Ab Initio Study of the Ammonia–Ammonia Dimer: BSSE-Free Structures and Intermolecular Harmonic Vibrational Frequencies

A. BENDE,[1,3]* Á. VIBÓK,[1] G. J. HALÁSZ,[2] S. SUHAI[3]

[1]*Debrecen University, Department of Theoretical Physics, H-4010 Debrecen, P.O. Box 5, Hungary*

[2]*University of Debrecen Institute of Mathematics and Informatics, H-4010 Debrecen, P.O. Box 12, Hungary*

[3]*Molecular Biophysics Department, German Cancer Research Center, Im Neuenheimer Feld 280, D-69120 Heidelberg, Germany*

ABSTRACT: The influence of basis set superposition error (BSSE) in optimized geometries, force constants and intermolecular harmonic vibrational frequencies of the ammonia–ammonia dimer have been studied both at the Hartree–Fock and correlated (second-order Møller–Plesset perturbation theory) levels of theory using several different basis sets as (6-31G, 6-311G, 6-31++G, 6-311++G, 6-31G(d,p), 6-311G(d,p), 6-31++G(d,p) 6-311++G(d,p) and 6-311++G(2d,2p)). The widely used a posteriori Boys–Bernardi "counterpoise" (CP) correction scheme has been compared with the a priori method utilizing the chemical Hamiltonian approach (CHA). The results show that practically there is no difference between these two methods, so the a priori CHA scheme can be considered as an ultimate solution of the BSSE problem. It is also concluded that the BSSE influence is very significant, so removing this effect is very important.   © 2004 Wiley Periodicals, Inc. Int J Quantum Chem 99: 585–593, 2004

Key words: basis set superposition error; chemical Hamiltonian approach; harmonic vibrational frequencies; intermolecular interactions

Correspondence to: Á. Vibók; e-mail: vibok@cseles.atomki.hu
Permanent address: National Institute for Research and Development of Isotopic and Molecular Technologies P.O. Box 700, R-3400, Cluj-Napoca, Romania

1. Introduction

Recently a number of different theoretical [1–8] and experimental [9–16] methods have been developed to study the structures of the ammonia–ammonia hydrogen-bonded complex. Considering the experimental data, it has been generally accepted that the ammonia dimer may have a linear hydrogen-bonded structure, but in 1985 Nelson et al. [11] gave strong evidence for a cyclic rather than linear structure by microwave study. On the other hand, the theoretical studies showed that one can find stationary points on the NH_3–NH_3 with two C_s and C_{2h} symmetries [4], respectively. In 1994 Olthof et al. [12] proposed a new potential with parameters for ammonia dimer by calculating the six-dimensional vibration–rotation–tunneling states, which were constructed from previous ab initio results and also were adjusted to reproduce the interchange splittings in the far-infrared (FIR) spectrum. Using this new potential it was possible to explain the existing experimental FIR data and other observed properties such as the decreased dipole moment of $(ND_3)_2$ compared to $(NH_3)_2$. The Olthof's potential shows that the ammonia dimer has an intermediate structure between the centrosymmetric cyclic and the linear hydrogen-bonded structure which could not have been obtained before by pure ab initio study. Almost all the theoretical (perturbational and density functional theories) studies have shown a linear hydrogen-bonded structure, except Lee and Park's work [4] who predict the aforementioned intermediate structure using a series of correlation consistent basis sets, cc-pVXZ and aug-cc-pVXZ ($X = D, T, Q$) at the Hartree–Fock (HF), second-order and fourth-order Møller–Plesset perturbation theory (MP2, MP4) levels.

The potential energy surface appears to be very flat near its equilibrium structure, and the values of the equilibrium energies belonging to the different symmetries are very close to each other and depend strongly upon the basis sets and the methods applied. The focal point of these studies was to find the global equilibrium structure and characteristic features of the PES of these dimers. In this paper, we examine the BSSE effects of equilibrium structures, force constants and harmonic vibrational frequencies of the ammonia–ammonia dimer using Hartree–Fock method and Møller–Plesset perturbation theory. Our aim is to give a better and much more accurate description for these quantities. Most of the calculations for the hydrogen-bonded complexes are based on the supermolecular approach, in which the interaction energy of the dimer is obtained as an energy difference between the supermolecule and the monomers. However, this interaction energy often shows minima that are too deep, especially for the case of weakly bonded intermolecular systems, as a consequence of using finite basis sets in the calculations. This phenomenon is called "basis set superposition error," and it is due to the fact that the description of the monomer is actually better within the supermolecule than that which one has for the free monomers by applying the same basis set. So, the BSSE is a purely "mathematical effect" that appears only due to the use of finite basis sets, leading to an incomplete description in the individual monomers. Several numerical studies and analytical considerations [17–19] show that the magnitude of this BSSE effect can be very large even for fairly large basis sets, so removing it in the practical calculations is very important. Different techniques have been proposed [20–26] to correct this artificial effect.

More than 30 years ago, Jansen and Ros [20] and, independently, Boys and Bernardi [21] suggested an a posteriori "counterpoise correction" (CP) scheme of calculating the monomer energies in the same basis set as used for the supermolecule. This means that the description of the monomers is adjusted to the dimer problem, and the energies and other quantities of the free monomers become distance-dependent.

In 1983, Mayer proposed a new a priori procedure to tackle the BSSE problem. This is the so-called "chemical Hamiltonian approach" (CHA) [27, 28], which permits one to identify those terms of the Hamiltonian that are responsible for the BSSE effects. By omitting these terms, one can obtain wave functions that are free from artificial non-physical delocalizations. Using this CHA scheme, several different approaches have been developed both at the HF [29–39] and correlated [40–47] levels of theory.

According to previous studies, the results obtained from the Boys–Bernardi and CHA methods are very close to each other, despite the fact that these schemes are conceptually very different. In this work, we apply both methods in order to study the structures, the force constants and harmonic vibrational frequencies of the ammonia–ammonia hydrogen-bonded complex. Similar studies have been performed in an our earlier work [48] for the hydrogen fluoride and water dimers.

The methods employed (CP, CHA/CE, and CHA/MP2) are briefly explained in the section 2. In section 3, the results for the ammonia–ammonia dimer are presented in several different basis sets, and the force constants and harmonic vibrational frequencies obtained are compared and discussed. The conclusions of the paper are given in the final section.

2. Methods Applied (CP, CHA/CE and CHA/MP2)

In this section, the CP and CHA methods presented in earlier papers [20, 21, 27] are briefly reviewed.

2.1. CP SCHEME

The most popular posteriori method correcting the BSSE is the Boys–Bernardi counterpoise correction (CP) scheme introduced by Jansen and Ross [20] and, independently, by Boys and Bernardi [21]. Applying this CP scheme one has to recalculate the monomers in the basis of the whole supermolecule for every geometrical arrangement. The CP-corrected interaction energy ΔE^{CP} can be defined as the difference of the supermolecule and monomer energies, all computed in the same supermolecule basis set:

$$\Delta E^{CP}_{AB} = E_{AB}(AB) - E_A(AB) - E_B(AB). \quad (1)$$

The uncorrected binding energy $\Delta E^{unc.}$ can be obtained as

$$\Delta E^{unc.}_{AB} = E_{AB}(AB) - E_A(A) - E_B(B). \quad (2)$$

Using Eqs. (1) and (2), one can define the BSSE content in the interaction energy as

$$\delta E_{BSSE} = \Delta E^{unc.}_{AB} - \Delta E^{CP}_{AB} = E_A(AB) - E_A(A)$$
$$+ E_B(AB) - E_B(B). \quad (3)$$

According to the Eq. (3), the CP-corrected potential energy surface (PES) of the dimer becomes

$$E^{CP}(AB) = E^{unc.}_{AB}(AB) - \delta E_{BSSE} = E^{unc.}_{AB}(AB) - E_A(AB)$$
$$+ E_A(A) - E_B(AB) + E_B(B). \quad (4)$$

Using Eq. (4), in addition to the monomer energies one has to calculate three different energy values [29] at every geometrical arrangement of the system in order to determine the CP-corrected PES.

2.2. CHA SCHEME

A conceptually different way of handling the BSSE problem is to apply the a priori "chemical Hamiltonian approach" (CHA) introduced by Mayer [27, 28]. The CHA procedure permits the supermolecule calculations to keep consistency with those for the free monomer performed in their original basis sets. The most important aspect of Mayer's scheme is that one can devide the Hamiltonian into two parts and omit those terms that are responsible for the BSSE:

$$\hat{H}_{BO} = \hat{H}_{CHA} + \hat{H}_{BSSE}. \quad (5)$$

Here $\hat{H}_{BO}$ is the original Born–Oppenheimer Hamiltonian, $\hat{H}_{CHA}$ is the BSSE-free part of the Hamiltonian, while the second term on the right hand side corresponds to the BSSE. It must be emphasized that, as BSSE is not a physical quantity, one cannot expect the remaining part of the Hamiltonian $\hat{H}_{CHA}$ to be Hermitian. Applying this non-Hermitian BSSE-free CHA Hamiltonian $\hat{H}_{CHA}$ and using the method of momenta instead of the variational principle appropriate Hartree–Fock type CHA-SCF [30] equations were derived in order to calculate BSSE-free wave functions:

$$\hat{H}_{CHA}\Psi_{CHA} = \Lambda\Psi_{CHA}. \quad (6)$$

As a result of several numerical and analytical considerations [34–37] using this BSSE-free wave function the energy of the system can be calculated as a conventional expectation value of the original Born–Oppenheimer Hamiltonian and not of the "chemical" one. (This is indicated by the expression "CHA with conventional energy," CHA/CE.) Here is our working formula:

$$E_{CHA/CE} = \frac{\langle \Psi_{CHA}|\hat{H}_{BO}|\Psi_{CHA} \rangle}{\langle \Psi_{CHA}|\Psi_{CHA} \rangle}. \quad (7)$$

While obtaining Hartree–Fock-type equations from the CHA Hamiltonian is a relatively straightforward procedure, the generalization of it to the Møller–Plesset perturbation theory was a bigger task. As it was shown by Mayer [49], the appropri-

ate second-order energy can be obtained as follows. Firstly, one has to calculate the first-order CHA wave function χ by using the non-Hermitian Hamiltonian partitioned as $\hat{H}_{CHA} = \hat{H}^0 + \hat{V}_{CHA}$, where $\hat{H}^0$ is the unperturbed Hamiltonian. The perturbed $\hat{V}_{CHA}$ operator is also non-Hermitian because it is built up of the nonorthogonal eigenvectors of the non-Hermitian CHA-SCF equations [30]. The original Hermitian Born–Oppenheimer Hamiltonian $\hat{H}_{BO}$ can also be partitioned as a sum of the same non-Hermitian unperturbed Hamiltonian $\hat{H}^0$ and some new (also non-Hermitian) perturbation $\hat{V}$: $\hat{V} = \hat{H}_{BO} - \hat{H}^0$. Using the first-order CHA wave function χ, the generalized Hylleraas functional J_2 can easily be calculated:

$$J_2 = \frac{1}{\langle \Psi_0 | \Psi_0 \rangle} \left[2\,Re(\langle \hat{Q}\chi | \hat{V} | \Psi_0 \rangle) \right.$$
$$\left. + Re(\langle \chi | \hat{H}^0 - E_0 | \chi \rangle) \right], \quad (8)$$

and the second-order energy will be given by

$$E^{(2)} = \frac{\langle \Psi_0 | \hat{H}_{BO} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} + J_2. \quad (9)$$

Here Ψ_0 is the unperturbed wave function, E_0 is the zero-order energy ($\hat{H}^0 \Psi_0 = E_0 \Psi_0$), and $\hat{Q}$ is the projection operator an to the orthogonal complement to Ψ_0. These equations define our working formula at the second order perturbation level. This formalism is called "CHA/MP2" theory [42].

3. Results and Discussion

The calculations were carried out partly in Heidelberg on a Hewlett-Packard cluster and partly in Debrecen on a Pentium 200 PC and Compaq Alpha running under Linux. The standard HF, MP2 and the CP-corrected HF, MP2 calculations were performed with the Gaussian 98 software [50]. The CHA/CE- and CHA/MP2-type calculations were done by generating the input data (integrals and RHF orbitals) with a slightly modified version of HONDO-8 [51].

In these calculations the CHA/SCF code [30] and the CHA/MP2 program of Mayer and Valiron [42, 44] were used. For the frequency calculations based on Wilson's G-F method, the program written by Beu [52] was applied. The NH_3–NH_3 dimer geometries was optimized using conventional Hartree–

Fock and second-order Møller–Plesset perturbation theories for each basis set. We considered different standard Pople basis sets as 6-31G, 6-311G, 6-31++G, 6-311++G, 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p) 6-311++G(d,p), and 6-311++G(2d,2p).

The conventional supermolecule geometries were optimized both at HF and MP2 levels applying the analytical gradient method included in Gaussian 98, while the CHA and CP-corrected geometries were calculated by using a numerical gradient method (inverse parabolic interpolation [53]) in internal coordinates. To test the applicability of our numerical gradient method, we performed several sample calculations using both this latter method and the analytical gradient built into Gaussian 98, respectively. As a consequence, there is practically no difference between them for conventional uncorrected cases; we have also performed similar calculations to check the values of the force constans and harmonic vibrational frequencies. The uncorrected HF and MP2 results for the force constants (in internal coordinates) and for the harmonic vibrational frequencies were obtained by using the standard routines of Gaussian 98. As for the CHA and CP-corrected calculations, the numerical second derivatives of the energies were first calculated to obtain the CHA and CP force constants, and then the NOMAD program [52] was applied to obtain the appropriate CHA and CP harmonic vibrational frequencies. As we were interested in the BSSE content in the interaction energies, only those components of the force constant matrix were recalculated which correspond to intermolecular interactions.

The results calculated are summarized in Tables I–III. Table I shows the results obtained for the geometry of the dimer for the conventional, CHA, and Boys–Bernardi schemes both at the Hartree–Fock and second-order Møller–Plesset perturbation levels of theory. Table II contains the results obtained for the diagonal force constants of the dimer for the uncorrected, CHA, and CP-corrected cases both at the Hartree–Fock and second-order Møller–Plesset perturbation levels of theory. In Table III, we present the conventional, CHA, and CP-corrected results both at the HF and second-order Møller–Plesset perturbation levels of theory for the intermolecular harmonic vibrational frequencies ($\omega_2 - \omega_6$) of the ammonia–ammonia dimer.

A full BSSE-free geometry optimization has been reported by Muguet et al. [2, 3] using an a priori BSSE exclusion technique (BSSE-MCSCF) based on the localized molecular orbital method. Their result

TABLE I

Intermolecular coordinates for NH$_3$–NH$_3$ dimer computed at the Hartree–Fock and second-order Møller–Plesset perturbation theory (uncorr., CHA, CP) level, using 6-31G, 6-311G, 6-31++G, 6-311++G, 6-31G(d,p), 6-311G(d,p), 6-31++G(d,p), 6-311++G(d,p), and 6-311++G(2d,2p) basis sets.

Basis set	Method	r_{NN} (Å)		α_{HNN} (deg)		α_{NNH} (deg)		Config.	
		SCF	MP2	SCF	MP2	SCF	MP2	SCF	MP2
6-31G	Uncorr.	3.27044	3.15915	39.020	38.348	39.019	38.348	Cyclic	Cyclic
(30)	CHA	3.32887	3.27304	85.836	87.619	5.736	5.785	Asymm.	Asymm.
	CP	3.35513	3.32433	83.722	84.652	6.768	7.106	Asymm.	Asymm.
6-311G	Uncorr.	3.25798	3.14432	39.998	39.524	39.998	39.524	Cyclic	Cyclic
(44)	CHA	3.37535	3.31263	87.197	88.504	6.154	6.403	Asymm.	Asymm.
	CP	3.39196	3.37575	85.832	86.249	6.694	7.547	Asymm.	Asymm.
6-31++G	Uncorr.	3.31842	3.21519	88.573	78.528	6.567	12.592	Asymm.	Asymm.
(44)	CHA	3.39594	3.32434	76.032	64.922	12.843	21.186	Asymm.	Asymm.
	CP	3.40294	3.34718	76.800	71.385	12.452	16.822	Asymm.	Asymm.
6-311++G	Uncorr.	3.32551	3.21757	92.624	81.988	5.054	10.759	Asymm.	Asymm.
(58)	CHA	3.38087	3.31480	77.584	76.027	12.457	14.218	Asymm.	Asymm.
	CP	3.38039	3.33264	77.633	74.330	12.649	15.612	Asymm.	Asymm.
6-31G(d,p)	Uncorr.	3.27596	3.13437	41.234	40.647	41.234	40.647	Cyclic	Cyclic
(60)	CHA	3.39126	3.30106	92.585	92.609	5.540	6.481	Asymm.	Asymm.
	CP	3.41875	3.33417	90.358	89.929	6.537	7.660	Asymm.	Asymm.
6-311G(d,p)	Uncorr.	3.28708	3.11678	41.784	41.244	41.783	41.244	Cyclic	Cyclic
(74)	CHA	3.45301	3.32905	92.333	92.104	6.568	7.890	Asymm.	Asymm.
	CP	3.48886	3.38795	91.292	90.577	6.867	8.309	Asymm.	Asymm.
6-31++G(d,p)	Uncorr.	3.40270	3.23422	87.783	85.780	10.063	12.466	Asymm.	Asymm.
(74)	CHA	3.44118	3.31066	77.128	73.363	15.170	19.114	Asymm.	Asymm.
	CP	3.44586	3.31185	77.180	69.866	14.914	20.916	Asymm.	Asymm.
6-311++G(d,p)	Uncorr.	3.44761	3.25961	90.992	91.413	8.629	10.082	Asymm.	Asymm.
(88)	CHA	3.47140	3.31352	80.070	76.171	13.703	17.136	Asymm.	Asymm.
	CP	3.46760	3.31682	80.130	73.615	13.838	18.857	Asymm.	Asymm.
6-311++G(2d,2p)	Uncorr.	3.49518	3.25790	83.116	78.799	12.686	15.908	Asymm.	Asymm.
(118)	CHA	3.50573	3.28425	81.003	75.933	13.594	17.412	Asymm.	Asymm.
	CP	3.50137	3.27440	78.695	68.033	14.954	22.099	Asymm.	Asymm.

also shows an intermediate geometry configuration, but the $\alpha_{HNN} = 53.2°$ and $\alpha_{NNH} = 39.7°$ (Fig. 1a) are much closer to the cyclic structure than the linear hydrogen-bonded one, while our values are closer to the linear configuration ($\alpha_{HNN} = 75.9°$ and $\alpha_{NNH} = 17.4°$ in CHA using 6-311G++(2d,2p) at the MP2 level at theory).

The r_{NN} intermolecular distance also shows an important BSSE dependence, but this effect became smaller and smaller in case of using large and well-balanced basis sets and came near the experimental value ($r_{NN} = 3.337$ Å) [11]. Moreover, it is very important to note that the existence of cyclic configurations (Fig. 1b) as the global minimum symmetry is definitely a BSSE effect. When a BSSE-free optimization technique is used, this configuration becomes only a transition-state structure.

Another significant remark is that when density functional theory methods are used, the intermediate configuration is very difficult to obtain; in almost all cases, the linear-bonded hydrogen structure were preferred [5, 6].

Considering the results, the following conclusions can be drawn:

1. As can be expected, the BSSE-free CP and CHA interaction energies usually show less deep minima than those obtained from the uncorrected methods both at the HF and at the second-order Møller–Plesset perturbation level of theory. From Table II it can be concluded that apart from a few cases the values of the intermolecular diagonal force constans are significantly larger in the uncorrected

TABLE II

Intermolecular force constants for the NH₃–NH₃ dimer computed at the Hartree–Fock and second-order Møller–Plesset perturbation theory (Uncorr., CHA, CP) level, using 6-31G, 6-311G, 6-31++G, 6-311++G, 6-31G(d,p), 6-311G(d,p), 6-31++G(d,p), 6-311++G(d,p), and 6-311++G(2d,2p) basis sets.

Basis set	Method	f_{rr} (a.u./A²)		$f_{\alpha_1\alpha_1}$ (a.u./Rad²)		$f_{\alpha_2\alpha_2}$ (a.u./Rad²)	
		SCF	MP2	SCF	MP2	SCF	MP2
6-31G	Uncorr.	.020959	.031705	.029226	.039164	.029116	.039164
(30)	CHA	.026128	.026053	.013131	.014801	.037030	.043124
	CP	.017096	.020452	.012212	.014838	.035060	.044515
6-311G	Uncorr.	.019896	.028001	.028340	.037001	.028339	.037001
(44)	CHA	.020664	.023314	.011556	.013189	.033747	.040037
	CP	.016672	.019060	.013131	.013000	.033616	.036505
6-31++G	Uncorr.	.019300	.028067	.014563	.015793	.041412	.046379
(44)	CHA	.014080	.018001	.012765	.017692	.032732	.035477
	CP	.014424	.017531	.012433	.015035	.032529	.036372
6-311++G	Uncorr.	.019290	.027378	.015322	.013708	.042041	.043462
(58)	CHA	.015558	.018595	.013025	.015293	.032383	.037885
	CP	.015132	.018056	.012890	.014686	.032720	.037056
6-31G(d,p)	Uncorr.	.019350	.028546	.022292	.028567	.022293	.028567
(60)	CHA	.019060	.023498	.008929	.009895	.026525	.030508
	CP	.015600	.019712	.008010	.010374	.026525	.033485
6-311G(d,p)	Uncorr.	.017829	.027752	.020948	.027653	.020949	.027654
(74)	CHA	.021340	.021716	.007616	.008699	.022717	.027574
	CP	.013440	.017416	.006434	.008535	.021141	.026525
6-31++G(d,p)	Uncorr.	.015886	.025999	.009571	.011179	.027586	.036429
(74)	CHA	.012666	.017393	.010111	.011271	.023768	.028468
	CP	.012956	.017512	.009323	.010899	.023374	.027050
6-311++G(d,p)	Uncorr.	.013463	.022475	.008407	.009974	.024836	.034293
(88)	CHA	.012048	.016426	.008010	.009962	.021667	.027150
	CP	.012140	.016868	.008010	.010374	.021273	.026262
6-311++G(2d,2p)	Uncorr.	.010893	.019707	.006704	.008705	.020386	.029553
(118)	CHA	.010229	.017751	.006855	.009093	.019781	.027635
	CP	.010242	.017790	.007059	.010601	.019592	.026188

case. In spite of this tendency, sometimes the opposite effect also occurs, especially when the basis sets used are not large enough. We must emphasize that the results are very sensitive to the applied basis sets and some of them, such as 6-31G, 6-31G(d,p), etc., are not really appropriate to describe the structure and the molecular properties. But when diffuse or diffuse and polarization functions are used in the applied basis sets, in practically all cases the counterpoise-corrected results are fairly close to those given by the CHA-based methods for all studied quantities. Concerning the calculation of the harmonic vibrational frequencies, there is no unambiguous tendency between the corrected and uncorrected results because the frequency values can strongly depend upon the modified dimer geometries.

2. We also note that agreement between the CP and CHA-corrected results both at the HF and at correlated levels is very good. This observation is consistent with our previous studies in the field of intermolecular interactions. Similarly to our earlier results, the difference between the uncorrected and corrected values becomes smaller for large enough basis sets as the values of the intermolecular interactions converge.

3. It is also interesting to note, however, that the values of the diagonal force constants and harmonic vibrational frequencies of ammonia–ammonia dimer calculated at the correlated level are larger than those obtained from

TABLE III

Intermolecular frequencies for the NH_3–NH_3 dimer computed at the Hartree–Fock and second-order Møller–Plesset perturbation theory (Uncorr., CHA, CP) level, using 6-31G, 6-311G, 6-31++G, 6-311++G, 6-31G(d,p), 6-311G(d,p), 6-31++G(d,p), 6-311++G(d,p), and 6-311++G(2d,2p) basis sets.

Basis set	Method	ω_2 (cm^{-1})		ω_3 (cm^{-1})		ω_4 (cm^{-1})		ω_5 (cm^{-1})		ω_6 (cm^{-1})	
		SCF	MP2	SCF	MP2	SCF	MP2	SCF	MP2	SCF	MP2
6-31G	Uncorr.	104.8	126.5	131.9	161.4	145.7	182.6	247.7	279.1	470.8	526.7
(30)	CHA	126.3	132.7	150.6	155.0	209.9	234.7	355.7	374.5	515.0	539.4
	CP	107.6	127.5	127.4	163.1	218.1	249.4	428.1	465.1	614.2	663.0
6-311G	Uncorr.	98.9	117.1	128.9	151.2	131.5	158.0	245.2	270.4	482.5	527.4
(44)	CHA	118.1	125.3	142.1	155.0	206.9	227.3	365.7	381.3	496.8	523.2
	CP	115.7	116.9	150.6	145.9	215.4	239.4	428.0	439.8	583.2	601.7
6-31++G	Uncorr.	125.9	119.8	135.0	141.0	138.6	155.6	292.7	296.9	404.7	449.5
(44)	CHA	80.5	61.6	87.5	103.5	113.1	124.7	224.9	230.3	395.3	430.0
	CP	81.9	76.6	89.7	118.4	114.7	126.6	225.8	244.2	393.9	427.0
6-311++G	Uncorr.	125.9	114.9	144.6	149.4	149.5	156.7	313.9	306.4	421.6	436.0
(58)	CHA	75.0	92.5	93.1	123.1	117.5	129.9	237.3	253.7	404.8	436.9
	CP	74.0	88.3	93.0	118.1	118.6	127.5	237.1	247.8	404.7	430.0
6-31G(d,p)	Uncorr.	89.8	107.1	118.6	140.0	127.0	151.6	231.9	254.5	437.6	473.9
(60)	CHA	106.4	111.1	134.9	149.3	189.7	203.6	374.4	389.1	550.3	547.5
	CP	93.6	120.5	120.7	148.3	193.0	208.1	376.3	405.0	623.0	605.2
6-311G(d,p)	Uncorr.	88.2	120.6	116.4	135.9	122.4	151.1	222.1	246.1	423.8	463.0
(74)	CHA	100.3	97.9	140.2	146.1	185.0	197.5	347.7	370.1	516.3	510.9
	CP	77.8	100.9	112.2	134.4	189.8	202.8	339.4	367.0	589.1	555.5
6-31++G(d,p)	Uncorr.	95.6	105.9	114.6	127.4	123.6	155.2	251.8	286.8	383.5	424.1
(74)	CHA	78.3	49.4	89.0	99.2	117.6	131.5	202.9	226.0	377.1	404.3
	CP	71.1	37.6	90.0	93.3	118.3	130.7	210.2	226.5	364.1	394.1
6-311++G(d,p)	Uncorr.	90.5	102.3	114.7	131.7	116.0	146.8	248.3	290.3	363.3	407.2
(88)	CHA	65.3	59.3	85.3	95.0	109.3	125.1	197.2	219.8	355.6	388.7
	CP	59.2	62.3	84.6	88.5	110.7	131.2	202.7	221.5	347.6	380.3
6-311++G(2d,2p)	Uncorr.	65.2	65.3	100.2	110.1	104.7	137.6	218.1	248.1	335.3	390.7
(118)	CHA	63.0	57.4	96.0	104.9	101.5	129.2	205.4	229.0	339.0	392.5
	CP	60.9	52.7	91.3	93.4	102.2	129.9	195.7	202.0	339.4	393.8

the Hartree–Fock calculation. This behavior is a direct consequence of the fact that, at the correlated level, the interactions between the molecules are much stronger.

4. In the BSSE-corrected calculations, both the HF and MP2 levels of the cyclic state of the ammonia–ammonia dimer disappeared and instead, a new, so-called intermediate asymmetric configuration is preferred. On the other hand, by using diffuse functions in the basis set, the quasilinear geometry of the dimer is distorted, and an intermediate configuration is favored.

5. Focusing to the correlated level, the amount of BSSE in the intermolecular interaction energies is much larger than that at the HF level, and this effect is also conserved in the values

of the force constants and harmonic vibrational frequencies. All these results clearly indicate the importance of the proper BSSE-free correlation treatment with the well-defined basis functions.

In this paper we performed calculations for the geometries, force constants, and the intermolecular harmonic vibrational frequencies of the ammonia dimers. The calculations have been taken at both Hartree–Fock and correlated (second-order Møller–Plesset perturbation theory) levels of theory in several different basis sets. Comparisons have been made between the a posteriori Boys–Bernardi "counterpoise" correction scheme and the a priori "chemical Hamiltonian approach." It can be concluded from the results that there is practically no
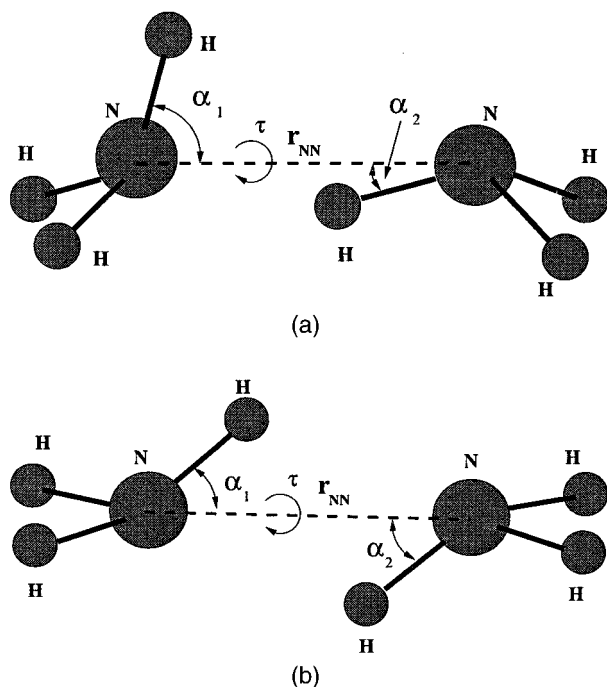
FIGURE 1. (a) Asymmetric structure of the ammonia–ammonia dimer. (b) Cyclic structure of the ammonia–ammonia dimer.

difference between these two methods, so the a priori CHA scheme can be considered as an ultimate solution of the BSSE problem. We also found that the basis set superposition error influence is fairly significant in the studied quantities, so removing this effect is very important.

References

1. Yeo, A. G.; Ford, T. A. J Mol Struct (TheoChem) 1988, 168, 247.

2. Muguet, F. F.; Robinson, G. W. J Chem Phys 1994, 102(9), 3648.

3. Muguet, F. F.; Robinson, G. W. J Chem Phys 1994, 102(9), 3655.

4. Lee, J. S.; Park, S. Y. J Chem Phys 2000, 112, 230.

5. Kieninger, M.; Suhai, S. J Comp Chem 1996, 17(13), 1508.

6. Jursic, B. S. J Mol Struct (TheoChem) 1998, 434, 29.

7. Beu, T. A.; Buck, U. J Chem Phys 2001, 114, 7848.

8. Beu, T. A.; Buck, U. J Chem Phys 2001, 114, 7853.

9. Linnartz, H.; Meerts, W. L.; Havenith, M. Chem Phys 1995, 193, 327.

10. Behrens, M.; Buck, U.; Fröchtenicht, R.; Hartmann, M.; Havenith, M. J Chem Phys 1997, 107(18), 7179.

11. Nelson, D. D.; Fraser, G. T.; Kelemperer, W. J. Chem Phys 1985, 83, 6201.

12. Olthof, E. H. T.; van der Avoird, A.; Wormer, P. E. S. J Chem Phys 1994, 101, 8430.

13. Snels, M.; Fantoni, R.; Sanders, S.; Meerts, W. L. Chem Phys 1987, 115, 79.

14. Heijmen, B.; Bizzarri, A.; Stolte, S.; Reuss, J. J Chem Phys 1988, 126, 201.

15. Huisken, F.; Pertsch, T. Chem Phys 1988, 126, 213.

16. Havenith, M.; Linnartz, H.; Zwart, E.; Kips, A.; ter Meulen, J. J.; Meerts, W. L. Chem Phys Lett 1992, 193(4), 261.

17. Alagona, G.; Ghio, C. J. J Mol Struct (TheoChem) 1995, 330, 77.

18. de Oliveira, G.; Dykstra, C. E. J Mol Struct (TheoChem) 1995, 337, 1.

19. Novoa, J. J.; Planas, M.; Rovira, M. C. Chem Phys Lett 1996, 251, 33.

20. Jansen, H. B.; Ross, P. Chem Phys Lett 1969, 3, 140.

21. Boys, S. B.; Bernardi, F. Mol Phys 1970, 19, 553.

22. Daudey, J. P.; Malrieu, J. P.; Rojas, O. Int J Quant Chem 1974, 17, 8.

23. Loushin, S.; Dykstra, C. E. J Comp Chem 1987, 8, 81.

24. Schwenke, D. W.; Truhlar, D. G. J Chem Phys 1985, 82, 2418.

25. Hobza, P.; Zahradnik, R. Chem Rev 1988, 88, 871.

26. Gianinetti, E.; Raimondi, M.; Tornaghi, E. Int J Quant Chem 1996, 60, 157.

27. Mayer, I. Int J Quant Chem 1983, 23, 341.

28. Mayer, I. Int J Quant Chem 1998, 70, 41.

29. Mayer, I.; Surján, P. R. Chem Phys Lett 1992, 191, 497.

30. (a) Mayer, I.; Vibók, Á. Chem Phys Lett 1987, 136, 115; (b) Mayer, I.; Vibók, Á. Chem Phys Lett 1987, 140, 558; (c) Vibók, Á.; Mayer, I. J Mol Struct (TheoChem) 1988, 170, 9.

31. (a) Mayer, I.; Vibók, Á.; Halász, G. J.; Valiron, P. Int J Quant Chem 1996, 57, 1049; (b) Halász, G. J.; Vibók, Á.; Valiron, P.; Mayer, I. J Phys Chem 1996, 100, 6332.

32. Halász, G. J.; Vibók, Á.; Suhai, S. Int J Quant Chem 1998, 68, 151.

33. Mayer, I.; Turi, L. J Mol Struct (TheoChem) 1991, 227, 43.

34. Mayer, I.; Surján, P. R. Int J Quant Chem 1989, 36, 225.

35. Mayer, I.; Surján, P. R.; Vibók, Á. Int J Quant Chem, Quant Chem Symp 1989, 23, 281.

36. Mayer, I.; Vibók, Á. Int J Quant Chem 1991, 40, 139.

37. Vibók, Á.; Mayer, I. Int J Quant Chem 1992, 43, 801.

38. Hamza, A.; Vibók, Á.; Halász, G. J.; Mayer, I. J Mol Struct (TheoChem) 2000, 501, 427.

39. Halász, G. J.; Vibók, Á.; Suhai, S.; Mayer, I. Int J Quant Chem 2002, 89, 190.

40. Mayer, I.; Vibók, Á. Mol Phys 1997, 92, 503.

41. Vibók, Á.; Halász, G. J.; Mayer, I. Mol Phys 1998, 93, 873.

42. Mayer, I.; Valiron, P. J Chem Phys 1998, 109, 3360.

43. Vibók, Á.; Halász, G. J.; Mayer, I. In BSSE-Corrected Perturbation Theories of Intermolecular Interactions; Electron Correlation and Material Properties; Gonis, A.; Kioussis, N.; Ciftan, M., Eds.; Kluwert Academic/Plenum Publishers: New York 2003, 263–283.

44. Mayer, I.; Valiron, P. Program CHA-MP2 (1998).

45. Valiron, P.; Vibók, Á.; Mayer, I. J Comp Chem 1993, 275, 46.

46. Halász, G. J.; Vibók, Á.; Mayer, I. J Comp Chem 1999, 20, 274.

47. Bende, A.; Vibók, Á.; Halász, G. J.; Suhai, S. Int J Quant Chem 2001, 84, 617.

48. Bende, A.; Knapp-Mohammady, M.; Suhai, S. Int J Quant Chem 2003, 92, 152.

49. Mayer, I. Mol Phys 1996, 89, 515.

50. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E., Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. W.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1998.

51. HONDO-8, from MOTECC-91, contributed and documented by M. Dupuis, A. Farazdel, IBM Corporation Center for Scientific & Engineering Computations: Kingston, NY, 1991.

52. Beu, T. A. Program NOMAD (1997).

53. Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. Numerical Recipes; Cambridge University Press: Cambridge, England, 1986.