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Performance of single-reference coupled-cluster methods for quasidegenerate problems: The H_4 model

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Summary. Several coupled-cluster methods based on a single-determinantal reference function have been applied to the model system composed of four hydrogen atoms in a trapezoidal arrangement. For nondegenerate regions all methods with the exception of CCD provide results within 1 mhartree of the exact (FCI) value. For degenerate regions such an accuracy can be achieved with the inclusion of the T_3 and T_4 clusters, in an iterative and in a noniterative manner. We report results for CCSDT, CCSDTQ-1, CCSD + TQ*(CCSD), CCSD + Q(CCSDT) plus other methods. In particular, the ACP method which has been proposed to indirectly account for T_4 terms is critically analyzed by including all T_3 contributions.

Key words: Single-reference coupled-cluster – H_4 model system – Quasidegenerate problems

1. Introduction

Since the introduction of coupled-cluster (CC) theory into quantum chemistry by Čížek [1], dramatic progress has been achieved in the reliability and accuracy of CC results. The expanding literature on the subject (cf. e.g. [2–4]) shows that the CC approach is taking a leading position among the methods developed for the inclusion of electron correlation. The currently available collection of various CC approximations is a result of much effort expended both in the theoretical development and in the computer programs. However, the fact that so many variants came into existence is a direct consequence of the impossibility of performing the full CC (FCC = full CI (FCI)) calculations for real chemical systems, i.e., those containing more than several electrons. Nonetheless, when developing, implementing and testing various CC approaches, typically we

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* *Permanent address*: Silesian University, Department of Chemistry, Szkolna 9, 40-006 Katowice, Poland

** *Permanent address*: Slovak Technical University, Department of Organic Chemistry, Bratislava, Czech and Slovak Federative Republic attempt to obtain the closest possible reproduction of the FCI results for energies and other properties.

As we speak about classification of CC approaches, the first distinction lies between single- and multi-reference formulations. The latter is deemed important when the state of the system requires a multi-reference zeroth-order description to introduce essential effects, usually termed "nondynamic correlation." Bond breaking phenomena, excited states, and other situations where by symmetry or otherwise more than one configuration is required, constitute such examples. Such approaches are now available and, although they are more difficult to implement, the results are encouraging [4–9]. However, if we would like to be more precise with respect to the distinction between single- and multi-reference approaches we should instead recognize that the need for a multi-reference (MR) function arises from the fact that the applicable single-reference (SR) approach is too severely truncated to be adequate. If we would be able to include high enough clusters in the CC scheme to approach the FCI results, then we would never need a MR approach. However, the higher clusters that are included the more difficult and more costly the method. Obviously, this is connected with the fact that we must include in the wavefunction expansion a very large number of configurations. It may happen that most of them are comparatively unimportant, with some being essential. This is usually the case when we apply the MR approach, which is simply an intelligent technique to select from the higher excitation clusters those that are most important and incorporate them preferentially into a computational scheme.

Alternatively, the SRCC approach has several appealing features compared to the MRCC. First, the method is straightforward and easier to implement. Second, it lends itself to routine applications to a large number of chemistry problems. Third, when considering the decomposition of a molecule to *all* of its possible fragments, we do not have to use exorbitant sized reference spaces to treat the different decomposition pathways equivalently. Fourth, we need not worry about the intruder states which can be a nightmare in MR methods, whose avoidance often requires the use of an "incomplete" model space which adds formal and computational difficulties. Fifth, there are many more problems with converging the MRCC equations than in the case of the SR approach.

We gather from the above that the main problem with the SRCC calculations is the high computational n-dependence of some terms included in the CC equations (n is the size of the basis set). For very advanced approaches, we may encounter some terms which are computed as n^8, sometimes even as n^9 or n^{10} procedures. Hence, the main effort in studies of the SRCC approaches is directed towards developing methods which should include high rank clusters and consequently give results close to those of FCC, while at the same time should exhibit low n-dependence in computations.

The attempts in developing such SRCC methods are of two types. The first is aimed at inclusion into the expansion of still greater numbers of connected cluster operations T_n, retaining at the same time all the features of the standard CC theory. We will call such formulations *standard* CC approximations. The second group of methods attempts to reproduce the exact results by modifying to some extent the inherent iterative nature of the standard CC theory either by the inclusion of some contributions in a noniterative manner or by adding or removing some terms that do not result directly from the standard CC approach. We will refer to these approximations as *nonstandard* CC methods.

The aim of the present paper is to investigate how the variety of *single-reference* approaches work for a difficult case where the reference function is usually considered to have a *multi-reference* character. This problem has already been addressed in the literature several times, from polyene model problems with semiempirical Hamiltonians [10], to *ab initio* examples like the simultaneous bond breaking in H_2O, dissociating the triple bond of N_2, or the insertion of Be into H_2, which have been considered even in the first *ab initio* CCD [11], CCSD [12] and CCSDT-1 [13] applications. A particularly informative example is offered by the study of the bond breaking of N_2 and F_2 [14] using both a SRCC and MRCC. Since we have now at our disposal a great number of SRCC methods at varied levels of sophistication, we have decided that it would be worthwhile to test them also for a case where the MR approach would be more appropriate.

The system of interest is the H_4 model, introduced by Jankowski and Paldus [15] which is composed of four hydrogen atoms in a trapezoidal arrangement. All the nearest-neighbor internuclear separations are fixed ($a = 2$ a.u.) while the angle $\phi = H_1H_2H_3 - \pi/2$ varies in the interval $\phi \in (0, \pi/2)$. This model is an example of a system in which wavefunction degeneracy is observed [15–18]. The range of degeneracy of this model is determined by a parameter α defining angle $\phi = \alpha\pi$. This means that for the square configuration ($\alpha = 0.0$) the FCI coefficients of the ground state Hartree–Fock wavefunction ϕ and of that corresponding to double excitation from highest occupied to lowest unoccupied levels are equal [15, 16, 18]. Wavefunction degeneracies usually create a more difficult situation for SRCC methods than orbital degeneracies which do not occur in the present case. The latter are generally well handled by infinite order CC approaches, although finite-order MBPT schemes may fail [14, 21]. On the other hand, for wavefunction degeneracies some of the CC methods like LCC(S)D (the (S) indicates with or without the single excitations) schemes will fail completely due to the occurrence of singularities [18].

The H_4 system has also been studied using various CEPA like approaches [22], Hilbert space MRCC techniques [7–9, 18], quasidegenerate perturbation theory [23] and Fock space MRCC methods [24].

In the next section we will briefly discuss the CC approaches used in the present study.

2. Coupled-cluster approximations

Using the exponential type wavefunction the Schrödinger equation may be written as:

$$H_N e^T|\Phi_0\rangle = E_{CC}\, e^T|\Phi_0\rangle \tag{1}$$

where Φ_0 represents a reference function, most often obtained by the Hartree–Fock procedure, and H_N is defined as the usual normal-ordered operator:

$$\begin{aligned} H_N &= \sum_{pq} f_{pq} N[p^\dagger q] + \tfrac{1}{4} \sum_{pqrs} \langle pq||rs\rangle N[p^\dagger q^\dagger sr] \\ &= \sum_{p} \varepsilon_p N[p^\dagger p] + W_N = H_N^0 + W_N \end{aligned} \tag{2}$$

The T operator in Eq. (1) is expressed as the sum of all possible cluster operators that can occur for a given system:

$$T = T_1 + T_2 + T_3 + \cdots + T_N \tag{3}$$

where N is the number of electrons in the system.

The CC equations may be formally written as:

$$\langle \Phi_{ijk\ldots}^{abc\ldots} | (H_N e^T)_c | \Phi_0 \rangle = 0 \tag{4}$$

and $\Phi_{ijk\ldots}^{abc\ldots}$ is a one-determinantal configuration in which occupied orbitals $i, j, k, \ldots$ have been replaced by virtuals $a, b, c, \ldots$.

2.1. *Standard* CC *approximations*

The various CC approaches which we assign to the *standard* group can be created by effecting the truncation either at the level of the cluster expansion, Eq. (3), or, once the T operator has been chosen, by truncating the e^T expansion in Eq. (4). The first case generates a group of methods with the full inclusion of the particular sequence of cluster operators. Thus by considering in Eq. (1) only the T_2 cluster we obtain the CCD method [11], by adding the T_1 cluster we arrive at the CCSD approximation [12]. Next, the inclusion of triple excitations, T_3, [13, 25] culminates in the full inclusion of all terms, CCSDT [26, 27] in addition to the previous ones. Finally, also adding the T_4 cluster creates the CCSDTQ method [28]. We note that the inclusion of the given rank cluster is revealed directly in the acronym used for the method. The principal characteristic of the computer efficiency of the particular method is given by the n-dependence, describing roughly the dependence of the required computer effort on the size of the basis set. Both CCD and CCSD methods scale as n^6 (actually $n_{occ}^2 n_{virt}^4$), while the CCSDT method is two powers worse, n^8 (actually $n_{occ}^3 n_{virt}^5$ and $n_{occ}^4 n_{virt}^4$), and finally the last of the considered methods (CCSDTQ) is an n^{10} ($n_{occ}^4 n_{virt}^6$) procedure.

It follows from the above that the full inclusion of the given sequence of cluster operators, particularly T_3 and T_4 clusters, makes the resulting equations very complicated and computationally difficult, hence the need for having methods with an intermediate level of complexity and, hopefully, with the corresponding level of accuracy. Thus we come to the second truncation technique performed at the exponential expansion level. Respective CC approaches are indicated by the arabic number preceded by a hyphen, e.g. various CCSDT-n approaches [13, 25, 26] differ mainly in the number of T_1, T_2, and T_3 operators and their products included in the equation for the t_{ijk}^{abc} amplitude. Following this procedure the CCSDT-1 method [13] is defined by the following set of equations:

$$\begin{aligned} \langle \Phi_i^a | [H_N(e^{T_1+T_2} + T_3)]_c | \Phi_0 \rangle &= 0 \\ \langle \Phi_{ij}^{ab} | [H_N(e^{T_1+T_2} + T_3)]_c | \Phi_0 \rangle &= 0 \\ \langle \Phi_{ijk}^{abc} | (H_N T_2)_c | \Phi_0 \rangle &= 0 \end{aligned} \tag{5}$$

The method defined in this way is correct through the fourth-order energy in MBPT and second-order wavefunction, as is the full CCSDT method, but contrary to the latter scales only as n^7. Furthermore, unlike full CCSDT, it does not require intermediate storage of T_3 amplitudes. In an analogus manner we define a method which partially includes connected quadruples on top of the full

CCSDT approach, as CCSDTQ-1 [28]. The CC equations pertinent to this method are the following:

$$\langle \Phi_i^a | (H_N e^{T_1+T_2+T_3})_c | \Phi_0 \rangle = 0 \tag{6a}$$

$$\langle \Phi_{ij}^{ab} | [H_N (e^{T_1+T_2+T_3} + T_4)]_c | \Phi_0 \rangle = 0 \tag{6b}$$

$$\langle \Phi_{ijk}^{abc} | (H_N e^{T_1+T_2+T_3})_c | \Phi_0 \rangle = 0 \tag{6c}$$

$$\langle \Phi_{ijkl}^{abcd} | [H_N (T_2^2/2 + T_3)]_c | \Phi_0 \rangle = 0 \tag{6d}$$

The latter method gives the energy correct through the fifth order of MBPT and scales as n^9.

To explore in a more detailed way the importance of the T_4 equation for the present model we have introduced another approximation called CCSDTQ-2a which includes additional diagrams. Now the last line of Eqs. (6) will become:

$$\langle \Phi_{ijkl}^{abcd} | [H_N (T_2^2/2 + T_3 + T_2 T_3)]_c | \Phi_0 \rangle = 0 \tag{7}$$

where the new term corresponding to the disconnected pentuples gives a sixth-order MBPT contribution and is computed with the same n-dependence. An important thing about T_4 contributions as given by Eqs. (6, 7) is that when they are included in a noniterative manner their n-dependence is lower than n^9.

We may benefit more from this when we go to the nonstandard CC approaches, which is the topic of the next subsection.

2.2. *Nonstandard* CC *approximations*

First we discuss schemes in which the higher rank clusters are included in a noniterative manner. The general strategy in these approaches relies on determining T_2 (and T_1) amplitudes by performing standard CCD (CCSD) calculations and then using the converged values of t_{ij}^{ab} (and t_i^a) to perturbatively include effects of triple and quadruple contributions. In the following we give a very brief description of the approximations applied in the present calculations.

2.2.1. CCSD + T(CCSD). The simplest approach in this spirit is a T(CCSD) method [29] which on top of CCSD evaluates the triple contribution (in the canonical SCF case) according to the formula:

$$E_T^{[4]} = \sum_{abcijk} \frac{|\langle \Phi_{ijk}^{abc} | H_N T_2 | \Phi_0 \rangle_c|^2}{\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c} \tag{8}$$

and the total energy is expressed as:

$$E = E_{\text{CCSD}} + E_T^{[4]} \tag{9}$$

In this way we avoid the n^7 procedure when iterating CC equations; however the last step, according to Eq. (8) requires an n^7 step, or the same as in the standard CCSDT-1 method. We should mention here that in our notation $X^{(n)}$ refers to the nth-order MBPT correction to the quantity X, whereas $X^{[n]}$ represents what we call an nth-order-type contribution which is created by taking the nth order MBPT expression and replacing the first-order T_2 amplitudes by their converged (usually at the CCSD level) equivalents.

2.2.2. CCSDT + Q(CCSDT). It appears that there is much more to gain in the noniterative inclusion of the T_4 contribution. In a simplification that is not readily apparent from standard CC methods, the fifth-order T_4 contribution can be factorized in such a way that all resulting diagrams are computed with n^7 and lower procedures [30–32]. Analogously we replace the W_N vertex with converged T_2, T_1, and T_3 coefficients and generate a noniterative fifth-order-type correction for the CCSDT method. The respective algebraic expression is the following:

$$E_{Qa}^{[5]} = \langle \Phi_0 | T_2^{(1)\dagger} T_2^{\dagger}/2 [W_N (T_2^2/2 + T_3)]_c | \Phi_0 \rangle \tag{10}$$

and the total energy within this approach is evaluated according to the formula:

$$E = E_{\mathrm{CCSDT}} + E_{Qa}^{[5]} \tag{11}$$

In this way we obtain a method which is correct through fifth order and the most time consuming contribution is that already present in the CCSDT approach. Since we include the full T_3 contribution in an iterative way and this is an n^8 scheme, the addition of the n^6 step (the $T_2^2/2$ part) and n^7 step (the T_3 part) in Eq. (10) costs only a fraction of the time required for converged results of the CCSDT method.

2.2.3. CCSD + TQ*(CCSD). Another approximation proposed is to carry out CC iterations only at the CCSD level, with all the terms required for the scheme to be correct through fifth order added on top of the CCSD method. We designate this scheme as TQ*(CCSD) [32] because the derivation starting from CCSD requires a somewhat different, i.e. Q^*, approximation. Here the total energy is expressed as follows:

$$E = E_{\mathrm{CCSD}} + E_T^{[4]} + E_{ST}^{[5]} + E_{TD}^{[5]} + E_{TT}^{[5]} + E_{Qb}^{[5]} \tag{12}$$

The second term in Eq. (12) has already been defined in Eqs. (8), while:

$$E_{Qb}^{[5]} = \langle \Phi_0 | (T_2^{\dagger 2}/2) [W_N (T_2^2/2 + T_3^{[2]})]_c | \Phi_0 \rangle \tag{13}$$

The other terms are:

$$E_{ST}^{[5]} = \langle \Phi_0 | T_1^{\dagger} W_N T_3^{[2]} | \Phi_0 \rangle \tag{14}$$

$$E_{TD}^{[5]} = \langle \Phi_0 | T_3^{[2]\dagger} W_N T_2^2/2 | \Phi_0 \rangle \tag{15}$$

$$E_{TT}^{[5]} = \langle \Phi_0 | T_3^{[2]\dagger} W_N T_3^{[2]} | \Phi_0 \rangle \tag{16}$$

The $T_3^{[2]}$ amplitudes are calculated according to the formula:

$$T_3^{[2]} = \sum_{abcijk} \frac{\langle \Phi_{ijk}^{abc} | W_N T_2 | \Phi_0 \rangle}{\varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c} \tag{17}$$

Equation (13) differs from Eq. (10) in that all T_2 amplitudes are the converged infinite order quantities, as required by the derivation [32]. The T_4 correction defined by Eq. (10) was considered in an originally proposed TQ(CCSD) method (see, e.g. [32]), where the converged T_3 amplitudes present in Eq. (10) are replaced by $T_3^{[2]}$.

The rate-determining step in the present method is the $E_{TT}^{[5]}$ contribution which scales as n^8, however it is computed only once. Out of the remaining components of the TQ*(CCSD) contribution $E_{ST}^{[5]}$ scales as n^6, $E_T^{[4]}$ and $E_{TD}^{[5]}$ can be combined together to form a single n^7 step and, finally, the last term, $E_{Qb}^{[5]}$ requires also an n^7 step. Bearing in mind, however, that all the terms occurring in Eq. (12), are computed only once, and only CCSD equations are iterated, we arrive at substantial savings in the cost of calculations.

A different rationale lies behind the approximate schemes introduced by Paldus and others [15, 33–37], denoted as ACP-D45 ≡ ACP ≡ ACCD and ACP-

D45(9) ≡ ACPQ. These approaches are based on the observation that neglecting certain disconnected quadruple diagrams within the CC(S)D method significantly improves the results. Since the diagram(s) in question are the most difficult to compute in the CCD method their elimination simplifies the method considerably. Paldus et al., by analyzing the UHF solution to the cyclic polyenes in the PPP model, which is exact for the cases considered in the fully correlated limit, were able to demonstrate that the good performance of the ACP schemes is associated with the fact that the elimination of the respective diagrams corresponds to their approximate cancellation with certain connected T_4 contributions [33]. The ACP approaches usually work well for such quasidegenerate situations. However, this conclusion may be less appropriate outside the analyzed PPP model.

In the present study we have employed only one of the discussed approximations, namely ACP, which relies on the elimination of two out of four $1/2\ T_2^2$ diagrams (see [33] for details). Though the other variant, ACPQ is superior [35], the behavior of the simpler ACP is sufficiently indicative of both methods to be adequate for our purposes.

3. Results and discussion

The calculations have been performed for the DZP basis set, taken from [18]. The computed correlation energies are presented in Tables 1 and 2 for the standard and nonstandard CC methods respectively, for the sequence of values of the α parameter. Analogously, in Figs. 1 and 2 the energy vs. α curves are presented for the same group of methods. In Table 3 we have collected results of CCD and CCSD methods modified in different ways to account for approximate

Table 1. Comparison of the FCI and the selected single-reference CC correlation energies for the H_4 model as a function of parameter α (all values in mH). The numbers indicate the difference of CC energies from corresponding exact FCI values (the first column)

α	FCI[a]	CCD[a]	CCSD	CCSDT-1	CCSDT	CC SDTQ-1	CC SDTQ-2a
0.0	−131.361	8.243	5.508	−0.965	−2.302	−0.654	−0.625
0.005	−123.831	7.024	4.474	−0.494	−1.546	−0.448	−0.427
0.01	−117.956	5.987	3.603	−0.205	−1.017	−0.299	−0.285
0.015	−113.412	5.166	2.928	−0.044	−0.671	−0.201	−0.189
0.02	−109.870	4.540	2.431	0.046	−0.450	−0.134	−0.123
0.05	−98.647	2.890	1.262	0.142	−0.071	−0.019	−0.007
0.1	−91.006	2.227	0.911	0.128	−0.022	−0.001	0.009
0.12	−89.169	2.121	0.860	0.120	−0.021	−0.001	0.008
0.15	−87.121	2.032	0.811	0.110	−0.022	−0.001	0.008
0.2	−84.953	1.987	0.770	0.099	−0.023	−0.001	0.007
0.3	−83.042	2.040	0.748	0.088	−0.023	−0.001	0.006
0.4	−82.460	2.112	0.751	0.086	−0.020	−0.001	0.007
0.5	−82.333	2.141	0.753	0.084	−0.020	−0.001	0.008

[a] Results for some geometries have already been published [18] but for completeness we reproduce all of them here. The FCI results are obtained from the algorithm and program of Zarrabian S, Sarma, CR, Paldus J (1989) Chem Phys Lett 155:183; Harrison RJ, Zarrabian S (1989) Chem Phys Lett 158:393

Table 2. The deviations of the single-reference CC correlation energies for DZP H_4 model from corresponding FCI values as a function of parameter α (all values in mH). (See text for the explanation of abbreviations used for individual approximate CC approaches.)

α	FCI[a]	ACP (CCD)	ACP (CCSD)	ACP (CCSDT)	CCSD+ T(CCSD)	CCSD+ TQ*(CCSD)	CCSDT+ Q(CCSDT)
0.0	−131.361	7.746	5.059	−0.784	−3.969	−0.869	0.475
0.005	−123.831	5.690	3.142	−1.843	−1.999	−0.526	0.063
0.01	−117.956	4.352	1.940	−2.243	−1.015	−0.310	−0.062
0.015	−113.412	3.527	1.241	−2.246	−0.526	−0.194	−0.080
0.02	−109.870	3.027	0.862	−2.056	−0.276	−0.133	−0.067
0.05	−98.647	2.179	0.513	−0.890	0.040	−0.041	−0.007
0.1	−91.006	1.894	0.562	−0.392	0.077	−0.004	0.002
0.12	−89.169	1.833	0.558	−0.340	0.077	0.002	−0.002
0.15	−87.121	1.777	0.544	−0.303	0.073	0.007	−0.001
0.2	−84.953	1.749	0.521	−0.286	0.067	0.011	0.001
0.3	−83.042	1.791	0.489	−0.298	0.058	0.012	0.001
0.4	−82.460	1.848	0.475	−0.314	0.056	0.012	0.002
0.5	−82.333	1.870	0.471	−0.320	0.056	0.012	0.003

[a] See footnote to Table 1

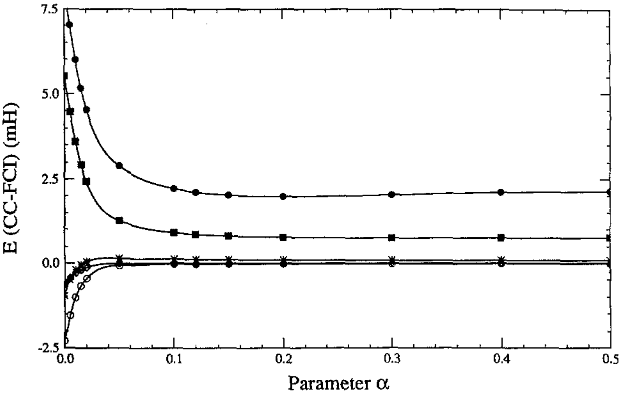

Fig. 1. The single-reference CC relative energies ΔE, $\Delta E = E_{CC} - E_{FCI}$, (in mH) as a function of parameter α (see text) for the ground state of the DZP H_4 model system. The various methods are identified as follows: (●) CCD; (■) CCSD; (*) CCSDT-1; (○) CCSDT; (◇) CCSDTQ-1, CCSDTQ-2

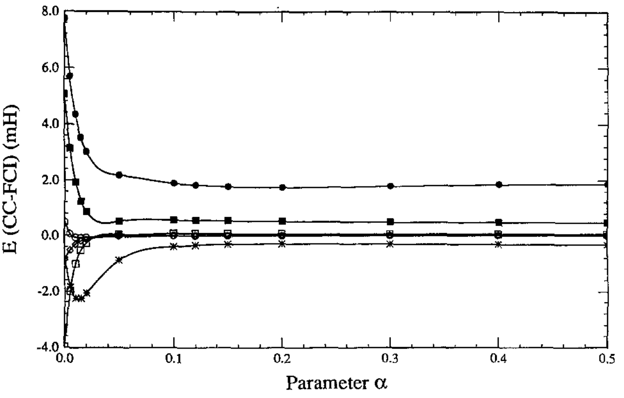

Fig. 2. Comparison of the single-reference CC relative energies ΔE (see Fig. 1) as a function of parameter α for the ground state of the H_4 (all values in mH). The various CC approaches are identified as follows: (●) ACP(CCD); (■) (ACP(CCSD); (*) ACP(CCSDT); (○) CCSDT + Q(CCSDT); (□) CCSD + T(CCSD); (◇) CCSD + TQ*(CCSD)

Table 3. Effect of the quadruples on the CCD and CCSD correlation energies for the H_4 model as a function of parameter α (all values in mH). The numbers indicate the difference of CC energies from corresponding exact FCI values (the first column) (see text for the explanation of abbreviations used for approximate CC methods)

α	FCI[a]	CCD[a]	ACP (CCD)	CC DQ-1a	CCSD	ACP (CCSD)	CC SDQ-1a
0.0	−131.361	8.243	7.746	9.337	5.508	5.059	6.663
0.005	−123.831	7.024	5.690	7.730	4.474	3.142	5.228
0.01	−117.956	5.987	4.352	6.438	3.601	1.940	4.090
0.015	−113.412	5.166	3.527	5.456	2.928	1.241	3.245
0.02	−109.870	4.540	3.027	4.728	2.431	0.862	2.638
0.05	−98.647	2.890	2.179	2.905	1.262	0.513	1.281
0.1	−91.006	2.227	1.894	2.227	0.911	0.562	0.913
0.12	−89.169	2.121	1.833	2.124	0.860	0.558	0.865
0.15	−87.121	2.032	1.777	2.038	0.811	0.544	0.820
0.2	−84.953	1.987	1.749	1.997	0.770	0.521	0.783
0.3	−83.042	2.040	1.791	2.051	0.748	0.489	0.763
0.4	−82.460	2.112	1.848	2.123	0.751	0.475	0.765
0.5	−82.333	2.141	1.870	2.151	0.753	0.471	0.766

[a] See footnote to Table 1

connected quadruple contributions. As has already been mentioned, the value of the α parameter determines the multi-configurational character of the reference function. The FCI coefficients given in [18] have been recalculated by us to show that for α greater than 0.02 the reference function recovers its single-configurational character, the weight of the ground state configuration exceeding 90%. This can be inferred also from the dependence of the correlation corrections on the α parameter shown in all three tables. We see that for the nondegenerate region, $\alpha > 0.02$, all the contributions are stable, showing no substantial changes and even the simplest of methods applied gives good results. Because of the above dichotomy we can address the two regions separately.

3.1. Region of quasidegenerate reference function: $\alpha < 0.02$

The present range of α values creates rather a severe test for the single reference based CC methods. For the standard approaches, see Table 1, n^6 methods, i.e. CCD and CCSD give errors of several mhartrees, the latter being better by about 2.5 mhartree. At first sight those discrepancies seem to be insignificant, however, we should be aware that the system is rather small and those errors amount to about 6–7% of the total correlation energy for the first point and decrease to about 4% for the last point of the region assumed by us to be of quasidegenerate nature. The inclusion of triples radically improves the results. It is unusual that the approximate CCSDT-1 method works so well for the degenerate region, where the results are better than those obtained with the full CCSDT scheme. We consider this inverted hierarchy of the two methods accidental. The accumulated evidence demonstrates that for the great majority of cases the latter method works substantially better also for the degenerate case. However, in many quasidegenerate examples in the literature, the CCSDT correction overshoots the exact results. This is also the case in the present calculations. The full CCSDT error is smaller than the corresponding CCSD one being for the first point at $\alpha = 0.0$ equal to -2.302 mhartree and at the last point in the region, -0.450 mhartree. One may note that this performance of the CCSDT method is in line with what we have observed for other systems for which the FCI values are known. For example, for the distorted geometries of the several first row hydrides studied [26a] the error is about 1–2 mhartrees, while for the equilibrium geometries it goes down to a few tenths of a millihartree.

For methods correct through fifth order we observe substantial improvements of the results compared to the CCSDT method. It is obvious that for the degenerate reference function connected quadruples play a much more important role. For $\alpha = 0.00$ the quadruple correction is equal to 1.633 mhartrees and is positive. An inclusion into T_4 of disconnected pentuples improves the results only slightly by a few hundredths of a millihartree.

The results collected in Table 2 are generally improved with respect to those in Table 1. First of all we observe that the ACP corrections bring the respective CCD and CCSD values closer to the FCI limit. They are in all cases negative with rather insignificant differences between the CCD and CCSD methods. The improvement, however, is meaningful and oscillates around 1.5 mhartree, with the exception of the first point, where it is smaller (ca. 0.5 mhartree). In Table 3 we present CCD, CCSD and their ACP modified equivalents. In addition, we have also computed the corrections originating from the inclusion into both methods of fifth-order-type quadruples, see Eq. (10), denoted as CC(S)DQ-1a. We observe that the sign of the ACP and CC(S)DQ-1a corrections are opposite. The latter, in fact, shows that T_4 moves the results away from the exact value. The positive values of the T_4 type corrections can be explained in the context of the full CCSDT results. Since the latter method overshoots, the quadruple correction is expected to bring the correlation back to the correct value. In fact the CCSDT based quadruple corrections are even more positive than those found for the CCSD method due to the inclusion of the T_3 operator into the T_4 equations, see Eq. (10). It is interesting that the T_4 correction decreases very rapidly as the reference function regains its single-configurational character. This is true both for CCSDT as well as CC(S)D schemes. In fact, moving from one point to another over the whole quasidegenerate region the T_4 correction is reduced by about 40%. When going from $\alpha = 0.02$ to $\alpha = 0.05$, which designate the region where the reference function most radically changes its multiconfigurational character, the correction is reduced 5 to 10 times. This is also true to some extent for the T_3 correction evaluated with respect to the CC(S)D methods. We may conclude this discussion by observing that including the T_4 correction alone into the CCSD method may in certain cases be worse than the corresponding CCSD results. On the other hand, when this correction is included into the CCSDT method the results are always significantly improved. Consequently, when we include the ACP correction – supposed to be negative – into the CCSDT method which already gives too negative values for this example, we may expect that ACP corrected results will be worse. This is in fact the case (see the respective column in Table 2) for all points studied with the exception of the first one corresponding to the strongest degeneracy, where this correction is positive and nicely improves the correlation correction to the value obtained by the CCSDTQ-1 scheme.

For the noniterative methods even CCSD + T(CCSD) works fairly well for this case, but is clearly poorer in the degenerate region as would be expected. Relatively good behavior has also been observed in polyene model problems [38].

Finally the best results for the degenerate region out of all the methods considered here are obtained with the Q(CCSDT) method. Generally, this approximation gives results comparable in accuracy to those of CCSDTQ-1, and perhaps fortuitously, somewhat better. In the case of the H_4 system the improvement is significant. Here this approach gives results better by 0.18, 0.38, 0.24, and 1.2 for the values of α: 0.000, 0.005, 0.010, 0.015, respectively (all energies in mhartrees). Thus, besides the first point, the Q(CCSDT) corrections added to the CCSDT energy give an answer different from the FCI limit by only a few hundredth of a mhartree. We emphasize here that this occurs for the multi-reference region where, in general, one cannot expect the single-reference methods to work well. However, as this is only a four electron example, methods including T_4 should be close to the FCI results. The additional positive aspect of the Q(CCSDT) approach is that the connected quadruple contributions are computed in a fraction of the time required for the CCSDT calculations due to the fact that *i*) they are computed only once and *ii*) they are computed with an n^7 procedure. We would like to mention that the good performance of this method does not appear to be accidental, as we have found it to work very well also for other cases [28], but still a small number of cases.

The main disadvantage of the Q(CCSDT) approach is that its base method, i.e., CCSDT requires an n^8 procedure thereby limiting its application. In order to circumvent this difficulty there has been proposed a CCSD + TQ*(CCSD) method [32], also correct through fifth order which is based on the CCSD method, see Eqs. (12, 13). The results shown in the last column of Table 2 are also very plausible; in fact they are very close to those obtained for the CCSDTQ-1 method but at a fraction of the cost required for the latter.

The same information about the behavior of different methods may be obtained from Figs. 1 and 2, where the deviations from FCI are plotted vs. the α parameter. We observe that the curves corresponding to the methods which include quadruple contributions in an iterative or noniterative manner nearly coincide with the FCI line. Note that the latter line – not drawn in the Figures for the sake of transparency – is a horizontal straight line passing through the 0.000 point.

3.2. *Region of nondegenerate reference function*: $\alpha > 0.02$

The general feature shared by all methods considered is that for the region of $\alpha > 0.02$, all the values are very stable and practically do not change from point to point. In addition, here we observe that all the approaches behave more regularly, i.e. the more elaborate method gives better results. Since this is a region where the reference state is supposed to be well described by a single configuration, the results should be much better. We observe that this is true here. All the values in Table 1 with the exception of the CCD method are smaller than 1 mhartree, with the latter results being slightly over 2 mhartrees. As we may expect, the inclusion of singles brings the correlation energy down by about 1.4 mhartree, thus reducing the FCI error to 0.75–0.9 mhartree. It seems that those limited CC methods are incapable of a more accurate reproduction of the

FCI values primarily due to the neglect of triples. Hence they introduce an error already at the fourth-order level. The simplest method which is able to include fourth-order triples, the CCSDT-1, gives excellent results, differing from the exact values throughout the nondegenerate region by less than 0.1 mhartree. Consequently, the full inclusion of triples occurring at the full CCSDT level reduces the error to 0.02 mhartree, although it should be noted that this method overshoots for that region. Comparing the CCSDT values with the CCSDTQ-1 approach, we observe that the error in the former method should be assigned entirely to fifth-order-type connected quadruples. We see that the inclusion of quadruples recovers nearly exactly the FCI values, the error being of the order of 1 μhartree. The same is true for the second T_4 scheme including disconnected pentuples although in this case the differences are of the order of a few μhartree. The presented spectrum of results shows what can be expected from each CC method for a situation where the reference is well defined in terms of a single configurational wavefunction.

Within the same region, we may compare the performance of the second group of methods. First of all we observe that the inclusion of the Paldus and Dykstra modification into CCD and CCSD methods to obtain ACP improves the results; we get closer to the FCI values by about 0.3 mhartree. However, incorporating the same correction into the CCSDT method gives significantly worse results, again the same situation as for the other region is repeated. The deviation from the FCI values increases from -0.02 mhartree for CCSDT to ca. -0.3 mhartree for ACP-CCSDT results. The two noniterative schemes give practically full agreement with the exact values. The first CCSDT + Q(CCSDT) provides results practically identical to those obtained with the iterative CCSDTQ-1 scheme, matching the exact values with an accuracy of 1 μhartree. The second method, CCSD + TQ*(CCSD) (last column in Table 2), gives also excellent results, differing from the exact ones by about 2–12 μhartree.

It is obvious that for a system with a greater number of electrons the deviations from the exact values may increase. In particular for O_3, frequencies computed at the CCSD + T(CCSD) and CCSDT-1 level, are poorer than those from CCSD [39], attesting to some imbalance in the approximations involved. On the other hand, the CCSDT method works very well for this difficult example [40]. Similarly, the very shallow potential curve for Be_2 is not described adequately compared to FCI except in the full CCSDT method, with CCSD and CCSDT-1 showing no minimum [26b]. Hence, the potential inadequacy of the H_4 problem as a model for more difficult cases has to be borne in mind.

4. Conclusion

We have studied the behavior of various coupled-cluster methods as applied to the H_4 system with varied degree of degeneracy for the reference function. The results show that the most sophisticated methods can recover the correlation energy even for the exactly degenerate situation with an accuracy up to 0.5 mhartree. It also follows that for the degenerate region higher clusters become important and, in particular, the inclusion of the T_4 cluster may improve the results by up to two mhartrees. It is also evident that one cannot expect accurate results for this case from the CCD or CCSD method, although the latter is considerably better. The ACP corrected methods give slightly better results, although this correction in all but one case works in the opposite direction to that obtained from the connected T_4 contribution. In particular when applied to the CCSDT method, the ACP corrections go in the wrong direction.

On the other hand, it is not just the final value of the correlation corrections for the energy and other properties which is important from the viewpoint of an efficient computational method. We should rather consider a proper balance between the accuracy and the cost efficiency. At least for this simple example, the superior approach is that denoted as CCSD + TQ*(CCSD). From the discussion presented in the previous sections it follows that this scheme requires only one step of n^8 procedure and two steps of n^7, all of them computed noniteratively. The quality of the results for this example favors this method as that suitable for efficient and accurate calculations of correlation corrections. However, more difficult examples must also be considered [32, 41].

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