Lee, Yang, Parr correlation[36]) and B3LYP (Becke's three-parameter exchange[37] and Lee, Yang, Parr correlation[36]) potentials only, because previous DFT[20, 22, 27] studies clarified that one has to apply gradient correction in both the exchange and the correlation part of the potential to get meaningful results in the intermolecular framework. Throughout the calculations, the (50, 194) grid (50 radial shells, 194 angular points per shell) was used (keyword: scf = tight).

To save space and to avoid the presentation of many similar figures we only show the TZV, TZV**, and TZV + + ** potential curves of the systems investigated (Figs. 1–4). However, we report minimum interaction energies for the case of all investigated basis sets and hydrogen-bonded complexes (Tables I–IV). Because the B3LYP and BLYP interaction energies usually do not fall far
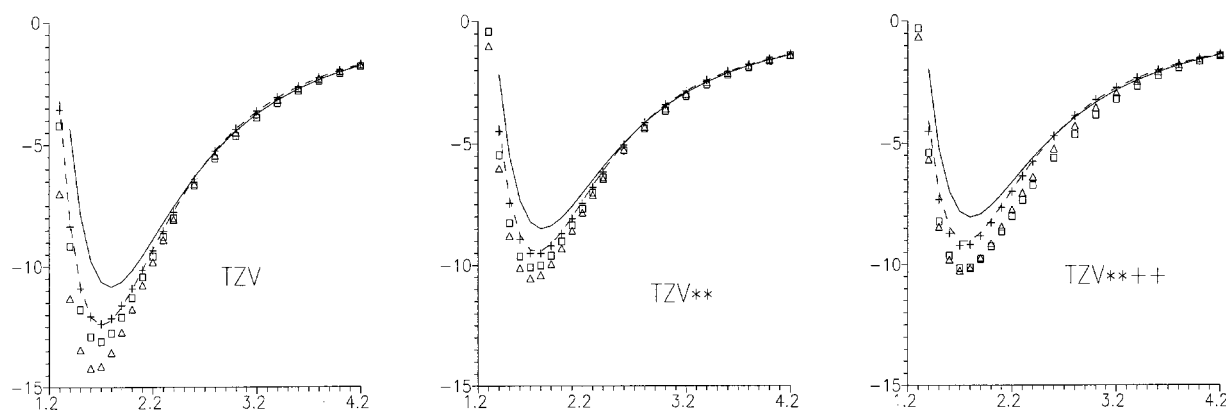
Interaction energy (kcal/mol)

FIGURE 1. Potential curves of the H_2O—HF system calculated in the TZV, TZV**, and TZV + + ** basis sets. The coordinates of the atoms (Å) are as follows: H_A (−0.58268, 0.06124, 0.75669); H_A (−0.58268, 0.06124, −0.75669); O_A (0, 0, 0); H_B (R, 0, 0); and F_B (R + 0.9171, 0, 0). R is the distance between the oxygen and the hydrogen-bonded hydrogen atoms. The curves: squares—MP2; solid line—MP2-BB; triangles—DFT(B3LYP); dashed line—DFT(B3LYP)-BB; crosses—CHA/F-DFT(B3LYP).
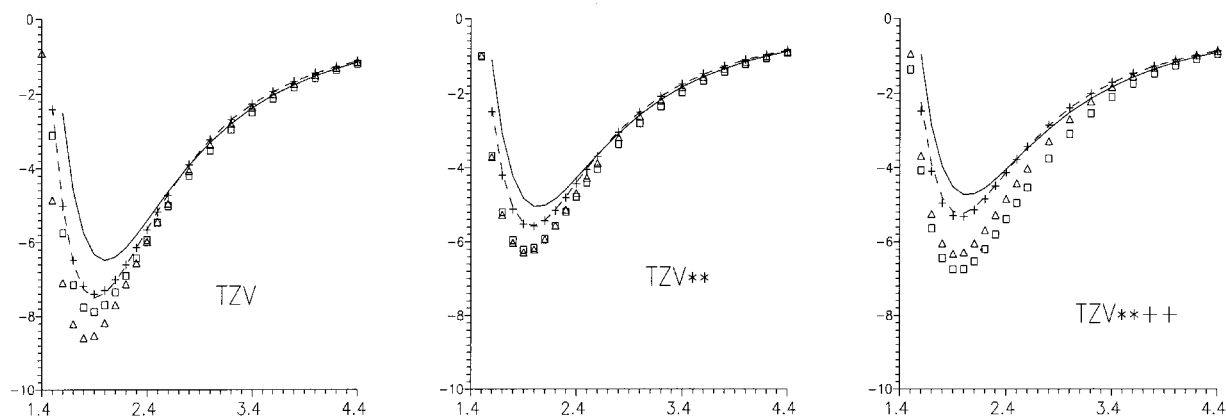
Interaction energy (kcal/mol)

FIGURE 2. Potential curves of the H_2O—H_2O system calculated in the TZV, TZV**, and TZV + +** basis sets. The coordinates of the atoms (Å) are as follows: H_A ($-0.46791, 0.3526, 0.75669$); H_A ($-0.46791, 0.3526, -0.75669$); O_A $(0, 0, 0)$; H_B $(R, 0, 0)$; O_B $(R + 0.957, 0, 0)$; and H_B $(R + 1.1966, -0.9265, 0)$. R is the distance between the oxygen and hydrogen-bonded hydrogen atoms. The curves: squares—MP2; solid line—MP2-BB; triangles—DFT(B3LYP); dashed line—DFT(B3LYP)-BB; crosses—CHA / F-DFT(B3LYP).

from each other, only the curves determined by using the B3LYP functional are presented.

Comparison of *a Posteriori* (BB) and *a Priori* (CHA) BSSE Corrections at DFT Level of Theory

Except for a few cases, the CHA/F-DFT and DFT-BB interaction energies were very close to each other, independent of whether the BLYP or B3LYP functional was used (Tables I–IV, Figs. 1–4). Similar to the observations in ref. 12, the largest differences could be found in the case of the 6-31G and DZV basis sets. In these cases, the CHA interaction energies fell between the BB-corrected and the uncorrected DFT values in agreement with the well-known fact that, when using small basis sets, the BB scheme tends to overcompensate[40] the BSSE. By comparing the *a priori-* and
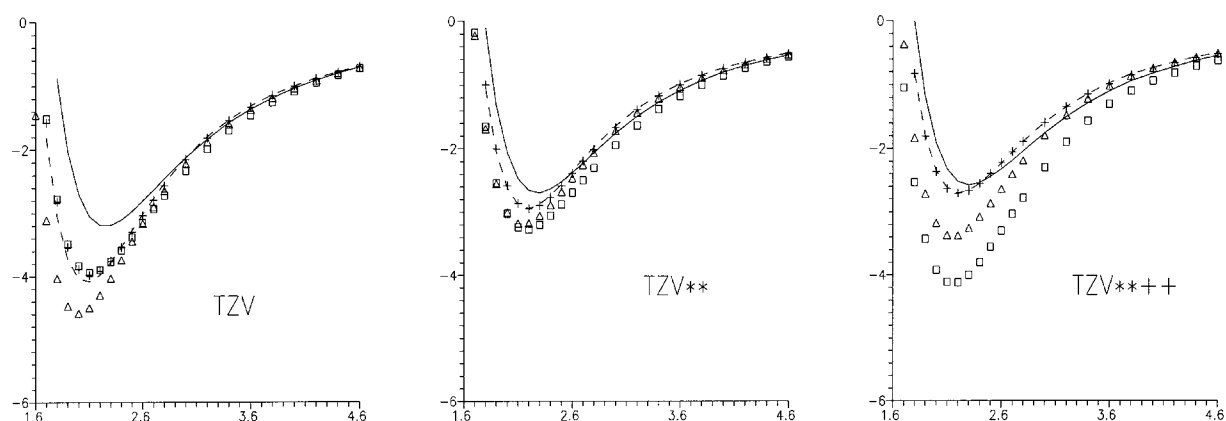
Interaction energy (kcal/mol)

FIGURE 3. Potential curves of the H_2O—H_2S system calculated in the TZV, TZV**, and TZV + +** basis sets. The coordinates of the atoms (Å) are as follows: H_A ($-0.54323, 0.21948, 0.75669$); H_A ($-0.54323, 0.21948, -0.75669$); O_A $(0, 0, 0)$; H_B $(R, 0, 0)$; S_B $(R + 1.32829, 0, 0)$; and H_B $(R + 1.37928, -1.32731, 0)$. R is the distance between the oxygen and hydrogen-bonded hydrogen atoms. The curves: squares—MP2; solid line—MP2-BB; triangles—DFT(B3LYP); dashed line—DFT(B3LYP)-BB; crosses—CHA / F-DFT(B3LYP).
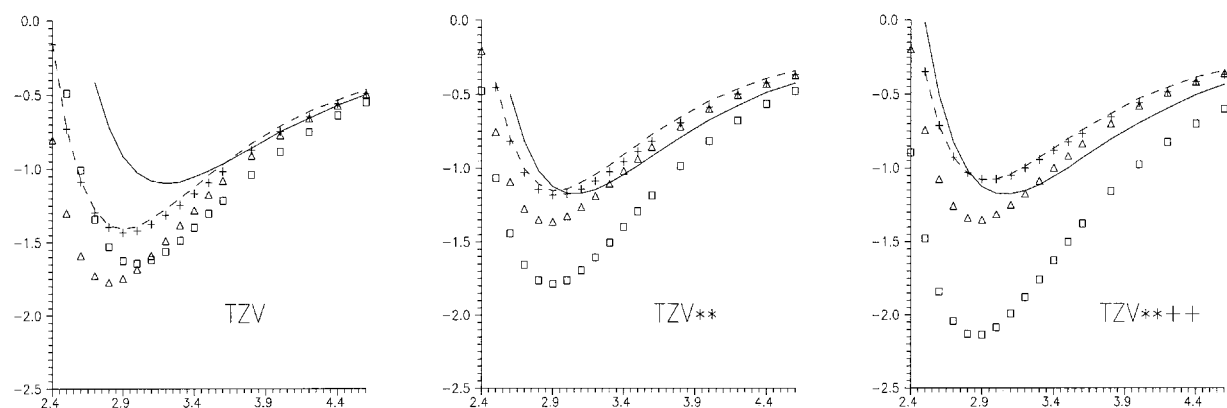
Interaction energy (kcal/mol)

FIGURE 4. Potential curves of the H_2S—H_2S system calculated in the TZV, TZV**, and TZV + +** basis sets. The coordinates of the atoms (Å) are as follows: H_A (−0.26929, 0.88079, 0.9571); H_A (−0.26929, 0.88079, −0.9571); S_A (0, 0, 0); H_B (R, 0, 0); S_B (R + 1.32829, 0, 0); and H_B (R + 1.37928, −1.32731, 0). R is the distance between the sulfur and hydrogen-bonded hydrogen atoms. The curves: squares — MP2; solid line — MP2-BB; triangles — DFT(B3LYP); dashed line—DFT(B3LYP)-BB; crosses—CHA / F-DFT(B3LYP).

TABLE I.
Minimum Interaction Energies (Kilocalories per Mole) of the H_2O—HF Potential Curves Calculated in Nine Different Basis Sets at Uncorrected and Corrected MP2 and DFT Levels of Theory.

	MP2	MP2-BB	DFT(BLYP)	DFT(BLYP)-BB	CHA / F-DFT(BLYP)	DFT(B3LYP)	DFT(B3LYP)-BB	CHA / F-DFT(B3LYP)
6-31G	− 12.6	− 11.1	− 13.4	− 11.5	− 12.2	− 14.1	− 12.5	− 13.1
6-31G**	− 9.8	− 8.1	− 9.5	− 7.8	− 8.5	− 10.0	− 8.6	− 9.2
6-31 + + G**	− 9.6	− 7.8	− 8.7	− 7.8	− 8.0	− 9.5	− 8.5	− 8.7
DZV	− 13.2	− 11.5	− 14.2	− 12.8	− 13.0	− 14.8	− 13.6	− 13.6
DZV**	− 10.0	− 8.6	− 9.9	− 8.8	− 9.2	− 10.4	− 9.5	− 9.7
DZV + + **	− 9.7	− 7.8	− 8.8	− 8.0	− 8.2	− 9.6	− 8.7	− 8.9
TZV	− 13.1	− 10.9	− 13.4	− 11.5	− 11.5	− 14.2	− 12.4	− 12.4
TZV**	− 10.1	− 8.5	− 9.9	− 8.7	− 8.8	− 10.5	− 9.4	− 9.5
TZV + + **	− 10.2	− 8.0	− 9.5	− 8.3	− 8.4	− 10.2	− 9.0	− 9.2

TABLE II.
Minimum Interaction Energies (Kilocalories per Mole) of H_2O—H_2O Potential Curves Calculated in Nine Different Basis Sets at Uncorrected and Corrected MP2 and DFT Levels of Theory.

	MP2	MP2-BB	DFT(BLYP)	DFT(BLYP)-BB	CHA / F-DFT(BLYP)	DFT(B3LYP)	DFT(B3LYP)-BB	CHA / F-DFT(B3LYP)
6-13G	− 8.1	− 6.5	− 8.8	− 7.0	− 7.7	− 9.2	− 7.7	− 8.2
6-31G**	− 6.5	− 5.0	− 6.5	− 4.8	− 5.3	− 6.7	− 5.3	− 5.7
6-31 + + G**	− 6.3	− 4.8	− 5.3	− 4.5	− 4.5	− 5.8	− 5.0	− 5.1
DZV	− 8.2	− 6.7	− 8.7	− 7.4	− 7.7	− 9.0	− 8.0	− 8.1
DZV**	− 6.1	− 5.0	− 6.0	− 5.1	− 5.3	− 6.3	− 5.5	− 5.7
DZV + + **	− 6.3	− 4.6	− 5.3	− 4.5	− 4.6	− 5.7	− 5.0	− 5.1
TZV	− 7.9	− 6.5	− 8.0	− 6.8	− 6.8	− 8.6	− 7.5	− 7.4
TZV**	− 6.2	− 5.0	− 5.9	− 5.1	− 5.1	− 6.3	− 5.6	− 5.6
TZV + + **	− 6.8	− 4.7	− 5.8	− 4.7	− 4.8	− 6.3	− 5.2	− 5.3

TABLE III.

Minimum Interaction Energies (Kilocalories per Mole) of H₂O—H₂S Potential Curves Calculated in Nine Different Basis Sets at Uncorrected and Corrected MP2 and DFT Levels of Theory.

OS	MP2	MP2-BB	DFT(BLYP)	DFT(BLYP)-BB	CHA/F-DFT(BLYP)	DFT(B3LYP)	DFT(B3LYP)-BB	CHA/F-DFT(B3LYP)
6-31G	−4.6	−3.4	−5.5	−4.1	−4.7	−5.7	−4.5	−5.1
6-31G**	−3.9	−2.6	−4.0	−2.8	−3.1	−4.1	−3.0	−3.4
6-31 + +G**	−4.0	−2.6	−2.8	−2.3	−2.3	−3.2	−2.6	−2.7
DZV	−4.1	−3.0	−4.3	−3.6	−3.8	−4.6	−4.0	−4.3
DZV**	−3.1	−2.4	−2.9	−2.4	−2.6	−3.1	−2.7	−2.9
DZV + +**	−3.7	−2.5	−2.6	−2.1	−2.2	−2.9	−2.5	−2.6
TZV	−4.0	−3.2	−4.1	−3.6	−3.5	−4.6	−4.1	−4.0
TZV**	−3.3	−2.7	−2.9	−2.6	−2.6	−3.2	−2.9	−2.9
TZV + +**	−4.1	−2.6	−3.0	−2.3	−2.3	−3.4	−2.7	−2.7

a posteriori-corrected interaction energies one can therefore determine whether the quality of the applied basis set is good enough to avoid over-compensation of the BB method. In the H_2O—HF, H_2O—H_2O, and H_2O—H_2S complexes (Tables I–III), the differences between the corrected DFT interaction energies were smaller using the DZV basis sets than in the case of the 6-31G basis. In the case of the weakest H_2S—H_2S complex (Table IV), the difference between the BB- and CHA-corrected interaction energies was surprisingly large using the DZV basis with or without polarization functions. However, the same effect was also observed at the SCF level.[12] It must be emphasized that the TZV basis set, even without polarization functions, provided very small differences between the *a priori-* and *a posteriori*-corrected DFT models throughout the calculations, regardless of the system investigated. This is probably the smallest

basis set that can be safely applied for the investigation of hydrogen-bonded complexes by using correlation methods.

Comparison of Corrected and Uncorrected MP2 and DFT Interaction Energies

In the ideal case, if DFT were to behave similarly to the intramolecular framework, we would have two groups of curves, one consisting of the uncorrected MP2 and DFT curves and the other consisting of the corrected MP2-BB, DFT-BB, and CHA/F-DFT curves, respectively. In both of these groups, the individual curves would be close to each other. However, this is not always the case. In the following we examine which effects are responsible for the deviation from the ideal case.

TABLE IV.

Minimum Interaction Energies (Kilocalories per Mole) of H₂S—H₂S Potential Curves Calculated in Nine Different Basis Sets at Uncorrected and Corrected MP2 and DFT Levels of Theory.

SS	MP2	MP2-BB	DFT(BLYP)	DFT(BLYP)-BB	CHA/F-DFT(BLYP)	DFT(B3LYP)	DFT(B3LYP)-BB	CHA/F-DFT(B3LYP)
6-31G	−1.59	−1.18	−1.64	−1.39	−1.40	−1.82	−1.54	−1.60
6-31G**	−1.68	−1.14	−1.32	−1.12	−1.14	−1.44	−1.24	−1.32
6-31 + +G**	−2.03	−1.15	−1.20	−1.02	−0.97	−1.39	−1.17	−1.20
DZV	−1.47	−1.07	−1.73	−1.32	−1.52	−1.83	−1.47	−1.69
DZV**	−1.66	−1.15	−1.51	−1.08	−1.31	−1.56	−1.20	−1.45
DZV + +**	−1.72	−1.17	−1.12	−0.97	−0.97	−1.28	−1.12	−1.17
TZV	−1.64	−1.10	−1.60	−1.26	−1.25	−1.77	−1.41	−1.43
TZV**	−1.78	−1.17	−1.21	−0.99	−1.00	−1.36	−1.15	−1.18
TZV + +**	−2.13	−1.17	−1.17	−0.90	−0.88	−1.35	−1.08	−1.07

Examining our results in Tables I–IV one can conclude that there is no large difference among the behavior of the 6-31G, DZV, and TZV basis set families with respect to the deviations from the ''ideal case'' just described. The only conclusion that can be drawn is that the scatter of the interaction energies for a given complex is always smallest in the case of the TZV basis set family.

However, rather significant deviations can be connected to the nature of the chemical system investigated. Among the calculated hydrogen-bonded complexes, one can find models with both strong (H_2O—HF) (Fig. 1 and Table I) and weak (H_2S—H_2S) (Fig. 4 and Table IV) interactions. In the latter case, the hydrogen bond is so weak that the dispersion forces become significant.

In the case of the strong hydrogen-bonded complexes (H_2O—HF, H_2O—H_2O) (Figs. 1 and 2, Tables I and II), the uncorrected MP2 and DFT curves are relatively close to each other and show almost the same behavior, independent of whether the BLYP or B3LYP potential is used. As the interaction becomes weaker the distance between the DFT and MP2 curves increases, reaching the maximum deviation in the case of the H_2S—H_2S complex (Fig. 4 and Table IV) where the uncorrected DFT curve comes close to the corrected MP2-BB curve. At the same time, the uncorrected MP2 model predicts interaction energies that are much larger than the ones calculated using the other methods. Comparing the behavior of the BLYP and B3LYP potentials the most striking fact is that there are some cases where the BLYP results are closer to MP2 values than the B3LYP values. For example, in the case of the H_2O—HF and H_2O—H_2O complexes and 6-31G**, DZV**, and TZV** basis sets, the differences between the uncorrected BLYP and MP2 interaction energies are small, whereas the respective B3LYP results are farther from the MP2 values than those of BLYP.

The same behavior of the BLYP, B3LYP, and MP2 methods can sometimes also be observed in the BSSE-free case (H_2O—HF complex: 6-31G**, DZV**, TZV**, 6-31G + + **, DZV + + **, and TZV + + ** basis sets). This means that, when using relatively small basis sets, the B3LYP potential cannot be favored unambiguously against the BLYP one in the calculation of intermolecular complexes. This interesting behavior of the BLYP and B3LYP models can be referred to from the calculations of Hobza et al.[28] on the hydrogen-fluoride and water dimers using small and moderate size basis sets and BLYP and B3LYP potentials. They calculated the equilibrium geometries of the complexes just indicated, and their BLYP intermolecular distances are generally closer to the MP2 results than those of B3LYP. However, using high-quality basis sets, Novoa et al.[27] and Kim et al.[22] found that the B3LYP intermolecular parameters were rather close to the MP2 parameters.

The differences between the behavior of the MP2 and DFT models can be rationalized by examining BSSE as a function of an applied basis set. Let us calculate the BSSE content of the interaction energy (the geometry and the theoretical model being given) with several basis sets. In principle, one expects a curve exhibiting a maximum by putting the quality of the basis sets on the abscissa and the BSSE content of the interaction energy on the ordinate. The flexibility of a small basis set is insufficient for the appearance of a significant BSSE-type correlation energy contribution. With the growing size of the basis set such contributions appear and the BSSE content increases. Using even larger basis sets, the BSSE content will again decrease, as we get closer to the saturated basis. Comparing our results from the point of view of such a BSSE content curve, the DFT and MP2 methods behave in a different manner (Table V). Our DFT calculations can generally be placed near

TABLE V.
BSSE Content (in Percentage) of MP2 and B3LYP Minimum Interaction Energies of Investigated Complexes by Using TZV, TZV, and TZV $+ +$ ** Basis Sets.[a]**

	H_2O—HF		H_2O—H_2O		H_2O—H_2S		H_2S—H_2S	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
TZV	18.7	15.0	19.8	16.8	22.2	15.0	37.2	21.3
TZV**	18.6	10.1	22.2	12.0	19.2	8.8	37.0	13.4
TZV $+ +$ **	23.4	9.8	33.3	16.8	39.4	20.4	47.3	20.5

[a]In the MP2 calculations the MP2-BB method was used to evaluate the BSSE content of the MP2 interaction energy. The BSSE content of the B3LYP interaction energy was determined as the difference between the uncorrected and BSSE-free (CHA / F) B3LYP interaction energies.

the maximum part of this curve, whereas the MP2 results are clearly situated in the premaximum interval. In this respect, the behavior of the DFT method is closer to that of the SCF than to MP2. This difference is not significant in the case of strong hydrogen bonds dominated by electrostatic effects, where the DFT and MP2 curves are close to each other, but it becomes rather large in the case of weak hydrogen bonds for which dispersion is important.

At first sight the underlying reason for the different behavior of the DFT and MP2 models is that, in the traditional methods, the basis set describes the electron–electron cusp, whereas in DFT only the density has to be described. However, if only this effect was responsible for the different behavior of the DFT and MP2 models we would not observe any difference regarding the strength of the complexes investigated. A more elaborate explanation can be put forward if one takes into account that the DFT and the MP2 models do not approach the correlation problem in the same manner. DFT as a local model cannot describe true correlation effects like the London dispersion forces with the available functionals. However, dispersion is important in the binding of weak hydrogen-bonded complexes as it can be seen from the behavior of the MP2 model.

It should also be mentioned that the large MP2 energy lowering, which can be observed in the case of the $H_2O—H_2S$ (Fig. 3 and Table III) complex, is mostly due to BSSE. This can be seen extremely clearly in the case of the $H_2S—H_2S$ (Fig. 4 and Table IV) complex, where polarized basis sets were used with or without diffuse functions. Therefore, one has to be very careful using either MP2 or DFT for the investigation of systems with weak hydrogen bonds: DFT fails to describe the true physical situation—perhaps the level of correlation included in MP2 is also insufficient. MP2 behaves as a classical correlation method that can get close to the saturated state by using only extremely large basis sets. The corrected DFT and MP2 curves are much closer to each other than the uncorrected ones indicating the importance of the BSSE correction.

It is to be noted that our calculated interaction energies can be compared with experimental data in the case of the $H_2O—HF$[41] and $H_2O—H_2O$[42] complexes. In the first case, the difference between the experimental (-8.4 kcal/mol) and the computed interaction energy is the smallest if one uses the CHA/F-DFT(BLYP)/TZV $+ +$** theoretical model (-8.4 kcal/mol, Table I). However, it must

be noted that the TZV $+ +$** basis set cannot be considered saturated even in the case of DFT methods. It means that further extension of the basis sets can dramatically change this situation, getting the MP2 energies closer to and the DFT interaction energies farther from the experimental results. Similar conclusions can be drawn from the comparison of experimental (-5.4 kcal/mol) and calculated interaction energies in the case of the $H_2O—H_2O$ complex. The only difference is that the best theoretical result (-5.3 kcal/mol, Table II) is predicted by the CHA/F-DFT(B3LYP)/TZV $+ +$** level of theory.

Comparison of Results with Literature Data

At this point, we compare our results with the calculations available from the literature. One finds contrasting opinions regarding the applicability of DFT methods for the investigation of hydrogen-bonded intermolecular complexes. Del Bene et al.[25] calculated binding energies, intermolecular distances, and X—H vibrational frequency shifts for eight hydrogen-bonded complexes and compared the DFT results with MP2 and experimental values. They used Pople's 6-31G(d,p) and 6-31 + G(d,p) basis sets and the B3LYP functional. Their calculated binding energies (uncorrected for BSSE) were generally close to the experimental values (if the latter are available). The only exceptions were the $H_2O—H_2O$ and HF—HF complexes for which they could not find the experimental "open" structures using the B3LYP/6-31G(d,p) model.* Serious discrepancies appeared when they compared the DFT, MP2, and experimental intermolecular distances and, especially, the X—H frequency shifts. The B3LYP/6-31G(d,p) values were far from the experimental values. The B3LYP/6-31G + (d,p) and MP2/6-31G + (d,p) results were usually close to each other, but "in those cases where noticeable differences exist between computed B3LYP/6-31G + (d,p) and MP2/6-31G + (d,p) results the MP2/6-31G + (d,p) values are in better agreement with experimental data." On the basis of these findings, Del Bene et al.[25] suggested not to use the

---

* It must be mentioned that the experimental open structure for the water dimer recovered at the B3LYP/6-31G(d,p) level of theory has been reported by Barone et al.[38] Hobza et al.[28] also reported B3LYP/6-31G(d,p) calculations on the water dimer. They were able to find the experimental open structure that corresponds to a first-order saddle point on the potential energy surface.

B3LYP/6-31G(d,p) model for the calculation of hydrogen-bonded complexes and stressed the importance of further refinement of present functionals.

Examining our curves one can observe that the differences between the DFT(B3LYP) and MP2 potential energy surfaces are not very large if one uses the polarized basis sets with or without diffuse functions in the cases of the H_2O—H_2O (Fig. 2 and Table II) and HF—HF (Fig. 1 and Table I) complexes. However, the remaining differences between them are large enough to cause slight deviations in the computed interatomic distances. The accurate determination of the X—H frequency shifts by theoretical methods is a rather complicated problem. The experimental results can be reproduced only by using the most sophisticated models and highest quality basis sets available (see, e.g., a recent study on the water dimer[39]). Therefore, it is not surprising that there are, in some cases, large differences between the computed B3LYP/6-31G + (d,p) and MP2/6-31G + (d,p) X—H frequency shifts. Moreover, it is rather surprising that the computed MP2/6-31G + (d,p) interaction energies, intermolecular distances, and X—H frequency shifts are in such good agreement with the experimental data despite the fact that the BSSE content of this model is not negligible. It is likely that the various errors cancel each other in the MP2/6-31G + (d,p) calculations.

There are several further studies in the literature that report more or less successful investigations on hydrogen-bonded complexes using DFT methods.[20, 22, 27, 28, 30] In what follows, we compare our calculations with the examples given by Novoa and Sosa[27] where equilibrium geometries and interaction energies were reported for the hydrogen-fluoride, water, and ammonia dimers as well as C_2H_2—H_2O and CH_4—H_2O complexes at the DFT (including the BLYP and B3LYP potentials), MP2, MP3, and MP4 levels of theory, respectively. The geometries were determined using Pople's 6-31 + +G(2d,2p) basis set (in the case of the MP3 and MP4 methods the MP2 geometries were used), whereas the uncorrected and BB-corrected interaction energies were calculated using those just indicated and Dunning's correlation-consistent polarized-valence double-zeta (cc-pVDZ) and augmented correlation-consistent polarized-valence triple-zeta (aug-cc-pVTZ) basis sets.

Their investigated complexes can be divided into three groups. The HF and water dimer are examples of strong hydrogen-bonded complexes, and the ammonia dimer and C_2H_2—H_2O are moderately bound ones. The CH_4—H_2O complex is one of the weakest hydrogen-bonded systems, and the effect of dispersion forces in the binding is significant. Comparing the strength of these complexes to the ones presented in our calculations, the HF dimer is about as strong as the water dimer, the ammonia dimer is stronger than the H_2O—H_2S and H_2S—H_2S dimers, and CH_4—H_2O is the weakest among the systems discussed. (One must mention that the following conclusions were drawn by us, and Novoa and Sosa[27] interpreted their results as an overall success of DFT.) In the first two groups, the BSSE content of the interaction energy was about 40% and 10% using the cc-pVDZ or 6-31 + +G(2d,2p) and aug-cc-pVTZ basis sets, respectively. Generally, the DFT results, especially the B3LYP values, were close to the MPn values. Using the 6-31 + +G(2d,2p) and aug-cc-pVTZ basis sets, the BSSE content of the interaction energy was smaller in the case of the DFT methods than in the case of MPn. Considering the CH_4—H_2O complex, the MPn and DFT methods behaved in a completely different manner. A large part of the uncorrected interaction energy was due to the BSSE, but the attractive nature of the intermolecular potential was described by MPn. On the other hand, the corrected DFT methods predicted a repulsive potential and the dispersion forces were so significant that DFT failed to account for the physics of the interaction.

Conclusions

In the systems investigated, the *a priori-* and *a posteriori-*corrected DFT intermolecular potential curves are generally close to each other. From the point of view of the basis sets we can suggest the use of at least valence triple-zeta-quality basis sets (TZV, 6-311G) augmented by diffuse functions in the DFT studies of hydrogen-bonded complexes. Using small basis sets, the B3LYP functional cannot be favored against the BLYP one, because, by using the latter, one can get results that are closer to the MP2 values than the B3LYP values. From the point of view of the systems investigated, strong and moderate hydrogen-bonded systems can be well described by using DFT, whereas weak systems must be treated with care, keeping in mind that, as the dispersion forces become significant, DFT fails to give a correct description. Correction for BSSE seems mandatory in all cases.

References

1. (a) T. Ziegler, *Chem. Rev.*, **91**, 651 (1991); (b) J. K. Laba-nowski and J. Andzelm, Eds., *Density Functional Methods in Chemistry*, Springer, New York, 1991; (c) B. G. Johnson, P. M. W. Gill, and J. A. Pople, *J. Chem. Phys.*, **98**, 5612 (1993); (d) N. C. Handy, C. W. Murray, and R. D. Amos, *J. Phys. Chem.*, **97**, 4392 (1993); (e) J. Andzelm and E. Wimmer, *J. Chem. Phys.*, **96**, 1280 (1992); (f) A. St-Amant and D. R. Salahub, *Chem. Phys. Lett.*, **169**, 387 (1990).

2. (a) L. Fan and T. Ziegler, *J. Chem. Phys.*, **98**, 8004 (1993); (b) L. Fan and T. Ziegler, *J. Am. Chem. Soc.*, **114**, 10890 (1992); (c) P. M. Kozlowski, G. Rauhut, and P. Pulay, *J. Chem. Phys.*, **103**, 5650 (1995).

3. B. G. Johnson, C. A. Gonzalez, P. M. W. Gill, and J. A. Pople, *Chem. Phys. Lett.*, **221**, 100 (1994).

4. (a) H. B. Jansen and P. Ross, *Chem. Phys. Lett.*, **3**, 140 (1969); (b) S. B. Boys and F. Bernardi, *Mol. Phys.*, **19**, 553 (1970).

5. I. Mayer and P. R. Surján, *Chem. Phys. Lett.*, **191**, 497 (1992).

6. (a) J. H. van Lenthe, J. G. C. M. van Duijneveldt-van de Rijdt, and F. B. van Duijneveldt, *Adv. Chem. Phys.*, **69**, 521 (1987); (b) P. Hobza and R. Zahradnik, *Chem. Rev.*, **88**, 871 (1988).

7. (a) F. M. Tao and Y. K. Pan, *J. Phys. Chem.*, **95**, 3582 (1991); (b) M. Gutowski, J. G. C. M. van Duijneveldt-van de Rijdt, J. H. van Lenthe, and F. B. van Duijneveldt, *J. Chem. Phys.*, **98**, 4728 (1993).

8. (a) I. Mayer, *Int. J. Quantum Chem.*, **23**, 341 (1983); (b) I. Mayer, In *Modelling of Structure and Properties of Molecules*, Z. B. Maksic, Ed., Ellis Horwood, Chichester, UK, 1987, p. 145.

9. I. Mayer and Á. Vibók, *Chem. Phys. Lett.*, **140,** 558 (1987).

10. I. Mayer and P. R. Surján, *Int. J. Quantum Chem.*, **36**, 225 (1989).

11. I. Mayer, P. R. Surján, and Á. Vibók, *Int. J. Quantum Chem.* (*Quantum Chem. Symp.*), **23**, 281 (1989).

12. P. Valiron, Á. Vibók, and I. Mayer, *J. Comput. Chem.*, **14**, 401 (1993).

13. M. Kieninger, S. Suhai, and I. Mayer, *Chem. Phys. Lett.*, **230**, 485 (1994).

14. I. Mayer, Á. Vibók, and P. Valiron, *Chem. Phys. Lett.*, **224**, 166 (1994).

15. B. Paizs and I. Mayer, *Chem. Phys. Lett.*, **220**, 97 (1994).

16. B. Paizs and I. Mayer, manuscript in preparation.

17. B. Paizs and S. Suhai, manuscript submitted for publication.

18. F. M. Tao and W. Klemperer, *J. Chem. Phys.*, **99**, 5976 (1993).

19. B. Paizs and S. Suhai, *J. Comput. Chem.*, **18**, 694 (1997).

20. F. Sim, A. St-Amant, I. Pápai, and D. R. Salahub, *J. Am. Chem. Soc.*, **114**, 4391 (1992).

21. K. Laasonen, M. Parrinello, R. Car, C. Lee, and D. Vander-bilt, *Chem. Phys. Lett.*, **207**, 208 (1993).

22. K. Kim and K. D. Jordan, *J. Phys. Chem.*, **98**, 10089 (1994).

23. S. Kristyán and P. Pulay, *Chem. Phys. Lett.*, **229**, 175 (1994).

24. J. M. Pérez-Jordá and A. D. Becke, *Chem. Phys. Lett.*, **233**, 134 (1995).

25. J. E. Del Bene, W. B. Person, and K. Szczepaniak, *J. Phys. Chem.*, **99**, 10705 (1995).

26. E. Ruiz, D. R. Salahub, and A. Vela, *J. Am. Chem. Soc.*, **117**, 1141 (1995).

27. J. J. Novoa and C. Sosa, *J. Phys. Chem.*, **99**, 15837 (1995).

28. P. Hobza, J. Šponer, and T. Reschel, *J. Comput. Chem.*, **16**, 1315 (1995).

29. S. Suhai, *J. Phys. Chem.*, **99**, 1172 (1995).

30. W.-G. Han and S. Suhai, *J. Phys. Chem.*, **100**, 3942 (1996).

31. S. Suhai, *J. Phys. Chem.*, **100**, 3950 (1996).

32. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Reploge, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, *GAUSSIAN-92*, Gaussian, Inc., Pittsburgh, PA, 1992.

33. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. 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. Challa-combe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Reploge, 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*, Gaussian, Inc., Pittsburgh, PA, 1995.

34. HONDO-8, from MOTECC-91, contributed and docu-mented by M. Dupuis and A. Farazdel, IBM Corporation Center for Scientific and Engineering Computations, Kingston, NY, 1991.

35. A. D. Becke, *Phys. Rev. A*, **38**, 3098 (1988).

36. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, **37**, 785 (1988).

37. A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).

38. V. Barone, L. Orlandini, and C. Adamo, *Chem. Phys. Lett.*, **231**, 295 (1994).

39. O. N. Ventura, K. Irving, and Z. Latajka, *Chem. Phys. Lett.*, **217**, 436 (1994).

40. I. Mayer and L. Túri, *J. Mol. Struct.* (*Theochem*), **227**, 43 (1991).

41. A. C. Legon, D. J. Millen, and H. M. North, *Chem. Phys. Lett.*, **135**, 303 (1987).

42. J. A. Odutola and T. R. Dyke, *J. Chem. Phys.*, **72**, 5062 (1980).