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Effects of counterpoise correction and basis set extrapolation on the MP2 geometries of hydrogen bonded dimers of ammonia, water, and hydrogen fluoride†

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We study the combined effects of counterpoise correction and basis set extrapolation on the second-order Møller–Plesset (MP2) geometries of three hydrogen bonded dimers, namely $(NH_3)_2$, $(H_2O)_2$ and $(HF)_2$. For $(NH_3)_2$, we study three characteristic structures on its potential energy surface. In addition, we look at the basis set convergence when diffuse functions on the hydrogen atoms are left out, as well as the errors introduced by including core correlation with valence-only correlation-consistent basis sets. Overall, the counterpoise-corrected and extrapolated geometries appear to be very reliable and are in convincing agreement with the geometries from explicitly correlated MP2-F12 calculations. Obtaining geometries with errors of less than 0.001 Ångstrom and 0.5 degrees compared to the basis set limit is, however, even with these advanced methods a difficult task.

I. Introduction

Due to their importance in biology and solvation processes, hydrogen bonded systems are a fundamental subject of research interest.[1,2] The most important characteristic of a hydrogen bonded system is the total intermolecular interaction energy at the global minimum structure of the potential energy surface. In order to obtain a structure that is a good approximation to the global minimum *via* geometry optimizations with standard supermolecular *ab initio* methods, precise gradients and energies are needed. In order to obtain these in the case of intermolecular interactions

1. the basis set superposition error (BSSE) has to be corrected[3–5] and

2. the slow convergence of the intermolecular interaction energy, in particular of the dispersion contribution, with the size of the basis set has to be taken into account.

Concerning item 1, there is nowadays a wide consensus that the BSSE can be removed[3] by the counterpoise (CP) procedure of Boys and Bernardi.[6]

The slow convergence of the intermolecular interaction energy with the size of the basis set can be remedied in three different ways:

One method is to add bond functions which improve the convergence of the intermolecular dispersion energy contribution.[7–12] Secondly, the slow convergence of the correlation energy with basis set size can be overcome by extrapolation of the results obtained from a series of correlation consistent basis sets with increasing X-tuple-ζ quality.[13,14] Albeit a literature search reveals that in the last decade many extrapolation formulae have been suggested that are more intricate, we will use the simple X^{-3} expression with two consecutive X-tuple-ζ basis sets.[15–17] This approach is theoretically well-founded and known to result in good basis set limit interaction energies for hydrogen bonded dimers in conjunction with the CP correction.[18]

At this point, one should note the following difficulty: Since the BSSE is a spurious contribution resulting from the incompleteness of the basis sets, it should vanish if the energies are extrapolated to the basis set limit. For example, upon application of the basis set extrapolation to the energies involved in the calculation of the supermolecular interaction energy, counterpoise corrected and uncorrected interaction energies should become equal. However, in their review[19] van Mourik *et al.* point out that in the case of intermolecular interactions the BSSE destroys the well behaved convergence patterns with the basis set size of the involved energies which is a prerequisite for the applicability for basis set extrapolation formulae. Halkier *et al.*[18] provide the following explanation for this phenomenon: They conclude from experience with the basis set convergence of dipole moments[20] that basis set extrapolations cannot remedy significant basis set errors other than those originating from the description of the electronic Coulomb cusp. Non-removal of BSSE results in an unsystematic, non-monotonic convergence of the correlation contribution to the interaction energy with increasing basis set size. As soon as the BSSE is removed by the CP procedure, the basis set convergence behavior is nearly exclusively determined by the electronic Coulomb cusp, which makes the basis set extrapolation formula work properly.

The third method to overcome the problem of the slow convergence of the intermolecular interaction energy with the

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size of the basis is the use of explicitly correlated wave functions (see, *e.g.* ref. 21). These are better suited than ordinary Slater-determinant based wave function expansions to describe the electronic Coulomb cusp.[15,22,23] Descendants of the explicitly correlated methods are the R12 methods of Kutzelnigg and coworkers (see, *e.g.* ref. 24–26). These methods avoid molecular integrals involving the coordinates of more than two electrons by insertion of the resolution of the identity. In contrast to the basis set extrapolation methods, the R12 methods eliminate the BSSE of the *correlated* contribution to the intermolecular interaction energy quite well: In ref. 27 it is mentioned that for the benzene–X and X–X systems with X = Ne,Ar the CP correction is very small (smaller than 0.16 kJ mol^{-1}) and the equilibrium distances are nearly unaffected by the CP correction. This reference uses the "old" MP2-R12 theory where the one-particle orbital basis set is used for the resolution of the identity. For these calculations large uncontracted orbital basis sets had to be used which yielded nearly converged Hartree–Fock (HF) energies. Nowadays, R12 methods use auxiliary basis sets for the resolution of the identity,[28,29] which makes them work well with small orbital basis sets, too, where the Hartree–Fock energies are not converged and the BSSE of the Hartree–Fock contribution to the intermolecular interaction energies is not negligible any more. On the other hand, the BSSE of the *correlated* contribution to the intermolecular interaction energies becomes so small with modern R12 methods that an application of the CP procedure is not necessary any more[30] (for numerical evidence for the dimers He_2, Be_2 and Ne_2 see ref. 31). Consequently, when intermolecular interaction energies are computed with modern R12 methods using a small orbital basis set, the CP procedure has to be applied to correct for BSSE of the Hartree–Fock contribution to the intermolecular interaction energy.[30]

In this work, our interest will be focused on the combined effects of BSSE and basis set extrapolation on the optimized geometries of hydrogen bonded dimers. Even nowadays it is common practice to optimize dimer geometries without CP correction or basis set extrapolation. A compilation of literature results for geometries of the HF dimer can be found in Table 8 of ref. 32 and for geometries of the water dimer in Table 1 of ref. 33. High-level CP corrected water dimer minimum geometries obtained with the MP2 method are reported in ref. 34, and with the MP2, MP4, and CCSD(T) methods in ref. 35 and 36. State-of-the-art non-CP corrected ammonia dimer geometries obtained with the MP2 and MP4 methods are given in ref. 37 and with the CCSD(T) and CCSDT(Q) methods in Table 4 of ref. 38. Highly reliable CP corrected ammonia dimer geometries obtained with the MP2 method can be found in ref. 39. For a more complete list of the literature on the hydrogen bonded dimers encountered in this work the reader is referred to the references cited in the works mentioned above.

II. Methods

An inspection of the literature reveals that since the MP2 method works very well for hydrogen bonded systems, geometrical parameters and interaction energies will change only slightly upon improving the correlation method from MP2 to CCSD(T).[32,33,35,37] A slight drawback of the MP2 level for obtaining optimized geometrical parameters for hydrogen bonded dimers is the exaggeration of the XH bond elongation of the hydrogen bond donor upon hydrogen bond formation.[33] In the case of the HF dimer, the CP corrected MP2 and CCSD(T) interaction energies for the hydrogen bonded dimer differ by at most 0.63 kJ mol^{-1},[18] and at most 0.27 kJ mol^{-1} for the water dimer.[18,33] Changing the correlation method from MP2 to MP4 affects the CP corrected interaction energies of the characteristic ammonia dimer geometries by only about 0.1 kJ mol^{-1}.[37] On the other hand, the geometrical parameters change significantly with the change of the basis set size[33–35,37,39] and the inclusion of CP correction.[19,33–35,39] In particular, the ammonia dimer has been found to be very sensitive with respect to these two items: Stationary points found with one basis set may even disappear with another basis set[37–39] and/or inclusion of the CP correction.[37]

This shows that CP corrected, extrapolated geometries of hydrogen bonded complexes, especially of the ammonia dimer, are of great interest. Methods for CP corrected[4,5,41] and extrapolated[40,42] geometry optimizations have been developed. In contrast to automatic extrapolated geometry optimizations, CP corrected geometry optimizations have been implemented nowadays in several standard *ab initio* packages. For this work, we have implemented the automatic combination of CP correction and basis set extrapolation for geometry optimizations.

Three years ago, two of us published an extensive overview for 16 hydrogen bonded species[43] to continue on a set of accurate reference data for hydrogen bonds,[44] concentrating on overall trends, comparing several methods with several basis sets to accurate coupled-cluster results.

In the present work, we focus on the basis set convergence of MP2 geometrical parameters. In particular, we investigate three geometries of the ammonia dimer, which is known to have a very flat potential energy surface. The cyclic ammonia dimer structure (see Fig. 1) has D_{2h} symmetry, while both the asymmetrical and linear structures exhibit C_s symmetry. The difference between the latter two structures is the eclipsed *vs.* staggered conformation of the non-hydrogen bonded hydrogen atoms. Both of them are minima, with the asymmetrical structure as the global minimum. As we will see later that, especially for these cases, very subtle differences in the basis set can have large effects on the geometrical parameters. The cyclic structure corresponds to a first-order saddle point on the potential energy surface between two asymmetrical minima. The investigated global minimum structures of both the water and hydrogen fluoride dimers display C_s symmetry.

Additionally, the effect of core correlation as well as of the diffuse functions on the hydrogen atoms are studied.

A. Counterpoise corrected geometry optimizations

CP corrected geometry optimizations have to be performed by searching the geometry where the energy

$$E_{\text{total,CP}} = E_{\text{AB}}^{\text{a}\cup\text{b}}(\text{AB}) - E_{\text{AB}}^{\text{a}\cup\text{b}}(\text{A}) - E_{\text{AB}}^{\text{a}\cup\text{b}}(\text{B}) + E_{\text{AB}}^{\text{a}}(\text{A}) + E_{\text{AB}}^{\text{b}}(\text{B}) \quad (1)$$

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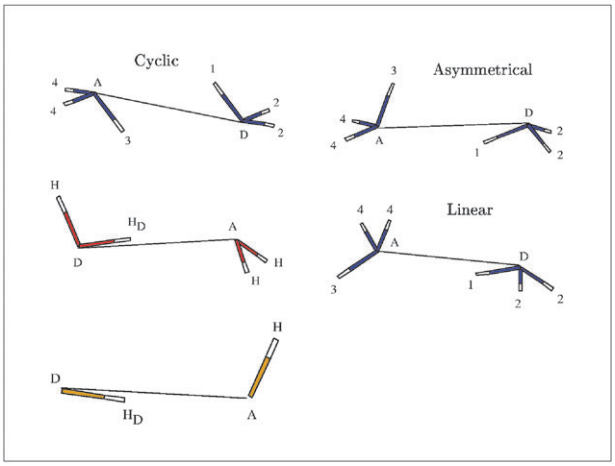


Fig. 1 Dimer geometries. According to our convention, the central atom of a hydrogen bond donor is termed *D* and of an acceptor *A*. In the case of the H_2O and HF dimer the hydrogen atom participating in the hydrogen bond is termed 'H_D' and all other hydrogen atoms are termed 'H'. In all cases where an ambiguity might arise whether the geometrical parameters are to be assumed as intra- or intermolecular, they should be considered as intramolecular.

becomes minimal (*cf.* eqn (5) of ref. 4 and eqn (3) of ref. 5). In this equation, the superscripts a∪b, a, and b indicate that the calculations have been performed in the basis set of the full dimer, in the basis set of monomer A, and the basis set of monomer B, respectively. The labels between the parentheses designate the fragment, *i.e.*, the dimer AB, monomer A, and monomer B. The subscript AB indicates that the corresponding fragment adopts the geometry it has in the dimer AB. The CP corrected energy gradients with respect to the atomic coordinates are obtained by substituting the energies in eqn (1) by the corresponding gradients (*cf.* eqn (5) in ref. 5). Non-CP corrected geometries are simply obtained from minimization of the first term on the right hand side of eqn (1).

B. Extrapolation techniques

To obtain correlation contributions to the intermolecular interaction energy corresponding to a nearly complete basis set, we apply the two-point extrapolation formula of ref. 17 to the correlation energies of the fragments.

For the computation of the CP- and non-CP corrected intermolecular interaction energies and for eqn (1), we use

$$E^{\mathrm{corr,ext}}_{(X-1)X} = \frac{X^3}{X^3-(X-1)^3}E^{\mathrm{corr}}_X - \frac{(X-1)^3}{X^3-(X-1)^3}E^{\mathrm{corr}}_{(X-1)}, \tag{2}$$

where E^{corr}_X and $E^{\mathrm{corr}}_{(X-1)}$ are the fragment correlation energies obtained with a *X*-tuple- and $(X-1)$-tuple-ζ correlation consistent basis set respectively. The extrapolated Hartree–Fock and total fragment energies are obtained *via*

$$E^{\mathrm{HF,ext}}_{(X-1)X} \approx E^{\mathrm{HF}}_X, \tag{3}$$

$$E^{\mathrm{total,ext}}_{(X-1)X} = E^{\mathrm{HF,ext}}_{(X-1)X} + E^{\mathrm{corr,ext}}_{(X-1)X}. \tag{4}$$

Eqn (3) can be employed because the smallest value for *X* we used corresponds to a quadruple-ζ basis set (in case of the TQ extrapolations), where the Hartree–Fock energies already can be assumed to be converged (as shown by comparison to the 5Z basis set results).

Since eqn (2) is linear with respect to the energies, the corresponding extrapolated energy gradients can be obtained by substitution of the energies by the equivalent gradients in eqn (2) through (4).

C. MP2-F12

For comparison, we optimized all dimer geometries with respect to MP2-F12 energies. In MP2-F12 theory, the conventional expansion of the MP2 wave function is supplemented with geminals

$$|\chi_{kl}\rangle = \hat{Q}_{12}f_{12}|\varphi_k\varphi_l\rangle \tag{5}$$

that depend explicitly on the interelectronic distance r_{12}. In this notation, $\hat{Q}_{12}$ denotes a projection operator, $f_{12} = f(r_{12})$ the correlation factor, and $|\varphi_k\varphi_l\rangle$ a properly antisymmetrized product of occupied Hartree–Fock orbitals.

Typically, the projection operator $\hat{Q}_{12}$ is chosen to make the geminals strongly orthogonal on the Hartree–Fock reference and to project out all of the conventional excitations, which is sometimes denoted as Ansatz 3[29] but for consistency with previous publications[45,46] will be denoted as Ansatz 2 in the following. In this formulation, the coupling of the conventional pairs with the explicitly correlated pairs is very small and can be neglected, which is indicated with an asterisk. This leads to an energy correction of the form

$$\Delta E^{*}_{\mathrm{F12}} = \frac{1}{8}\sum_{ij}\sum_{klmn} c^{kl}_{ij}\langle\chi_{kl}|(\hat{F}_{12}-\varepsilon_i-\varepsilon_j)|\chi_{mn}\rangle c^{mn}_{ij} + \frac{1}{2}\sum_{ijkl} c^{kl}_{ij}\langle\chi_{kl}|g_{12}|\varphi_i\varphi_j\rangle. \tag{6}$$

Note that $\hat{F}_{12}$ denotes the sum of the Fock operator of electrons 1 and 2, whereas ε_i denotes an orbital energy. g_{12} is the conventional electron repulsion.

One approach to determine the amplitudes c^{kl}_{ij} of the explicitly correlated excitations is the fixed coefficient version[47] where the geminal coefficients are determined from the singlet and triplet pair cusp conditions.[15,23]

This means that the geminal coefficients are not optimized, which results in absolute as well as interaction energies being not as favorable as with optimized coefficients. For our work, we have chosen the fixed coefficient R12 approach since it still yields good results for intermolecular interactions.[30]

From a computational point of view the fixed-coefficient R12 approach is the numerically most stable. Since the energy it yields is invariant with respect to unitary transformations among the occupied Hartree–Fock orbitals, it fulfils the cusp conditions exactly (see Table 1 of ref. 48) and it is free of a geminal BSSE. The geminal BSSE is not to be confused with the ordinary orbital BSSE and cannot be be removed by the CP correction or any other simple procedure alike.

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D. CABS singles

Furthermore, in case of MP2-F12 we also carry out the computation of the perturbative complementary basis set (CABS) singles correction[49] (see also ref. 50):

$$\Delta E_s = \sum_{ip'} \frac{F_{ip'}^2}{\varepsilon_i - \varepsilon_{p'}}, \quad (7)$$

where $F_{ip'}$ are elements of the extended Fock matrix. This provides a correction to the Hartree–Fock results and significantly improves the result of the reference determinant.

III. Computational details

A. Counterpoise corrected geometry optimizations

The "jobex" script of TURBOMOLE 5.7[51] has been modified in order to perform combined CP corrected and basis set extrapolated geometry optimizations at the MP2 level of theory. The basis sets used are the standard augmented correlation consistent basis sets of Dunning and co-workers.[52,53] These will, for brevity, be denoted as XZ basis set rather than aug-cc-pVXZ in the Discussion section. All calculations have been performed using the resolution of Identity (RI)–MP2 implementation using density fitting with standard auxiliary basis sets[54,55] and analytical gradients.

In the case of the water dimer at its minimum geometry, the invocation of core correlation lowers the interaction energy by only 0.11 kJ mol^{-1}, for ammonia by 0.05 and for the hydrogen fluoride dimer by 0.07 kJ mol^{-1}.[43] The influence of core correlation on the ammonia dimer potential energy surface in the hydrogen bond region has been shown to be small,[37] so the neglect of core correlation should lead to reasonable geometrical parameters. The geometry optimizations have been assumed to be converged when the largest Cartesian gradient component became smaller than 10^{-5} E_h/a_0.

B. MP2-F12 calculations

The MP2-F12 calculations were performed using ansatz 2A* with a complementary basis set to approximate three electron integrals.[29] In ref. 45, the effect of the neglected exchange commutator terms and coupling terms in the 2A* approximation was tested by performing 2A*, 2A, 2B* and 2B calculations using numerical gradients on small, covalently bound molecules such as CO, H_2O, NH_3 and others. The differences between the approximations (2A*, 2A, 2B*, 2B) were found to be smaller than the remaining basis set errors and the CABS singles contributions. Hence, the calculation of analytical gradients was implemented using the simplest approximation (2A*), and this implementation is used here. We assume that the differences between the approximations are also very small for the equilibrium geometries of weakly bound complexes. This point in fact requires additional numerical tests. For the orbital basis set, we use the aug-cc-pVTZ and aug-cc-pVQZ basis sets. The computation of two electron integrals was carried out using density-fitting techniques[56] using the correlation fitting basis sets aug-cc-pwCVQZ and aug-cc-pwCV5Z, respectively.[57,58] As advocated in ref. 31, we use a Slater-type geminal correlation factor f_{12}.[59] The exponent of the Slater-type geminal, which is approximated by a contraction of 6 Gaussians (STG-6G), has been chosen according to the recommendations by Yousaf and Peterson.[60] To circumvent two-electron integrals involving commutators of the kinetic energy, we applied a resolution of the identity similar to that of Kedžuch and coworkers.[61]

All explicitly correlated computations have been performed with the TURBOMOLE program package 6.1. The geometry optimizations have been performed with analytical gradients computed in a modified TURBOMOLE version.[45,46]

C. CABS singles

As mentioned above, the BSSE of the correlated contribution to the intermolecular interaction energy is small for modern R12 methods. In the case of the orbital basis set actually used, the Hartree–Fock energy is nearly converged and the BSSE of the Hartree–Fock contribution to the intermolecular interaction energy is small (a CP correction of the Hartree–Fock contribution of 0.05/0.05/0.05/0.12/0.23 kJ mol^{-1} of the $((NH_3)_2$ asym/$(NH_3)_2$ cycl/$(NH_3)_2$ lin/$(H_2O)_2$/$(HF)_2$ system in the TZ basis set, respectively). This Hartree–Fock BSSE is reduced further because we include the computation of the perturbative CABS singles correction. Therefore, we do not apply CP corrections to the interaction energies for our explicitly correlated computations.

The Fock matrix elements needed according to eqn (7) were computed using the RI-JK approximation. For this, the JK-aug-cc-pVTZ and JK-aug-cc-pVQZ basis sets were used.[62]

IV. Results

A. CP correction and extrapolation

Looking at the results in Table 1, we conclude that the use of the CP correction is vital when extrapolating intermolecular geometries. Since the intramolecular parameters are basically converged with a QZ basis set for all geometries (distances within 0.001 Ångstrom and angles within 0.15 degrees), we restrict ourselves to the discussion of the intermolecular values. For completeness, full tables are given in the supplementary material.† In Table 1, E_{int} denotes the interaction energies computed with reference to the monomer geometries as found in the dimer, whereas E_{stab} denotes the stabilization energies with reference to separately optimized monomer geometries. Thus, E_{int} will be larger in magnitude than E_{stab}. 'CP' stands for the counterpoise corrected results and 'non-CP' for the non-counterpoise corrected energies, respectively.

Note that the difference between E_{stab} and E_{int}, sometimes denoted as relaxation energy, is essentially independent of the basis set and on the application of the CP correction—at least when using basis sets of TZ quality and better. In case of the asymmetrical structure of the ammonia dimer, it amounts to 0.07, for the cyclic structure to 0.05 kJ mol^{-1}, and for the linear structure to 0.09 kJ mol^{-1}. For the water dimer, it is 0.17 kJ mol^{-1}, and for the hydrogen fluoride dimer 0.14 kJ mol^{-1}. In all cases, the deviations from these values are at most 0.01 kJ mol^{-1}.

The convergence of the stabilization energies with basis set size shows the usual pattern, as demonstrated in Fig. 2: The CP

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Table 1 Intermolecular geometry parameters and energies of the NH_3, H_2O and HF dimers as obtained by counterpoise corrected as well as uncorrected geometry optimizations with the aug-cc-pVTZ to aug-cc-pV5Z basis sets as well as basis set extrapolated results. Site names used to specify distances and angles may be inferred from Fig. 1. Distances R are given in Ångstrom, angles θ in degrees, and energies E in kJ mol^{-1}

		Not counterpoise corrected					Counterpoise corrected				
		TZ	QZ	5Z	ext(TQZ)	ext(Q5Z)	TZ	QZ	5Z	ext(TQZ)	ext(Q5Z)
$(NH_3)_2$	R_{DA}	3.234	3.218	3.213	3.202	3.207	3.232	3.219	3.213	3.208	3.208
asymm.	θ_{1DA}	17.07	19.47	20.70	22.39	22.03	22.92	22.14	22.29	22.32	22.32
	θ_{3AD}	76.31	72.24	70.14	67.52	67.98	66.96	68.01	67.70	67.63	67.62
	E_{int}	−13.83	−13.56	−13.39	−13.40	−13.27	−12.66	−13.02	−13.13	−13.26	−13.26
	E_{stab}	−13.76	−13.48	−13.32	−13.32	−13.20	−12.60	−12.95	−13.06	−13.19	−13.18
$(NH_3)_2$	R_{DA}	3.168	3.164	3.164	3.161	3.163	3.190	3.175	3.169	3.165	3.164
cyclic	θ_{1DA}	42.34	42.37	42.38	42.42	42.40	42.55	42.47	42.44	42.42	42.42
	E_{int}	−13.62	−13.43	−13.29	−13.34	−13.18	−12.60	−12.94	−13.06	−13.19	−13.19
	E_{stab}	−13.56	−13.38	−13.23	−13.29	−13.12	−12.55	−12.89	−13.01	−13.14	−13.14
$(NH_3)_2$	R_{DA}	3.250	3.243	3.243	3.237	3.241	3.270	3.254	3.249	3.244	3.243
linear	θ_{1DA}	12.94	13.48	13.64	13.90	13.85	14.18	13.98	13.98	13.98	13.98
	θ_{3AD}	140.14	141.11	141.37	141.94	141.76	142.48	142.02	142.02	142.02	142.00
	E_{int}	−13.63	−13.33	−13.14	−13.14	−13.00	−12.40	−12.76	−12.87	−13.00	−12.99
	E_{stab}	−13.54	−13.23	−13.05	−13.04	−12.90	−12.32	−12.67	−12.78	−12.90	−12.90
$(H_2O)_2$	R_{DA}	2.907	2.903	2.904	2.898	2.905	2.933	2.918	2.913	2.908	2.907
	θ_{H_DDA}	5.55	5.50	5.42	5.58	5.30	5.54	5.53	5.55	5.58	5.60
	θ_{acc}^{a}	123.35	124.39	124.82	124.54	125.26	124.72	125.01	124.99	124.95	124.87
	E_{int}	−21.86	−21.49	−21.24	−21.29	−21.10	−19.89	−20.50	−20.69	−20.88	−20.90
	E_{stab}	−21.69	−21.31	−21.06	−21.10	−20.93	−19.74	−20.34	−20.52	−20.71	−20.73
$(HF)_2$	R_{DA}	2.746	2.736	2.739	2.732	2.740	2.771	2.753	2.749	2.745	2.744
	θ_{H_DDA}	6.37	6.41	6.32	6.60	6.26	6.74	6.64	6.71	6.72	6.77
	θ_{HAD}	111.12	111.49	111.92	111.32	112.20	111.66	111.80	111.68	111.64	111.53
	E_{int}	−19.85	−19.54	−19.30	−19.35	−19.26	−17.83	−18.44	−18.62	−18.74	−18.80
	E_{stab}	−19.72	−19.39	−19.16	−19.19	−19.13	−17.71	−18.31	−18.48	−18.61	−18.66

[a] θ_{acc} is the angle between the bisection line of the HOH angle of the hydrogen bond acceptor water monomer and the OO-axis.

corrected results converge from above, the non CP-corrected from below. The difference between the two gets smaller after extrapolation. For the HF dimer, the difference still amounts to about 0.4 kJ mol^{-1}, whereas it drops to 0.2 kJ mol^{-1} for the water dimer and nearly vanishes for the ammonia dimer.

Already when using an extrapolation with basis sets of triple- and quadruple-ζ quality, the geometries are essentially converged, provided that the CP correction has been employed. Specifically, the deviations of the distances are smaller than 0.001 Ångstrom and the angles smaller than 0.1 degrees among the quadruple- and quintuple-ζ extrapolated geometries. These geometries are basically converged. In contrast, the difference between the non CP-corrected extrapolated TQZ and Q5Z geometries are within 0.008 Ångstrom and almost one degree. The latter point is illustrated in Fig. 3. From this, it can be concluded that only the CP-corrected results allow for a systematic extrapolation. For example, the non CP-corrected angle of the HF dimer does not seem to converge at all from the TZ to QZ to 5Z basis set. Similar trends are also observed when comparing the results of the non-extrapolated 5Z basis set and the extrapolated Q5Z geometries. Again, the CP-corrected results appear much more stable than the non-corrected ones. Ideally, at the basis set limit the extrapolated non-corrected and corrected results should coincide. However, we can still see sizeable differences between both Q5Z extrapolations. These can become as large as 0.004 Ångstrom and 0.7 degrees. Without extrapolations, these differences increase to 0.009 Ångstrom and 2.4 degrees for the 5Z basis set. The stability of the CP corrected results suggests that the Q5Z extrapolated values are closest to the true basis set limit. Note that this also holds for the stabilization energies.

B. Removal of diffuse basis functions on the hydrogen atoms

In order to save computational time, it is sometimes advocated to leave out the diffuse functions of the hydrogens when doing quantum *ab initio* calculations,[63] resulting in so-called aug′-cc-pVXZ basis sets. The rationale behind this is that in many chemical species such as water, the hydrogen atoms are positively charged and, thus, the remaining electron density of the hydrogen will be mainly located at the nuclei.

The non CP-corrected aug′-cc-pVXZ stabilization energies shown in Fig. 2 are quite different from those of the aug-cc-pVXZ basis sets. When the CP correction is employed, both aug and aug′ results are very close to one another.

Comparing Tables 1 and 2, it becomes immediately clear that the non-CP corrected geometries are much less stable with aug′-cc-pVXZ than with the full aug-cc-pVXZ basis sets. While the results for the individual basis sets with a given X are relatively close to each other, the extrapolation becomes problematic without counterpoise correction: In the worst case, the ammonia dimer, the intermolecular angles differ by as much as 4 degrees between the TQZ and Q5Z extrapolations. The CP correction dramatically ameliorates the situation: Now the angles for all of the three investigated dimer structures agree within about 0.3 degrees. While the ext(Q5Z) geometries for $(HF)_2$ and $(H_2O)_2$ agree well with the corresponding results from the full basis sets, agreement somewhat detoriates for $(NH_3)_2$ and for the lower level ext(TQZ) extrapolation.

In conclusion, the geometries obtained by an approach like W1,[63] which uses ext(TQZ) extrapolation with aug′ basis sets for the double excitation correlation contribution without CP

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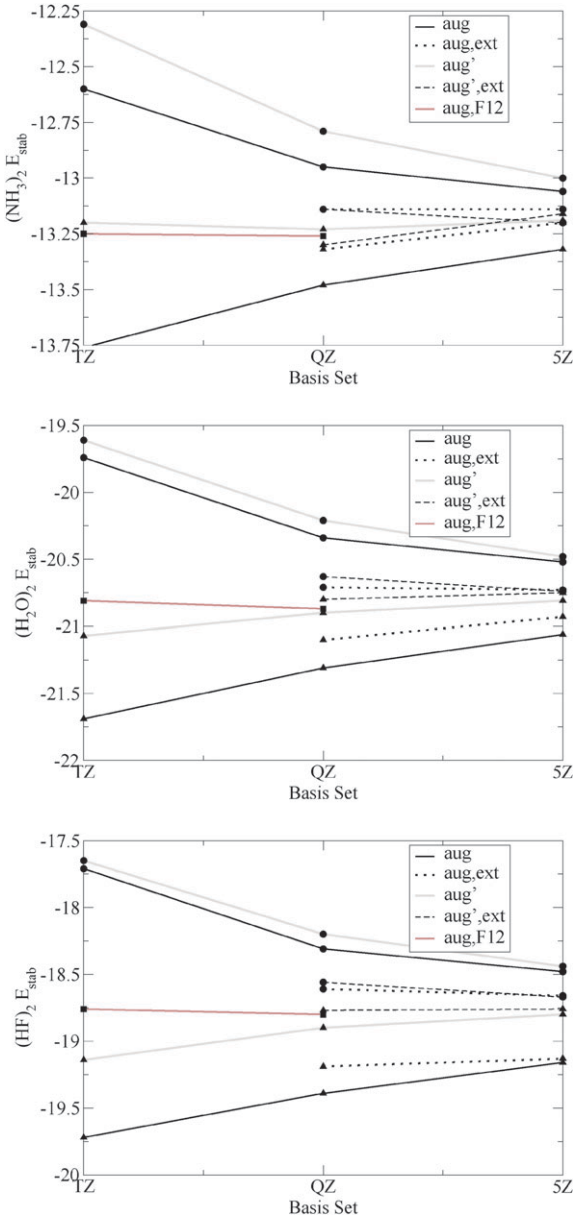


Fig. 2 Convergence of stabilization energies (in kJ mol^{-1}) for the asymmetrical $(NH_3)_2$ (top), $(H_2O)_2$ (middle) and $(HF)_2$ (bottom) dimers. Circles denote CP-corrected results, triangles results without CP correction. The values from two-point extrapolations of two consecutive aug-cc-pVXZ (aug′-cc-pVXZ) basis sets are labeled as aug,ext (aug′,ext).

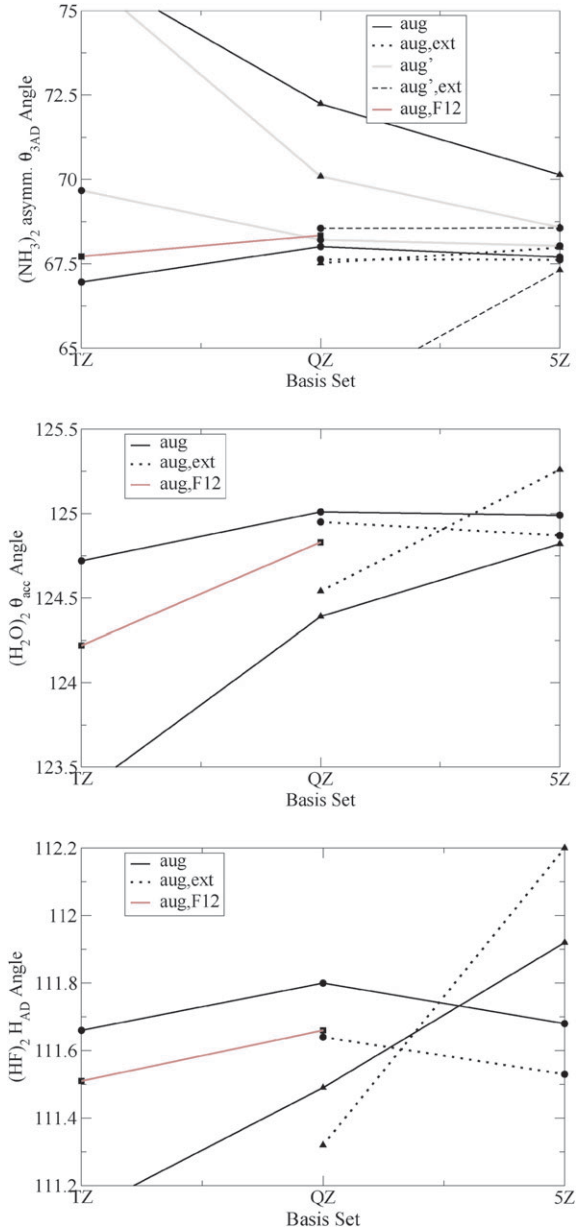


Fig. 3 Convergence of characteristic intermolecular angles (in degrees) for the asymmetrical $(NH_3)_2$ (top), $(H_2O)_2$ (middle) and $(HF)_2$ (bottom) dimers. Circles denote CP-corrected results, triangles results without CP correction. The values from two-point extrapolations of two consecutive aug-cc-pVXZ (aug′-cc-pVXZ) basis sets are labeled as aug,ext (aug′,ext). For clarity, aug′ results are only displayed for the ammonia dimer.

correction cannot be expected to be very accurate for hydrogen bonded systems. In contrast, neglecting diffuse basis functions on the hydrogen atoms in Q5Z extrapolations, as done in the W2 method, appears to be a valid approach.

C. Core correlation and valence basis sets

In addition, we have calculated all results including core-correlation with the basis sets mentioned above. A table with the corresponding results is presented in the ESI.† Inclusion of core correlation introduces a large extra BSSE caused by the core electrons. Although in this case the use of basis sets without specific core–core and core–valence correlation functions is generally not recommended, some groups advocated such an approach in order to obtain an error cancellation of the extra BSSE obtained with the missing correlation energy of the MP2 method. Even at the extrapolated Q5Z level (corrected or non-CP-corrected), we encounter large deviations from the MP2 results where the core electrons are not correlated. Even worse, at the lower basis set levels, the extrapolated non-corrected TQZ asymmetrical ammonia dimer geometry collapses into the cyclic one, yielding an inappropriate global minimum geometry. This leads to the conclusion that the

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Table 2 Intermolecular geometry parameters and energies of the NH_3, H_2O and HF dimers as obtained by counterpoise corrected and uncorrected geometry optimizations with the aug′-cc-pVTZ to aug′-cc-pV5Z basis sets as well as basis set extrapolated results. Site names used to specify distances and angles may be inferred from Fig. 1. Distances R are given in Ångstrom, angles θ in degrees, and energies E in kJ mol^{-1}

		Not counterpoise corrected					Counterpoise corrected				
		TZ	QZ	5Z	ext(TQZ)	ext(Q5Z)	TZ	QZ	5Z	ext(TQZ)	ext(Q5Z)
$(NH_3)_2$	R_{DA}	3.236	3.214	3.209	3.193	3.207	3.245	3.221	3.215	3.210	3.210
asymm.	θ_{1DA}	17.32	20.92	21.70	25.08	22.46	21.21	22.12	22.25	21.70	21.74
	θ_{3AD}	76.10	70.09	68.58	63.40	67.31	69.67	68.21	68.03	68.55	68.56
	E_{stab}	−13.20	−13.23	−13.19	−13.30	−13.16	−12.31	−12.79	−13.00	−13.14	−13.20
$(H_2O)_2$	R_{DA}	2.911	2.906	2.906	2.903	2.906	2.936	2.918	2.913	2.907	2.907
	θ_{H_DDA}	5.45	5.60	5.46	5.76	5.46	5.61	5.51	5.57	5.53	5.59
	θ_{acc}[a]	123.53	124.41	124.91	124.75	125.19	124.46	125.14	124.96	125.13	124.97
	E_{stab}	−21.07	−20.90	−20.81	−20.80	−20.75	−19.61	−20.21	−20.48	−20.63	−20.74
$(HF)_2$	R_{DA}	2.750	2.742	2.741	2.736	2.741	2.774	2.753	2.749	2.744	2.744
	θ_{H_DDA}	6.34	6.49	6.52	6.71	6.61	6.75	6.57	6.66	6.58	6.78
	θ_{HAD}	111.57	111.61	111.84	111.39	111.91	111.87	111.92	111.75	111.87	111.53
	E_{stab}	−19.14	−18.90	−18.80	−18.77	−18.76	−17.65	−18.20	−18.44	−18.56	−18.67

[a] θ_{acc} is the angle between the bisection line of the HOH angle of the hydrogen bond acceptor water monomer and the OO-axis.

combination of using basis sets without core correlation functions but nevertheless correlating core electrons in a post-HF method is clearly not suitable for the calculation of intermolecular interactions. Moreover, these calculations are computationally more demanding than the non-core correlated ones.

D. MP2-F12

The MP2-F12 results are collected in Table 3 and in Fig. 2 and 3. The stabilizition energies are already well converged with the TZ basis set. For the water and hydrogen fluoride dimers, they are close to the CP corrected, extrapolated results. For the ammonia dimer, they are slightly outside of the range of the CP corrected and non-CP corrected extrapolated results. Still, in all cases they agree within 0.15 kJ mol^{-1}.

The differences between the TZ and the QZ basis set geometries are very small, indicating that all results are close to the basis set limit within this framework. Only for the angles shown in Fig. 3, there are differences of up to 0.6 degrees between the TZ and QZ basis set values. The largest difference can again be found for the asymmetrical structure of the ammonia dimer: Here, the differences become as large as 0.003 Ångstrom and 0.6 degrees, respectively. This is roughly comparable to the difference between the CP corrected QZ and 5Z values of Table 1. The F12 results for the water dimer are in nearly perfect agreement with the R12 results of ref. 64, which were obtained with a specifically designed basis set of QZ quality.

In general, all results are in agreement with the best available basis set extrapolation results. For the water and the hydrogen fluoride dimers, the intermolecular distances agree within 0.002 Ångstrom and the angles within 0.15 degrees. Usually, the non-counterpoise corrected, extrapolated values and those where the CP correction is used bracket the exact results. As indicated before, especially the bond angles are very sensitive to the basis set. Taking a closer look at these values, we see that for the water and hydrogen fluoride dimers, the MP2-F12 results lie nicely between the CP and non-CP extrapolations or are very close to them. Namely, 5.30 and 5.60 (with the F12 value of 5.52), 124.87 and 125.56 (124.83), 6.77 and 6.26 (6.62), as well as 111.53 and 112.20 (111.66) degrees.

Table 3 Intermolecular geometry parameters and energies of the NH_3, H_2O and HF dimers as obtained by MP2-F12 geometry optimizations. Site names used to specify distances and angles may be inferred from Fig. 1. Distances R are given in Ångstrom, angles θ in degrees, and energies E in kJ mol^{-1}

Molecule		TZ	QZ	QZ/R12[b]
$(NH_3)_2$	R_{DA}	3.205	3.208	
asymm.	θ_{1DA}	22.28	21.84	
	θ_{3AD}	67.72	68.34	
	E_{int}	−13.33	−13.34	
	E_{stab}	−13.25	−13.26	
$(NH_3)_2$	R_{DA}	3.163	3.163	
cyclic	θ_{1DA}	42.44	42.43	
	E_{int}	−13.25	−13.25	
	E_{stab}	−13.19	−13.20	
$(NH_3)_2$	R_{DA}	3.241	3.243	
linear	θ_{1DA}	13.78	13.81	
	θ_{3AD}	141.67	141.63	
	E_{int}	−13.06	−13.07	
	E_{stab}	−12.97	−12.98	
$(H_2O)_2$	R_{DA}	2.906	2.906	2.907
	θ_{H_DDA}	5.74	5.52	5.57
	θ_{acc}[a]	124.22	124.83	124.87
	E_{int}	−20.99	−21.04	
	E_{stab}	−20.81	−20.87	
$(HF)_2$	R_{DA}	2.745	2.742	
	θ_{H_DDA}	6.72	6.62	
	θ_{HAD}	111.51	111.66	
	E_{int}	−18.90	−18.94	
	E_{stab}	−18.76	−18.80	

[a] θ_{acc} is the angle between the bisection line of the HOH angle of the hydrogen bond acceptor water monomer and the OO-axis. [b] A specifically designed QZ basis set, in conjunction with MP2-R12, ref. 64.

For the ammonia dimer, the deviations are larger, as shown in Fig. 3. Notably, for the asymmetrical structure of the ammonia dimer, the angles of the F12/QZ method are outside the bracket ranges of 22.03–22.32 (*vs.* 21.84), and 67.62–67.98 (*vs.* 68.32) degrees. However, both F12/TZ values are within these bounds, so it is not quite clear where the source of the remaining basis set error is coming from. We cannot exclude that they could be due to neglected terms in the 2A*

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approximation, although according to the results presented in ref. 45 this appears to be unlikely. Interestingly, the Q5Z extrapolated results without diffuse functions on the hydrogen atoms are closer to the QZ MP2-F12 results for the ammonia dimer. Clearly, it is very difficult to determine the angles of the basis set limit minimum structures for systems like the ammonia dimer with a very flat well region to better than about one degree.

V. Conclusions

We can conclude that for intermolecular interactions, the CP-corrected, extrapolated geometries are yielding very stable results, suggesting that they are very close to the basis set limit. In our cases, an extrapolation of triple- and quadruple-ζ quality was sufficient at the MP2 level. Of course, for quantitative results, correlation effects going beyond perturbation theory of second order are very important. For intermolecular interactions, they could be estimated by calculating the difference of CCSD(T) and MP2 at a lower level basis set. Similarly, in this way core correlation as well as relativistic effects might be estimated. Nevertheless, an efficient first step within such an approach is the estimation of the MP2 basis set limit. For this purpose, CP-corrected, extrapolated results or the F12 method may be used. The geometries and interaction energies of these methods agree very well, with the exception of the two minimum structures of the ammonia dimer. The deviations of 0.2 to 0.8 degrees for the intermolecular angles between our best extrapolated results and the F12 method at present cannot be resolved. Leaving out the diffuse functions on the hydrogen atoms gives results in closer agreement to the F12 values for the ammonia dimer. The inclusion of core correlation with valence basis sets for intermolecular interactions cannot be recommended, as wrong structures are predicted.

For larger hydrogen-bonded systems than considered here, the use of augmented quadruple-ζ and larger basis sets may become prohibitively expensive. Yet, our results demonstrate that with MP2-F12 at the augmented triple-ζ level one can expect maximal deviations from converged valence-only MP2 results of about 0.005 Ångstrom for intermolecular distances, 1 degree for intermolecular angles, and 0.1 kJ mol^{-1} per hydrogen bridge for interaction and stabilization energies. This should be similar for other *ab initio* methods. If F12 approaches are not available, a somewhat more expensive strategy yielding similar accuracy is to extrapolate CP-corrected energies and gradients from augmented triple- and quadruple-ζ basis sets, omitting the diffuse functions on the hydrogen atoms.

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References

1 J. C. Dore and J. Teixeira, *Hydrogen Bonded Liquids: Proceedings of the NATO Advanced Study Institute on Hydrogen-Bonded Liquids*, Institut Scientifique de Cargèse, Corsica, April 13–15 1989, Kluwer Academic Publishers, Dordrecht, 1991.
2 M. C. Bellissent-Funel and J. C. Dore, *Hydrogen Bond Networks*, Kluwer Academic Publishers, Dordrecht, 1994.
3 F. B. van Duijneveldt, J. G. C. M. van Duijneveldt-van de Rijdt and J. H. van Lenthe, *Chem. Rev.*, 1994, **94**, 1873, and references cited therein.
4 S. S. Xantheas, *J. Chem. Phys.*, 1996, **104**, 8821.
5 S. Simon, M. Duran and J. J. Dannenberg, *J. Chem. Phys.*, 1996, **105**, 11024.
6 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.
7 (*a*) F. M. Tao and Y. K. Pan, *Chem. Phys. Lett.*, 1992, **194**, 162; (*b*) F. M. Tao and Y. K. Pan, *J. Chem. Phys.*, 1992, **97**, 4989; (*c*) F. M. Tao, *J. Chem. Phys.*, 1993, **98**, 3049; (*d*) F. M. Tao and W. Klemperer, *J. Chem. Phys.*, 1994, **101**, 1129.
8 S. M. Cybulski, *Chem. Phys. Lett.*, 1994, **228**, 451.
9 B. Kukawska-Tarnawska, G. Chałasiński and K. Olszewski, *J. Chem. Phys.*, 1994, **101**, 4964.
10 R. Burcl, G. Chałasiński, R. Bukowski and M. M. Szczęśniak, *J. Chem. Phys.*, 1995, **103**, 1498.
11 H. L. Williams, E. M. Mas, K. Szalewicz and B. Jeziorski, *J. Chem. Phys.*, 1995, **103**, 7374.
12 M. Torheyden and G. Jansen, *Theor. Chem. Acc.*, 2000, **104**, 370.
13 J. M. L. Martin, *Chem. Phys. Lett.*, 1996, **259**, 669.
14 W. Klopper, K. L. Bak, P. Jørgensen, J. Olsen and T. Helgaker, *J. Phys. B: At., Mol. Opt. Phys.*, 1999, **32**, R103.
15 W. Kutzelnigg and J. D. Morgan III, *J. Chem. Phys.*, 1992, **96**, 4484, (E) 1992, **97**, 8821.
16 T. Helgaker, W. Klopper, H. Koch and J. Noga, *J. Chem. Phys.*, 1997, **106**, 9639.
17 A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen and A. K. Wilson, *Chem. Phys. Lett.*, 1998, **286**, 243.
18 A. Halkier, W. Klopper, T. Helgaker, P. Jørgensen and P. R. Taylor, *J. Chem. Phys.*, 1999, **111**, 9157.
19 T. van Mourik, A. K. Wilson, K. A. Peterson, D. E. Woon and T. H. Dunning Jr., *Adv. Quantum Chem.*, 1998, **31**, 105.
20 A. Halkier, W. Klopper, T. Helgaker and P. Jørgensen, *J. Chem. Phys.*, 1999, **111**, 4424.
21 J. Rychlewski, *Explicitly Correlated Wave Functions in Chemistry and Physics*, Kluwer Academic Publishers, Dordrecht, 2003.
22 T. Kato, *Commun. Pure Appl. Math.*, 1957, **10**, 151.
23 R. T. Pack and W. Byers-Brown, *J. Chem. Phys.*, 1966, **45**, 556.
24 W. Kutzelnigg, *Theor. Chim. Acta*, 1985, **68**, 445.
25 W. Kutzelnigg and W. Klopper, *J. Chem. Phys.*, 1991, **94**, 1985.
26 W. Klopper, F. R. Manby, S. Ten-no and E. F. Valeev, *Int. Rev. Phys. Chem.*, 2006, **25**, 427.
27 W. Klopper, H. P. Lüthi, T. Brupbacher and A. Bauder, *J. Chem. Phys.*, 1994, **101**, 9747.
28 W. Klopper and C. C. M. Samson, *J. Chem. Phys.*, 2002, **116**, 6397.
29 E. F. Valeev, *Chem. Phys. Lett.*, 2004, **395**, 190.
30 O. Marchetti and H.-J. Werner, *Phys. Chem. Chem. Phys.*, 2008, **10**, 3400.
31 D. P. Tew and W. Klopper, *J. Chem. Phys.*, 2006, **125**, 094302.
32 W. Klopper, M. Quack and M. A. Suhm, *J. Chem. Phys.*, 1998, **108**, 10096.
33 W. Klopper, J. G. C. M. van Duijneveldt-van de Rijdt and F. B. van Duijneveldt, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2227.
34 P. Hobza, O. Bludský and S. Suhai, *Phys. Chem. Chem. Phys.*, 1999, **1**, 3073.
35 S. S. Xantheas, *Struct. Bonding*, 2005, **116**, 119.
36 J. R. Lane and H. G. Kjaergaard, *J. Chem. Phys.*, 2009, **131**, 034307.
37 J. S. Lee and S. Y. Park, *J. Chem. Phys.*, 2000, **112**, 230.
38 A. D. Boese, A. Chandra, J. M. L. Martin and D. Marx, *J. Chem. Phys.*, 2003, **119**, 5965.
39 J. Stålring, M. Schütz, R. Lindh, G. Karlström and P.-O. Widmark, *Mol. Phys.*, 2002, **100**, 3389.
40 Y.-Y. Chuang and D. G. Truhlar, *J. Phys. Chem. A*, 1999, **103**, 651.
41 A. Bende, Á. Vibók, G. J. Halász and S. Suhai, *Int. J. Quantum Chem.*, 2004, **99**, 585.

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42 M. Heckert, M. Kállay, D. P. Tew, W. Klopper and J. Gauss, *J. Chem. Phys.*, 2006, **125**, 044108.
43 A. D. Boese, J. M. L. Martin and W. Klopper, *J. Phys. Chem. A*, 2007, **111**, 11122.
44 C. Tuma, A. D. Boese and N. C. Handy, *Phys. Chem. Chem. Phys.*, 1999, **1**, 3939.
45 S. Höfener, C. Hättig and W. Klopper, *Z. Phys. Chem.*, 2010, **224**, 695.
46 S. Höfener and W. Klopper, *Mol. Phys.*, 2010, **108**, 1783.
47 S. Ten-no, *J. Chem. Phys.*, 2004, **121**, 117.
48 S. Ten-no, *J. Chem. Phys.*, 2007, **126**, 014108.
49 T. B. Adler, G. Knizia and H.-J. Werner, *J. Chem. Phys.*, 2007, **127**, 221106.
50 J. Noga and J. Šimunek, *Chem. Phys.*, 2009, **356**, 1.
51 R. Ahlrichs, M. Bär, H.-P. Baron, R. Bauernschmitt, S. Böcker, P. Deglmann, M. Ehrig, K. Eichkorn, S. Elliott, F. Furche, F. Haase, M. Häser, H. Horn, C. Hättig, C. Huber, U. Huniar, M. Kattannek, A. Köhn, C. Kölmel, M. Kollwitz, K. May, C. Ochsenfeld, H. Öhm, H. Patzelt, O. Rubner, A. Schäfer, U. Schneider, M. Sierka, O. Treutler, B. Unterreiner, M. von Arnim, F. Weigend, P. Weis and H. Weiss, *TURBOMOLE 5.7*, Universität Karlsruhe, 2004.
52 T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007.
53 D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.*, 1995, **103**, 4572.
54 F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.*, 1998, **294**, 143.
55 F. Weigend, A. Köhn and C. Hättig, *J. Chem. Phys.*, 2002, **116**, 3175.
56 F. R. Manby, *J. Chem. Phys.*, 2003, **119**, 4607.
57 F. Weigend, A. Köhn and C. Hättig, *J. Chem. Phys.*, 1993, **14**, 907.
58 C. Hättig, *Phys. Chem. Chem. Phys.*, 2005, **7**, 59.
59 S. Ten-no, *Chem. Phys. Lett.*, 2004, **398**, 56.
60 K. E. Yousaf and K. A. Peterson, *Chem. Phys. Lett.*, 2009, **476**, 303.
61 S. Kedžuch, M. Milko and J. Noga, *Int. J. Quantum Chem.*, 2005, **105**, 929.
62 F. Weigend, *J. Comput. Chem.*, 2008, **29**, 167.
63 J. M. L. Martin and G. de Oliveira, *J. Chem. Phys.*, 1999, **111**, 5.
64 E. Kordel, C. Villani and W. Klopper, *Mol. Phys.*, 2007, **105**, 2565.

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