BSSE-Free Description of Intermolecular Force Constants in Hydrogen Fluoride and Water Dimers

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ABSTRACT: Theoretical studies have been performed to calculate the force constants and harmonic vibrational frequencies in the hydrogen fluoride and water dimers. The calculations have been undertaken both at the Hartree–Fock and correlated (second-order Møller–Plesset perturbation theory) levels of theory using several different basis sets ranging from the weak to the intermediate. The basis set superposition error (BSSE) has been excluded by using the chemical Hamiltonian approach. The results show that the BSSE influence is significant in the force constants and harmonic vibrational frequencies even if electron correlation is accounted for, so removing the BSSE is important. The results are compared with those obtained by the basis independent density-functional tight-binding method. © 2003 Wiley Periodicals, Inc. Int J Quantum Chem 92: 152–159, 2003

Key words: basis set superposition error; chemical Hamiltonian approach; force constants; HF dimer; H_2O dimer

Introduction

Hydrogen bonds play an essential role in biophysics and biochemistry. In the recent past a number of different theoretical and also experimental methods have been developed to study the interaction energies and structures of hydrogen-bonded complexes [1, 2]. The main goal is to give better and more accurate description of 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 inter-

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molecular systems as a consequence of using finite basis sets in the calculations. This "phenomenon" is called a basis set superposition error (BSSE) and 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, which leads to an incomplete description in the individual monomers. Several numerical studies and analytic considerations [3–5] show that the amount of this BSSE effect can be large even for fairly big basis sets, so removing it in the practical calculations is important. During the last three decades different approaches have been developed to take into account this "finite basis effect" [6–13]. The most simple and straightforward a posteriori correction scheme, introduced by Boys and Bernardi, is usually called "BB or CP (counterpoise correction) method" [7]. In the CP scheme the energy of the monomers are recalculated by using the full basis of the supermolecule and these corrected monomer energies are used when one computes the interaction energy of the complex. A conceptually different a priori method to solve the BSSE problem was developed by Mayer [14] in 1983. This procedure is based upon the so-called "chemical Hamiltonian approach" (CHA) and permits one to identify those terms of the Hamiltonian that actually cause BSSE. Omitting these terms, one gets a "physical" Hamiltonian, which leads to wave functions that are free from the nonphysical delocalizations caused by BSSE. Several approaches have been developed using the CHA scheme both at the Hartree–Fock (HF) level [15–24] and using second-order perturbation theory [25–28]. A huge number of calculations has been performed in the last decade by applying this CHA to study the structures and interaction energies for different van der Waals and hydrogen-bonded systems [29–32]. In these calculations different systems were inves-
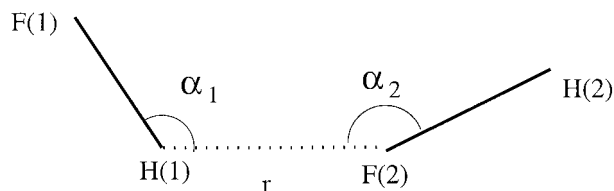

FIGURE 2. The geometry of the H_2O dimer; r = distance between the O(1) and O(2); α_1 = angle between H(1) − O(1) and O(1) . . . O(2) bonds; α_2 = angle between O(1) . . . O(2) and O(2) − H(2) bonds.

tigated, from the small to the large and biologically interesting "bimolecular complex" (like formamid dimers and DNA basis pairs) [31, 32] by using a variety of different basis sets. It has been concluded that in all cases a remarkable agreement has been found with the results given by Boys and Bernardi's CP method.

Our aim in this article is to perform calculations of the force constants and harmonic frequencies of different bimolecular complexes to test the applicability of the CHA scheme for this particular problem, which has not been studied previously. As a starting point we chose two relatively small and simple hydrogen-bonded systems, the $(HF)_2$ and $(H_2O)_2$ dimers, for which numerous experimental and theoretical data exist [33–35]. We also compared the results obtained for the $(H_2O)_2$ dimer with the results obtained by the self-consistent charge, density-functional tight-binding (SCC-DFTB) [35–41] method.

The methods applied (CHA/F, CHA/MP2, and SCC-DFTB) are briefly reviewed in the next section. In the third section the results of the calculations performed on hydrogen fluoride and water dimers are presented in several different basis sets and the force constants and harmonic vibrational frequencies obtained are compared and discussed.

Methods (CHA/HF, CHA/MP2, and SCC-DFTB)

CHA SCHEME

In the *a priori* CHA scheme we omit those terms of the Hamiltonian that cause BSSE. The CHA procedure permits the supermolecule calculations to keep consistency with those for the free monomers

FIGURE 1. The geometry of the HF dimer; r = distance between the H(1) and F(2); α_1 = angle between F(1) − H(1) and H(1) . . . F(2) bonds; α_2 = angle between H(1) . . . F(2) and F(2) − H(2) bonds.
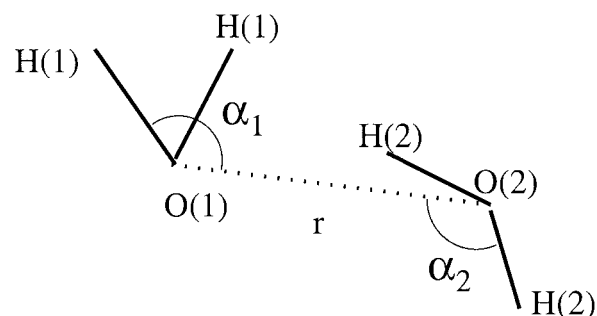
performed in their original monomer basis sets. The only difficulty of this scheme is that the resulting CHA Hamiltonian is not Hermitian: As the BSSE is not a physical phenomenon, there cannot be any Hermitian operator corresponding to it—so one cannot expect the BSSE-free Hamiltonian $\hat{H}_{CHA}$ to be Hermitian, either. Based on this CHA Hamiltonian Mayer and Vibók developed different SCF-type equations [15]; and, this was extended by Mayer and Valiron to the second-order Møller–Plesset perturbational level [27]. These methods provide the appropriate BSSE-free wave functions. Both the numerical calculations [21–24] and the analytic considerations [19] indicated that the energy of the system should be calculated as a conventional expectation value of the original Born–Oppenheimer Hamiltonian by using the BSSE-free wave function, and not of the expectation value of "physical Hamiltonian" [20]. (This complex scheme of calculating the energies is usually denoted by the expression "CHA with conventional energy," CHA/CE.)

While the derivation of the SCF-type equations in the CHA framework is a relatively simple procedure, the generalization of it to the Møller–Plesset perturbational theory was a bigger task. As shown by Mayer [42], the appropriate second-order energy can be obtained in the following manner: First, one has to calculate the first-order CHA wave function χ by using the non-Hermitian CHA Hamiltonian partitioned as $\hat{H}_{CHA} = \hat{H}^0 + \hat{V}_{CHA}$, where $\hat{H}^0$ is a Møller–Plesset-type unperturbed Hamiltonian. The latter is also non-Hermitian, as it is built up of the nonorthogonal eigenvectors of the non-Hermitian CHA-SCF equations [15]. The usual Hermitian Born–Oppenheimer Hamiltonian $\hat{H}$ can then be partitioned as a sum of the same non-Hermitian unperturbed Hamiltonian $\hat{H}^0$ and of some (also non-Hermitian) perturbation $\hat{V}$, that is, $\hat{V} = \hat{H} - \hat{H}^0$. Using the first-order CHA wave function χ, one can calculate the generalized Hylleraas functional J_2 and obtain the second-order energy correction as [42].

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

(1)

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 to the orthogonal complement to Ψ_0. This generalized Hylleraas functional repre-

TABLE I
Diagonal force constants [$r = H(1)\ldots F(2)$, $\alpha_1 = F(1) - H(1)\ldots F(2)$, $\alpha_2 = H(1)\ldots F(2) - H(2)$] for HF dimers computed at the HF/CHA-HF and MP2/CHA-MP2 levels using 6-31G, 6-311G, 6-31G**, 6-311G**, 6-31++G**, 6-311++G**, cc-pVDZ, cc-pVTZ, Aug-cc-pVDZ and Aug-cc-pVTZ basis sets.

Basis/method	f_{rr} (a.u./Å²)				$f_{\alpha_1\alpha_1}$ (a.u./Rad²)				$f_{\alpha_2\alpha_2}$ (a.u./Rad²)			
	HF	CHA-HF	MP2	CHA-MP2	HF	CHA-HF	MP2	CHA-MP2	HF	CHA-HF	MP2	CHA-MP2
6-31G	0.055487	0.057040	0.058727	0.055521	0.009898	0.011227	0.009484	0.009484	0.008320	0.006890	0.012536	0.009741
6-311G	0.051080	0.047344	0.055844	0.050747	0.009146	0.009454	0.009675	0.009775	0.007721	0.004946	0.012759	0.008319
6-31G**	0.043460	0.040076	0.068733	0.050747	0.008191	0.008845	0.043237	0.008881	0.012627	0.009677	0.033023	0.012084
6-311G**	0.039213	0.036181	0.046077	0.039721	0.007891	0.007598	0.009225	0.007950	0.009426	0.007718	0.011176	0.009446
6-31++G**	0.031542	0.030964	0.037344	0.029616	0.008148	0.008211	0.009055	0.007787	0.008966	0.007952	0.012047	0.009397
6-311++G**	0.030859	0.027840	0.033917	0.027925	0.008066	0.007299	0.008271	0.007324	0.07094	0.005967	0.009409	0.007716
cc-pVDZ	0.043990	0.040600	0.056050	0.044018	0.008773	0.008517	0.010278	0.008612	0.009338	0.009265	0.012253	0.010469
cc-pVTZ	0.028016	0.028752	0.040342	0.041568	0.008010	0.008065	0.009811	0.009576	0.007740	0.007204	0.011561	0.009869
Aug-cc-pVDZ	0.028050	0.029212	0.038363	0.033253	0.008128	0.007653	0.009941	0.007926	0.007575	0.007569	0.011234	0.009444
Aug-cc-pVTZ	0.026943	0.026026			0.007897	0.007897			0.007046	0.007149		

TABLE II

Intermolecular frequencies for the HF dimer computed at the HF/CHA-HF and MP2/CHA-MP2 levels using 6-31G, 6-311G, 6-31G**, 6-311G**, 6-31++G**, 6-311++G**, cc-pVDZ, cc-pVTZ, Aug-cc-pVDZ, and Aug-cc-pVTZ basis sets.

| Basis/method | ω_1 (cm^{-1}) | | | | ω_2 (cm^{-1}) | | | | ω_3 (cm^{-1}) | | | |
	HF	CHA-HF	MP2	CHA-MP2	HF	CHA-HF	MP2	CHA-MP2	HF	CHA-HF	MP2	CHA-MP2
6-31G	165.34	180.16	137.91	173.96	223.84	221.88	246.12	248.64	568.27	559.71	620.91	575.36
6-311G	152.47	160.74	135.44	173.34	215.09	193.40	235.41	224.06	551.11	507.64	618.12	531.68
6-31G**	127.10	154.03	131.74	144.63	230.85	226.72	233.60	224.81	600.44	544.91	746.61	561.81
6-311G**	144.55	147.97	107.02	151.50	200.94	203.54	208.91	214.68	538.25	497.53	584.95	520.18
6-31++G**	142.23	139.58	156.32	135.41	203.85	202.81	218.33	199.24	523.36	509.17	569.27	514.10
6-311++G**	141.10	133.76	145.75	133.48	191.92	180.97	202.58	191.44	503.37	466.10	536.72	482.27
cc-pVDZ	152.28	162.00	122.94	163.10	209.37	217.19	232.28	222.35	560.49	568.68	643.51	546.43
cc-pVTZ	135.69	138.20	153.48	161.65	190.36	193.48	208.24	221.24	509.56	498.17	599.50	557.27
Aug-cc-pVDZ	135.59	138.88	159.78	146.47	198.11	195.51	220.60	198.71	502.71	492.45	581.62	524.58
Aug-cc-pVTZ	134.05	131.28			193.50	193.03			497.84	493.83		
Exp.	125				161				475			

sents the appropriate application of the CHA scheme with conventional energy calculation for the perturbational problem. This formalism is called CHA/MP2 [27]. In this perturbation theory the zeroth-order energy can be calculated as the sum of the occupied orbitals energies. Despite the fact that the CHA Hamiltonian is not Hermitian, the occupied orbital energies were always obtained as real numbers, providing E_0 to be real. In few cases one obtains complex virtual orbital energies, but because they always appear in complex conjugate pairs the calculated CHA/MP2 energy corrections are always real [27].

SCC-DFTB METHOD

Recently the approximate quantum mechanical (SCC-DFTB) method was developed for organic molecules [36–39]. This method is comparable in computational speed with the AM1 and PM3 methods and is derived from DFT by an expansion of the DFT total energy up to second order in the charge density fluctuations $\Delta\rho$ around a reference density ρ_0 [38, 39]. The subsequent approximations lead to a generalized eigenvalue problem that has to be solved self-consistently for atomic charges. The method can be seen as an extension of so-called tight binding (TB) methods to charge self-consistency. All parameters of this model are calculated from DFT and the method is therefore called the SCC-DFTB scheme.

The second-order terms in the density fluctuations are approximated by a simple distribution of atom-centered point charges $\Delta\rho_\alpha = q_\alpha - q_\alpha^0$, estimated by a Mulliken charge analysis. The approximate DFT energy functional becomes

$$E_{\text{tot}} = \sum_i^{\text{occ}} \sum_{\mu\nu} c_\mu^i c_\nu^i H_{\mu\nu}[\rho_0] + \frac{1}{2}\sum_{\alpha\beta}\Delta q_\alpha \Delta q_\beta \gamma_{\alpha\beta} + E_{\text{rep}}[\rho_0].$$

(2)

The Hamilton matrix elements $H_{\mu\nu}[\rho_0]$ are calculated within DFT-GGA in a two-center approximation using a minimal basis of atomic-like wave functions ϕ_μ. The second term on the right side of Eq. (2) represents the long-range Coulomb interactions between point charges at different sites and includes the self-interaction contributions of the single atoms. $E_{\text{rep}}[\rho_0]$ is approximated as a sum of two-body interactions, $E_{\text{rep}} = \sum_{\alpha\neq\beta} U(R_{\alpha\beta})$, which are determined by comparing bond stretching energies calculated from the SCC-DFTB method with those from DFT calculations.

The results for reaction energies, geometries, and frequencies for small organic molecules have been presented elsewhere [36, 37]. The mean average deviations from experimental values are comparable to full DFT calculations. The method has also been benchmarked for biologically relevant molecules, H-bonded complexes, small peptides, and H-bonded stacking DNA base pair interactions

TABLE III
Diagonal force constants [$r = O(1)\ldots O(2)$, $\alpha_1 = H(1) - O(1)\ldots O(2)$, $\alpha_2 = O(1)\ldots O(2) - H(2)$] for HF dimers computed at the HF/CHA-HF and MP2/CHA-MP2 levels using 6-31G, 6-311G, 6-31G**, 6-311G**, 6-31++G**, 6-311++G**, cc-pVDZ, cc-pVTZ, Aug-cc-pVDZ, and Aug-cc-pVTZ basis sets.

Basis/method	f_{rr} (a.u./A²)				$f_{\alpha 1\alpha 1}$ (a.u./Rad²)				$f_{\alpha 2\alpha 2}$ (a.u./Rad²)			
	HF	CHA-HF	MP2	CHA-MP2	HF	CHA-HF	MP2	CHA-MP2	HF	CHA-HF	MP2	CHA-MP2
6-31G	0.051759	0.054411	0.052598	0.054696	0.035060	0.036595	0.036847	0.039026	0.018561	0.019114	0.016563	0.018173
6-311G	0.058066	0.054571	0.065119	0.057633	0.035891	0.033682	0.039052	0.036979	0.021555	0.018485	0.021506	0.018249
6-31G**	0.034197	0.036847	0.043317	0.039503	0.024449	0.025606	0.031675	0.029652	0.011268	0.011564	0.013156	0.012091
6-311G**	0.035496	0.032001	0.043514	0.036011	0.021717	0.020797	0.026915	0.024370	0.011500	0.010571	0.011488	0.010680
6-31++G**	0.033215	0.028103	0.043253	0.029863	0.022075	0.020887	0.027886	0.022368	0.013176	0.010530	0.015692	0.010895
6-311++G**	0.030704	0.027448	0.038343	0.028633	0.020697	0.019032	0.027052	0.021762	0.012675	0.010152	0.014707	0.010323
cc-pVDZ	0.034986	0.031769	0.044424	0.033326	0.023163	0.021174	0.031868	0.024643	0.010750	0.010349	0.012213	0.010190
cc-pVTZ	0.025030	0.024869	0.034986	0.039670	0.019456	0.020747	0.023160	0.029057	0.009536	0.008822	0.010750	0.009960
Aug-cc-pVDZ	0.024287	0.025944	0.035439	0.032955	0.020022	0.019065	0.028130	0.024518	0.009205	0.009216	0.010838	0.010793
Aug-cc-pVTZ	0.023583	0.023732			0.019861	0.019303			0.008963	0.008896		

[38–40]. Vibrational frequencies for small model peptides have been compared with results of B3LYP/6 − 31G* and MP2/6 − 31G* calculations and the vibrational absorption and the vibration circular dichroism spectra have been evaluated within an SCC-DFTB/DFT hybrid scheme, leading to a good agreement with the results of *ab initio* methods [41]. The benchmarks performed so far have been satisfactory, showing that the SCC-DFTB method is able to give a reliable description of several biologic model molecules.

Results and Discussion

The calculations have been carried out partly in Heidelberg on a Hewlett-Packard cluster and partly in Debrecen on a Pentium 200 PC running Linux. In the standard HF and MP2 calculations the Gaussian 98 computer code [43] was utilized while the CHA-type calculations were performed by generating the input data (integrals and RHF orbitals) with a slightly modified version of HONDO-8 [44].

In these calculations we used the same CHA/HF program as in [15] and the CHA/MP2 program of Mayer and Valiron [27, 45]. For the frequencies calculations based on the Wilson's G-F method, the program written by Beu [46] was applied. The HF and H_2O dimers geometries were optimized using the conventional HF and second-order Møller–Plesset perturbation theory (MP2) for each basis set.

Several different basis sets were used: 6-31G, 6-311G, 6-31G**, 6-311G**, 6-31G**++, 6-311G**++, cc-pVDZ, cc-pVTZ, aug-cc-pVDZ, and aug-cc-pVTZ. From the 6-31G to the 6-311G**++ are standard Polpe basis sets, while cc-pVDZ to aug-cc-pVTZ are Dunning's correlation consistent basis sets. We had to enter the cc-pVXZ and aug-cc-pVXZ (X = D, T) basis sets in to HONDO-8 as external basis sets. A small difficulty should be noted in this connection: HONDO-8 only performs calculations by using *6d* and *10f* functions, while the cc-pVXZ and aug-cc-pVXZ basis sets are assumed to use pure *d* and *f* functions. This may cause minor discrepancies in the comparisons.

The uncorrected dimer geometries were optimized both at HF and MP2 levels using the analytic gradient method implemented in Gaussian 98, while the CHA geometries were calculated using a numerical gradient method in internal coordinates. To test the latter method we performed some sample calculations using both the analytic gradient method implemented in Gaussian 98 and our nu-

TABLE IV

Intermolecular frequencies for H_2O dimer computed at the HF/CHA-HF and MP2/CHA-MP2 levels using 6-31G, 6-311G, 6-31G**, 6-311G**, 6-31++G**, 6-311++G**, cc-pVDZ, cc-pVTZ, Aug-cc-pVDZ, and Aug-cc-pVTZ basis sets.

| Basis/method | ω_1 (cm^{-1}) | | | | ω_2 (cm^{-1}) | | | | ω_3 (cm^{-1}) | | | |
	HF	CHA-HF	MP2	CHA-MP2	HF	CHA-HF	MP2	CHA-MP2	HF	CHA-HF	MP2	CHA-MP2
6-31G	177.12	181.96	151.91	173.74	205.43	211.30	205.74	211.96	407.01	412.57	409.21	418.86
6-311G	186.52	179.23	163.63	153.81	217.45	210.19	229.94	214.34	404.56	391.52	403.73	390.23
6-31G**	137.91	142.14	141.77	144.54	177.04	190.59	204.63	204.22	377.18	380.23	428.78	413.20
6-311G**	135.91	127.88	134.88	125.20	171.75	164.02	187.05	173.99	347.87	340.35	384.32	368.91
6-31++G**	144.82	136.51	169.26	141.30	174.55	162.59	202.55	171.06	338.62	328.04	373.81	339.58
6-311++G**	148.79	138.07	170.50	147.43	165.71	157.13	202.83	172.24	324.01	311.05	384.74	352.65
cc-pVDZ	140.72	128.33	149.73	113.32	170.39	164.05	195.02	170.11	348.65	336.58	408.10	367.22
cc-pVTZ	132.86	132.92	148.60	157.89	149.86	152.37	180.50	193.76	319.85	324.61	372.12	376.90
Aug-cc-pVDZ	129.73	129.29	154.47	143.12	154.90	156.21	186.63	179.05	320.22	314.28	371.15	350.79
Aug-cc-pVTZ	130.57	128.56			151.48	151.29			307.76	304.02		
Exp.	150				—				320			

merical gradient code, respectively. Practically no difference has been found between them in conventional uncorrected cases. A similar test has been made for the force constants and harmonic frequencies. The conventional HF and MP2 calculations for the force constants (in internal coordinates) and harmonic vibrational frequencies have been calculated with the standard routines of Gaussian 98 code. In the CHA framework at first we calculated the numerical second derivatives of the energies to obtain the CHA force constants; then, using these data the NOMAD program [46] was applied to calculate the appropriate CHA harmonic frequencies. As we were interested in the BSSE content in the interaction energies between the monomers, only those components of the force constant matrix were recalculated which correspond to the intermolecular interactions.

Table I displays the results obtained for the diagonal force constants of the HF dimer for the uncorrected and CHA schemes both at the HF and MP2 perturbation levels of theory.

Table II shows the results obtained for the harmonic vibrational frequencies using the force constants presented in Table I. In Tables III and IV the same kind of results as Tables I and II are presented but for the H_2O dimer. For the sake of comparison, in Table V we present harmonic vibrational frequencies obtained from the basis-independent SCC-DFTB method.

Considering the results, the following conclusions can be drawn:

1. In accord with the observation that the BSSE-free CHA interaction energies usually exhibit less deep minima than those given by the uncorrected methods both at the HF and at the correlated levels of theory, in most cases the values of the diagonal force constants are significantly larger in the uncorrected case. Sometimes the opposite effect also can be observed, which probably is the consequence of using not large enough basis sets. It has also been found that the BSSE-uncorrected geometries, both as the HF and correlated levels of the theory calculated in the 6-31G** basis set, differ much from the others. However, this discrepancy, already observed by Salvador et al. [47], more or less has been restored by using our CHA scheme. Turning to the calculation of the harmonic vibrational frequencies, no rigorous tendency was found because the frequency values can strongly depend on the modified dimer geometries.

2. As can be expected, the difference between

TABLE V

Intermolecular frequencies for H_2O dimer computed at the SCC-DFTB theory level.

Method	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})
SCC-DFTB	143.19	212.63	322.16
Exp.	150	—	320

the values of the uncorrected and CHA-corrected results become smaller in large enough basis sets as the values of the intermolecular interactions converge to each other.

3. Another interesting observation is that the values of the diagonal force constants and harmonic vibrational frequencies calculated at the correlated level are larger than those obtained from the HF-type calculation. This effect is a direct consequence of the fact that at the correlated level the interactions between the molecules are much stronger.

4. Turning to the correlated level, the amount of the BSSE content in the intermolecular interaction energies is much larger than that at the HF level and this effect manifests in the values of the force constants and harmonic vibrational frequencies too.

5. Concerning the experimental and basis set-independent (SCC-DFTB) results, they are fairly close to each other and the CHA results converge slightly better to these numbers than those obtained from the conventional uncorrected calculations.

Summary

We performed calculations of the force constants and harmonic vibrational frequencies of the hydrogen fluoride and water dimers. The calculations have been undertaken both at the HF and correlated (MP2) levels of theory using several different basis sets ranging from the small to the intermediate. The results were compared with those given by the basis set-independent (SCC-DFTB) method. We also took into account the BSSE by applying the CHA. The results show that the influence of BSSE content is significant on the force constants and harmonic vibrational frequencies, so removing it is important.

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