

# Convergence of the Interaction Energies in Noncovalent Complexes in the Coupled-Cluster Methods Up to Full Configuration Interaction

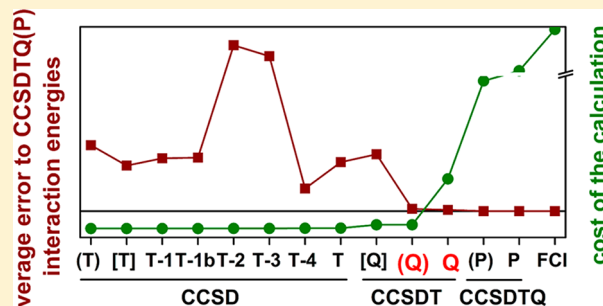
Lucia Šimová,<sup>†,§</sup> Jan Řezáč,<sup>‡</sup> and Pavel Hobza<sup>\*,†,‡</sup>

<sup>†</sup>Regional Center of Advanced Technologies and Materials, Department of Physical Chemistry, Palacký University, 771 46 Olomouc, Czech Republic

<sup>‡</sup>Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 166 10 Prague, Czech Republic

## Supporting Information

**ABSTRACT:** The CCSD(T) method stands out among various coupled-cluster (CC) approximations as the “golden standard” in computational chemistry and is widely and successfully used in the realm of covalent and noncovalent interactions. The CCSD(T) method provides reliable interaction energies, but their surprising accuracy is believed to arise partially from an error compensation. The convergence of the CC expansion has been investigated up to fully iterative pentuple excitations (CCSDTQP); for the smallest eight electron complexes, the full CI calculations have also been performed. We conclude that the convergence of interaction energy at noncovalent accuracy (0.01 kcal/mol) for the complexes studied is reached already at CCSDTQ or CCSDT(Q) levels. When even higher accuracy (spectroscopic accuracy of 1 cm<sup>-1</sup>, or 3 cal/mol) is required, then the noniterative CCSDTQ(P) method could be used.



## INTRODUCTION

Quantum-mechanical computational methods can, in principle, provide an exact description of molecules and molecular systems. However, such calculations are prohibitively complex and can be applied only to the simplest model systems. In other cases, approximations must be employed to make the calculations tractable. The error introduced by these approximations is not well-defined, and the only way to quantify the accuracy of a method is to compare the results to an experiment or a more-accurate calculation. In the case of noncovalent interactions, the calculated quantity, interaction energy, cannot be directly observed experimentally. Therefore, computational data are often used as a reference in this field. However, even these benchmark calculations are only approximate, which means that the absolute accuracy of the calculations can not be defined. Because noncovalent interactions are important in many areas of chemistry, and because their computational description is rather difficult, it is important to develop an unambiguous reference that can be used for evaluation of accuracy of the approximate methods.

In a given basis set and within the common assumptions (Born–Oppenheimer approximation, neglect of relativistic effects), the full configuration interaction (FCI) method provides the exact solution. In practice, it can be applied only to systems with up to ~10 electrons (when a sufficiently large basis set is used). In terms of noncovalent interactions, this method has been applied to rare gas dimers, but there have not been any results reported for molecular complexes (where the interactions are more complex). In this work, we use FCI to

evaluate interaction energies in the few noncovalent complexes where these calculations are possible. This gives us the ultimate reference (exact, with respect to the correlation energy treatment in a given basis set), which is then used to quantify the accuracy of high-order coupled-clusters methods with the possibility of application to larger systems. Only after we show that these methods yield results close to the FCI, we can use them as a benchmark for more-approximate calculations.

Since the first introduction by Čížek et al.,<sup>1</sup> the coupled-clusters method has become, in its various implementations, one of the most important tools in quantum chemical calculations. It relies on the formulation of an excitation operator in an exponential form, which can be expanded into a Taylor series, in terms of components representing single, double, etc. excitations:

$$\begin{aligned} e^T &= e^{T_1+T_2+\dots} \\ &= 1 + T_1 + T_2 + \frac{T_1^2}{2} + T_1T_2 + \frac{T_2^2}{2} + \dots \end{aligned}$$

Depending on the particular components included in coupled-cluster equations and on the manner of doing so, several methods have been developed. The first general implementation of coupled-cluster doubles (CCD) was done by Bartlett and Purvis in 1978,<sup>2</sup> followed in 1982 by the derivation of coupled cluster singles and doubles (CCSD) equations.<sup>3</sup> Since

Received: April 4, 2013

Published: July 3, 2013



connected triple excitations are important for an accurate description of covalent as well as noncovalent interactions, soon various approximations to coupled-cluster singles, doubles, and triples (CCSDT) emerged. So far, the most employed are noniterative CCSD(T),<sup>4</sup> which is the “golden standard” of computational chemistry, and CCSD[T],<sup>5</sup> together with the iterative methods introduced by Bartlett and co-workers:<sup>5–8</sup> CCSDT-1, CCSDT-1b, CCSDT-2, CCSDT-3, CCSDT-4. In the last series of methods, the cluster operator is defined as

$$e^T \approx e^{T_1+T_2+T_3}$$

The difference between the methods lies in the process of defining excitation amplitudes, where some terms are neglected, depending on the approximation of the projection of the wave function onto the space of triple excitations. Both noniterative variants include triple excitations perturbatively and are based upon the CCSDT-1 approach. The CCSD(T) method includes one more fifth-order term than CCSD[T]. Despite CCSD(T) being preferred and established as the golden standard of computational chemistry, we have shown, in our previous work,<sup>9</sup> that, at times, the CCSD[T] method might provide more accurate interaction energies of noncovalently bound complexes when compared to the benchmark data obtained at the CCSDT(Q) and CCSDTQ levels. It is equally important that both of these noniterative approximations outperform the much more expensive CCSDT method in the calculations of interaction energies. This is clearly caused by an error cancellation, which is more prominent in CCSD[T].

The iterative CCSDTQ<sup>10</sup> method covers a large portion of correlation energy and it is thus possible to expect that the interaction energy evaluated at this level is already converged. Nevertheless, to confirm this, it is necessary to calculate the interaction energy of various types of noncovalent complexes beyond the CCSDTQ level. Within the coupled cluster theory, pentuple excitations can be covered either in a noniterative CCSDTQ(P) way<sup>11</sup> or an iterative CCSDTQP way.<sup>12</sup> The respective interaction energies should be close to the exact values (within a given basis set), which can be obtained by performing the FCI calculations. It would be of course desirable to compare the calculations to experiment, but it is not straightforward if we are interested in interaction energies. First, experimental data on noncovalent interactions are rather scarce and the selection of reasonable model systems is limited. Second, the experimental results are associated with uncertainty which is often larger than the effects we are discussing here (errors of ~0.1 kcal/mol are common; only few systems had been measured with higher accuracy). Furthermore, the measured quantity, the dissociation energy ( $D_0$ , i.e., interaction enthalpy at 0 K) includes the zero-point vibration energy, which must be calculated if we want to isolate the interaction energy ( $D_e$ ). Even the most advanced vibrational analysis based on an accurate potential introduces further error. In the case of the most accurate experiment (HF dimer),  $D_0$  had been measured with error of 3 cal/mol,<sup>13</sup> while the best estimate of interaction energy has an uncertainty of ~50 cal/mol. Another advantage of comparing calculations to calculations is that we can use the same approximations (such as Born–Oppenheimer approximation, neglect of relativistic effects etc.) on both sides, while for accurate comparison with the experiment, they cannot be neglected.

The aim of the present paper is to investigate the performance of different coupled-cluster approaches in calculations of noncovalently bonded complexes and compare

them to a relevant benchmark. Therefore, we chose several small model complexes, for which calculations up to CCSDTQP or FCI are possible, to study common trends and the convergence of interaction energies for hydrogen-bonded structures, electrostatically and dispersion-bound complexes. To the best of our knowledge, there is no such study available yet.

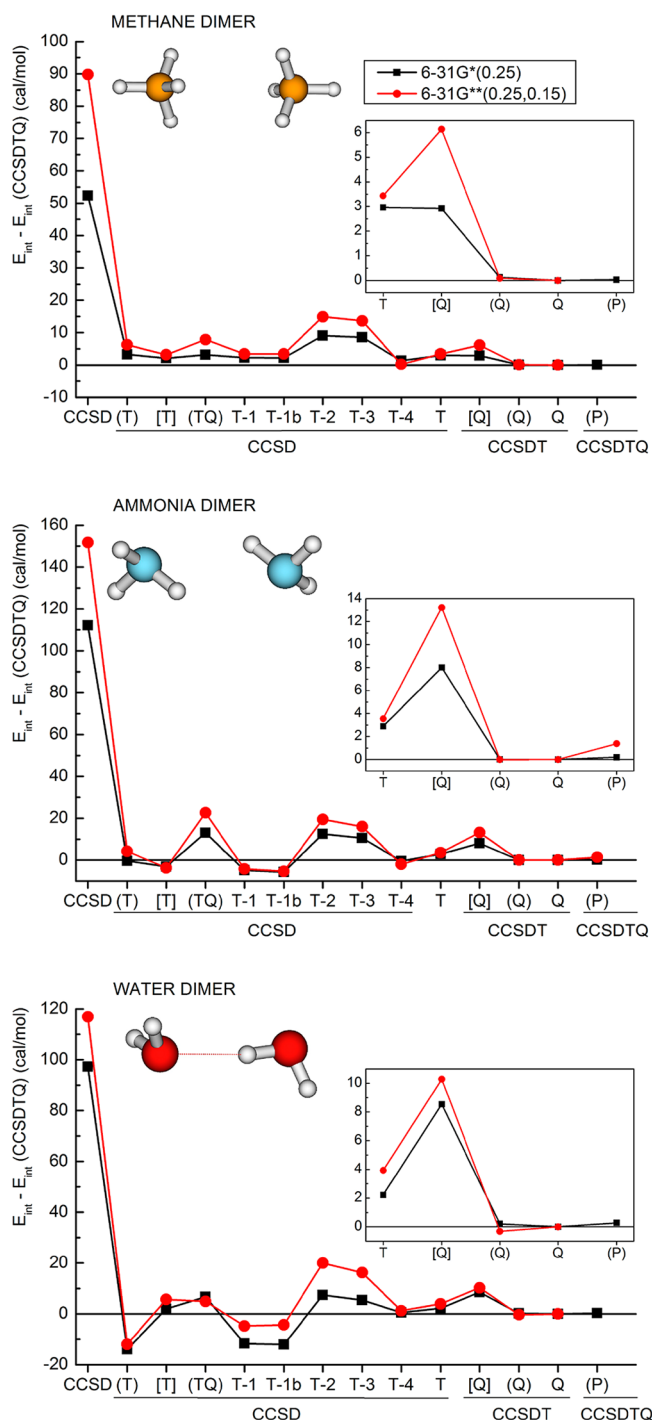
The convergence of correlation energy within the sequence of coupled cluster methods, with the condition of employing a suitable basis set, is established: CCSD < CCSD(T) < CCSDT < CCSDT(Q) < CCSDTQ < CCSDTQ(P) < CCSDTQP < FCI. A lot of research has been done in investigating properties (ionization potential, electron affinity, excitation energies) of small isolated molecules.<sup>14,15</sup> It has been shown that these properties converge within the mentioned sequence and we intend to study also the behavior of interaction energies of weakly bound complexes.

There are several studies where the interaction energies of noncovalent complexes were determined at a computational level beyond CCSD(T). In 2004, a CCSDT study of hydrogen-bonded and stacked complexes was published by Pittner and Hobza,<sup>16</sup> followed by the work of Hopkins and Tschumper,<sup>17</sup> where some dispersion-bound and stacked structures were investigated using the CCSD(TQ)<sup>18</sup> method. Later, the CCSD(TQ) method was used in calculations of benzene dimer.<sup>19</sup> The conclusions of these papers cannot be overestimated, because neither fully iterative CCSDT nor noniterative CCSD(TQ) provide converged values of interaction energies. Coupled-cluster methods with the inclusion of higher excitations have been used in studies of small isolated structures or rare-gas dimers,<sup>20–22</sup> which are, however, not the best choice of models of interactions in noncovalently bound molecular complexes. Recently, CCSDT(Q) and CCSDTQ methods have been employed in our laboratory for small model (hydrogen-bonded, dispersion-bound,  $\pi$ – $\pi$  stacked) complexes as a benchmark in the investigation of the performance of CCSD(T) and CCSD[T] methods.<sup>9</sup> An FCI study of noncovalent ionized complexes was done by Pieniazek et al.,<sup>23</sup> who, however, did not evaluate interaction energies. Also, an electronic structure study has recently been published by Verdicchio et al.,<sup>24</sup> where potential energy curves and dissociation energies were calculated at the valence FCI level. The lithium–thiophene complex was studied by Harding and Klopper, using an accurate composite scheme involving the CCSDT(Q) method.<sup>25</sup>

Presently studied complexes include eight for which FCI and CCSDTQP calculations were feasible. FCI was performed for linear lithium hydride dimer (8 electrons), possessing the lithium bond, as well as for the electrostatically bonded complexes of lithium hydride with hydrogen anion and lithium cation. The latter two complexes have 6 electrons and both are again linear. Further, the FCI calculations were done for dispersion bound T-shaped  $\text{Li}_2\text{--H}_2$  complex (8 electrons), linear  $\text{LiH--H}_2$  (6 electrons) and  $\text{HBeH--H}_2$  (8 electrons) complex. For the 10-electron linear complex of beryllium hydride interacting with lithium hydride and planar complex  $\text{BH}_3\text{--H}_2$  calculations, only up to CCSDTQP were performed.

We also investigated typical hydrogen-bonded systems, the water dimer, and the ammonia dimer, together with dispersion-bound methane dimer. For these 20-electron complexes, calculations only up to the CCSDTQ(P) level were possible. The structures of these complexes are visualized in Figure 1.

The Cartesian coordinates of all the structures are reported in Supporting Information.



**Figure 1.** Interaction energies [cal/mol], relative to CCSDTQ results.

## COMPUTATIONAL DETAILS

The QCISD/6-31++G (d,p) optimized geometry of the LiH dimer was taken from ref 26, and subsequently the  $\text{H}^-$ -LiH, LiH-Li<sup>+</sup>, LiH-H<sub>2</sub>, Li<sub>2</sub>-H<sub>2</sub>, HBeH-LiH, HBeH-H<sub>2</sub>, and BH<sub>3</sub>-H<sub>2</sub> complexes were optimized at the same level. Water, ammonia, and methane dimer structures were optimized at the CCSD(T)/CBS level. Gaussian 09<sup>27</sup> and ACESII<sup>28</sup> packages were used for geometry optimizations.

The calculations of interaction energies were done using the iterative coupled-cluster methods CCSDT, CCSDTQ and CCSDTQP, along with such methods where the highest excitations are treated approximately-iterative CCSDT-1, CCSDT-1b, CCSDT-2, CCSDT-3, CCSDT-4 methods and noniterative CCSD(T), CCSD[T], CCSD(TQ), CCSDT(Q), CCSDT[Q], and CCSDTQ(P). All coupled-cluster and FCI interaction energies were calculated using the CFOUR<sup>29</sup> quantum chemical software with the MRCC program of M. Kállay.<sup>30</sup>

To compare these methods with DFT, we used the B3LYP and BLYP functionals, together with the def2-QZVP basis set. The DFT calculations were done using Grimme's dispersion correction.<sup>31</sup>

In all CC calculations, we used the 6-31G\*(0.25) basis set, which is a modified version of the 6-31G\* basis set, where the exponents of the polarization functions are changed from the original value to 0.25;<sup>32</sup> in the case of lithium, we used the standard 6-31G\* basis set with the exponent of the polarization function being 0.20. We also employed the slightly larger 6-31G\*\*(0.25,0.15) basis set, where the polarization function exponent for the hydrogen atom is set to 0.15. These basis sets, developed specifically for the treatment of noncovalent interactions, have been used in our laboratory for treating extended complexes, specifically hydrogen-bonded and stacked DNA base pairs.<sup>33,34</sup> Spherical d-functions were used in all calculations.

We are certainly aware that the basis sets considered are small and miss higher polarization functions. However, the high-order CC and FCI calculations in larger basis set are not tractable, even for rather small complexes. The objective of the present study is not to generate highly accurate stabilization energies for these complexes, but merely to evaluate the role of higher electron excitations. In our laboratory we have started an ambitious project to determine highly accurate stabilization energies for selected noncovalent complexes. Here, as large basis sets as possible will be used for CCSD(T) calculations while corrections for higher excitations (Q, P) will be calculated with smaller basis sets, similar to those used in the present study.

All interaction energies were corrected for the basis set superposition error, using the counterpoise method of Boys and Bernardi.<sup>35</sup> All electrons were correlated in all calculations and we used tight convergence criteria for both SCF and CC procedures ( $10^{-10}$  a.u.).

## RESULTS

Since we are investigating the convergence of the interaction energy, we must establish a threshold to define, when the convergence occurs. We've chosen the value of 10 cal/mol, which is close to the definition of spectroscopic accuracy ( $1 \text{ cm}^{-1}$ ). We designate this threshold as noncovalent accuracy. It is very tight, in fact, 10 times tighter than the subchemical accuracy (0.1 kcal/mol).

The total stabilization energies obtained with both basis sets at the CCSD(T), CCSDT, CCSDT(Q), CCSDTQ(P), CCSDTQP, and FCI levels are shown in Table 1. It is obvious that stabilization energies are not converged with the basis set, because both 6-31G\*(0.25) and 6-31G\*\*(0.25,0.15) basis sets are small. Where possible, we compare stabilization energies with FCI data. The average difference from FCI is 0.02 cal/mol for CCSDTQ(P) and 0.01 cal/mol for CCSDTQP, respectively. This allows us to use the CCSDTQP and CCSDTQ(P)

Table 1. Interaction Energies (Their Negative Values)<sup>a</sup>

	Interaction Energy (kcal/mol)							FCI
	CCSD(T)	CCSD(TQ)	CCSDT	CCSDT (Q)	CCSDT Q	CCSDT Q(P)	CCSDT QP	
Li <sub>2</sub> ...H <sub>2</sub>	0.0350	0.0347	0.0367	0.0371	0.0373	0.0373	0.0373	0.0373
	0.0882	0.0875	0.0919	0.0924	0.0926	0.0926	0.0926	0.0926
BH <sub>3</sub> ...H <sub>2</sub>	0.0460	0.0475	0.0474	0.0477	0.0478	0.0478	0.0478	
	0.1195	0.1220	0.1225	0.1229	0.1229	0.1229	0.1229	
BeH <sub>2</sub> ...H <sub>2</sub>	0.0731	0.0748	0.0747	0.0750	0.0751	0.0752	0.0752	0.0752
	0.1922	0.1955	0.1960	0.1964	0.1966	0.1966	0.1966	0.1966
CH <sub>4</sub> dimer	0.0673	0.0674	0.0676	0.0705	0.0706	0.0705		
	0.2926	0.2910	0.2955	0.2988	0.2989			
LiH...H <sub>2</sub>	0.2682	0.2683	0.2735	0.2745	0.2750	0.2750	0.2750	0.2750
	0.5775	0.5864	0.5875	0.5885	0.5889	0.5889	0.5889	0.5889
NH <sub>3</sub> dimer	2.2629	2.2494	2.2596	2.2625	2.2625	2.2623		
	2.6536	2.6352	2.6543	2.6578	2.6578	2.6564		
H <sub>2</sub> O dimer	3.9655	3.9449	3.9493	3.9513	3.9515	3.9513		
	4.2189	4.2021	4.2030	4.2073	4.2070			
BeH <sub>2</sub> ...LiH	6.4828	6.4866	6.4884	6.4892	6.4890	6.4890	6.4891	
	6.8953	6.8999	6.9029	6.9033	6.9027	6.9030	6.9031	
LiH dimer	22.5940	22.6186	22.6334	22.6370	22.6385	22.6385	22.6385	22.6385
	23.5763	23.6010	23.6164	23.6185	23.6190	23.6189	23.6190	23.6190
H <sup>-</sup> ...LiH	50.1931	50.2411	50.2727	50.2810	50.2851	50.2851	50.2851	50.2851
	52.1584	52.2048	52.2353	52.2397	52.2413	52.2413	52.2413	52.2414
LiH...Li <sup>+</sup>	54.8442	54.8439	54.8442	54.8442	54.8442	54.8442	54.8442	54.8442
	55.1372	55.1372	55.1374	55.1375	55.1375	55.1375	55.1375	55.1375

<sup>a</sup>The data shown in the first and second rows were obtained using the 6-31G\*(0.25) and 6-31G\*\*(0.25,0.15) basis sets.

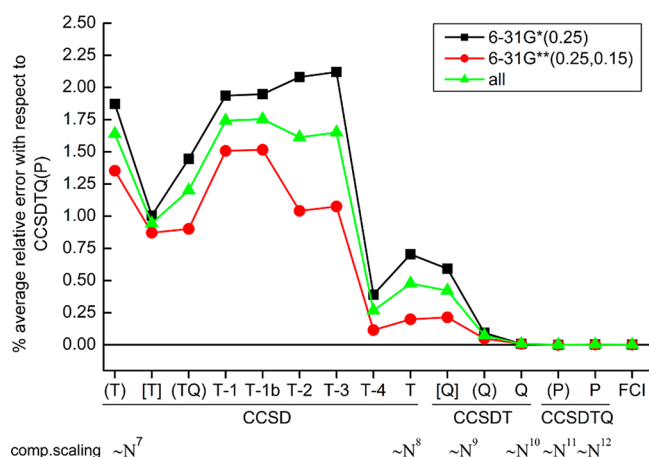
data as our benchmark in such cases, where FCI calculations are not possible.

For six complexes (LiH dimer, H–LiH, LiH–Li<sup>+</sup>, LiH–H<sub>2</sub>, Li<sub>2</sub>–H<sub>2</sub>, and HBeH–H<sub>2</sub>), we are able to compare the performance of the coupled-cluster methods to FCI. The differences are very small, on the order of cal/mol. The CCSDTQP and CCSDTQ(P) methods give practically the same results. The performance of the latter method, being considerably less CPU-time demanding, is remarkable. Nevertheless, neither method can be used in routine calculations of larger noncovalent complexes. The CCSDTQ and CCSDT(Q) methods yield also very accurate data, and, for the six complexes, we can safely claim that the interaction energy is converged (at the noncovalent accuracy) at these levels of theory. The mean unsigned error (MUE, which is exactly the same as the mean absolute error MAE) for the six complexes and both basis sets is 0.01 cal/mol in the case of CCSDTQ method and 0.78 cal/mol for the CCSDT(Q) method. For the latter, the largest difference in the interaction energy is observed for the H<sup>-</sup>–LiH complex with a value of 4.116 cal/mol (in this case, the interaction energy is very large).

Let us examine the results for all the complexes obtained using both basis sets and analyze the convergence of interaction energies in general. Since the accuracy of the CCSDTQ(P) method has been established and these calculations have been

feasible for (almost) all the complexes studied, we will further compare the interaction energies to this benchmark. Besides the total stabilization energies, we also report relative errors with respect to the CCSDTQ(P) results in Figure 2. The absolute differences from the benchmark are generally small, and the relative errors might provide more information on the performance of a particular method. Evidently, the larger basis set having polarization functions also on hydrogen atoms performs better, and the relative errors of all methods studied are <1.52%. It is clear from Table 1 that the stabilization energy is already quite converged (at the noncovalent accuracy) at the CCSDTQ level, with the CCSDT(Q) data differing from those of the CCSDTQ(P) (and FCI, respectively) only slightly. The convergence of the interaction energies for all the complexes studied might be better observed from Figures 1, 3, and 4. The interaction energies for smaller 6-electron (H<sup>-</sup>–LiH, LiH–Li<sup>+</sup>), 8-electron (LiH dimer), and 10-electron (HBeH–LiH) systems are plotted in Figure 3, relative to CCSDTQP data. Similarly, in Figure 4, the interaction energies of dispersion-bound complexes Li<sub>2</sub>–H<sub>2</sub>, LiH–H<sub>2</sub>, HBeH–H<sub>2</sub>, and BH<sub>3</sub>–H<sub>2</sub> are shown, relative to CCSDTQ(P) data. Water, ammonia, and methane dimers interaction energies are plotted in Figure 1, relative to the CCSDTQ results. The trends are generally consistent for both basis sets. The interaction energies of the water dimer and methane dimer data obtained with the 6-





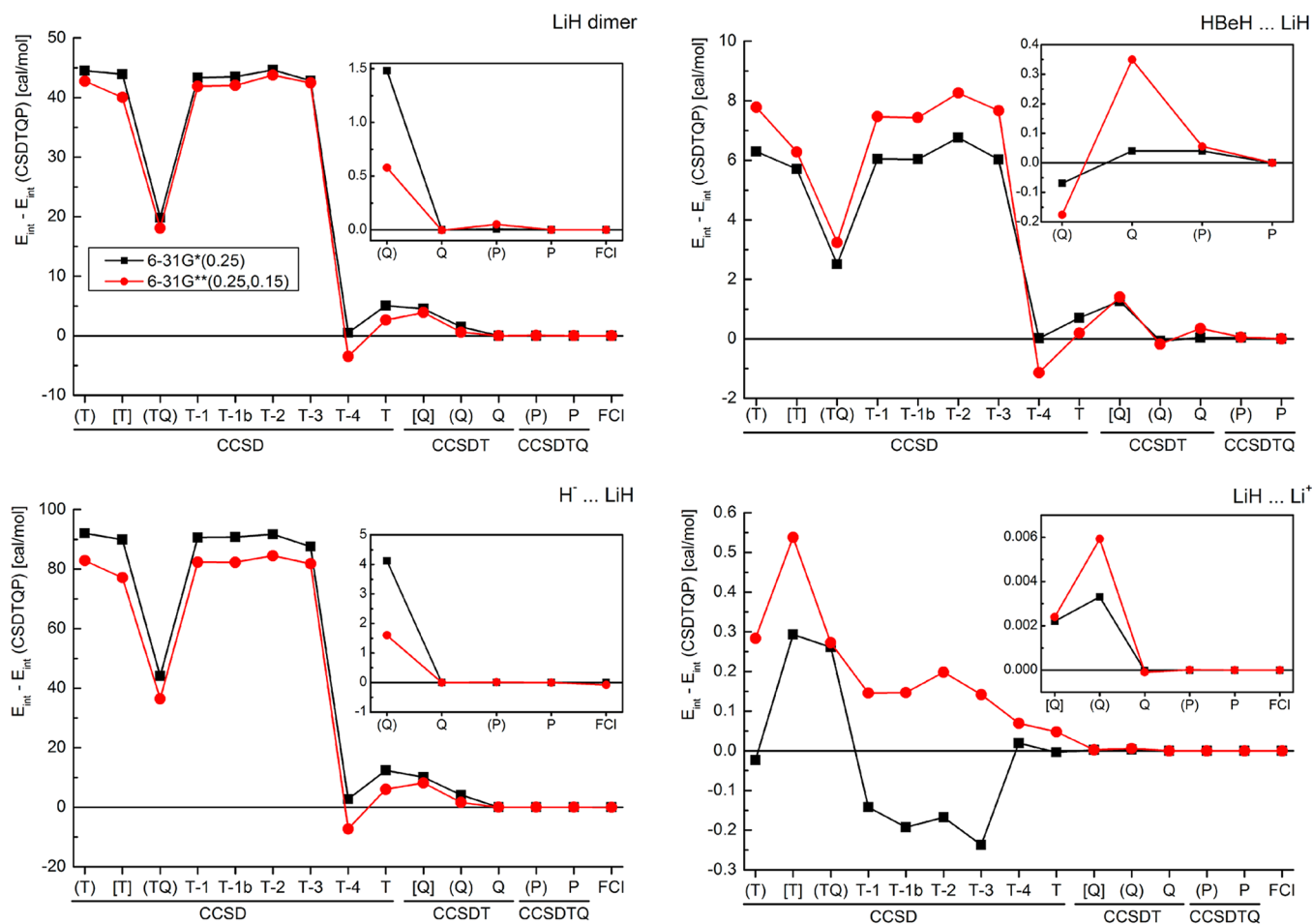
**Figure 2.** Average relative errors, with respect to the CCSDTQ(P) data. For water and methane dimers, the data obtained using 6-31G\*\* (0.25,0.15) are omitted. FCI calculations were performed for the LiH dimer, H–LiH, LiH–Li<sup>+</sup>, LiH–H<sub>2</sub>, Li<sub>2</sub>–H<sub>2</sub> and HBeH–H<sub>2</sub> complexes.

31G\*\* (0.25,0.15) basis set have been omitted, because the CCSDTQ(P) calculations are extremely demanding. The difference of CCSDTQ data from the benchmark is negligible—the average relative error considering both basis sets is <0.01%, with the largest difference of 1.37 cal/mol being observed for the ammonia dimer. Based on these results, we

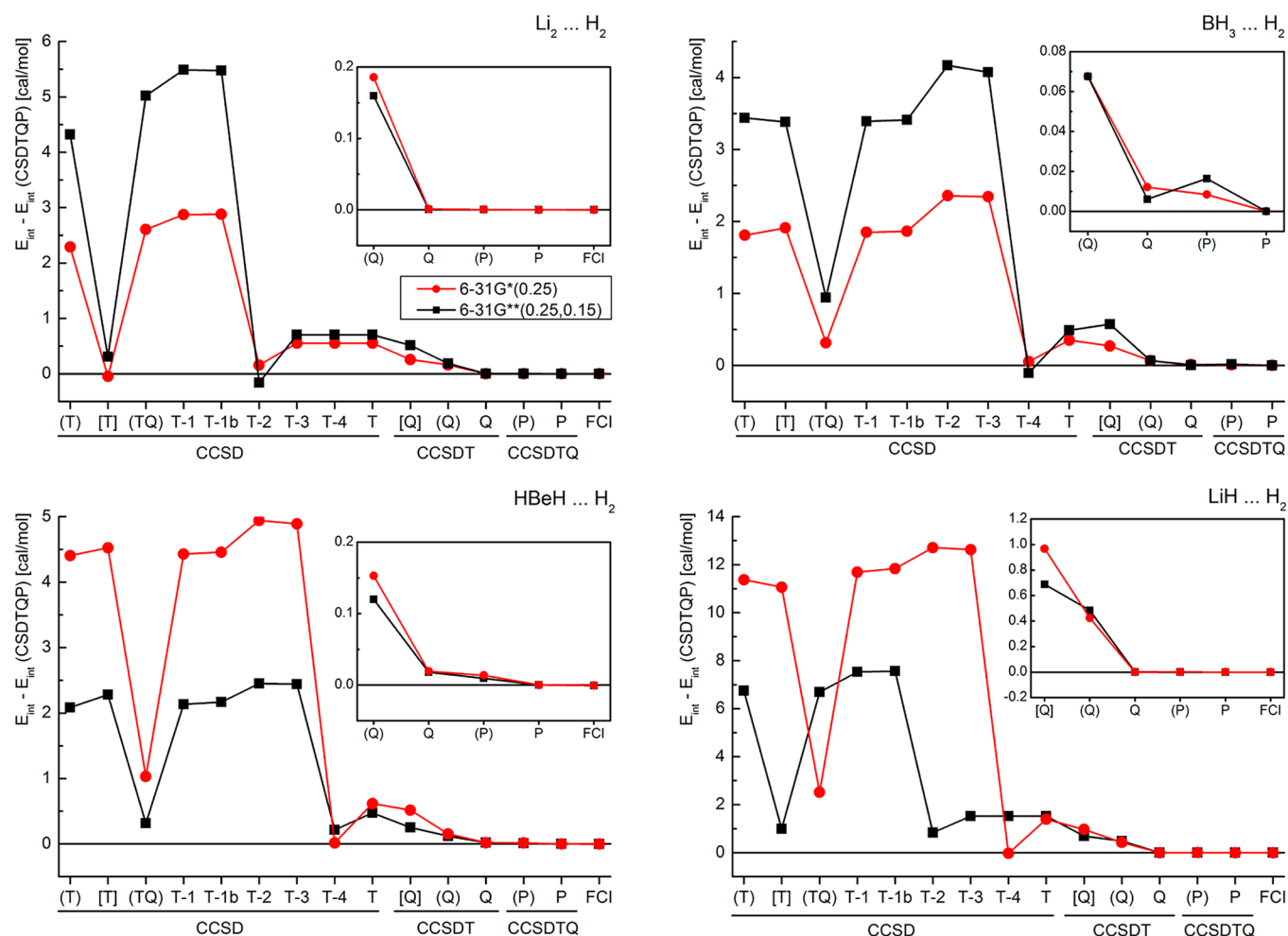
can consider the CCSDTQ interaction energy converged. Calculations at this level of theory, however, are still extremely demanding for most noncovalent complexes. If high accuracy in describing noncovalent interactions is required, the CCSDT(Q) method should also be considered. Calculations at this level are not so demanding, while high accuracy is still preserved. Our results show the average difference (the mean unsigned error, MUE) of the CCSDT(Q) values from those of the CCSDTQ(P) to be 0.57 cal/mol, which is <0.07%, in terms of the relative error. The largest deviation from the benchmark in our set of model complexes has been observed in the case of H<sup>−</sup>–LiH interaction and is 4.11 cal/mol.

Further, the performance of another method with the noniterative treatment of quadruple excitations—CCSDT[Q]—will be investigated. The computational demands of both CCSDT[Q] and CCSDT(Q) methods are comparable, but the performance of the CCSDT[Q] in describing noncovalent interactions appears to be inferior. The average relative error is 0.42%, and the average difference from the CCSDTQ(P) is <3.5 cal/mol. The relative and absolute errors of this method are clearly much larger than those of the CCSDT(Q) method. According to our data, we conclude that the interaction energies are converged at the CCSDT(Q) level. When even higher accuracy is needed, one can rely on the CCSDTQ method.

Here, we mention the CCSD(TQ) method, which treats both triple and quadruple excitations perturbatively. The results



**Figure 3.** Interaction energies [cal/mol], relative to CCSDTQ(P) values.



**Figure 4.** Interaction energies [cal/mol] of dispersion-bound complexes, relative to CCSDTQP results.

obtained with this method are inferior to methods where triple excitations are treated iteratively with MUE 9.4 cal/mol (1.2%). However, it has been shown, that the performance of CCSD(TQ), which scales only  $N^7$ , improves upon enlargement of the basis set. This makes it a promising method for application to larger complexes.

Next, we focus on the performance of the CCSDT method and its several iterative and noniterative approximations. First, we analyze the data obtained at the CCSDT level of theory. From Figure 2, it is clear that we obtain results closer to the CCSDTQ(P) values with the CCSDT method than with the CCSDT[Q] method. The MUE of the CCSDT method, with respect to the benchmark, is 2.13 cal/mol, expressed as a relative error of 0.47%. In our previous study, we demonstrated that noniterative approximations to CCSDT, i.e., CCSD(T) and CCSD[T], provide closer agreement to the benchmark data than the iterative CCSDT method. However, in the previous study, the benchmark data were generated at the CCSDT(Q) level, while in the present study it is at the higher CCSDTQ(P) level. When only the smaller basis set is used, the relative errors indicate that the CCSDT method performance is almost comparable to that of the CCSD[T] approach. When the larger 6-31G\*\*(0.25,0.15) basis set is employed, the performance of CCSDT improves, with the average relative error being as small as 0.2%.

The trends in the behavior of various approximations to CCSDT are particularly interesting, because of their relatively

low requirement of computational resources and the high accuracy that can be achieved. These calculations are routinely performed for systems with tens of electrons and hundreds of basis functions. In five cases—the LiH dimer, H–LiH, LiH–Li<sup>+</sup>, HBeH–H<sub>2</sub>, and BH<sub>3</sub>–H<sub>2</sub>—there is a prominent change in interaction energy when going from the CCSDT-3 method to the CCSDT-4 method. In fact, these differences are on the order of cal/mol, so the average relative error, although higher than for the methods where quadruple excitations are included, is no larger than 1.26% in the case of CCSDT-1b. The data obtained with the CCSDT-1 and CCSDT-1b methods show generally the highest error of all CCSDT approximations, up to 91 cal/mol. The largest relative error is observed for the dispersion-bound Li<sub>2</sub>–H<sub>2</sub> complex (namely, 7.7%). An accurate assessment of correlation energy is particularly important in the description of dispersion interactions, and it is expected that the interaction energy of such complexes will be sensitive to the choice of the method. In this case, the absolute deviation from the benchmark is not large, but the relative error is significant. In general, the CCSDT-3 method performs slightly better than CCSDT-2. Exceptionally accurate results were obtained using the CCSDT-4 method, but the time of the calculation is very close to that of the CCSDT method. These data are quite close to the CCSDTQ(P) benchmark, with the average error being 1.21 cal/mol. Among the noniterative methods CCSD[T] and CCSD(T), the higher accuracy is exhibited in results obtained with the CCSD[T] method (0.95% vs 1.64% relative error),

regardless of the basis set used. Moving from the 6-31G\*(0.25) basis set to the larger 6-31G\*\*(0.25,0.15) improves the results significantly in the case of all the methods up to CCSDT[Q], as can be seen from Figure 1A.

There are four complexes in our set that can be classified as hydrogen-bonded. The typical hydrogen-bonded complexes are water and ammonia dimers. The lithium hydride dimer, together with beryllium hydride interacting with a single lithium-hydride molecule, both contain the so-called “lithium bond”,<sup>36</sup> which is considered to be a special type of hydrogen bond where the hydrogen atom has a partial negative charge. A part of the stabilization energy of the  $\text{H}^-$ –LiH complex also originates in hydrogen bonding. For the water dimer, we have not been able to obtain the CCSDTQ(P) data with the larger basis set; therefore, we have compared the interaction energies in this group to a common benchmark at the CCSDTQ level of theory. In Figure 2, we can see a small deviation of the CCSDTQ data from the CCSDTQ(P) data for ammonia dimer, which is 0.0014 cal/mol (or 0.05%). Also, for the HBeH\_LiH complex, there is a small difference between more-accurate CCSDTQ(P) and the CCSDTQ data, which is 0.29 cal/mol (or 0.004%); however, both of these differences are negligible. In the group of the hydrogen-bonded models of noncovalent interaction, it is clear that, at the CCSDTQ and also CCSDT(Q) level, the interaction energies are already converged. The iterative CCSDT-4 approximation shows consistently high accuracy, but its computational cost is closer to that of the CCSDT method than to the other approximate methods. On average, for these five complexes, where hydrogen bonding is responsible for the interaction, the most accurate method with the inclusion of triple excitations is CCSDT-4, followed by the CCSD[T] and CCSD(T) methods.

In the case of the LiH–Li<sup>+</sup> complex, the interaction energy calculated with the smaller 6-31G\*(0.25) basis set does not vary from the FCI benchmark, regardless of the method used. This is clearly caused by the dominant electrostatic contribution, which is known to be accurately described already at the Hartree–Fock level. Similar results are obtained when the larger basis set is used; the largest error (0.54 cal/mol) was found for the CCSD[T] method.

The CCSD(T) and CCSD[T] calculations might be performed using much-larger basis sets than could be employed in higher-level calculations, thus covering a significant portion of interaction energy. Higher-level calculations could be performed with smaller basis sets, providing correction contributions to the interaction energies. When starting with the CCSDT(Q) data, the contributions of higher excitations are small and the interaction energies at this level, with a possible inclusion of correction to CCSDTQ, are converged. If we start with the CCSD(T) interaction energies, corrections at least to CCSDT(Q) should be calculated, in the basis set, as large as possible. The basis sets used in this work are sufficient for the qualitative comparison of different methods, but larger basis sets would be needed if quantitative results are sought. Also, for our small model complexes, the differences in interaction energies upon including higher excitations in CC calculations are small. That might not apply for larger complexes, and this will be investigated in our future work.

A much less-expensive way to study weakly interacting complexes is to use the DFT methods; for larger systems, it also is often the only way. We calculated interaction energies using the popular BLYP and B3LYP functionals in combination with def2-QZVP basis set (this was necessary for calculation of

dispersion correction). In order to compare these results properly, we evaluated interaction energies for all the complexes using this basis set also at the second-order Möller–Plesset (MP2) and CCSD(T) level of theory (see Table 2). The accuracy of the DFT results is inferior, compared

**Table 2. Interaction Energies (Their Negative Values) for Weakly Bonded Complexes Calculated at the MP2, CCSD(T), and DFT-D3 Level in the def2-QZVP Basis Set**

	Interaction Energy (kcal/mol)			
	MP2	CCSD(T)	BLYP	B3LYP
$\text{Li}_2\cdots\text{H}_2$	0.1055	0.1059	0.0064	0.0449
$\text{BH}_3\cdots\text{H}_2$	0.1022	0.1191	0.0691	0.1014
$\text{BeH}_2\cdots\text{H}_2$	0.2036	0.2150	0.1273	0.1778
$\text{CH}_4$ dimer	0.5290	0.5535	0.5638	0.5286
$\text{LiH}\cdots\text{H}_2$	0.6488	0.6375	0.5198	0.6033
$\text{NH}_3$ dimer	3.2593	3.2188	3.1353	3.2554
$\text{H}_2\text{O}$ dimer	5.2915	5.2639	5.3240	5.5162
$\text{BeH}_2\cdots\text{LiH}$	7.8048	7.6856	8.1360	8.3640
LiH dimer	25.8757	25.4196	24.1597	25.0446
$\text{H}^-\cdots\text{LiH}$	64.6380	64.5822	63.7794	63.8996
$\text{LiH}\cdots\text{Li}^+$	59.2607	58.6786	58.4572	59.2298

even to the MP2 data, because MP2 describes interactions of this type well (while in the case of larger dispersion-bound complexes the DFT-D setup outperforms MP2 significantly).

An important factor to consider in the calculations of interaction energies is not only the accuracy of a given method but also the computational resources, which are necessary for such a calculation. For the most-demanding calculations—FCI, CCSDTQP, and CCSDTQ(P)—an extended memory up to 500 GB was required. In Figure 1, we also mentioned the computational scaling of methods used in this work. For iterative procedures, this is the scaling of one step, which must be repeated until the convergence is reached.

To conclude our investigation of the interaction energy convergence of noncovalently bound complexes, we summarize our findings as follows:

- (1) The use of the CCSDTQP and CCSDTQ(P) methods results in highly accurate results, which differ from FCI by <0.02 cal/mol (i.e., by  $<2 \times 10^{-3}\%$ ). Computational demands for such calculations are very high and are feasible for complexes containing up to 10 (CCSDTQP) or 20 (CCSDTQ(P)) electrons, depending on the computational facilities available. CCSDTQ(P) interaction energies are very close to the CCSDTQP or FCI ones and the average error is as small as 0.015 cal/mol, i.e.,  $1.9 \times 10^{-3}\%$ . The CCSDTQ(P) thus represents a promising method for generating benchmark interaction energies for 4–5 atomic complexes.
- (2) Comparison of the CCSDT(Q) and CCSDTQ methods to FCI demonstrates their accuracy, with the mean unsigned error (MUE) being 0.78 cal/mol (<0.1%) and 0.01 cal/mol (0.003%), respectively.
- (3) CCSDTQ and CCSDT(Q) methods can be compared to a CCSDTQ(P) benchmark, from which the results differ, on average, by <0.11 cal/mol (0.01%) and <0.57 cal/mol (0.07%), respectively. The performance of the CCSDT-[Q] method is comparably inferior with a considerably larger MUE, with respect to CCSDTQ(P), of ~3.5 cal/mol (or 0.5%). Computational demands are still high, but CCSDT(Q) calculations can be carried out for



relatively large complexes with 10–12 atoms (4–6 non-hydrogen atoms).

- (4) The iterative CCSDT method generally outperforms the CCSDT[Q] method in describing noncovalent interactions. When compared to CCSDTQ(P), the average error is <2.2 cal/mol (MUE), or 0.47%.
- (5) The performance of approximations to CCSDT: CCSD(T), CCSD[T], and CCSDT-1, CCSDT-1b, CCSDT-2, CCSDT-3, CCSDT-4 is an interesting issue, because they usually provide results with an acceptable accuracy at a relatively low cost. The most accurate, in terms of relative errors, is the CCSDT-4 method (the average relative error of 0.2%, with respect to CCSDTQ(P)), with computational demands close to those of the CCSDT method, followed by the less-demanding CCSD[T] (0.9%), CCSDT-2 (1.61%), CCSD(T) (1.64%), CCSD-3 (1.65%), CCSDT-1 (1.74%), and CCSDT-1b methods (1.75%). In our previous study,<sup>9</sup> we have shown that the CCSD[T] method might, at times, outperform the more popular CCSD(T) method. In this work, the CCSD(T) method gives a higher average relative error, with respect to CCSDTQ(P), than the CCSD[T] method and so we can again confirm this conclusion, although it might not apply to calculations in larger basis sets.
- (6) The results produced using the CCSD(TQ) method show an average error of 9.4 cal/mol, with respect to the CCSDTQ(P) benchmark. Despite the inclusion of noniterative treatment of quadruple excitations, a significant drop in accuracy is observed, compared to methods with iterative triples.
- (7) The necessity of including triple and higher excitations is demonstrated on results calculated at CCSD level; the errors are as large as 70 cal/mol (10% error, with respect to CCSDTQ(P)).
- (8) The interaction energies converge to the FCI limit, similar to the correlation energy (and other properties) of isolated molecules.

According to these results, the convergence of interaction energy (noncovalent accuracy) is reached at the CCSDTQ, or CCSDT(Q), level. Although these calculations are more computationally demanding, with the constant development of computational resources, they promise a path to highly accurate interaction energies of noncovalent systems, which can serve as a reliable benchmark for other computational approaches. If even higher accuracy (spectroscopic accuracy) is required, the use of noniterative CCSDTQ(P) approximation is recommended. Finally, for extended complexes with up to 50 atoms (25 non-hydrogen atoms), the noniterative alternatives to the CCSDT–CCSD[T] and CCSD(T) methods giving still highly accurate interaction energies can be applied.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Cartesian coordinates of optimized complexes are provided together with the table of interaction energies obtained at CCSD and MP2 levels. Interaction energies without counterpoise correction are also reported. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [pavel.hobza@uochb.cas.cz](mailto:pavel.hobza@uochb.cas.cz).

### Notes

The authors declare no competing financial interest.

<sup>§</sup>On leave from the Institute of Chemistry, Center for Glycomics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 38, Bratislava, Slovak Republic.

## ■ ACKNOWLEDGMENTS

This work was part of the Research Project RVO: 61388963 of the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic. This work was also supported by the Czech Science Foundation [P208/12/G016] and the operational program Research and Development for Innovations of European Social Fund (CZ 1.05/2.1.00/03/0058). This project is further cofinanced by the European Social Fund and the state budget of the Czech Republic (POST-UP II, CZ.1.07/2.3.00/30.0041).

## ■ REFERENCES

- (1) Čížek, J. *Adv. Chem. Phys.* **1969**, *14*, 35.
- (2) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561.
- (3) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.
- (4) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
- (5) Urban, M.; Noga, J.; Cole, S. J.; Bartlett, R. J. *J. Chem. Phys.* **1985**, *83*, 4041.
- (6) Lee, Y. S.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1984**, *81*, 5906.
- (7) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 7041.
- (8) Noga, J.; Bartlett, R. J.; Urban, M. *Chem. Phys. Lett.* **1987**, *134*, 126.
- (9) Řezáč, J.; Šimová, L.; Hobza, P. *J. Chem. Theory Comput.* **2013**, *9*, 364.
- (10) Bomble, Y. J.; Stanton, J. F.; Kállay, M.; Gauss, J. *J. Chem. Phys.* **2005**, *123*, 054101.
- (11) Kállay, M.; Gauss, J. *J. Chem. Phys.* **2005**, *123*, 214105.
- (12) Kállay, M.; Surján, P. R. *J. Chem. Phys.* **2001**, *115*, 2945.
- (13) Bohac, E. J.; Marshall, M. D.; Miller, R. E. *J. Chem. Phys.* **1992**, *96*, 6681.
- (14) Bartlett, R. J.; Musial, M. *Rev. Mod. Phys.* **2007**, *79*, 291.
- (15) Bartlett, R. J. *WIREs Comput. Mol. Sci.* **2012**, *2*, 126.
- (16) Pittner, J.; Hobza, P. *Chem. Phys. Lett.* **2004**, *390*, 496.
- (17) Hopkins, B. W.; Tschumper, G. S. *J. Phys. Chem. A* **2004**, *108*, 2941.
- (18) Raghavachari, K.; Pople, J. A.; Replogle, E. S.; Head-Gordon, M. *J. Phys. Chem.* **1990**, *94*, 5579.
- (19) Pitoňák, M.; Neogrády, P.; Řezáč, J.; Jurečka, P.; Urban, M.; Hobza, P. *J. Chem. Theory Comput.* **2008**, *4*, 1829.
- (20) Hellmann, R.; Bich, E.; Vogel, E. *Mol. Phys.* **2008**, *106*, 133.
- (21) Jager, B.; Hellmann, R.; Bich, E.; Vogel, E. *Mol. Phys.* **2009**, *107*, 2181.
- (22) Patkowski, K.; Szalewicz, K. *J. Chem. Phys.* **2010**, *133*, 094304.
- (23) Pieniazek, P. A.; Arnstein, S. A.; Bradforth, S. E.; Krylov, A. I.; Sherrill, C. D. *J. Chem. Phys.* **2007**, *127*, 164110.
- (24) Verdichio, M.; Bendazolli, G. L.; Evangelisti, S.; Leininger, T. *J. Phys. Chem. A* **2013**, *117*, 192.
- (25) Harding, M. E.; Klopper, W. *ChemPhysChem* **2013**, *14*, 708.
- (26) McDowell, S. A. C. *J. Comput. Chem.* **2003**, *24*, 1201.
- (27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.



Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; 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.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford, CT, 2009.

(28) ACES II is a program product of the Quantum Theory Project, University of Florida. Authors: Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Gwaltney, S. R.; Beck, S.; Balkova, A.; Bernholdt, D. E.; Baeck, K.-K.; Rozyczko, P.; Sekino, H.; Hober, C.; Bartlett, R. J. The integral packages included are VMOL (Almlöf, J.; Taylor, P. R.), VPROPS (Taylor, P.), and ABACUS (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Taylor, P. R.).

(29) CFOUR, a quantum chemical program package written by: Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G. With contributions from: Auer, A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; Cheng, L.; Christiansen, O.; Heckert, M.; Heun, O.; Huber, C.; Jagau, T.-C.; Jonsson, D.; Jusélius, J.; Klein, K.; Lauderdale, W. J.; Matthews, D. A.; Metzroth, T.; Mück, L. A.; O'Neill, D. P.; Price, D. R.; Prochnow, E.; Puzzarini, C.; Ruud, K.; Schiffmann, F.; Schwalbach, W.; Stopkiewicz, S.; Tajti, A.; Vázquez, J.; Wang, F.; Watts, J. D. and the integral packages MOLECULE (Almlöf, J. Taylor, P. R.), PROPS (Taylor, P. R.), ABACUS (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.), and ECP routines by Mitin, A. V.; van Wüllen, C. For the current version, see: <http://www.cfour.de> (accessed Sept. 2012).

(30) MRCC, a string-based quantum chemical program suite written by M. Kállay. Also see: Kállay, M.; Surján, P. R. *J. Chem. Phys.*, **2001**, *115*, 2945, as well as [www.mrcc.hu](http://www.mrcc.hu) (accessed Sept. 2012).

(31) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(32) Kroon-Batenburg, L. M. J.; van Duijneveldt, F. B. *J. Mol. Struct.* **1985**, *121*, 185.

(33) Hobza, P.; Šponer, J. *Chem. Rev.* **1999**, *99*, 3247.

(34) Svozil, D.; Hobza, P.; Šponer, J. *J. Phys. Chem.* **2010**, *114*, 1191.

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

(36) Sannigrahi, A. B.; Kar, T.; Niyogi, B. G.; Hobza, P.; Schleyer, P. v. R. *Chem. Rev.* **1990**, *90*, 1061.