Triple and quadruple excitation contributions to the binding in Be clusters: calibration calculations on Be₃

John D. Watts, Ivan Cernusak[†], Jozef Noga[‡], and Rodney J. Bartlett
Quantum Theory Project
Departments of Chemistry and Physics
University of Florida
Gainesville, FL 32611-2085

Charles W. Bauschlicher, Jr., Timothy J. Lee, and Alistair P. Rendell
NASA Ames Research Center
Moffett Field, CA 94035-1000

Peter R. Taylor[§]
ELORET Institute
Palo Alto, CA 94303

Abstract

We have investigated the contribution of connected triple and quadruple excitations to the binding in Be₃ by comparing various coupled-cluster (CC) and truncated configuration-interaction (CI) treatments with multireference CI (MRCI) and full CI (FCI) calculations. The CC method with single and double excitations (CCSD) produces results that differ substantially from more elaborate treatments, but most extensions to CCSD that account approximately for connected triple excitations perform very well. In contrast, good agreement with FCI for Be₂ can be achieved only with the highest level CC and MRCI methods.

I. Introduction

For the diatomic molecule Be₂, the CCSD method gives a poor potential en-

[†] Permanent address: Department of Physical Chemistry, Comenius University, 842 15 Bratislava, Czech and Slovak Federated Republic

[‡] Permanent address: Institute of Inorganic Chemistry, Center for Chemical Research, Slovak Academy of Sciences, 842 36 Bratislava, Czech and Slovak Federated Republic

[§] Mailing address: NASA Ames Research Center, Moffett Field, California 94035-1000

ergy curve, but after inclusion of connected triple excitations (CCSDT) a more reasonable curve is obtained [1]. The curve is further improved after consideration of connected quadruple excitations [2]. While the bonding in the trimer and higher oligomers of Be is quite different from that in Be_2, Lee et al. [3] found in a recent study of structure and bonding in Be and Mg clusters that the CCSD method also did not satisfactorily reproduce the binding energies determined with large-scale multireference CI (MRCI) wave functions, even though the CCSD geometries were fairly good. In further investigations [4,5], however, it was observed that agreement with MRCI was greatly improved when the CCSD method was corrected approximately for the effect of connected triple excitations [6], using the CCSD+T(CCSD) method [7] or an improvement denoted CCSD(T) [8]. While both methods include, noniteratively, all fourth-order contributions of connected triple excitations, the latter adds one fifth-order contribution which is normally of the opposite (i.e. positive) sign. As such CC treatments are considerably cheaper than MRCI, they could provide a cost-effective means of studying larger Be and Mg clusters. However, these methods fail for Be_2 [2]. Hence, it would be desirable to establish that the apparently good performance of CCSD+T(CCSD) and CCSD(T) for the trimers and tetramers does not arise from some fortuitous cancellation of errors in the correlation treatment. Such errors could be due to the failure to treat the connected triple excitation contributions iteratively, to the neglect of many terms in the full CCSDT equations (including several fifth-order terms), or to the neglect of higher than connected triple excitations, particularly the connected quadruple excitations that first contribute to the correlation energy in fifth-order. Such errors are a conceivable problem in Be clusters because of the known multireference character of these systems caused by the quasi-degeneracy of the Be $2s$ and $2p$ orbitals.

In the present work we examine a number of different correlation treatments for the Be_3 cluster. We perform FCI calculations to provide an absolute comparison standard for all of the correlation treatments. We also perform CC calculations with full iterative inclusion of triple excitations (CCSDT) [9,10], several approximations to the full CCSDT treatment as proposed by Bartlett and co-workers [6,7,9,11] (as well as the CCSD(T) method [8]), and two noniterative CCSD corrected schemes, which are correct through fifth-order and account approximately for the effects of connected quadruple excitations [2]. Effects of connected quadruple excitations are also estimated with the CCSDT+Q and CCSDT+Q* methods [12]. We compare

these results with those of single reference and multireference CI calculations. Brief details of the computational methods are given in the next section, some details being deferred to section III, which contains our results and discussion. Conclusions are given in section IV.

II. Computational methods.

Two Be atomic natural orbital (ANO) basis sets [13] are used in this work. The larger is the [4s 2p 1d] basis given in Ref. 3, although in the present work the 3s contaminant function is included in the basis. The smaller basis is obtained by deleting the d ANO to give a [4s 2p] set.

The [4s 2p] basis has been used in conjunction with a variety of correlation treatments: FCI, MRCI, CISD, CISDT, CISDTQ, MBPT(4), CCSD, CCSDT, and various approximate CC schemes for handling connected triple and quadruple excitations. The particular CC schemes are described in the next section. FCI calculations in the [4s 2p 1d] basis are beyond our computational capabilities, but all other methods were applied in this basis. In all of our single-reference calculations (including FCI) the MOs were obtained from an SCF calculation; the highest-lying a_1' and e' MOs (these would correspond to 1s complement functions in a segmented contracted basis) were deleted. The MRCI calculations were based on a CASSCF wave function with all Be 2s and 2p orbitals in the active space: all CASSCF configurations were used as reference configurations. In the CASSCF/MRCI calculations the Be 1s orbitals were taken from an SCF calculation and frozen, and the highest a_1' and e' MOs were deleted after the SCF calculation. The Be 1s electrons were not correlated in any of the calculations.

Calculations were performed around the equilibrium bond length assuming a D_{3h} geometry. A rather large grid spacing (0.3 a_0) was used because the Be_3 potential is very flat. Optimum bond lengths were determined by fitting the computed energy points to a quadratic form in $1/r$.

All MBPT and CC methods are rigorously size-extensive and for this example separate correctly to closed-shell atoms. Hence, at the separated atom limit, three times the energy of one Be atom is obtained. Moreover, since the core electrons are not correlated, all of the CC methods used in this work give the FCI energy at the separated atom limit. In the [4s 2p] basis set, the SCF, MBPT(4), and CC atomic energies are −14.572920, −14.612790, and −14.617580 E_h. In the [4s 2p 1d] basis the

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atomic energies for these methods are −14.572942, −14.614290, and −14.618643 E_h respectively. MRCI, however, is not rigorously size-extensive. Consequently, for this method binding energies were computed using a supermolecule approach for the dissociation limit.

The SCF/CI and CASSCF/MRCI calculations were performed using the MOLECULE-SWEDEN [14] program system. Some CCSD and CCSD(T) calculations were performed with VCCSD, a vectorized CC program [15] interfaced to MOLECULE-SWEDEN. Other CC calculations were performed using ACES [16]. The FCI calculations were performed using a modified version of the Knowles-Handy [17] program. Calculations were performed on the NASA Ames Central Computer Facility CRAY Y−MP/832, the NAS Facility CRAY Y−MP/8128, and the Quantum Theory Project FPS-164/MAX.

III. Results and Discussion.

The results of calculations in the [4s 2p] basis are summarized in Table I. Energies are given explicity and differences relative to FCI are given in parentheses. One unfortunate consequence of using a basis set this small is that Be_3 is not bound at any level of calculation. As Be_3 is actually bound by at least 24 kcal/mol [3], this indicates a very significant coupling of the one-particle and n-particle spaces, at least for the binding energy. However, there is a local minimum in the energy at a bond length near 4.75 a_0 for most levels of treatment considered, and the r_e values given in Table I refer to this local minimum. Explicit calculations show that these local minima are genuine and do not result from basis set superposition errors.

The CC methods in Table I are listed in order of sophistication of the iterative component of the method. The CCSD method [18] includes all effects of the T_1 and T_2 cluster operators, which include disconnected triple and quadruple excitation effects. The CCSD+T(CCSD) [7], CCSD(T) [8], CCSD+T*(CCSD) [2], CCSD+TQ(CCSD) [2], and CCSD+TQ*(CCSD) [2] methods extend CCSD by providing noniterative estimates of the effects of the triple excitation cluster operator T_3 (ie connected triple excitation effects) and (for CCSD+TQ(CCSD) and CCSD+TQ*(CCSD) only) the effects of the quadruple excitation operator T_4 (ie connected quadruple excitation effects) from CCSD T_1 and T_2 amplitudes. All of these methods are correct through fourth order of perturbation theory. The CCSD(T) and CCSD+T*(CCSD) methods contain, in addition, nonitera-

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tive estimates of different fifth-order terms, while the CCSD+TQ(CCSD) and CCSD+TQ*(CCSD) methods are correct through fifth order. The noniterative fourth- and fifth-order corrections to the CCSD energies are shown in Table II. For brevity, in the tables and the rest of the text we refer to the CCSD+T(CCSD), CCSD+T*(CCSD), CCSD+TQ(CCSD), and CCSD+TQ*(CCSD) methods as CCSD+T, CCSD+T*, CCSD+TQ and CCSD+TQ*, it being understood that the noniterative corrections are evaluated with CCSD amplitudes. The various CCSDT-n methods [6,7,9,11] are all iterative schemes for estimating the effects of connected triple excitations; they differ by the number and type of terms included in the T_3 equation. The higher-numbered methods include more terms. The CCSDT method [9,10] includes all effects of the T_1, T_2, and T_3 cluster operators, and is exact for a three-electron system. The CCSDT+Q(CCSDT) and CCSDT+Q*(CCSDT) methods [12] estimate effects of connected quadruple excitations (ie the T_4 operator) noniteratively from converged CCSDT amplitudes. These estimates are also shown in Table II. These methods are hereafter referred to as CCSDT+Q and CCSDT+Q*, it being understood that the T_4 corrections are computed from CCSDT amplitudes.

One obvious conclusion to be drawn from Table I is that, as we have observed in many other situations (see Ref. 19 and references therein), the multireference calculations reproduce the FCI results almost exactly. (We have not employed a multireference Davidson correction in the present calculations: as discussed in Ref. 19 such a correction generally overshoots the FCI result when only six electrons are correlated and a complete reference space is used, as in the present MRCI calculations.) The MRCI results themselves differ from FCI by tens of μE_h at all geometries, a discrepancy more than an order of magnitude smaller than for any of the other methods, and the geometry dependence of the difference is also much smaller.

The CC methods that take some account of connected triple excitations offer substantial improvement over the CCSD method for Be$_3$, all giving energies in much better agreement with FCI and all giving a local minimum which is absent from the CCSD potential. The noniterative CCSD+T, CCSD(T), and CCSD+T* methods are in very close agreement, because of the small values of the fifth-order terms $E_{ST}^{[5]}$ and $E_{TD}^{[5]}$ (see Table II) which distinguish CCSD(T) and CCSD+T* from CCSD+T. These methods are also in very close agreement with CCSDT-1 and CCSDT-2, suggesting that iteration of the T_3 equation is not of great importance

in this case. CCSD(T) is slightly closer to FCI than is CCSD+T* since $E_{ST}^{[5]}$ is much smaller than $E_{TD}^{[5]}$ for this example (Table II). In other systems the reverse is sometimes true and the relative sizes of the two terms also vary with molecular geometry [2].

The more sophisticated noniterative methods CCSD+TQ and CCSD+TQ*, which are correct through fifth order, perform very well. They are in significantly better agreement with FCI than are the simpler noniterative methods and are competitive with CCSDT+Q and CCSDT+Q*, which are considerably more expensive. CCSD+TQ* is the more theoretically sound method for adding connected T_4 corrections to CCSD [2], and this method gives slightly better agreement with FCI than does CCSD+TQ.

Although the CCSDT-2 and CCSDT-3 methods are theoretically more complete than CCSDT-1, they are in slightly poorer agreement with FCI. The reason for this is the presence of additional terms in the T_3 equation which normally make positive contributions to the energy. This has been observed previously [9,11], and should not necessarily be viewed as a deficiency of these methods since the extra terms confer extra stability in some difficult cases. The CCSDT-4 method is in extremely good agreement with FCI, but this is fortuitous since the more complete CCSDT method is not in such good agreement. The CCSDT-4 method omits from the T_3 equation all nonlinear terms involving T_3, and consequently tends to give energies slightly lower than CCSDT, and sometimes in better agreement with FCI [9].

The quadruples corrected CCSDT results are in slightly better agreement with FCI than are the CCSDT results, with the CCSDT+Q* method, like CCSD+TQ*, having an error of only a fraction of a mE_h. The T_4 corrections are seen to be negative, which is usually the case near equilibrium geometries. As discussed in some detail in Ref. 2, for correcting CCSDT energies the correction Q is to be preferred on mathematical grounds to Q*, the reverse of the situation when correcting CCSD. However, in the present case the Q* correction to CCSDT agrees better with FCI than does Q.

The CC bond lengths given in Table I differ from the FCI value by more than 0.1 a_0 in some cases, which may appear disappointing in view of the perfect agreement between the FCI and MRCI values. This apparent deficiency should not be overemphasized, however, as the very flat potential around r_e magnifies the effect

of small energy differences on the computed bond length. It is more reasonable to view all of the (triples-corrected) CC bond lengths as being in fair agreement with one another and with FCI — more importantly, the connected triples appear to be entirely responsible for the local minima in the CC potentials, as the CCSD potential has no local minimum at all.

Additional insight into the importance of connected and disconnected higher excitations can be obtained from the CI results given in Table I. The agreement between CCSDT+Q and CISDTQ is very close, and both agree well with FCI. However, disconnected quadruples obviously play a central role in achieving this agreement, as CISDT differs from FCI by more than any result in the table (other than CISD). From the difference between CISD and CCSD it appears that disconnected triples and quadruples contribute some 13 mE_h to the energy: even in a case like Be$_3$, in which near-degeneracy effects increase the importance of disconnected triples, it is likely that much of this difference is due to disconnected quadruples [20]. It is, of course, hardly feasible to include quadruple excitations in CI calculations on most systems of interest because of the computational cost.

In Table III we show the results obtained with the more realistic [4s 2p 1d] basis set. The noniterative corrections to CCSD and CCSDT in this basis are shown in Table IV. With this larger basis set we do not have FCI values for comparison, but we may expect the MRCI method to produce closely similar results, and accordingly this is our reference point. The same general trends seen in Table I are observed here also. With the exception of CCSD and MBPT(4), the agreement between all methods is, on the whole, very good. The failure of MBPT(4) is a reflection of the need to include single and double excitation effects iteratively, which is not surprising for a system like Be$_3$. The good agreement between the noniterative methods and their iterative counterparts shows, however, that it is not necessary to include connected triple and quadruple excitation effects iteratively. The full CCSDT, CCSDT+Q, CCSDT+Q*, CCSD+TQ, and CCSD+TQ* results are in excellent agreement with MRCI, although the (small) difference between MRCI and these CC methods has a relatively large variation with distance.

In general, the variation among the computed bond lengths with different correlation treatments is smaller than is the case for the [4s 2p] basis set. Only the MBPT(4) value shows an error as large as 0.1 a_0, and most methods agree well with the MRCI result.

The binding energy results may be divided into two classes: apart from CCSD+TQ and CCSD+TQ*, the CC methods that account approximately for connected triples produce results of 12.0 kcal/mol or less, while CCSDT and CC methods that account for quadruple excitations yield binding energies around 13.5 kcal/mol. The discrepancy between the various CC values and the MRCI result of 14.5 kcal/mol may seem large as a relative error, but comparisons in larger basis sets [4,5] show that the absolute error, at least at the CCSD(T) level, remains much the same, and hence in large basis sets the relative error in the binding energy is rather small. We stress that the [4s 2p 1d] binding energies are far from the basis set limit values: the MRCI result in a complete basis is estimated to be 24 kcal/mol [3].

We now analyze the apparent success of the simple noniterative CC methods CCSD+T and CCSD(T) in more detail. The performance of these methods is good. For the larger basis set, they remove about 87% of the error of the CCSD method, while the CCSDT method removes an additional 10%. Hence, triple excitation effects beyond those included in CCSD(T) further increase the binding energy slightly, as do connected quadruple excitations, though not by as much. The fact that the residual triple and quadruple excitation effects are relatively small and of the same sign suggests that the good agreement of CCSD+T and CCSD(T) with MRCI and FCI is not fortuitous. It should be remembered, however, that the smallness of the residual triple excitation correction can be considered to be a consequence of a partial cancellation of several contributions to the energy of opposite sign (see Tables II and IV). To illustrate, we note that for the larger basis set the CCSDT method gives energies which are 1-1.7 mE_h lower than the CCSD+T or CCSD(T) energies. However, using the CCSD+TQ and CCSD+TQ* estimates, the contribution to the energy of the $E_{TT}^{[5]}$ term [2], arising from the presence of WT_3 (see Ref. 2) in the T_3 equation, is about -3 mE_h, which is partially offset by the nonlinear terms in the T_3 equation. From this analysis, therefore, one could argue that the closeness of the CCSD+T and CCSD(T) results to MRCI and FCI depends to some extent upon such cancellations.

On balance, we believe that it is reasonable to apply the CCSD(T) method to larger Be clusters, as we have previously suggested [5]. Of course, in any application of the method to systems with substantial nondynamical correlation effects the potential for large residual triple and quadruple excitation contributions should always be borne in mind. We note that for Be$_2$ it is precisely the residual triple

excitation effects absent from CCSD(T) which are necessary in order to get a correct potential curve [1], although, as we have stressed above and elsewhere [3], there are few parallels between the bonding in Be_2 and larger Be clusters. For Be_3 the residual triple and quadruple excitation effects are small and of the same sign, but this will by no means always be the case. Other systems show quite different correlation effects [2,21].

Finally, considering that the CCSD+T method actually gives slightly better agreement with FCI and MRCI here, it seems tempting to use the CCSD+T method instead of CCSD(T). We do not recommend this since adding the positive fifth-order $E_{ST}^{[5]}$ term will in general confer more stability, particularly in highly correlated systems, as has been discussed previously [2,4,8]. The cost of evaluating the $E_{ST}^{[5]}$ term is negligible compared with solving the CCSD equations or evaluating the fourth-order triples correction. CCSD+T* will have similar advantages over CCSD+T.

IV. Conclusions

Benchmark FCI, CASSCF/MRCI, and a variety of single-reference CI and CC calculations have been performed on Be_3 to determine the effects of connected triple and quadruple excitations and to compare with the simple noniterative CC method CCSD(T). The MRCI results are in excellent agreement with FCI. The most sophisticated single-reference CI and CC methods, CISDTQ and CCSDT+Q, give very similar results and are in very good agreement with MRCI and FCI. It is found that connected triple excitations account for almost all of the difference between the CCSD and FCI energies, while the contribution of connected quadruple excitations is rather small, but also increases the binding energy. In this case, it appears not to be essential to include either T_3 or T_4 iteratively, since the noniterative methods give results very similar to their iterative counterparts. The failure of MBPT(4) shows, however, that the iterative inclusion of T_1 and T_2 is important, at least as measured in the modest basis sets used in this work. The closeness of the CCSD(T) results to those of more extended treatments of electron correlation is seen not to arise from a cancellation of errors between neglected triple excitation contributions and higher excitations, in the sense that the residual triple and quadruple excitation corrections are both small and of the same sign. Our previous work [4] has also shown good agreement between CCSD(T) and extensive MRCI treatments for Be_4, and it seems this also is a genuine agreement and not a cancellation of errors.

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This reinforces our earlier optimism about the potential for success in applying the CCSD(T) method to larger beryllium clusters, although the possibility of terms neglected in this simple approach being significant should always be borne in mind when studying these highly correlated systems.

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Table I. Comparison of SCF, MBPT(4), CC, CI, MRCI, and FCI results for Be with the [4s 2p] ANO basis set[a].

Method	r=4.5	r=4.8	r=5.1	r_e (n.c.)[b]
SCF	−43.709033	−43.708482	−43.708272	4.787
MBPT(4)	−43.837089(11.174)	−43.838295(10.106)	−43.837180(10.120)	—[c]
CCSD	−43.836688(11.575)	−43.839322(9.079)	−43.840515(6.785)	4.820
CCSD+T	−43.844744(3.519)	−43.845600(2.801)	−43.845094(2.206)	4.810
CCSD(T)	−43.844815(3.448)	−43.845584(2.817)	−43.845063(2.237)	4.860
CCSD+T*	−43.844272(3.991)	−43.845338(3.063)	−43.844984(2.316)	4.741
CCSD+TQ	−43.847081(1.182)	−43.847571(0.830)	−43.846702(0.598)	4.723
CCSD+TQ*	−43.847508(0.755)	−43.847912(0.489)	−43.846950(0.350)	4.786
CCSDT−1a	−43.844679(3.584)	−43.845264(3.137)	−43.844716(2.584)	4.813
CCSDT−1b	−43.844443(3.820)	−43.845188(3.213)	−43.844702(2.598)	4.876
CCSDT−2	−43.843741(4.522)	−43.844826(3.575)	−43.844557(2.743)	4.868
CCSDT−3	−43.843853(4.410)	−43.844876(3.525)	−43.844579(2.721)	4.651
CCSDT−4	−43.848521(−0.258)	−43.848550(−0.149)	−43.847396(−0.096)	4.763
CCSDT	−43.846468(1.795)	−43.847029(1.372)	−43.846313(0.987)	4.740
CCSDT+Q	−43.846979(1.284)	−43.847430(0.971)	−43.846618(0.682)	4.704
CCSDT+Q*	−43.847601(0.662)	−43.847880(0.521)	−43.846938(0.362)	(n.c.)
CISD	−43.823917(24.346)			(n.c.)
CISDT	−43.833038(15.225)			(n.c.)
CISDTQ	−43.847001(1.262)			
MRCI	−43.848235(0.028)	−43.848373(0.028)	−43.847274(0.026)	4.673
FCI	−43.848263	−43.848401	−43.847300	4.673

[a] Total energy in E_h, differences relative to FCI (in parentheses) in mE_h, r and r_e in a_0.
[b] Not computed.
[c] No local minimum in potential.

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Table II. Fourth- and fifth-order noniterative corrections to the CCSD and CCSDT energies at different bond lengths for the $[4s\ 2p]$ basis set[a,b].

Correction	$r = 4.5$	$r = 4.8$	$r = 5.1$
$E_T^{[4]}$	−0.008055	−0.006277	−0.004579
$E_{ST}^{[5]}$	−0.000071	0.000015	0.000031
$E_{DT}^{[5]}$	0.000472	0.000261	0.000109
$E_{TT}^{[5]}$	−0.002334	−0.001912	−0.001495
Q(T(CCSD))	−0.000403	−0.000336	−0.000253
Q*(T(CCSD))	−0.000830	−0.000678	−0.000501
Q(CCSDT)	−0.000511	−0.000401	−0.000305
Q*(CCSDT)	−0.001133	−0.000851	−0.000625

[a] Energies in E_h, r in a_0.

[b] For definitions of the corrections see references 2 and 12.

Table III. Comparison of SCF, MBPT(4), CC, and MRCI results for Be with the [4s 2p 1d] ANO basis set[a].

Method	$r=4.2$	$r=4.5$	$r=4.8$	r_e	D_e[b]
SCF	−43.713496	−43.713874	−43.712582	(n.c.)	(n.c.)
MBPT(4)	−43.866785(10.330)	−43.868581(9.159)	−43.865257(8.996)	4.437	16.2
CCSD	−43.860364(16.751)	−43.862039(15.701)	−43.860368(13.885)	4.480	3.8
CCSD+T	−43.873044(4.071)	−43.873878(3.862)	−43.870714(3.539)	4.398	11.4
CCSD(T)	−43.872954(4.161)	−43.873711(4.029)	−43.870480(3.773)	4.393	11.3
CCSD+T*	−43.872245(4.870)	−43.873221(4.519)	−43.870220(4.033)	4.408	11.0
CCSD+TQ	−43.875379(1.736)	−43.876157(1.583)	−43.872856(1.397)	4.393	12.9
CCSD+TQ*	−43.875665(1.450)	−43.876399(1.341)	−43.873044(1.209)	4.390	13.0
CCSDT−1a	−43.873048(4.067)	−43.873534(4.206)	−43.870095(4.158)	4.376	11.3
CCSDT−1b	−43.872804(4.311)	−43.873448(4.292)	−43.870098(4.155)	4.386	11.2
CCSDT−2	−43.871606(5.509)	−43.872529(5.211)	−43.869455(4.798)	4.404	10.6
CCSDT−3	−43.871943(5.622)	−43.872755(4.985)	−43.869628(4.625)	4.397	10.7
CCSDT−4	−43.878127(−1.012)	−43.878373(−0.633)	−43.874656(−0.403)	4.360	14.4
CCSDT	−43.875088(2.027)	−43.875729(2.011)	−43.872447(1.806)	4.386	12.6
CCSDT+Q	−43.875488(1.627)	−43.876033(1.707)	−43.872654(1.599)	4.380	12.8
CCSDT+Q*	−43.875993(1.122)	−43.876388(1.352)	−43.872891(1.362)	4.370	13.1
MRCI	−43.877115	−43.877740	−43.874253	4.387	13.9

[a] Total energy in E_h, differences relative to MRCI (in parentheses) in mE_h, r and r_e in a_0, and D_e in kcal/mol.
[b] Not computed.

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Table IV. Fourth- and fifth-order noniterative corrections to the CCSD and CCSDT energies at different bond lengths for the $[4s\ 2p\ 1d]$ basis set[a,b].

Correction	$r = 4.2$	$r = 4.5$	$r = 4.8$
$E_T^{[4]}$	−0.012680	−0.011839	−0.010345
$E_{ST}^{[5]}$	0.000090	0.000167	0.000234
$E_{DT}^{[5]}$	0.000800	0.000658	0.000493
$E_{TT}^{[5]}$	−0.002973	−0.002890	−0.002706
Q(T(CCSD))	−0.000251	−0.000294	−0.000163
Q*(T(CCSD))	−0.000538	−0.000480	−0.000351
Q(CCSDT)	−0.000400	−0.000304	−0.000206
Q*(CCSDT)	−0.000905	−0.000660	−0.000444

[a] Energies in E_h, r in a_0.

[b] For definitions of the corrections see references 2 and 12.