AB INITIO STUDY OF THE AMMONIA - WATER DIMER: BSSE-FREE STRUCTURES AND INTERMOLECULAR HARMONIC VIBRATIONAL FREQUENCIES.

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Abstract

The optimized geometries, force constants and the intermolecular harmonic vibrational frequencies of the ammonia - water dimer have been studied both at the Hartree-Fock and second-order Møller-Plesset perturbation theory (MP2) levels of theory using several different basis sets as (6-31G, 6-311G, 6-31G**, 6-311G**, 6-31++G** and 6-311++G**). 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 basis set superposition error (BSSE) influence is very significant, so removing this effect is very important.

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Introduction

Studies of the intermolecular fundamentals of molecular complexes can give important information on molecular interactions. Recently a number of different theoretical and experimental [1-7] methods have been developed to study the structures of the ammonia - water hydrogen-bonded complex. Theoretical studies showed that one can find stationary points on the $NH_3 - H_2O$ potential energy surface (PES) with two different C_s symmetries [6]. The values of the equilibrium energies belonging to the different symmetries are very close to each other and strongly depend upon the basis sets and the methods applied. The focal point of these studies was to find the equilibrium structure and characteristic features of the PES of this dimer. In this paper, we examine the equilibrium structure, the force constants and the harmonic vibrational frequencies of the ammonia - water dimers 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 too deep minima 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" (BSSE) and it is due to the fact that the description of the monomer is actually better within the supermolecule than the treatment of the free monomers by applying the same basis set. So, the BSSE is a purely "mathematical effect" which 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 show that the amount of this BSSE effect can be very large even for fairly big basis sets, so removing it in the practical calculations is very important. Different techniques have been proposed to correct this artificial effect.

More than 30 years ago, Jansen and Ross [8] and, independently, Boys and Bernardi [9] 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

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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) [10,11] which permits one to identify those terms of the Hamiltonian which are responsible for the BSSE effects. By omitting these terms, one can get wave functions free from artificial nonphysical delocalizations. Using this CHA scheme several different approaches have been developed both at the HF [12-21] and correlated [22-29] levels of theory. In our paper we use the "CHA with conventional energy" (CHA/CE) version [13] to compute the HF energy and Møller-Plesset perturbation theory applied to CHA Hamiltonian (CHA-MP2) [24] for correlated level.

According to the previous studies, the results obtained from the Boys-Bernardi and CHA methods are very close to each other, despite of 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 - water hydrogen-bonded complex. Similar studies have been performed in an our earlier work [30] for the hydrogen fluoride and water dimers.

The methods employed (CP, CHA/CE and CHA/MP2) are briefly explained in the next section. In section 3. the results for the ammonia - water dimer are presented in several 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.

The methods applied (CP, CHA/CE and CHA/MP2)

The most popular *a posteriori* method correcting the BSSE is the Boys-Bernardi counterpoise correction (CP) scheme introduced by Jansen and Ross [8] and, independently, by Boys and Bernardi [9]. Applying this CP scheme one has to recalculate the monomers in the basis of the whole super-molecule 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:

$$
\begin{aligned}
E^{CP}(AB) &= E_{AB}(AB) - \delta E_{BSSE} \tag{1} \\
&= E_{AB}(AB) - E_A(AB) + E_A(A) - E_B(AB) + E_B(B).
\end{aligned}
$$

Using eq. (1), in addition to the monomer energies one has to calculate five different energy values [12] at every geometrical arrangement of the system in order to determine the CP-corrected PES.

A conceptually different way of handling the BSSE problem is to apply the *a priori* "chemical Hamiltonian approach" (CHA) introduced by Mayer [10,11]. 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 divide the Hamiltonian into two parts and omit those terms that are responsible for the BSSE:

$$
\hat{H}_{BO} = \hat{H}_{CHA} + \hat{H}_{BSSE}. \tag{2}
$$

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 has to be emphasized that as BSSE is not a physical quantity, one cannot expect 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 [13] equations were derived in order to calculate BSSE-free wavefunctions. As a results of several numerical and analytical considerations [16-19] using this BSSE-free wavefunction 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:

$$
E_{CHA/CE} = \frac{< \Psi_{CHA} | \hat{H}_{BO} | \Psi_{CHA} >}{< \Psi_{CHA} | \Psi_{CHA} >}. \tag{3}
$$

While to obtain 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 [31], the appropriate second order energy can be obtained as follows. Firstly one has to calculate the first order CHA wavefunction 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 non-orthogonal eigenvectors of the non-Hermitian CHA-SCF equations [13]. 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 $\hat{V}$ defined by $\hat{V} = \hat{H}_{BO} - \hat{H}^0$. Using the first order CHA wavefunction χ, the *generalized Hylleraas functional* J_2 for non-Hermitian operators applied in the framework of the varitational-perturbational method [24], can easily be calculated:

$$J_2 = \frac{1}{<\Psi_0|\Psi_0>}[2Re(<\hat{Q}\chi|\hat{V}|\Psi_0> + Re(<\chi|\hat{H}^0 - E_0|\chi>)]. \quad (4)$$

and the second order energy will be given by

$$E^{(2)} = \frac{<\Psi_0|\hat{H}_{BO}|\Psi_0>}{<\Psi_0|\Psi_0>} + J_2. \quad (5)$$

Here Ψ_0 is the unperturbed wavefunction, 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 [24].

Computational Details

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 by the Gaussian 98 computer code [32]. 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 [33].

In these calculations the CHA/SCF code [13] and the CHA/MP2 program of Mayer and Valiron [24,26] were used. For the frequency calculations based on GF Wilson method [34], the program written by Beu [35] was applied. The $NH_3 - H_2O$ dimer geometries were optimized using conventional Hartree-Fock and second order Møller-Plesset perturbation theories for each basis set.

We considered six different basis sets as 6-31G, 6-311G, 6-31G**, 6-311G**, 6-31++G** and 6-311++G**, which are standard Pople basis sets.

The conventional supermolecule geometries were optimized both at HF and MP2 levels applying the analytical gradient method included in the Gaussian 98, while the CHA and CP-corrected geometries were calculated by using a numerical gradient method (Inverse Parabolic Interpolation [36]) in internal coordinates. So as to test the applicability of our numerical gradient method we have 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 constants 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 the Gaussian 98 program. As for the CHA and CP-corrected calculations at first the numerical second derivatives of the energies were calculated to obtain the CHA and CP force constants and then the NOMAD program [35] 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 calculated by Gaussian98 program were recalculated which correspond to intermolecular interactions.
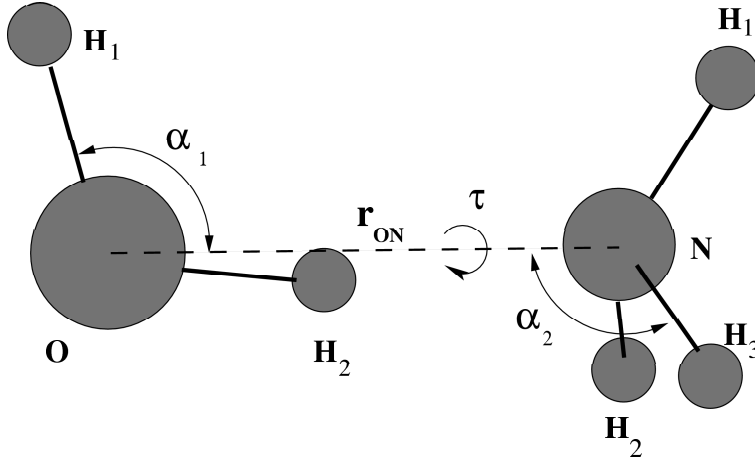
Figure 1: *Structure I of the ammonia - water dimer.*

Results and Discussions

The results obtained for the geometry of the ammonia - water dimer using the conventional, CHA and CP schemes, both at the HF and MP2 levels, are presented in Table 1. The uncorrected and BSSE-corrected (CHA and CP) values show that ammonia - water complex has two different equilibrium geometry (Structure I. and Structure II.) both having C_s symmetries. Structure I (Fig. 1) is typical for HF level where H_1, O, H_2 of water and N, H_1 of ammonia define the σ_h symmetry plane of molecular complex (H_2 and H_3 are out of this σ_h symmetry plane) while Structure II (Fig. 2) is characteristic for MP2 level where H_1, O, H_2 of water and N, H_2 of ammonia define the σ_h symmetry plane of the dimer (H_1 and H_3 are out of σ_h symmetry plane).

Table 1

Intermolecular coordinates for the $NH_3 - H_2O$ dimer computed at the Hartree-Fock and second-order Møller-Plesset perturbation theory (uncorrected, CHA and CP) levels, using 6-31G, 6-311G, 6-31G**, 6-311G**, 6-31++G** and 6-311++G** basis sets. r_{ON} the distance between O and N atoms given in Angstrom (Å) while α_1 and α_2 are angles defined by $H_1 - O$ bond of water and r_{ON} and by $N - H_3$ bond of ammonia and r_{ON}, respectively. Angles are given in degree (Deg.).

/The number of basis functions are given in parenthesis/

Basis set	Method	$r_{ON}(Å)$		$\alpha_1(Deg.)$		$\alpha_2(Deg.)$	
		SCF	MP2	SCF	MP2	SCF	MP2
6-31G	Uncorr.	2.9551	2.9391	115.18	113.91	99.43	112.47
(28)	CHA	2.9896	3.0044	116.07	104.64	99.09	107.21
	CP	2.9812	2.9840	116.45	115.44	99.00	112.72
6-311G	Uncorr.	2.9392	2.8910	115.00	114.02	101.37	111.94
(41)	CHA	3.0303	3.0301	115.71	107.51	100.14	108.84
	CP	3.0471	3.0643	115.76	115.10	100.24	112.97
6-31G**	Uncorr.	3.0504	2.9614	108.25	107.02	105.27	100.70
(55)	CHA	3.0742	3.0275	108.98	107.66	105.40	101.08
	CP	3.0784	3.0248	109.15	108.38	105.27	100.13
6-311G**	Uncorr.	3.0545	2.9359	107.17	103.63	106.47	116.06
(68)	CHA	3.1363	3.0676	107.52	98.22	105.83	114.03
	CP	3.1470	3.0987	107.53	104.10	105.76	117.28
6-31++G**	Uncorr.	3.0443	2.9355	111.89	112.54	104.38	117.76
(68)	CHA	3.0934	3.0483	111.75	101.69	103.73	112.40
	CP	3.1054	3.0253	111.90	112.50	103.57	118.63
6-311++G**	Uncorr.	3.0750	2.9386	110.40	109.94	105.23	118.05
(81)	CHA	3.1102	3.0305	110.25	100.02	104.43	113.42
	CP	3.1105	3.0217	110.54	109.56	104.25	118.95

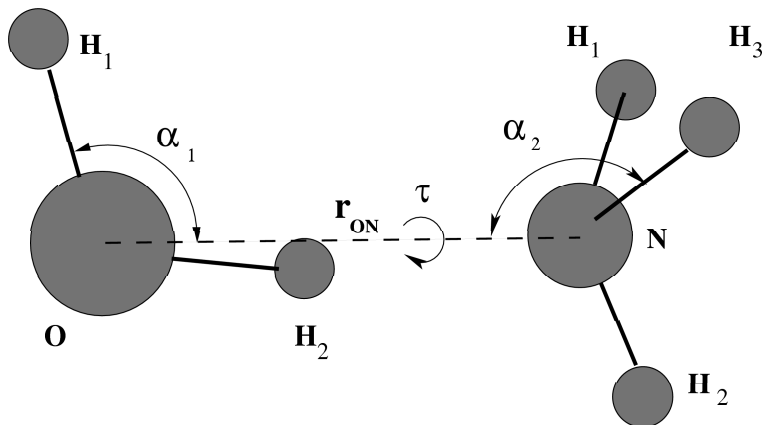r_{ON}(exp.) $\approx$ 2.983 Å Ref.[5]

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Figure 2: *Structure II of the ammonia - water dimer .*

The $r(O \cdots N)$ bond shows an important BSSE content, which converges
to the experimental value ($\approx$ 2.983 Å) if we use large basis sets with high-
polarization functions. At the same time we made comparative calcula-
tions using *Aug-cc-pVDZ* and *cc-pVTZ* Dunning's basis sets at MP2-CHA
and MP2-CP levels and we got 2.9790 Å and 2.9874 Å value, respectively
for $r(O \cdots N)$ bond distance. Whereas, in case of $\alpha(H_1 - O \cdots N)$ and
$\alpha(O \cdots N - H_3)$ angles this BSSE-content is imperceptible, only at MP2
level can be found small deviations. Furthermore the BSSE effects cannot
change the geometry structure obtained in uncorrected case.

Table 2. contain the results obtained for the diagonal force constants
of the ammonia - water dimer for the uncorrected, CHA and CP-corrected
cases, both at the HF and MP2 levels. In Table 3. we present the con-
ventional, CHA and CP-corrected results, both at the HF and MP2 levels
for the intermolecular harmonic vibrational frequencies (ν_8,ν_9, ν_{10} and ν_{13})
of the ammonia - water dimer. The molecular complex has fifteen non-
degenerated normal modes: three normal modes are characteristic to water
molecule, six are characteristic to ammonia molecule while the six normal
modes left have intermolecular trait. The previous frequency notation (in-
dex) were introduced by Yeo *et al.* (Ref.[2]) where ν_8, ν_9, ν_{10}, ν_{13}, ν_{14} and
ν_{15} represent frequencies corresponding to intermolecular normal modes.

Table 2

Intermolecular force constants for the $NH_3 - H_2O$ dimer computed at the Hartree-Fock and second-order Møller-Plesset perturbation theory (uncorrected, CHA and CP) levels, using 6-31G, 6-311G, 6-31G**, 6-311G**, 6-31++G** and 6-311++G** basis sets. f_{rr} is the diagonal force constant corresponding to r_{ON} internal coordinate given in atomic unit/ Angstrom square ($a.u./\text{Å}^2$), $f_{\alpha_1\alpha_1}$ is the diagonal force constant corresponding to α_1 angle given in atomic unit/ Radian square ($a.u./Rad^2$), while $f_{\alpha_2\alpha_2}$ is the diagonal force constant corresponding to α_2 angle given in atomic unit/Radian square ($a.u./Rad^2$).
/The number of basis functions are given in parenthesis./

Basis set	Method	f_{rr} $(a.u./\text{Å}^2)$		$f_{\alpha_1\alpha_1}(a.u./Rad^2)$		$f_{\alpha_2\alpha_2}(a.u./Rad^2)$	
		SCF	MP2	SCF	MP2	SCF	MP2
6-31G	Uncorr.	.04904	.05430	.05314	.06061	.02488	.02411
(28)	CHA	.04949	.05092	.05226	.05510	.02495	.02497
	CP	.04650	.04951	.06894	.06145	.03611	.02521
6-311G	Uncorr.	.05234	.06281	.05268	.06176	.02661	.02688
(41)	CHA	.04745	.05296	.04911	.05430	.02167	.02246
	CP	.03996	.04153	.04281	.04675	.02101	.02035
6-31G**	Uncorr.	.03669	.04577	.03750	.04762	.01524	.01704
(55)	CHA	.03857	.04231	.03887	.04613	.01589	.01866
	CP	.03535	.03993	.03834	.04465	.01641	.01720
6-311G**	Uncorr.	.03737	.05095	.03583	.04664	.01606	.01946
(68)	CHA	.03122	.03768	.03125	.03741	.01431	.01542
	CP	.02868	.03214	.03138	.03651	.01405	.01550
6-31++G**	Uncorr.	.03512	.04720	.03855	.05221	.01818	.02027
(68)	CHA	.02945	.03137	.03506	.03979	.01471	.01567
	CP	.02868	.03373	.03322	.04123	.01287	.01353
6-311++G**	Uncorr.	.03157	.04341	.03538	.04795	.01691	.01970
(81)	CHA	.02552	.03429	.03217	.03877	.01366	.01486
	CP	.02787	.03374	.03257	.03782	.01444	.01261

Table 3

Intermolecular frequencies for the $NH_3 - H_2O$ dimer computed at the Hartree-Fock and second-order Møller-Plesset perturbation theory (uncorrected, CHA and CP) levels, using 6-31G, 6-311G, 6-31G**, 6-311G**, 6-31++G** and 6-311++G** basis sets. The ν_{10}, ν_9, ν_8 and ν_{13} are frequencies corresponding to intermolecular normal modes. /The number of basis functions are given in parenthesis./

Basis set	Method	$\nu_{10}(cm^{-1})$		$\nu_9(cm^{-1})$		$\nu_8(cm^{-1})$		$\nu_{13}(cm^{-1})$	
		SCF	MP2	SCF	MP2	SCF	MP2	SCF	MP2
6-31G	Uncorr.	205.5	193.3	214.8	220.6	505.5	518.3	793.4	793.6
(28)	CHA	203.1	201.2	212.8	211.7	485.8	464.3	701.6	713.5
	CP	231.9	201.4	287.1	219.3	573.3	522.5	795.8	792.6
6-311G	Uncorr.	198.5	180.5	217.3	231.6	513.4	528.9	802.8	819.6
(41)	CHA	187.3	174.2	205.9	207.0	472.2	465.4	713.9	722.8
	CP	159.3	112.7	188.4	189.2	467.2	464.0	799.7	816.0
6-31G**	Uncorr.	161.5	168.3	181.6	200.2	423.8	455.3	662.2	704.4
(55)	CHA	168.2	171.3	186.4	204.1	419.4	445.1	645.8	687.0
	CP	168.5	160.2	185.6	195.3	428.0	438.0	661.7	703.0
6-311G**	Uncorr.	165.1	171.5	181.2	207.8	423.3	459.2	656.1	717.5
(68)	CHA	150.9	140.6	166.7	178.3	384.8	396.2	639.4	704.6
	CP	148.7	133.2	164.2	166.4	396.6	409.4	654.8	715.5
6-31++G**	Uncorr.	187.6	202.9	193.6	212.6	435.8	485.1	692.1	757.8
(68)	CHA	161.6	157.1	178.1	163.7	402.7	406.1	671.4	748.4
	CP	153.6	151.7	174.0	181.6	406.1	435.2	690.3	755.9
6-311++G**	Uncorr.	182.3	201.2	185.8	206.8	423.8	469.6	666.7	731.8
(81)	CHA	155.1	158.9	171.5	170.3	390.9	407.1	649.5	726.0
	CP	165.5	148.0	173.9	179.6	405.7	422.8	665.5	729.8

Table 4

Bands observed in the region $800 - 10 \; cm^{-1}$ in cryogenic matrices and their possible assignment to the water - ammonia complex or to multimers.

Wavenumber (cm^{-1})						Assignment
N_2^a	N_2^b	Ne^c	Ar^a	Ar^b	Kr^c	
600		662	638	638	631	ν_{13}
440	439	430	419	420	417	ν_8
420	414	411	402	402	390	?
				295 $\Big\}$	334 311 $\Big\}$	Combinations
		202			197	ν_9
		180			193	ν_{10}
		20				ν_{15}

[a]Ref. [2].
[b]Ref. [3].
[c]Ref. [4].

Bands observed in the region $800 - 10 \; cm^{-1}$ in different N_2, Ne, Ar and Kr cryogenic matrices and their potential assignment to the water-ammonia complex or to multimers (Ref. [2]) are presented in Table 4.

Considering the results, the following conclusions can be drawn: *i)* As it 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 Tables 2 it can be concluded that apart from a few cases the values of the intermolecular diagonal force constants are significantly larger in the uncorrected case. In spite of this tendency sometimes opposite the effect also occurs, especially when the basis sets used are not large enough. We have to emphasize that the results are very sensitive to the applied basis sets and some of them as 6-31G, 6-31G** *etc.* are not really appropriate to describe the structure and the molecular properties. Concerning the calculation of the harmonical 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 but in generally the BSSE-free frequency values make up to the experimental values presented in Table 4. *ii)* We also note that the agreement between the CP and CHA-corrected results both at the HF and at correlated levels are very good. This observation is consistent with our previous studies in the field of intermolecular interactions. *iii)* Similarly to our earlier results, the difference between the uncorrected and corrected values become smaller for large enough basis sets as the values of the intermolecular interactions converge to each other. *iv)* It is also interesting to note, however, that the values of the diagonal force constants and harmonic vibrational frequencies calculated at correlated level are larger than those obtained from the Hartree-Fock calculation. This kind of behavior is a direct consequence of the fact that the correlated level the interactions between the molecules are much stronger. *v)* Focusing to the correlated level, the amount of BSSE in the intermolecular interaction energies is much larger than the one we get 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.

Summary

The optimized geometries, the intermolecular force constants and the harmonic vibrational frequencies of the ammonia - water 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, 6-31G**, 6-311G**, 6-31++G** and 6-311++G**). 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 a solution of the basis set superposition error (BSSE) problem. It is also concluded that the BSSE influence is very significant, so removing this effect is very important.

Acknowledgement

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