11122 *J. Phys. Chem. A* **2007,** *111,* 11122−11133

Basis Set Limit Coupled Cluster Study of H-Bonded Systems and Assessment of More Approximate Methods

A. Daniel Boese*

Institute of Nanotechnology, Forschungszentrum Karlsruhe, P.O. Box 3640, D-76021 Karlsruhe, Germany

Jan M. L. Martin

Department of Organic Chemistry, Weizmann Institute of Science, IL-76100 Reovot, Israel

Wim Klopper

Lehrstuhl für Theoretische Chemie, Institut für Physikalische Chemie,
Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany

Received: March 28, 2007; In Final Form: July 13, 2007

Hydrogen bonds are of utmost importance in both chemistry and biology. As the applicability of density functional theory and ab initio methods extends to ever larger systems and to liquids, an accurate description of such interactions is desirable. However, reference data are often lacking, and ab initio calculations are only possible and done in very small basis sets. Here, we present high level [CCSD(T)] ab initio reference calculations at the basis set limit on a large set of hydrogen-bonded systems and assess the accuracy of second-order perturbation theory (MP2). The possibilities of using basis set extrapolations for geometries and dissociation energies are discussed as well as the results of R12 methods and density functional and local correlation methods.

1. Introduction

With ever-faster computers, researchers in the field of computational chemistry are able to investigate molecules of increasing size. Although 30 years ago, ab initio methods were only applicable to molecules with less than 10 atoms, these methods can now be used to compute molecules containing hundreds, if not thousands, of atoms. It is now feasible to calculate energies, geometries and spectra of such systems, assisting experimentalists to search for desired properties in molecules on the nanometer scale.

However, large molecules offer some challenging tasks to modern electronic structure theory methods. First, so-called near-linear scaling methods are needed, or at least methods that have both a modest prefactor and a low scaling exponent. Second, different minimization techniques are required, since the potential energy surfaces of such large clusters are far more complex and exhibit a plethora of local minima. Finally, the methods themselves must be capable of describing various subtle effects, which become increasingly important with larger system size.

One of the subtle effects is the van der Waals interaction between two molecules, resulting from the attractive forces between instantaneously induced dipole moments. This is often the weakest interaction of interest to chemists and can usually be described adequately by semiempirical potentials. Furthermore, the correct description of hydrogen bonds also becomes an issue because most systems will be modeled not in the gas phase but, rather, in the condensed phase. Thus, when describing molecular solids, associated liquids, or large biosystems, non-covalent interactions, such as hydrogen bonds and van der Waals interactions, play an important role and cannot be neglected. Semiempirical potentials, on the other hand, lack the accuracy for covalent interactions and hydrogen bonds.

There is ample evidence that wavefunction-based quantum chemistry methods are able to predict properties of molecular systems to virtually any desired accuracy by systematically improving the correlation treatment together with the one-particle representation. However, the numerical complexity, as for instance measured by the computer time needed for such studies, quickly becomes intractable before reaching either the level of accuracy or the size of system one would like to treat.[1−3] These methods can still be readily employed to compute small molecules, which in turn may serve as benchmarks to evaluate less sophisticated methods, such as density functional theory (DFT) or second−order Møller−Plesset perturbation (MP2) calculations. For medium-sized molecules, DFT and MP2 are the methods of choice for most calculations performed at the ab initio level of theory. Although common DFT methods seem to be more accurate than MP2 for the description of covalent interactions, they are inherently unable to correctly describe van der Waals interactions.[4−7] On the other hand, hydrogen bonds are known to be well within the capabilities of DFT approaches, despite their inconsistent description of the dispersion interaction.

Quantum chemical methodology always offers a variety of choices. In this contribution, we will investigate the effect of basis set on MP2 of several hydrogen-bonded complexes, detailing the basis set convergence and amount of basis set superposition error (BSSE) so that informed choices can be made. In addition, basis set extrapolations will be employed for both energies and geometries. We end with an investigation of the possibilities of adding the CCSD(T)-MP2 difference to large basis set MP2 calculations to estimate the CCSD(T) basis set limit.[8−10]

10.1021/jp072431a CCC: $37.00

2. Computational Details

We used three quantum chemical program packages; namely, Gaussian 03,[11] MOLPRO,[12] and TURBOMOLE.[13] The automatic basis set extrapolation and counterpoise correction algorithms[14−17] have been implemented into the TURBOMOLE package in the course of the present work.

As reference method, we used the W2 method.[1] This is essentially an extrapolation towards the full CCSD(T) basis set limit, including relativistic (but not non-Born−Oppenheimer) corrections. W2 energies are calculated at the CCSD(T)/A′VQZ geometry, this notation meaning an aug-cc-pVQZ basis set for all first- or second-row atoms and a cc-pVQZ basis set for hydrogen.[18] W2 is one of the most accurate standard ab initio methods currently available, with an average error of less than 0.5 kcal/mol for the G2-1 set[19] of molecules.[20] Although computationally much more expensive, it is more reliable and accurate than the G1, G2, and G3 methods.[20,21] For the NH_3 dimer, W2 has been shown to be extremely accurate.[22] In ref 22, even larger basis sets were considered than the extrapolated A′VQZ/A′V5Z extrapolation from W2 in conjunction with higher order contributions in the coupled-cluster amplitudes going beyond CCSD(T), which lead to no further noticeable improvement in the dissociation energy.

We considered several modifications of MP2, because some different approaches have been recently published in special consideration of treating weak interactions. The following MP2 methods have been tested:

- Conventional MP2 and RI-MP2, in which the resolution of the identity (RI) approximation has been shown to cause differences only in the microhartree region.[23]
- Local MP2 as implemented in the MOLPRO package by Schütz et al.[24]
- Spin-component scaled (SCS)-MP2,[25] in which the like-spin and unlike-spin MP2 correlation energy is scaled with different, semiempirically fitted coefficients. It has been tested thoroughly for dispersion energies and has been reported to yield much improved results.[26−30]
- Head-Gordon and co-workers suggested complete neglect of the like-spin correlation terms of MP2. That way, the energy can be evaluated with a fourth-order scaling algorithm using a combination of auxiliary basis functions and a Laplace transform, in contrast with the conventional fifth-order scaling MP2 method.[31]
- MP2-R12, using explicitly correlated wavefunctions that depend on the interelectronic coordinates to speed up the basis set convergence.[32−38]

The following exchange-correlation functionals were investigated:

- The BP86 generalized gradient approximation (GGA) functional, with Becke's 88 exchange and Perdew's 86 correlation functional.[39]
- The BLYP GGA functional, which uses the Becke 88 exchange and the LYP correlation functional, in which the correlation functional completely neglects like-spin correlation.[40]
- The PBE GGA functional by Perdew and co-workers, which has been developed by considering deviations of the uniform electron gas.[41]
- The HCTH/407 GGA exchange correlation functional by Handy and co-workers,[42] which is a parametrization of the B97-1 functional without exact exchange.
- The TPSS meta-GGA functional, which has been reported to be a vast improvement over PBE for the description of hydrogen-bonded complexes.[43] However, this conclusion was based on comparing with all-electron MP2 results obtained in a fairly small triple-ζ basis set.[44]
- The B3LYP hybrid functional of Becke (incorporating 20% of exact exchange), which is currently one of the most popular functionals.[45]
- The B97-1 functional, which is a reparametrization by Handy and co-workers of the B97 functional[46] and probably a slight improvement over B3LYP.[47]

In molecular dynamics techniques such as CPMD,[48,49] which are often used for simulations of the liquid phase, GGA functionals are far more efficient computationally than hybrid functionals. Therefore, we have considered several GGA functionals in the present study. Of course, it is crucial to estimate the error introduced by each GGA in such calculations, because for most liquids, the correct description of hydrogen bonded arrangements and energies is critical. In fact, the difference in speed for molecular dynamics codes is even larger than for electronic structure codes that use auxiliary basis sets, such as TURBOMOLE, in which, for example, BLYP is about an order of magnitude faster than B3LYP.

Furthermore, a variety of basis sets and extrapolation techniques, as well as the explicitly correlated R12 approach, have been used to investigate the convergence to the basis set limit for the MP2 method. For this study, Dunning's cc-pVnZ correlation consistent basis sets (going from double-ζ to quadruple-ζ quality) have been used for the first row,[18] and the cc-pV(n+d)Z basis sets of Wilson, Peterson, and Dunning[50] for chlorine. (The latter include additional high-exponent *d* functions, which have been shown to be important[51−53] for spectroscopic constants of molecules in which a second-row atom is surrounded by one or more highly electronegative first-row atoms.) Since we are investigating relatively weak intermolecular interactions, it is important to include diffuse functions. Hence, on all atoms except hydrogen, we augment the basis set, which is denoted A′V*n*Z (aug′-cc-pV*n*Z).

Unless indicated otherwise, extrapolations to the complete basis set limit for correlation energies are carried out using the simple formula[54] $E(n) = E_\infty + a/n^3$, where n is the ordinal number of the basis set (2 for A′VDZ, 3 for A′VTZ, 4 for A′VQZ, 5 for A′V5Z, and 6 for A′V6Z) and a is a constant. This formula is based on the leading term in the partial wave expansion of singlet-coupled pair energies.[55] For the SCF energy, $E(n) + a/n^5$ was employed.[1] For our purposes, as some tests showed, there was no difference between this extrapolation scheme and the more accurate $E(n) = E_\infty + a(n + 1)\exp(-9/\sqrt{n})$ extrapolation.[56−58] Alternatively, for the A′VDZ−A′VTZ extrapolation, we also tested Truhlar's empirical scheme with the exponential factor of 3.4 (rather than 5) for the Hartree−Fock (HF) basis set limit and 2.2 for the correlation energy (rather than 3).[59] All the extrapolation schemes as well as the nonextrapolated calculations have also been done with and without using the counterpoise correction to account for the basis set superposition error.

$$D_e = -E_{tot}\,(\text{complex}) + E_{mon}\,(\text{acceptor}) + E_{mon}\,(\text{donor}) \quad (1)$$

$$D_e^{cpc} = D_e - \Delta E\,(\text{BSSE}) \quad (2)$$

$$\Delta E\,(\text{BSSE}) = E_{tot}\,(\text{donor}) - E_{tot}\,(\text{donor, ghost}) + E_{tot}\,(\text{acceptor}) - E_{tot}\,(\text{acceptor, ghost}) \quad (3)$$

$$\Delta E\,(\text{BSSE}) > 0 \quad (4)$$

The subscript E_{tot} denotes the energy at the dimer geometry; E_{mon} denotes the energy at an optimized monomer geometry.

For the DFT calculations, we used a different basis set, which was the pc-2 basis set for hydrogen, the aug-TZ3P+f basis set for chlorine[60] and the aug-pc-2 basis set[61−63] for all other atoms. In all these calculations, large (pruned 99 × 590, using a Euler−Maclaurin grid for the radial and Lebedev grid for the angular part) grids have been used.[64]

Although the estimation of the MP2 basis set limit is of little interest due to the intrinsic error in the MP2 method itself, it might be used to estimate the CCSD(T) basis set limit for hydrogen-bonded systems. In this contribution, we compare our reference values to various estimations of the CCSD(T) basis set limit using MP2 calculations. This has been done in the past with small basis sets to estimate the strength of hydrogen bonds.[65,66] We put these proposed methods to the test and look at our reference values for a test set of molecules, for which we have reliable ab initio data. These have been computed for the $ClH\cdots NH_3$, $CO\cdots HF$, $FH\cdots NH_3$, $H_2O\cdots H_2O$, $HCl\cdots HCl$, $HF\cdots H_2O$, $HF\cdots HF$, $HF\cdots HCN$, $NH_3\cdots NH_3$, $NH_3\cdots H_2O$, $OC\cdots HF$, $H_3O^+\cdots H_2O$, $NH_4^+\cdots H_2O$, $HCC^-\cdots H_2O$, $CN^-\cdots H_2O$, and $OH^-\cdots H_2O$ molecules.

3. Results and Discussion

For all methods and basis sets, we investigate the following properties of hydrogen bonds:

- The dissociation energy D_e of the complex into two monomers, with the W2 results as reference,
- The hydrogen bond distance $X\cdots H-Y$ in comparison with CCSD(T)/A′VQZ values, and
- The hydrogen bond shift, which changes the H−Y distance (of the donor molecule HY) by some amount, as compared again with the CCSD(T)/A′VQZ values.

In a prior, less complete contribution,[67] we also looked at the harmonic frequency shifts of the H−Y stretches and compared those, as well as the geometries, to the MP2 values. CCSD(T) harmonic frequencies, however, are unfortunately too expensive to calculate for our test set of molecules, and since the MP2 values, as we shall see below, are not accurate enough to serve as reference, we restrict ourselves to energies and geometries. A part of the test set has been used extensively to examine the performance of density functionals[22,67−69] and has been augmented by a second set of hydrogen-bonded systems with the same purpose.[43,70]

We report two different error estimates. The first one is given by the simple formula for the "commonly" used rms error:

$$\text{rms error (kJ/mol)} = \sqrt{\frac{1}{16}\sum_{i}^{16}[\text{value (complex}(i)) - \text{value (reference}(i))]^2} \quad (5)$$

The second formula is a percent rms error and is given by

$$\%\ \text{rms error} = \sqrt{\frac{1}{16}\sum_{i}^{16}\left(\frac{\text{value (complex}(i))}{\text{value (reference}(i))} - 1\right)^2} \times 100\% \quad (6)$$

The first equation weights the strong hydrogen bonds more than the weak ones; the second equation does the opposite.

In Table 1, we summarize the individual interaction energies of all complexes, calculated using the W2 method. Here, we list the relativistic and nonrelativistic interaction energies, also including nonrelativistic values that exclude core correlation. These data are displayed together with evaluated geometric data, such as the hydrogen bond length and the hydrogen bond elongation (shift) exerted by the second monomer. As mentioned above, the underlying reference geometries are of CCSD(T)/A′VQZ quality.

TABLE 1: Individual Dimer Dissociation Energies, Using W2 (in kJ/mol) and CCSD(T)/A′VTZ Geometry Values (in pm)

	energies			geometries	
dimer	rel. + core	nonrel. + core	nonrel.	distance	shift
		Neutral			
$ClH\cdots NH_3$	34.78	34.91	34.96	179.3	4.3
$CO\cdots HF$	7.08	7.15	7.19	207.2	0.2
$FH\cdots NH$	52.11	52.22	51.99	169.7	3.2
$H_2O\cdots H_2O$	20.84	20.91	20.80	195.4	0.6
$HCl\cdots HCl$	8.39	7.32	7.26	255.9	0.4
$HF\cdots H_2O$	36.35	36.48	36.31	171.4	1.6
$HF\cdots HF$	19.10	19.18	19.11	182.4	0.6
$HF\cdots HCN$	30.93	31.06	30.85	184.9	1.2
$NH_3\cdots NH_3$	13.13	13.15	13.10	230.2	0.3
$NH_3\cdots H_2O$	26.82	26.87	26.75	197.8	1.2
$OC\cdots HF$	14.77	14.82	14.63	208.1	0.6
		Charged			
$H_3O^+\cdots H_2O$	141.16	141.32	140.93	119.5	21.8
$NH_4^+\cdots H_2O$	84.82	85.58	85.28	165.2	8.5
$HCC^-\cdots H_2O$	76.37	76.44	76.10	186.7	4.5
$CN^-\cdots H_2O$	64.55	64.60	64.58	192.7	3.4
$OH^-\cdots H_2O$	110.32	110.36	110.25	142.3	20.3

Core correlation, as expected, makes a very minor contribution to the complex dissociation energies, reaching a maximum of 0.4 kJ/mol for the $H_5O_2^+$ complex. Notably, it is less than 0.2 kJ/mol, even for both chlorine-containing molecules in the test set. It can thus be safely neglected when calculating the dissociation energies of hydrogen-bonded complexes. The relativistic corrections in W2 theory are sizable for only one molecule: for the HCl dimer, they amount to ∼1 kJ/mol. We note that the interaction energies range from 65 to 140 kJ/mol for the charged complexes (which naturally include some induction) and from 7 to 52 kJ/mol for the neutral complexes. The strongest neutral complex ($FH\cdots NH_3$) has an interaction energy comparable to the weakest charged complex ($CN^-\cdots H_2O$); hence, the division of these systems is somewhat arbitrary. Finally, we note that there is a wide spread of hydrogen-bond strengths, with the strongest 20 times larger than the weakest.

The hydrogen bond distances can easily be explained by correlating the bond strengths in Table 1 and the geometries in Figure 1. The HCl dimer has the longest hydrogen bond distance and is one of the weakest bonds, followed by $OC\cdots HF$ and $CO\cdots HF$. The ammonia dimer is a special case, since it has a nondirected hydrogen bond, or rather, two relatively weak bonds. The shortest hydrogen bonds are also the strongest ones, where either HF or HCl is the donor molecule (this is probably driven by the stability of the Cl and F anions) or the system is charged. Notable exceptions are the $H_3O^+\cdots H_2O$ and $OH^-\cdots H_2O$ system, since they have hydrogen bond lengths that are quite small. For $H_3O^+\cdots H_2O$, we have something between a hydrogen bond and a normal covalent OH bond, since the hydrogen bond distance is only 30 pm longer than the computed OH bond in H_2O. $HCC^-\cdots H_2O$ and $CN^-\cdots H_2O$ have rather long hydrogen bonds, in comparison, since they are not as strongly bound. Again, we have a large range from extremely short to very long bonds, spanning more than a factor of 2 between the shortest and the longest bond. The difference between these systems becomes even more obvious when looking at the shift that the bond of the donor molecule undergoes upon approach of the acceptor molecule. This seems to be a very subtle change and has a minimum value of 0.2 and maximum value of 22 pm. Here,

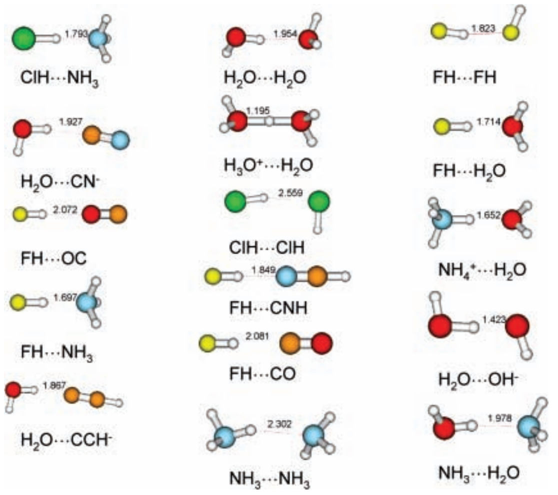

Figure 1. Geometries of all systems in our evaluation set. White = hydrogen, orange = carbon, blue = nitrogen, red = oxygen, yellow = fluorine, green = chlorine.

not only the strength and length of the hydrogen bond comes into play, but also how strongly the hydrogen is bound in the donor molecule. For example, CO shifts the H atom 0.2 pm in its direction away from the F atom (resulting in an interaction energy of 7 kJ/mol), while the NH_3 molecule exerts a shift of 3.2 pm on HF. The shifts for the H_2O molecule range from 0.6 pm (with another H_2O molecule) to 20 pm (having a hydrogen bond to a OH^- molecule). Despite excluding some of the weaker and weakest hydrogen bonds known, we nonetheless have a very large range of interaction energies and geometry shifts. This emphasizes the difficulty in treating such systems correctly, and we shall see in the following section that some DFT functionals have problems in describing even the interaction energies correctly.

3.1. Performance of Density Functional Methods and MP2. Before discussing the results of the density functional methods, however, we need to consider the dispersion interactions that are not naturally included in Kohn−Sham DFT. In some cases, they are added later to the functional in one of several post-Kohn−Sham fashions.[71−74] Of course, functionals such as LSDA include dispersion interactions for the exact limit of a uniform electron gas. However, since in the LSDA calculation, the correlation energy is calculated assuming a homogeneous electron density everywhere, it overbinds by a large amount and is thus useless for a quantitative, or even qualitative, description. On the other hand, GGAs cut off the long-range dispersion interactions. Thus, *any* attempt at describing molecular interactions dominated by these van der Waals interactions with the commonly used DFT functionals is bound to fail.

Because of this, we need to discuss the role of van der Waals interactions in our test systems and estimate the errors introduced. For example, the Ne dimer has an interaction strength of 0.4 kJ/mol and the Ar dimer 1.2 kJ/mol. Hartree−Fock, which does not include van der Waals interactions, is repulsive in the case of the Ne dimer by ∼0.2 kJ/mol at the MP2 minimum distance and is nonbinding for the Ar dimer at the MP2 minimum. We can assume the van der Waals effects to be more than 0.6 kJ/mol for systems containing first-row atoms and 1.2 kJ/mol for those containing second-row atoms. By symmetry-adapted perturbation theory (SAPT), the dispersion term can be estimated for several hydrogen-bonded species. For the water dimer, this contribution amounts to almost 9 kJ/mol at the minimum geometry,[75,76] which is almost half of the interaction energy. This amounts to ∼70% of the difference between the HF method and MP2 at this geometry. The same ratio can be seen at the geometry optimized by the HF method, for which the correlation energy is estimated by MP2 at 4.2 kJ/mol and the dispersion term is 3.4 kJ/mol, which is ∼15% of the overall interaction energy.[77]

Our weakest hydrogen bonds are the HCl dimer, with a dimer dissociation energy of 7.3 kJ/mol (including the van der Waals energy, since CCSD(T) should capture these effects well), and the CO···HF complex, with 7.2 kJ/mol. Whereas MP2 with an A′V5Z basis set overestimates the interaction energy of the HCl dimer, the Hartree−Fock contribution to this interaction energy at the MP2 distance is almost nonbinding, with 0.1 kJ/mol. At the Hartree−Fock optimized structure close to the basis set limit (using an A′V5Z basis), Hartree−Fock has an interaction energy of 3.2 kJ/mol. The HCl dimer is hence the only candidate in our set for which the van der Waals interaction amounts to ∼40% of the total interaction energy, assuming that the aforementioned 70% of the difference of MP2 and HF is due to van der Waals interactions. We will have to consider this in our discussion later. This is the main reason why we did not include even weaker hydrogen bonds in our set: Since neither DFT nor MP2[30,78] are known to describe van der Waals interactions well, one aim of this study is to test the limits of these methods by looking at hydrogen bonds that are not mainly determined by such effects.

1. Dissociation Energies. In Table 2, the errors of each functional and MP2/A′VTZ are presented for each individual complex in comparison to W2. We also give two sets of rms and mean errors using the definitions in Section III. Since DFT naturally should include core correlation, the DFT reference method is the second column in Table 1, whereas for MP2, it is the third. However, since the results without core correlation do not differ greatly from the results including core correlation , the overall conclusions are not affected.

- For the MP2 results, we display those obtained with an A′ VTZ basis set. This is because MP2 at all tested basis sets yields very similar results (see Supporting Information), and the lowest percentage errors are obtained with the least computationally demanding A′VTZ basis set. It overestimates all interaction energies except for the CO···HF complex. The MP2/A′VTZ correlation energy is far from converged, but increasing the basis to A′V6Z only reduces the mean absolute error from 1.3 to 0.7 kJ/mol. MP2/A′V6Z still systematically overestimates the interaction energies, with only CO···HF and the HF dimer underestimated. The largest error of MP2/A′VTZ for all complexes is the one for H_3O^+···H_2O: its interaction energy is overestimated by 3 kJ/mol. Large errors are also observed for both the CO···HF and OC···HF complexes, possibly because of the difficult electronic structure of carbon monoxide. Overall, the errors are fairly constant over the wide range of molecules and interaction energies investigated, which means that the relative errors of the weakly bound systems are somewhat large. The only exceptions are the ammonia and hydrogen fluoride dimers. In fact, for large basis sets, the ammonia dimer interaction energy is almost exactly equal to our W2 energy. This had led in previous contributions to an underestimation of the interaction energy,[79] since the difference between the MP2 and CCSD(T) energies was only estimated. Nevertheless, MP2 is not a great method for calculating hydrogen bonding interactions; the rms errors of 7.7% and 1.7 kJ/mol are quite large when one considers that it is very often used as reference method for estimating such interaction energies with DFT.

TABLE 2: Individual Dimer Dissociation Energy Errors for Different Functionals and MP2 (in kJ/mol)

dimer	MP2	(meta)-GGA BP86	BLYP	HCTH/407	PBE	TPSS	hybrid B3LYP	B97-1
				Neutral				
$ClH\cdots NH_3$	2.06	7.02	0.32	−0.39	10.68	6.12	0.46	5.07
$CO\cdots HF$	−0.58	−3.59	−2.13	0.04	−0.30	−1.49	−0.74	0.45
$FH\cdots NH_3$	1.61	4.58	1.44	−1.93	7.87	5.31	2.27	3.58
$H_2O\cdots H_2O$	0.27	−2.87	−3.34	−2.92	0.53	−1.68	−1.65	0.02
$HCl\cdots HCl$	1.77	−1.51	−2.15	0.86	1.93	−0.53	−1.56	1.13
$HF\cdots H_2O$	0.63	0.24	−1.16	−3.68	3.41	1.38	0.64	1.45
$HF\cdots HF$	0.03	−2.00	−1.59	−2.04	1.30	−0.80	−0.09	0.74
$HF\cdots HCN$	1.87	−1.00	−1.43	−2.88	2.35	0.63	0.15	0.95
$NH_3\cdots H_2O$	0.11	−3.25	−3.81	−1.37	0.08	−2.10	−2.64	−0.17
$NH_3\cdots H_2O$	0.72	−0.83	−2.61	−3.11	2.50	0.17	−1.35	0.83
$OC\cdots HF$	2.51	0.95	−0.02	0.12	4.35	2.51	0.39	2.06
mean %	4.5	−8.2	−11.5	−5.2	12.1	−0.5	−5.0	7.7
rms %	9.2	20.0	16.6	8.5	16.3	11.8	9.9	8.3
mean	1.0	−0.2	−1.5	−1.5	3.2	0.9	−0.4	1.5
rms	1.4	3.2	2.13	2.1	4.5	2.8	1.4	2.1
				Charged				
$H_3^+O\cdots H_2O$	3.02	10.40	5.20	1.34	13.71	8.89	5.84	6.85
$NH_4+\cdots H_2O$	0.65	0.75	−1.75	−4.04	4.17	1.15	0.42	1.78
$HCC^-\cdots H_2O$	2.56	4.06	0.16	−2.69	8.36	4.23	0.09	2.50
$CN^-\cdots H_2O$	2.50	4.10	0.63	−1.20	8.18	4.72	0.48	3.12
$OH^-\cdots H_2O$	0.81	5.41	−2.47	−7.44	8.89	4.26	0.52	3.20
mean %	1.9	5.0	0.1	−3.18	9.3	4.9	1.2	3.6
rms %	2.3	5.4	2.2	4.1	9.6	5.3	1.9	3.7
mean	1.9	4.9	0.4	−2.8	8.7	4.7	1.5	3.5
rms	2.2	5.9	2.7	4.05	9.2	5.3	2.6	3.9
				Errors for All Complexes				
mean %	3.7	−4.1		−4.6	11.2	1.2	−3.0	6.4
rms %	7.7	16.9		7.4	14.6	10.2	8.3	7.2
mean	1.3	1.4		−2.0	4.9	2.0	0.2	2.1
rms	1.7	4.2		2.9	6.4	3.7	1.9	2.8

- Although the BP86 functional is useful for applications to molecules containing many transition metal atoms,[80,81] it is not very accurate when determining heats of formation or structures of main-group elements, such as organic molecules.[82] It also fails for the description of hydrogen bonds and is more than two times less accurate for the percentage and the absolute rms error than MP2. The interaction energies are not a mere shift of the individual errors; the spread of errors is also much larger. The $H_3O^+\cdots H_2O$ complex has the largest error, followed by $ClH\cdots NH_3$ (about 7 kJ/mol), which is quite large, especially when considering that the interaction energy for $ClH\cdots NH_3$, for example, is only 35 kJ/mol. Even worse, the errors do not appear to be systematic.• The functional BLYP is quite often used in CPMD calculations. Although it offers only a minor improvement over BP86 in the relative (%) rms error, it provides a large improvement in the absolute rms error. This functional rather underestimates the dissociation energies, which would be in line with the view that dispersion interactions are excluded in DFT. With an additional term that includes these interactions, the mean error should be reduced further. Nevertheless, the large errors in the systems that include the weaker hydrogen bonds are somewhat worrisome, and these energies, with the exception of $OC\cdots HF$, are underestimated by 1−4 kJ/mol. The ammonia dimer shows one of the largest errors, rendering this functional less suited for CPMD calculations of liquid ammonia.

- The HCTH/407 functional, as an improved version of the original HCTH/93 functional (which failed to describe hydrogen-bonded complexes, despite yielding very good results for atomization energies[67,83,84]) is known to yield much better energetics than any other GGA functional.[69] In Table 2, we can see that over the range of functionals tested, it is one of the most accurate functionals and is of accuracy comparable to that of MP2. It is the only functional that shows a consistent mean percent error for the neutral and charged systems, underestimating both by ∼4% of the interaction energy. The errors for the neutral complexes are smaller than those of MP2 and BLYP, but the situation is reversed for the charged complexes. In the same way as for BLYP, most dissociation energies are underestimated, with the exception of the hydrogen chloride dimer.

- PBE overestimates all dissociation energies except the weak $CO\cdots HF$ complex. It has the largest rms error and a percent rms error close to the BP86 value. In comparison with MP2, its absolute rms error is 380% larger. It clearly shows an undesired behavior and cannot be recommended to be used for such weak interactions. At this stage, we can only speculate about the origin, but it is likely that the exchange-correlation hole is too delocalized for such interactions, and thus, its behavior is closer to LSDA than the other functionals. This, on the other hand, comes with an advantage: a functional such as PBE can be used for solid metals and yields much better results for them than for example BLYP.[81]

- TPSS is expected to yield much better results than PBE. It has been stated that the "TPSS functional matches, or exceeds in accuracy and, unlike semiempirical functionals, consistently provides a high-quality description of diverse systems and properties", including hydrogen-bonded complexes.[43] Both percent rms and absolute rms errors are improved by ∼40% when comparing it to PBE. It does not overestimate the hydrogen bonds by as much as the other functionals and exhibits the lowest mean percent error of all functionals. Despite this, it still has a sizable rms percent error, suggesting that the interaction energies are shifted only toward smaller values by TPSS, whereas the error range remains almost the same. This can be illustrated by looking at the span of the minimal and maximal error. PBE and BP86 span an error range of 13.6 kJ/

mol, and TPSS, of 11 kJ/mol. Although TPSS is an improvement over functionals such as PBE or BP86, it is still not as good as BLYP or HCTH/407, and unfortunately, we cannot confirm the above statement for the interaction energies computed here.

- The two hybrid functionals tested, B3LYP and B97-1, show quite similar errors, although for B97-1, every complex is systematically shifted to a larger estimate of the interaction energy. The percent rms error is thus almost the same (B3LYP rather underestimates the weak H-bonds). Both hybrid functionals overestimate most hydrogen bonds, although the HCl dimer is underestimated with B3LYP by 1.6 kJ/mol. This is somewhat surprising, since rare gas dimers are not bound by these functionals, and they are lacking any sort of van der Waals interactions. Thus, most errors will be even larger when adding such an additional term.

We tested additional functionals (see the Supporting Information). For example, BMK[69] has a percent rms error of 14.1 and an overall rms error of 2.1 kJ/mol, so although its overall rms error is comparable to the best functionals tested, it has quite large relative errors for the weak bonds. On average, it rather underestimates the dissociation energies, 8% (or 1.4 kJ/mol) on average. PBE0[85] does exactly the opposite: it has a percent rms error of 8.3 (which is close to MP2 and as good as B3LYP) but an overall error of 4.4 kJ/mol, worse than BP86. The charged and strong bonds are rather poorly described, and it overestimates almost all of the strengths of the bonds (6.2% or 3.2 kJ/mol, on average). PW91,[86] which has been reported to yield low errors for systems with weak interactions,[87] yields an even larger error than PBE; its rms error is 7.8 kJ/mol for all complexes, and its percent rms error is as large as 19%. Thus, for our set of hydrogen-bonded systems, we cannot confirm the findings of ref 87.[87] In B2-PLYP,[88] MP2 is combined with DFT to a semiempirical hybrid functional. The overall (1.4 kJ/mol) rms error is comparable to the accuracy of MP2, while the percent rms error is halved at 4.4%. Especially the weak hydrogen bond shows, thus, a much lower error with B2-LYP than with MP2.

Overall, we notice that MP2 is the most reliable method. Although both rms errors are almost the same as for B3LYP, the mean errors of the latter are somewhat larger. The much improved performance of MP2 becomes visible when regarding the span of errors: the errors for MP2 span only 3.6 kJ/mol; those of B3LYP, 7.6 kJ/mol and of B97-1, 7.1 kJ/mol. The latter two can be compared to BLYP and HCTH/407 with 9.0 and 8.8 kJ/mol, whereas the TPSS (11 kJ/mol), PBE (14.0 kJ/mol) and BP86 (13.7 kJ/mol) spans are almost three times larger than MP2. All methods describe the dissociation energies of the hydrogen-bonded systems reasonably well.

2. Hydrogen Bond Distances. Turning to the distances of the hydrogen-bonded systems, a different picture emerges for the GGA functionals, as Table 3 reveals. In this table, only the overall errors for all systems are shown; the individual bond lengths are given in the Supporting Information. MP2 again has the lowest error of all tested methods, for both the longer and the shorter hydrogen bonds. For nearly every molecule (except CO···HF), it underestimates the bond length by a small amount in the A′VTZ basis. Interestingly, almost all functionals underestimate most bond lengths by at least as much as the MP2 method does. This is somewhat surprising, since for all DFT methods, the magnitude of the missing van der Waals interaction is unknown, and the effect on the geometry is difficult to estimate. Thus, when including an extra van der Waals term, which is sometimes done,[71−74] none of these functionals can be used, since the geometry will be much worsened. Considering the HCl dimer, there is a large change of the interaction energy of the hydrogen chloride dimer when calculating the HF energy at its minimum distance and at the distance of the MP2 minimum. This indicates that the length could be changed by a large amount by the missing interactions, much more than we might expect. This is unfortunately confirmed by comparing the HF and the MP2 distance: The geometry change is almost 50 pm! This is because of a quite flat potential energy surface. Thus, when looking at the hydrogen bond distances, we probably look at the value most affected by a lack of dispersion interactions in DFT (of course, there are also other interactions missing in HF theory). The hybrid functionals yield the lowest errors of the DFT methods, and B3LYP is of similar quality to MP2: both underestimate the bond lengths. The percent rms error for B3LYP is almost twice as large as for MP2, showing that MP2 provides very good geometries, especially for the short, strong bonds (which gain a larger weight with the percent error). Among the GGA functionals, BLYP is the only functional that yields good, however underestimated, H-bond distances. However, in contradiction, it underestimates most interaction energies, as expected from a method that has too long hydrogen bond distances. Thus, the BLYP functional is somewhat inconsistent in describing such interactions. On the other hand, it is the only GGA functional that yields good bond distances and energies, which explains its common use in programs such as CPMD, in which the dispersion terms are missing.[89,90] TPSS, PBE, and BP86 overestimate the energies and underestimate the bond distances by a large amount, with TPSS a 20% improvement over PBE. Its errors are, however, more than twice as large as for the hybrid functionals and three times as large as for MP2. HCTH is the only method tested that underestimates the hydrogen bond lengths, consistent with the observation that DFT should lack a part of the interaction energy when it neglects dispersion interactions. It mainly overestimates the very weak bond lengths (for example, the HCl dimer by 21 pm), which has a shallow potential around the minimum geometry and is, hence, an ideal candidate for the addition of an extra dispersion term (although the interaction energy of the HCl dimer is already overestimated). MP2 is the most reliable method for bond lengths, and the hybrid and BLYP functionals also give geometries close to our reference values. Rather than investigating the XH···Y distances, we also investigated the X···Y distances (see Supporting Information). This, however, does not change the errors significantly with the exception of the PBE and TPSS functionals. These underestimate the XH···Y distance

TABLE 3: Errors in the Hydrogen Bond Distances for Some Functionals and MP2 (in pm)

dimer		(meta)-GGA					hybrid	
neutral	MP2	BP86	BLYP	HCTH/407	PBE	TPSS	B3LYP	B97-1
Errors for Neutral Complexes								
mean %	−0.8	−4.0	−0.5	5.1	−4.4	−3.9	−0.9	−1.3
rms %	1.1	4.1	1.8	5.8	4.4	4.0	1.3	2.0
mean	−1.3	−6.5	−0.6	9.0	−7.2	−6.5	−1.3	−2.1
rms	2.4	8.1	3.6	12.4	8.8	8.5	2.6	3.7
Errors for Charged Complexes								
mean %	−1.0	−5.1	−2.0	−1.2	−5.3	−2.9	−1.3	−1.8
rms %	1.4	6.9	3.1	2.4	7.1	3.9	1.8	2.6
mean	−2.5	−8.4	−3.5	−1.8	−8.8	−4.9	−2.2	−3.0
rms	3.1	10.7	4.9	2.0	11.0	6.2	2.9	3.9
Errors for All Complexes								
mean %	−1.0	−4.3	−1.0	3.2	−4.7	−3.6	−1.0	−1.5
rms %	1.4	5.1	2.3	4.9	5.4	4.0	2.3	2.2
mean	−1.7	−7.1	−1.5	5.6	−7.7	−6.0	−1.6	−2.4
rms	2.6	9.0	4.1	10.5	9.5	7.9	2.7	3.8

TABLE 4: Errors in the Hydrogen Bond Distance Shift for Some Functionals and MP2 (in pm)

dimer		(meta)-GGA					hybrid	
neutral	MP2	BP86	BLYP	HCTH/407	PBE	TPSS	B3LYP	B97-1
Errors for Neutral Complexes								
mean %	7.7	85.1	45.6	−0.5	80.2	36.0	31.0	34.0
rms %	18.9	90.8	47.7	25.5	85.6	72.4	31.9	37.6
mean	0.1	1.1	0.6	0.3	1.1	0.8	0.4	0.5
rms	0.2	1.7	1.00	0.7	1.7	1.3	0.6	0.9
Errors for Charged Complexes								
mean %	9.8	53.0	32.5	20.5	57.6	53.1	16.5	18.1
rms %	13.4	69.5	36.4	24.5	69.5	67.1	18.6	21.7
mean	0.7	4.3	2.3	1.6	4.3	4.2	1.2	1.4
rms	1.2	6.8	3.1	2.4	6.8	6.9	1.6	2.1
Errors for All Complexes								
mean %	8.3	75.1	41.5	6.0	73.1	41.3	26.4	29.0
rms %	17.4	84.1	44.5	25.2	80.9	70.8	28.4	33.5
mean	0.3	2.1	1.1	0.7	2.1	1.8	0.6	0.8
rms	0.7	4.1	1.9	1.5	4.1	4.0	1.0	1.4

but overestimate the XH distances, resulting in an error cancelation for the X•••Y distances.

3. Hydrogen Bond Distance Shifts. As a last property, we look at the shift that the bonded hydrogen atom undergoes when forming a hydrogen bond. Because the shifts are very small, which we can see from Table 1, the errors can become quite large (Table 4). Although the percent rms errors for the dissociation energies range from 8.4 (MP2) to 17.8 (BP86) and from 1.4 (MP2) to 5.4 (PBE) for the hydrogen bond distances, here, our percent rms errors become quite sizable and are as large as 27.4 (MP2) to 84.1 (BP86). Similarly to the distances of the hydrogen bonds (and as we would expect from a functional lacking some van der Waals interactions), the HCTH functional is the only method that underestimates the percent mean signed error for shift of the neutral complexes. It is the only functional that has errors that are comparable to MP2, including the hybrid functionals. For the neutral complexes, it is not clear for any of the methods whether the values contain a systematic error. Just as for the other properties looked at, PB86 and PBE are the worst performers, with TPSS barely improving upon PBE. BLYP is again much better than these functionals, but not as good as the hybrid functionals B3LYP and B97-1. Some of the (meta-)GGA functionals tested exhibit errors larger than 50%, corresponding to absolute errors that are unacceptable when studying H-bonding.

Summarizing the results of this section, we conclude that for hydrogen-bonded systems, DFT is worse than MP2. The hybrid functionals, especially B3LYP, are a possible alternative and in individual cases are as good as MP2, but for geometrical data, they still lack accuracy. When computing such properties with GGA functionals, BLYP is probably the best alternative. HCTH yields very good results for systems and properties when the dispersion interactions are not as important, and it probably would be the most suited candidate for the add-on terms that have been published. PB86, PBE, and to a lesser extent TPSS are not really suitable for the description of hydrogen-bonded systems, overestimating the energies and the shifts and consequently underestimating the hydrogen bond lengths by a large amount.

3.2. MP2 Basis Set Convergence and Approximate MP2 Methods. Having established that MP2 is the best method tested for our set of molecules, we now examine various approximate MP2 methods, such as local MP2, SCS-MP2, and SOS-MP2. We are also interested in which kinds of basis sets yield the best results. The basis set convergence of properties such as hydrogen bonds is of interest for researchers developing basis sets or extrapolation methods. In all cases, we have fully optimized the geometries when including extrapolation techniques or counterpoise corrections.

1. Dissociation Energies. Detailed data concerning basis set convergence is presented in Figure 2. The largest 6Z basis set for which we calculated the interaction energies is taken as the basis set limit. Since the calculations were too large for some complexes, we looked at only 12 of the 16 complexes, excluding all charged systems except $OH^-\cdots H_2O$. Since the errors for the double-ζ (DZ) basis sets are very large, we compare only the triple-ζ (TZ), quadruple-ζ (QZ), and quintuple-ζ (5Z) basis sets to our MP2/6Z reference values. Unfortunately, it is not clear whether the (counterpoise-corrected) extrapolated QZ,5Z results or the (counterpoise-corrected) 6Z results are the most accurate. Both the counterpoise-corrected and counterpoise-uncorrected results coincide at the QZ,5Z basis set level. This suggests that the ordinate could be shifted somewhat toward −0.1 kJ/mol. The rms error of the corrected TZ energies is two times larger than for the uncorrected energies, and for the QZ and 5Z basis set, ∼3 times as large. Only for the $ClH\cdots NH_3$ and HF•••HCN systems for the TZ and QZ basis sets are the 6Z reference values not within the span of both the counterpoise-uncorrected and -corrected results. The uncorrected, extrapolated MP2 results are somewhat disappointing, since the DZ,TZ extrapolated value has a larger rms error than the TZ basis set by itself. Only at the TZ,QZ level is the extrapolation useful, although the errors are still larger than expected, and the mean signed error is still larger than the uncorrected result. For the 5Z basis set, the errors become extremely small, and the corrected and uncorrected, extrapolated QZ/5Z results are very close to each other, suggesting that the BSSE tends to be zero after extrapolating to the CBS limit for those basis sets. The lowest error of the respective basis set is obtained when extrapolating the counterpoise-corrected MP2, rather than the uncorrected value. A measure of the accuracy of the extrapolation could be the difference of the uncorrected and corrected results. Generally, the extrapolated results are much closer together than the nonextrapolated ones. For the 5Z basis set, the differences between the CP-corrected and uncorrected interaction energies range between 0.19 and 1.38 kJ/mol, whereas the analogous differences are just 0.03 and 0.17 kJ/mol for the QZ,5Z extrapolated values. For the QZ basis set, the span is between 0.36 and 2.55 kJ/mol and between 0.15 and 0.54 kJ/mol for the TZ,QZ extrapolated values. For the TZ basis set, this is 0.93 and 4.65, and 0.62 and 2.86 for the DZ,TZ extrapolated values. This is, however, mainly due to the fact that the counterpoise-corrected values have very large errors. The extrapolated results are nevertheless more reliable than the nonextrapolated ones: When examining the span of errors, only the HF•••HCN molecule for the DZ,TZ basis set extrapolation and the $ClH\cdots NH_3$ molecule for the TZ,QZ extrapolation are not within the span of the uncorrected and corrected result, as can be seen in the detailed table of the Supporting Information. It appears that both of these molecules are particularly difficult cases. We also looked at a different basis set extrapolation advocated by Truhlar, who suggested using $n^{3.4}$ for HF and $n^{2.2}$ for the MP2 part rather than the n^5 for HF and n^3 for the correlation energy. This has been fitted to yield the correct total energies for the Ne atom and the HF and H_2O molecules. However, the difference between both extrapolation techniques for the dissociation energies of hydrogen-bonded complexes is quite small. Whereas the DZ,TZ extrapolation using a simple 5,3 formula yields a mean error of 0.78 kJ/mol and an rms error of 1.07 kJ/mo asl compared to our 6Z reference, Truhlar's 3.4,2.2

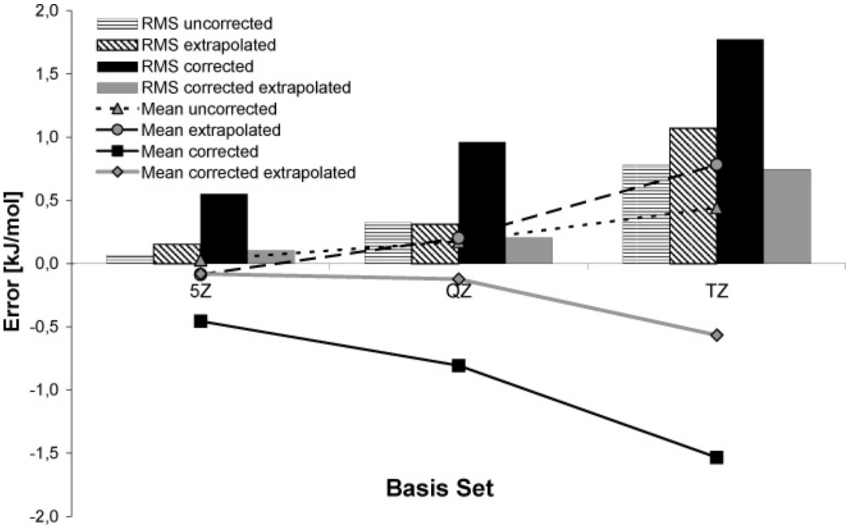

Figure 2. Energetic errors for the MP2 values in comparison to the A′V6Z basis set using extrapolations and counterpoise correction. The bars display the rms errors, and the dots the mean errors.

TABLE 5: Individual Dimer Dissociation Energy Errors for MP2 (in kJ/mol), Compared to the Counterpoise Corrected MP2-R12 Results[a]

neutral	6Z	6Z (CP)	5Z	5Z (CP)	QZ,5Z	QZ,5Z (CP)	d-5Z	R12
ClH$\cdots$NH$_3$	−0.39	−0.77	−0.49	−1.11	−0.40	−0.46		0.11
CO$\cdots$HF	0.11	−0.08	0.18	−0.12	−0.02	0.00	0.57	0.13
FH$\cdots$NH$_3$	−0.08	−0.47	−0.09	−0.71	−0.21	−0.22	0.32	0.10
H$_2$O$\cdots$H$_2$O	0.02	−0.18	0.04	−0.29	−0.02	−0.03	0.35	0.16
HCl$\cdots$HCl	−0.09	−0.23	−0.04	−0.36	−0.08	−0.08		0.10
HF$\cdots$H$_2$O	0.03	−0.29	0.07	−0.48	−0.02	−0.12	0.50	0.15
HF$\cdots$HF	0.05	−0.16	0.09	−0.27	0.05	−0.04	0.55	0.12
HF$\cdots$HCN	0.10	−0.21	0.13	−0.35	−0.16	−0.06	0.56	0.13
NH$_3\cdots$NH$_3$	−0.02	−0.11	−0.02	−0.21	−0.05	0.00	0.13	0.06
NH$_3\cdots$H$_2$O	−0.02	−0.23	−0.02	−0.37	−0.10	−0.07	0.24	0.11
OC$\cdots$HF	0.11	−0.12	0.16	−0.21	−0.06	−0.02	0.61	−0.11
Errors for Neutral Complexes								
mean %	−0.02	−0.26	0.00	−0.41	−0.08	−0.10		0.12
rms %	0.14	0.32	0.18	0.49	0.15	0.16		0.12

[a] d-5Z denotes a doubly augmented 5Z basis set; R12 refers to the noncorrected MP2-R12 results.

formula has a mean error of 0.88 kJ/mol and an rms error of 1.27 kJ/mol. This is mainly due to the fact that the basis sets are quite small by themselves, and it is unlikely that any extrapolation using just the DZ,TZ basis sets will lead to good results for the whole range of hydrogen-bonded systems.

Near-basis set limit calculations have been carried out for the neutral systems, and the results are compared to MP2-R12 results in Table 5 in order to evaluate the basis sets and the extrapolations. Hence, we will attempt to clarify the questions arising from the differences of the results from the different methods presented in Figure 2. The MP2-R12 energy calculations used basis sets of uncontracted, augmented 5Z quality and have been performed at the geometry of MP2 at the 5Z level.

Both the 5Z and 6Z uncorrected energies are almost converged. The R12 and 6Z HCl$\cdots$NH$_3$ interaction energies deviate by 0.26 kJ/mol; all other dissociation energies differ less. That the errors of the 6Z basis sets might be somewhat larger is indicated by the counterpoise-corrected results using these basis sets. Whereas at the 5Z basis set level, the MP2 interaction energies are on average the same as our reference counterpoise-corrected R12 values, at the 5Z counterpoise-corrected level, they are underestimated by 0.41 kJ/mol. At the 6Z level, these values become −0.02 and −0.26 kJ/mol. The difference between these values is still larger than the difference between the 5Z and 6Z basis sets. It looks, however, as if BSSE is almost completely eliminated when extrapolating the basis sets. The difference between the noncorrected and corrected results is smaller than that of the R12 method, but this accuracy is misleading because the dissociation values of the extrapolated basis sets are quite different from the R12 values. On the other hand, they are perfectly between the 6Z and counterpoise-corrected 6Z results.

The large difference of the 6Z results as compared to the dissociation energies of the R12 method might come from the fact that there are not enough diffuse functions on the 6Z basis set. The doubly augmented quintuple ζ basis set calculations (which, however, do have a larger basis set superposition error) seem to indicate that most interaction energies are higher by ~0.4 kJ/mol than it might have been indicated by the 6Z basis set and seem to favor the R12 results to be closer to the basis set limit. In addition, a different QZ,5Z extrapolation using separate extrapolations of singlet-coupled (as $E_\infty^{\mathrm{S}} + a_{\mathrm{S}}n^{-3}$) and triplet-coupled (as $E_\infty^{\mathrm{T}} + a_{\mathrm{T}}n^{-5}$) pair correlation energies advocated by one of us[91] did not lead to different results (at the 5Z optimized geometry). Only the mean error is slightly improved to −0.05 kJ/mol; the rms error is still 0.19 kJ/mol.

2. Hydrogen-Bonded Distances. The basis set convergence of the XH$\cdots$Y hydrogen bond distances, shown in Figure 3, shows behavior similar to the dissociation energies. The counterpoise-corrected geometries again yield the largest errors, ~3 times as large as the uncorrected results. The bond lengths are significantly overestimated, as can be expected from an interaction energy, which is too low. The overestimation is consistent across the test set, since the rms error is not that much larger than the mean error. The behavior of the noncounterpoise-corrected hydrogen bond lengths is very different from the noncounterpoise-corrected energies. The basis set superposition error makes the two systems move too closely together, and in all cases, the bond length is underestimated. However, it is not underestimated by as much as we could have expected, and the QZ basis set, not the TZ basis, has the largest mean error. This is because of error cancelation: The interaction energy between the monomers is simply underestimated, and the basis set error is larger than the basis set superposition error, leading to a fortuitous agreement.

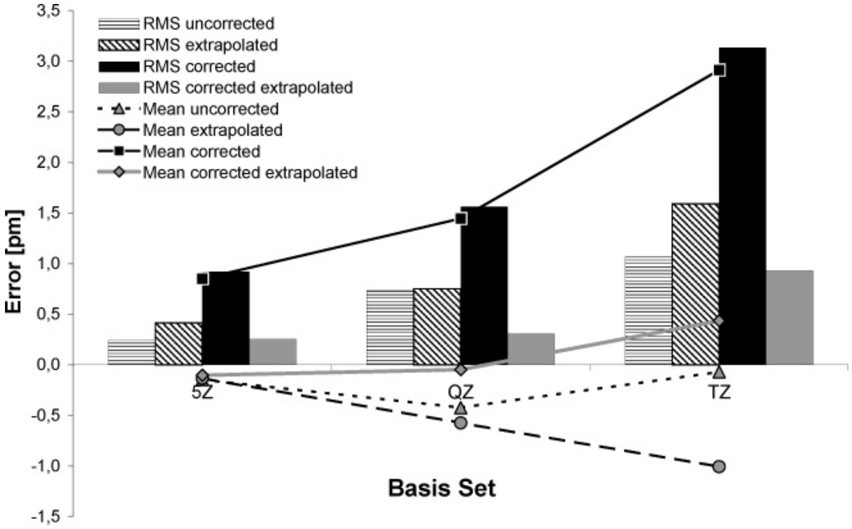

Figure 3. Errors for the MP2 values of the hydrogen-bonded distances in comparison to the A′V6Z basis set using extrapolations and counterpoise correction. The bars display the rms errors, and the dots the mean errors.

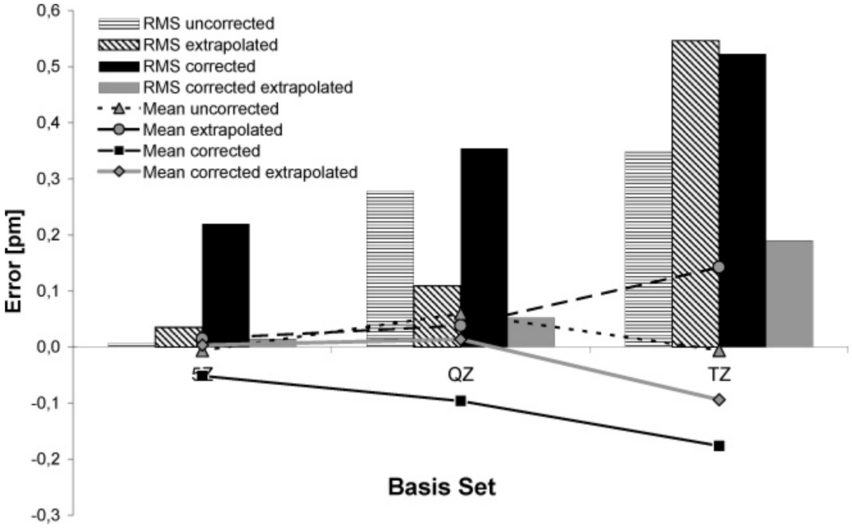

Figure 4. Errors for the MP2 values of the hydrogen bond geometry shifts in comparison to the A′V6Z basis set using extrapolations and counterpoise correction. The bars display the rms errors, and the dots the mean errors.

When the monomers are loosely bound and the interaction has a large fraction of van der Waals terms, the bond distances will be overestimated rather than underestimated. For example, the rms error of the ClH···NH_3 distance is overestimated by more than 2 pm in comparison to our 6Z reference data for the TZ basis set. Here, the X···Y distances show exactly the same behavior as the XH···Y distances.

As geometric properties are known to converge quickly with basis set size, extrapolation techniques become more rewarding. The extrapolated, corrected geometries are more accurate than the nonextrapolated ones, whereas the noncorrected bond lengths are better than the corrected ones. Thus, the errors of the bond lengths are in very close agreement with the errors obtained for the interaction energy. For the DZ,TZ extrapolated values, we must be cautious, however, in cases when the DZ basis set yields an unreasonable geometry. A different extrapolation scheme, such as the aforementioned one by Truhlar, does not bring any improvement: the rms error of this method is ∼2.5 pm. As was the case for the energies, the counterpoise-corrected, extrapolated distances are the most accurate ones. Both the noncorrected and corrected extrapolated values are again in much closer mutual agreement with each other than the nonextrapolated ones. As for the interaction energies, it is unclear which method yields the most accurate geometries. Even at the 6Z level (excluding the ClH···NH_3, $(NH_3)_2$ and NH_3···H_2O complexes), the counterpoise-corrected lengths differ by as much as 0.5 pm from the noncorrected ones.

3. Hydrogen Bond Distance Shifts. Figure 4 shows the error in the hydrogen bond shifts as compared to the 6Z basis set. The same trends as for both the energies and hydrogen bond lengths again apply; however, we note the large error for the counterpoise-corrected, extrapolated DZ,TZ values, larger than even the nonextrapolated ones. A closer look reveals that the DZ geometry of the OH^-···H_2O complex yields an inadequate description, and the error for this shift is as large as 1.9 pm. Excluding this molecule, the rms error for the DZ,TZ extrapolated shift would be only 0.06 pm, rather than 0.55 pm. At the TZ,QZ extrapolated level, the error for this complex is only 0.05 pm, which explains the very small error when using the uncorrected TZ,QZ values. When counterpoise-correcting the energies and gradients before extrapolation, excellent results can be obtained even for the DZ,TZ and the TZ,QZ hydrogen-bonded shifts. The errors for the counterpoise-corrected 5Z shifts remain large, mainly because of the shifts of the OH^-···H_2O (0.7 pm error) and ClH···NH_3 (0.2 pm error) molecules, which are still not very well described. The mean error of the

TABLE 6: Dimer Dissociation Energy Errors for Different MP2 Methods (in kJ/mol)[a]

	conv. MP2			SCS-MP2		local MP2	
	TZ	5Z	CBS	TZ	5Z	TZ	5Z
			Errors for Neutral Complexes				
mean %	4.5	3.3	2.2	−3.2	−5.0	−3.6	−1.2
rms %	9.2	10.9	10.7	4.5	5.8	7.8	10.0
mean	1.0	0.7	0.5	−0.7	−1.1	−0.8	−0.3
rms	1.4	1.3	1.2	0.9	1.2	1.2	1.2
			Errors for Charged Complexes				
mean %	1.9	1.5	1.1	−2.7	−3.3	−0.9	−0.7
rms %	2.3	2.1	1.9	3.1	3.7	1.5	1.0
mean	1.9	1.3	0.8	−2.2	−2.8	−2.0	−1.5
rms	2.2	1.7	1.5	2.4	3.1	2.6	2.0
			Errors for All Complexes				
mean %	3.7	2.3	1.8	−2.6	−3.9	−2.6	−1.0
rms %	7.7	9.1	8.9	4.1	5.3	6.5	8.3
mean	1.3	0.9	0.6	−1.2	−1.6	−1.3	−0.8
rms	1.7	1.4	1.3	1.6	2.0	1.8	1.5

[a] For the CBS limit of the MP2 method, we used the extrapolated QZ,5Z data.

TABLE 7: Dimer Dissociation Energy Errors for Different Composite MP2/CCSD(T) Methods (in kJ/mol)[a]

CCSD(T)	6-31G*(0.25)		DZ			TZ			QZ
MP2	DZ,TZ(T)	5Z	TZ	QZ	5Z	QZ	TZ,QZ	5Z	5Z
				Errors for Neutral Complexes					
mean %	10.0	4.8	2.0	0.7	0.0	1.7	0.6	0.9	0.9
rms %	13.3	8.4	5.5	4.1	3.7	3.9	4.1	3.4	3.5
mean	1.2	0.6	0.1	−0.1	−0.2	0.1	−0.1	0.0	0.0
rms	1.4	0.8	0.9	0.7	0.6	0.5	0.4	0.4	0.3
				Errors for Charged Complexes					
mean %	2.8	0.9	−0.1	−0.5	−0.7	0.1	−0.3	−0.1	−0.1
rms %	4.9	3.7	0.7	0.7	0.8	0.5	0.5	0.4	0.4
mean	2.0	0.3	0.0	−0.4	−0.7	−0.1	−0.3	−0.1	−0.1
rms	3.3	2.7	0.6	0.5	0.7	0.4	0.4	0.3	0.3
				Errors for All Complexes					
mean %	7.7	3.6	1.3	0.3	−0.2	1.2	0.3	0.6	0.6
rms %	11.4	7.3	4.6	3.4	3.1	3.2	3.4	2.9	2.9
mean	1.5	0.5	0.1	−0.2	−0.4	0.1	−0.1	−0.1	0.0
rms	2.2	1.6	0.8	0.6	0.6	0.5	0.4	0.4	0.3

[a] The first row shows the CCSD(T) basis set used; the second the MP2 basis set to estimate the basis set limit.

uncorrected values again has a maximum for the QZ basis set, as we have seen for the lengths of the hydrogen bonds. Overall, the errors for the shifts are small, and many of these (with respect to Table 4) are very small compared to the errors of the MP2 method itself.

4. Approximate MP2. Finally, we take a closer look at the performance of various approximate MP2 methods. The dissociation energies computed using local MP2 and SCS-MP2 with TZ and 5Z basis sets are presented in Table 6. Because SCS-MP2 gradients were unavailable, we performed single-point calculations at the corresponding minimum geometry given by conventional MP2 using the same basis set. It is somewhat disappointing that SCS-MP2 in a larger basis set does not give better results than for the smaller basis sets. In all cases, the A′VTZ basis set yields the lowest errors for the distances and dissociation energies of the hydrogen bonds as compared to our reference coupled-cluster calculations. For the shifts of the hydrogen bonds, only the error for the charged systems, in particular the anionic systems, is slightly reduced when increasing the basis set. The mean percent error for MP2 is decreased; however, the rms error is increased. For the absolute error, the rms error is decreased by a small amount. For SCS-MP2, the percent rms error is halved in comparison to conventional MP2. It no longer overestimates the interaction energies, but rather, underestimates them with much improved weak hydrogen bonds. However, the strong hydrogen bonds, especially in the charged complexes, yield worse interaction energies and are significantly underestimated, but the overall rms error is not much different from conventional MP2. SOS-MP2, on the other hand, yields much larger errors at the largest used basis set (A′V5Z). The percent rms error for all systems is 12.7, and the absolute rms error is 4.3 kJ/mol.

Local MP2 with the localization domains *not* kept fixed during the geometry optimization (our version of the program did not allow for this) also underestimates the interaction energy of the hydrogen-bonded complexes, as it seems to cut some of the correlated charge-transfer terms of MP2. Interestingly, the difference between the two basis sets (TZ and 5Z) seems to be the same for the local and the conventional MP2. Local MP2, however, underestimates the interaction energy more in the small basis sets, because some interaction terms are neglected after the localization. The basis set error is almost the same as the basis set error for the conventional MP2. Hence, despite the lack of "some sort of BSSE" for local MP2, the errors are still large in the small basis set. Simply because MP2 overestimates the dissociation energies, the somewhat underestimated dissociation energies yield lower rms errors, especially for the weaker hydrogen bonds, and the error of local MP2 is smaller than that of conventional MP2. When comparing these results to the density functionals in Table 2, we notice that these methods (SCS-MP2 and local MP2) are the ones with the smallest errors of all tested methods as compared to our reference values.

To summarize, the BSSE for MP2 in the A′V5Z basis is actually comparable to that for DFT at a TZ (aug′-pc2) level, 0.55 kJ/mol (for MP2) vs 0.43 kJ/mol (for B3LYP). For comparison, the MP2 TZ and QZ BSSE are 1.1 kJ/mol and 2.2 kJ/mol. Concerning basis set extrapolations, they seem to be worthwhile only for larger basis sets or when counterpoise-correcting the geometry gradients and energies beforehand. As expected, geometries converge much faster than energies. Counterpoise-corrected energies and gradients yield much worse results than the noncorrected ones for the properties under investigation, suggesting that for the uncorrected results, the basis set superposition error is canceling the basis set error. SCS-MP2 and local MP2 yield somewhat better results than conventional MP2, however not in a consistent manner. It is just a constant shift of the dissociation energies toward lower values, whereas MP2, as noted in the last section, consistently overestimates most of the interaction energies. The standard deviations of all MP2 methods are thus very similar.

3.3. Composite Methods. In this section, we combine MP2 and CCSD(T) in order to obtain CCSD(T) interaction energies at the basis set limit (Table 7). This seems to be an attractive approach, and some attempts already have been made in that direction, especially for the estimation of the interaction strengths of hydrogen bonds.[8,65,66] Here, we combine a low basis set CCSD(T) calculation with an estimate for the remaining basis set by MP2. We used the MP2 A′V5Z reference geometries. They are, of course, not the optimum and explain some of the errors that are still obtained, even when going close to the CCSD(T) basis set limit. Thus, even for CCSD(T)/A′VQZ at the MP2 geometry, the overall percent rms error is still 3.1%, and the overall error is 0.31 kJ/mol (as compared to MP2, which has 9.1% and 1.44 kJ/mol in Table 6). Because of the problem with the geometry, this is the best possible result that can be achieved by the CCSD(T)/MP2 combined methods. The minimum error for such methods should be close to MP2 at a basis set of triple-ζ quality; hence, 7.7% and 1.7 kJ/mol. For example, CCSD(T)/DZ,MP2/QZ means that we have computed the energy the following way: MP2/QZ + CCSD(T)/DZ − MP2/DZ at the MP2 geometry. Of course, if all of these energies would have been computed at another reasonable geometry, this probably would not have changed much. The geometry effects at the TZ level for MP2, hence, the difference MP2/TZ//MP2/5Z minus MP2/TZ, were on average less than 0.01 kJ/mol. We probably have a much larger error when going from the MP2 to the CCSD(T) geometry. The 6-31G*(0.25) basis set has been used previously to calculate the CCSD(T)-MP2 correction in conjunction with larger basis sets of the MP2 method or extrapolation techniques.[65,92] This, however, seems to be inadequate for our purposes. The rms errors, even when using a 5Z basis set, are still larger than when using the MP2 method by itself, indicating that calculating such a correction with an extremely small basis set does more harm than good. The picture, however, already changes for the A′VDZ basis set! This seems to be enough. Even when using this in conjunction with the A′VTZ basis set of MP2, the results are close to convergence. The overall percent rms error does not change by much when using MP2/A′VQZ or MP2/A′PV[T,Q]Z adding the CCSD(T)/A′VDZ correction term. All errors are reduced to about one-half to one-third when using these methods instead of regular MP2. Probably the safest way would be to include CCSD(T)/A′VTZ corrections, for which the rms error is now close to the results of the CCSD(T)/A′VQZ or CCSD(T)/A′V5Z results. For cost-efficiency reasons when benchmarking hydrogen-bonded systems, such methods are likely to be used more widely, albeit not with such small basis sets as 6-31G*(0.25).

To evaluate the usefulness of such methods, we have taken a closer look at the basis set convergence of the CCSD(T) method at the given geometry (see Supporting Information). It might be argued that the use of diffuse functions is impractical, since the use of a basis set with one additional cardinal number higher is almost as expensive. The rms errors of the CCSD(T) method for the neutral hydrogen-bonded dissociation energies (it is clear that for anions, only basis sets with diffuse functions make sense) are (in order) 6.2, 2.5, 1.1, and 0.4 kJ/mol for the cc-pVDZ up to the cc-pV5Z basis sets, respectively. Using diffuse functions, we get 0.7, 0.8, 0.4, and 0.3 kJ/mol. Hence, the addition of diffuse functions when evaluating such interactions is very important.

4. Conclusions

We have evaluated the basis set convergence of several methods to obtain a detailed picture of their nature and performance for hydrogen-bonded complexes. As reference methods, we used W2 (extrapolated CCSD(T)) for the energies and CCSD(T)/A′VQZ geometries. When using a basis set of triple-ζ quality, the tested density functional methods perform clearly worse than the MP2 method. Although sometimes individual functionals are able to surpass the accuracy of MP2 for individual categories, none of them is consistent. Probably the best functionals tested are the hybrid methods, followed by the GGA's BLYP and HCTH/407. HCTH/407 clearly lacks some sort of van der Waals interactions (as density functionals should), explaining the poor prediction of hydrogen-bonded distances. The performance of TPSS is somewhat disappointing. Although it is an improvement (between 10 and 50%) over PBE and BP86, errors are still large. For extremely large systems, the hybrid functionals B97-1 or B3LYP and the GGA functionals HCTH/407 or BLYP could be used, since the basis set superposition error at the triple-ζ DFT level is as small as at the quintuple-ζ MP2 level of theory. Hence, the basis set convergence is much quicker, and even a basis set of augmented-double-ζ quality might be sufficient.

The intrinsic error of the MP2 method is of the same order of magnitude as the basis set error at the triple-ζ level. Using basis sets of better than triple-ζ quality unfortunately does not lead to much improvement for the MP2 or related methods. For weaker bonds going into the van der Waals regime, such as bonding with the hydrogen molecule, an increased basis set leads to better results using MP2. Thus, it might be of interest to see how these methods converge to the basis set limit and which extrapolation or R12 methods are useful. Generally, when extrapolating energies or geometries for weak systems, better results are obtained when counterpoise-correcting beforehand, making such extrapolations at least 3 times as expensive and having to conduct 10 times as many calculations as when not correcting the extrapolation. Extrapolations without counterpoise corrections seem to be worthwhile only for very large basis sets close to the basis set limit. Counterpoise-corrected energies and geometries are, at least for the properties of the systems investigated in the present work, much worse than their noncorrected counterparts. SCS-MP2 and local MP2 yield mixed results as compared to conventional MP2, with lower percent rms errors but larger absolute rms errors for the hydrogen-bonded systems. Since for smaller basis sets, the interaction is underestimated rather than overestimated by almost the same amount as for conventional MP2 methods, it might be an interesting alternative to include local MP2 with some extrapolation to get to the basis set limit. Finally, a viable alternative to full CCSD(T) calculations is to correct MP2 by the CCSD(T)-MP2 difference in a small basis set. Here, even using a basis set of augmented-double-ζ quality yields reasonable results for our reference set.

Acknowledgment. Research at Weizmann was supported by the Minerva Foundation, Munich, Germany, by the Lise Meitner-Minerva Center for Computational Quantum Chemistry (of which the Baroness Thatcher Professor of Chemistry J.M.L.M. is a member ad personam) and by the Helen and Martin Kimmel Center for Molecular Design. Research in Karlsruhe has been supported by the Deutsche Forschungsgemeinschaft (DFG) through the Center for Functional Nanostructures (CFN, Project No. C3.3). It has been further supported by a grant from the Ministry of Science, Research and Arts of Baden-Württemberg (Az: 7713.14-300).

Supporting Information Available: Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Martin, J. M. L.; De Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843.
(2) Boese, A. D.; Oren, M.; Atasoylu, O.; Martin, J. M. L.; Kállay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *120*, 4129.
(3) Karton, A.; Rabinovich, E.; Martin, J. M. L. *J. Chem. Phys.* **2006**, *125*, 144108.
(4) Pérez-Jordá, J. M.; San-Fabián, E.; Pérez-Jiménez, A. J. *J. Chem. Phys.* **1999**, *110*, 1916.
(5) van Mourik, T.; Gdanitz, R. J. *J. Chem. Phys.* **2002**, *116*, 9620.
(6) Kamiya, M.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2002**, *117*, 6010.
(7) Rappe, A. K.; Bernstein, E. R. *J. Phys. Chem. A* **2000**, *104*, 6117.
(8) Klopper, W.; Lüthi, H. P. *Mol. Phys.* **1999**, *96*, 559.
(9) Dunning, T. H., Jr.; Peterson, K. A. *J. Chem. Phys.* **2000**, *113*, 7799.
(10) Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2004**, *108*, 10200.
(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K.

N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.02; Gaussian, Inc.: Pittsburgh PA, 2003.

(12) MOLPRO is a package of ab initio programs written by Werner, H.-J.; Knowles, P. J.; with contributions from Almlöf, J.; ; Amos, R. D.; Berning, A.; Deegan, M. J. O.; Eckert, F.; Elbert, S. T.; Hampel, C.; Lindh, R.; Meyer, W.; Nicklass, A.; Peterson, K.; Pitzer, R.; Stone, A. J.; Taylor, P. R.; Mura, M. E.; Pulay, P.; Schütz, M.; Stoll, H.; Thorsteinsson, T.; Cooper, D.L.

(13) TURBOMOLE, version 5.8, Developed by Ahlrichs, R.; Furche, F.; Hättig, C.; Klopper,W.; Sierka, M.; Weigend, F.; and co-workers.

(14) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(15) Simon, S.; Duran, M.; Dannenberg, J. J. *J. Chem. Phys.* **1996**, *105*, 11024.

(16) Chang, Y. -Y.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 651.

(17) Rodgers, J. M.; Fast, P. L.; Truhlar, D. G. *J. Chem. Phys.* **2000**, *112*, 3141.

(18) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. Kendall, R. A.; Dunning, T. H.; Harrison, R. J., Jr. *J. Chem. Phys.* **1992**, *96*, 6796.

(19) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(20) Parthiban, S.; Martin, J. M. L. *J. Chem. Phys.* **2001**, *114*, 6014.

(21) Sullivan, M. B.; Iron, M. A.; Redfern, P. C.; Martin, J. M. L.; Curtiss, L. A.; Radom, L. *J. Phys. Chem. A* **2003**, *107*, 5617.

(22) Boese, A. D.; Chandra, A.; Martin, J. M. L.; Marx, D. *J. Chem. Phys.* **2003**, *119*, 5965.

(23) Weigend, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97*, 331.

(24) Schütz, M.; Hetzer, G.; Werner, H.-J. *J. Chem. Phys.* **1999**, *111*, 7210.

(25) Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095.

(26) Grimme, S. *Chem.—Eur. J* **2004**, *10*, 3423.

(27) Gerenkamp, M.; Grimme, S. *Chem. Phys. Lett.* **2004**, *392*, 229.

(28) Piacenza, M.; Grimme, S. *Chem. Phys. Chem* **2005**, *6*, 1554.

(29) Piacenza, M.; Grimme, S. *J. Am. Chem. Soc.* **2005**, *127*, 14841.

(30) Hill, J. G.; Platts, J. A.; Werner, H.-J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4072.

(31) Young, Y. S.; Lochan, R. C.; Dutoi, A. D.; Head-Gordon, M. *J. Chem. Phys.* **2004**, *121*, 9793.

(32) For a review, see: W. Klopper, R12 methods, Gaussian geminals. In *Modern Methods Algorithms of Quantum Chemistry*, 2nd Ed.; Grotendorst, J., Ed.; John von Neumann Institute for Computing: Jülich, Germany, 2000, pp 181−229; available online at http://www.fz-juelich.de/nic-series/Volume3/klopper.pdf.

(33) Klopper, W.; Kutzelnigg, W. *Chem. Phys. Lett.* **1987**, *134*, 17.

(34) Klopper, W. *J. Chem. Phys.* **2002**, *116*, 6397.

(35) Klopper, W. *Chem. Phys. Lett.* **1991**, *186*, 583.

(36) Samson, C. C. M.; Klopper, W.; Helgaker, T. *Comp. Phys. Commun.* **2002**, *149*, 1.

(37) Manby, F. R. *J. Chem. Phys.* **2003**, *119*, 4607.

(38) Villani, C.; Klopper, W. *J. Phys. B: At., Mol. Opt. Phys.* **2005**, *38*, 2555.

(39) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098. Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822.

(40) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785.

(41) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(42) Boese, A. D.; Handy, N. C. *J. Chem. Phys.* **2001**, *114*, 5497.

(43) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129; *J. Chem. Phys.* **2004**, *121*, 11507.

(44) Tao, J. M.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

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

(46) Becke, A. D. *J. Chem. Phys.* **1997**, *107*, 8554.

(47) Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 6264.

(48) Marx, D.; Hutter, J. *Ab Initio Molecular Dynamics: Theory and Implementation* in *Modern Methods Algorithms of Quantum Chemistry*; Grotendorst, J., Ed.; NIC, FZ: Jülich, 2000; for downloads, see www.theochem.ruhr-uni-bochum.de/go/cprev.html.

(49) CPMD Program; Hutter, J.; Alavi, A.; Deutsch, T.; Bernasconi, M.; Goedecker, St.; Marx, D.; Tuckerman, M.; Parrinello, M. MPI für Festkörperforschung and IBM Zurich Research Laboratory.

(50) Wilson, A. K.; Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2001**, *114*, 9244.

(51) Martin, J. M. L. *J. Chem. Phys.* **1998**, *108*, 2791.

(52) Bauschlicher, C. W.; Partridge, H., Jr. *Chem. Phys. Lett.* **1995**, *240*, 533.

(53) Wilson, A. K.; Dunning, T. H., Jr. *J. Chem. Phys.* **2003**, *119*, 11712.

(54) Halkier, A.; Helgaker, T.; Jorgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.

(55) Kutzelnigg, W.; Morgan, J. D., III. *J. Chem. Phys.* **1992**, *96*, 4484, and references therein; **1992**, *97*, 8821.

(56) Klopper, W.; Kutzelnigg, W. *J. Mol. Struct.* **1986**, *135*, 339.

(57) Jensen, F. *Theor. Chem. Acc.* **2005**, *113*, 267.

(58) Karton, A.; Martin, J. M. L. *Theor. Chem. Acc.* **2006**, *115*, 330.

(59) Truhlar, D. G. *Chem. Phys. Lett.* **1998**, *294*, 45.

(60) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 716.

(61) Jensen, F. *J. Chem. Phys.* **2001**, *115*, 9113; **2002**, *116*, 3502.

(62) Jensen, F. *J. Chem. Phys.* **2002**, *116*, 7372.

(63) Jensen, F. *J. Chem. Phys.* **2002**, *117*, 9234.

(64) Lebedev, V. I. *Zh. Vychisl. Mat. Mat. Fiz.* **1975**, *15*, 48; *Zh. Vychisl. Mat. Mat. Fiz.* **1976**, *16*, 293; *Sibirsk. Mat. Zh.* **1977**, *18*, 132. Lebedev, V. I.; Skorokhodov, A. L. *Russ. Acad. Sci. Dokl. Math.* **1992**, *45*, 587.

(65) Jurecka, P.; Hobza, P. *Chem. Phys. Lett.* **2002**, *365*, 89.

(66) Jurecka, P.; Hobza, P. *J. Am. Chem. Soc.* **2003**, *125*, 15608.

(67) Tuma, C.; Boese, A. D.; Handy, N. C. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3939. Note that the HCTH/120 functional is denoted HCTH-38 in this paper.

(68) Boese, A. D.; Handy, N. C. *J. Chem. Phys.* **2002**, *116*, 9559.

(69) Boese, A. D.; Martin, J. M. L. *J. Chem. Phys.* **2004**, *121*, 3405.

(70) Rabuck, A. D.; Scuseria, G. E. *Theor. Chem. Acc.* **2000**, *104*, 439.

(71) Wu, Q.; Wang, Y. *J. Chem. Phys.* **2002**, *116*, 515.

(72) Zimmerli, U.; Parrinello, M.; Koumoutsakos, P. *J. Chem. Phys.* **2004**, *120*, 2693.

(73) Grimme, S. *J. Comp. Chem.* **2004**, *25*, 1463.

(74) Ortmann, F.; Bechstedt, F.; Schmidt, W. G. *Phy. Rev. B: Condens. Matter Mater. Phys.* **2006**, *73*, 205101.

(75) Torheyden, M.; Jansen, G. *Theor. Chem. Acc.* **2000**, *104*, 370.

(76) Mas, E. M.; Szalewicz, K. *J. Chem. Phys.* **1996**, *96*, 7606.

(77) Hesselmann, A. Ph.D. Thesis, University of Essen, Essen, 2003.

(78) Sinnokrot, M.; Valeev, E. F.; Sherrill, C. D. *J. Am. Chem. Soc.* **2003**, *124*, 10887.

(79) Stalring, J.; Schütz, M.; Lindh, R.; Karlström, G.; Widmark, P.-O. *Mol. Phys.* **2002**, *100*, 3389.

(80) Furche, F.; Perdew, J. P. *J. Chem. Phys.* **2006**, *124*, 044103.

(81) Bühl, M.; Kabrede, H. *J. Chem. Theor. Comput.* **2006**, *2*, 1282.

(82) Boese, A. D.; Martin, J. M. L.; Handy, N. C. *J. Chem. Phys.* **2003**, *119*, 3005.

(83) Cohen, A. J.; Handy, N. C. *Chem. Phys. Lett.* **2000**, *316*, 160.

(84) Ahlrichs, R.; Furche, F.; Grimme, S. *Chem. Phys. Lett.* **2000**, *325*, 317.

(85) Adamo, C.; Barone, V. *Chem. Phys. Lett.* **1998**, *298*, 113.

(86) Perdew, J. P.; Wang, Y. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *45*, 13244. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 6671.

(87) Tsuzuki, S.; Lüthi, H. P. *J. Chem. Phys.* **2001**, *114*, 3949.

(88) Grimme, S. *J. Chem. Phys.* **2006**, *124*, 034108.

(89) Boese, A. D.; Doltsinis, N. L.; Handy, N. C.; Sprik, M. *J. Chem. Phys.* **2000**, *112*, 1670.

(90) Vandevondele, J.; Mohamed, F.; Krack, M.; Hutter, J.; Sprik, M.; Parrinello, M. *J. Chem. Phys.* **2005**, *122*, 014515.

(91) Klopper, W. *Mol. Phys.* **2001**, *99*, 481.

(92) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 6624.