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Inclusion of the (T) Triples Correction into the Linear-r_{12} Corrected Coupled-cluster Model CCSD(R12)

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ABSTRACT: The recently developed singles-and-doubles linear-r_{12} corrected coupled-cluster model CCSD(R12) has been extended by inclusion of triples corrections in exactly the same manner as in the popular CCSD(T) model. The resulting model is denoted CCSD(T)(R12). An orthonormal auxiliary basis set is used for the resolution-of-the-identity approximation to calculate the three- and four-electron integrals needed in the linear-r_{12} Ansatz. CCSD(T)(R12) reaction energies are calculated for a test set of 15 chemical reactions involving 23 small molecules. The CCSD(T)(R12), CCSD(R12), and MP2-R12 results are compared with experimental data obtained by correcting experimental enthalpies of reaction for zero-point vibrational energies and finite temperature contributions. Conventional MP2, CCSD, and CCSD(T) results are presented for comparison. An estimate of the basis set limit is obtained by an aug-cc-pV(Q + d)Z/aug-cc-pV(5 + d)Z CCSD(T) extrapolation for a subset of 12 reactions. All CCSD(T) results are compared with the extrapolated values, and the errors are analyzed for the CCSD(T) and CCSD(T)(R12) models in various basis sets. © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 106: 2306–2317, 2006

Key words: coupled-cluster theory; triples correction; linear-r_{12} method

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Introduction

The recently developed coupled-cluster model CCSD(R12) has been found to be a promising alternative to conventional CCSD calculations when basis sets of triple-zeta quality or higher are used [1]. With quadruple-zeta basis sets, an accuracy similar to that of the CCSD-R12 model [2–7] developed by Noga and colleagues is observed, but with less computational costs for larger molecules and with the option to include an auxiliary basis for the calculation of the three- and four-electron integrals needed for the linear-r_{12} Ansatz [8, 9]. A natural extension of the CCSD(R12) approach is the inclusion of connected triples through the same perturbative correction used in the widely applied CCSD(T) model [10]. The resulting method, denoted CCSD(T)(R12), has been implemented based on the atomic orbital (AO) integral direct triples code [11] of the Dalton program package [12]. The performance of the CCSD(T)(R12) model has been investigated by calculating the reaction energies of 15 chemical reactions involving 23 molecules. These are the same reactions that were recently investigated with local coupled-cluster models by Pflüger [13]. The new CCSD(T)(R12) results are compared with MP2-R12 and CCSD(R12) results, as well as with experimental data obtained by correcting (at the density functional level) experimental enthalpies of reaction for zero-point vibrational energies (ZPVE) and finite temperature contributions. A comparison with conventional MP2, CCSD, and CCSD(T) results is also given. An estimate of the CCSD(T) basis-set limit is obtained through the aug-cc-pV(Q + d)Z/aug-cc-pV(5 + d)Z CCSD(T) extrapolation for a subset of 12 reactions. All CCSD(T) results are compared with the extrapolated values, and the errors are analyzed.

Theory

A detailed overview of the derivation of the CCSD(R12) model can be found in Ref. [1]. Here, we summarize the fundamental equations of the CCSD(R12) model.

The exponential Ansatz

$$|\mathrm{CC}\rangle = \exp(\hat{S})|\mathrm{HF}\rangle \tag{1}$$

is used for the wave function, with the Hartree–Fock state $|\mathrm{HF}\rangle$ as the reference state. The cluster operator $\hat{S}$,

$$\hat{S} = \hat{T}_1 + \hat{T}_2 + \hat{T}_{2'}, \tag{2}$$

contains the excitation operators $\hat{T}_i$ that create singles, doubles, and R12 double excitations [14]

$$\hat{T}_1 = \sum_{ai} t_a^i E_{ai}, \tag{3}$$

$$\hat{T}_2 = \tfrac{1}{2} \sum_{abij} t_{ab}^{ij} E_{ai} E_{bj}, \tag{4}$$

$$\hat{T}_{2'} = \tfrac{1}{2} \sum_{ijkl} c_{kl}^{ij} \sum_{\alpha\beta} w_{\alpha\beta}^{kl} E_{\alpha i} E_{\beta j}, \tag{5}$$

with the integrals

$$w_{\alpha\beta}^{kl} = \langle \varphi_\alpha(1)\varphi_\beta(2)|\hat{\mathrm{w}}_{12}|\varphi_k(1)\varphi_l(2)\rangle. \tag{6}$$

Coupled-cluster singles and doubles amplitudes are denoted t_a^i and t_{ab}^{ij}, and the R12 doubles amplitudes are denoted c_{kl}^{ij}. Operators E_{ai} correspond to spin-free single excitations. We use the usual convention that $i, j, \ldots$ denote occupied orbitals, and $a, b, \ldots$ unoccupied (virtual) orbitals. The index p is used for general molecular orbitals (MO) and $\alpha, \beta, \ldots$ for orbitals of a complementary subspace (vide infra). The operator $\hat{T}_{2'}$ contains a particular form of double excitations, which we denote R12 double excitations. These are double excitations into the correlated pair functions [15]

$$\hat{\mathrm{w}}_{12}|\phi_k(1)\phi_l(2)\rangle, \tag{7}$$

which can be expressed with the help of a complementary orbital subspace $\{\phi_\alpha\}$. For Ansatz 1 of R12 theory, which we use in the present study, the orbital subspace $\{\phi_\alpha\}$ consists of all orbitals that are orthogonal to the finite one-electron orbital basis $\{\phi_p\}$. Thus, $\{\phi_\alpha\}$ and $\{\phi_p\}$ together form a complete basis for the one-electron Hilbert space, and $\hat{\mathrm{w}}_{12}$ is expressed as

$$\hat{\mathrm{w}}_{12} = (1 - \hat{P}_1)(1 - \hat{P}_2) r_{12}, \tag{8}$$

with the projection operator $\hat{P}_1$ onto the finite one-electron orbital basis defined as

$$\hat{P}_1 = \sum_p |\phi_p(1)\rangle\langle\phi_p(1)|. \tag{9}$$

A description of $\hat{T}_{2'}$ in the context of Ansatz 2 can be found in Ref. [1], but here we focus on Ansatz 1. Since the CCSD(R12) model does not contain triple

excitations, $\hat{S}$ is truncated after the doubles. As usual in coupled-cluster theory, the ground-state energy is obtained from the expression

$$E = \langle \mathrm{HF}|\hat{H}^S|\mathrm{HF}\rangle, \tag{10}$$

where $\hat{H}^S$ is the similarity-transformed Hamiltonian

$$\hat{H}^S = \exp(-\hat{S})\hat{H}\exp(\hat{S}), \tag{11}$$

and where the amplitudes of the excitation operators are obtained by solving the projected Schrödinger equation

$$\langle \mu_i|\hat{H}^S|\mathrm{HF}\rangle = 0, \tag{12}$$

with $i = 1, 2$, and $2'$. The different expressions for the projection manifolds $\langle \mu_i|$ are given in detail in Refs. [1] and [14].

The above equations define the CCSD-R12 model. To highlight how the simplified CCSD(R12) model is derived from the full CCSD-R12 model, we partition the Hamiltonian (omitting the nuclear repulsion energy) into the many-electron Fock operator $\hat{f}$ and the fluctuation potential $\hat{\Phi}$,

$$\hat{H} = \hat{f} + \hat{\Phi}. \tag{13}$$

If the generalized Brillouin condition ($f^i_\alpha = f^\alpha_i = 0$) is assumed, the closed-shell CCSD-R12 equations can be written as

$$\langle \mu_1|[\hat{f}, \hat{T}_1] + \hat{\Phi}^S|\mathrm{HF}\rangle = 0, \tag{14}$$

$$\langle \mu_2|[\hat{f}, \hat{T}_2 + \hat{T}_{2'}] + \hat{\Phi}^S|\mathrm{HF}\rangle = 0, \tag{15}$$

$$\langle \mu_{2'}|[\hat{f}, \hat{T}_2 + \hat{T}_{2'}] + \hat{\Phi}^S|\mathrm{HF}\rangle = 0, \tag{16}$$

where $\hat{\Phi}^S$ is the complete singles-and-doubles similarity-transformed fluctuation potential

$$\hat{\Phi}^S = \exp(-\hat{S})\hat{\Phi}\exp(\hat{S}). \tag{17}$$

The CCSD(R12) model is obtained by approximating in the equation for the R12 doubles amplitudes [Eq. (16)] the similarity-transformed fluctuation potential $\hat{\Phi}^S$ with

$$\bar{\hat{\Phi}} = \exp(-\hat{T}_1 - \hat{T}_2)\hat{\Phi}\exp(\hat{T}_1 + \hat{T}_2), \tag{18}$$

that is, by neglecting the R12 double excitations in the similarity transformation. Hence, the projection onto the R12 doubles manifold in the CCSD(R12) model becomes

$$\langle \mu_{2'}|[\hat{f}, \hat{T}_2 + \hat{T}_{2'}] + \bar{\hat{\Phi}}|\mathrm{HF}\rangle = 0. \tag{19}$$

Furthermore, we retain in the equation for the conventional doubles amplitudes [Eq. (15)] only terms linear in $\hat{T}_{2'}$. The nonlinear terms will be very small if the R12 double excitations are orthogonal on the conventional double excitations and if reasonable basis sets are used. They vanish exactly in Ansatz 1 of R12 theory, which is used in this article. Using $\bar{\hat{\Phi}}$ in place of Φ^S in the projection onto the R12 doubles manifold avoids the calculation of small terms that are difficult to compute accurately and prone to errors if (too) small basis sets are used. The differences in energies from the CCSD(R12) and CCSD-R12 models are very small. They become almost negligible if basis sets of quadruple-zeta quality or higher are used [1].

It is straightforward to add noniterative triples corrections to the CCSD(R12) model, for instance, those of the CCSD(T) model [10]. The equations defining the triples amplitudes in CCSD(T)-R12 are

$$\langle \mu_3|[\hat{f}, \hat{T}_3] + [\hat{\Phi}, \hat{T}_2] + [\hat{\Phi}, \hat{T}_{2'}]|\mathrm{HF}\rangle = 0, \tag{20}$$

where the term with the commutator $[\hat{\Phi}, \hat{T}_{2'}]$ vanishes for Ansatz 1, which is employed in the present study. The calculation of the triples correction (T) therefore only requires the conventional singles and doubles amplitudes, and the CCSD(T)(R12) energy can be written as

$$E_{\mathrm{CCSD(T)(R12)}} = E_{\mathrm{CCSD(R12)}} + \Delta E_{\mathrm{CCSD(T)}}, \tag{21}$$

with the energy correction for the connected triples

$$\Delta E_{\mathrm{CCSD(T)}} = \sum_{ai} 2t^i_a \langle \overline{a}_i|[\hat{\Phi}, \hat{T}_3]|\mathrm{HF}\rangle + \sum_{abij} \left(2t^{ij}_{ab} - t^{ji}_{ab}\right)\langle \overline{ab}_{ij}|[\hat{\Phi}, \hat{T}_3]|\mathrm{HF}\rangle. \tag{22}$$

The definition of the conventional singles and doubles projection manifolds is given in Ref. [14]. It is important to realize that the triples amplitudes in Eq. (22) are calculated from the converged singles and doubles amplitudes of a CCSD(R12) calculation.

Computational Details

All CCSD(T)(R12) calculations were carried out using Ansatz 1 and standard approximation B of R12 theory [9]. They were carried out with the Dalton [12] program, using either an aug-cc-pV(T + d)Z or an aug-cc-pV(Q + d)Z basis set as the orbital basis and in either case a fully uncontracted aug-cc-pV(5 + d)Z basis as an auxiliary basis [16]. (Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 10/21/03, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352, and funded by the U. S. Department of Energy. In addition, conventional CCSD(T) calculations were carried out with the same program using an aug-cc-pV(X + d)Z basis set as the orbital basis with X = T, Q, or 5. The geometries of the investigated molecules were optimized at the MP2(FC)/aug-cc-pVTZ level and provided to us by H.-J. Werner (private communication, 2005). The geometries are available from the authors upon request. All calculations were performed using the frozen core approximation (1*s* for C, N, O; 1*s*, 2*s*, and 2*p* for S, Cl), but we shall omit the extension (FC) in the following. All experimental enthalpies of reaction [17a–h] were corrected for ZPVE and finite temperature terms obtained from unscaled harmonic vibrational frequencies, which were calculated at the B3LYP/TZVP level using the Turbomole program package [18–22]. The extrapolations to the basis-set limit were performed using the formula [23]

$$E_\infty = \frac{(X^3 E_X - Y^3 E_Y)}{(X^3 - Y^3)}, \qquad (23)$$

where E_X and E_Y are the correlation energies obtained in the basis sets aug-cc-pV(X + d)Z and aug-cc-pV(Y + d)Z with cardinal numbers X and Y, respectively. In the present work, we carried out extrapolations based either on $X = 3$ and $Y = 4$ (TZ/QZ extrapolation) or on $X = 4$ and $Y = 5$ (QZ/5Z extrapolation). The extrapolated correlation energies were added to the HF energies obtained in the largest of the two basis sets, i.e., to the aug-cc-pV(Q + d)Z HF values for the TZ/QZ extrapolation and to the aug-cc-pV(5+d)Z HF values for the QZ/5Z extrapolation.

Results and Discussion

The investigated reactions are listed in Table I. The MP2, MP2-R12, CCSD, CCSD(R12), CCSD(T), and CCSD(T)(R12) ground-state energies of the molecules involved in the reactions are given in Tables II and III for the aug-cc-pV(T + d)Z basis set and in Tables IV and V for the aug-cc-pV(Q + d)Z basis set. The MP2, CCSD, and CCSD(T) ground-state energies for the aug-cc-pV(5 + d)Z basis set are listed in Tables VI and VII. The calculated aug-cc-pV(T+d)Z and aug-cc-pV(Q+d)Z reaction energies are compared with the corresponding experimental data in Tables VIII–XI, where the differences between the calculated reaction energies and the experimental values ($\Delta H_{\mathrm{calc}} - \Delta H_{\mathrm{exp}}$) are listed and analyzed. They are depicted for the aug-cc-pV(Q + d)Z basis in Figure 1 for the conventional MP2, CCSD, and CCSD(T) models and in Figure 2 for the corresponding R12 methods.

It appears that the second-order level leads to inaccurate results for reactions 3 and 10, with errors as large as 81 kJ/mol for the triple-zeta basis and 88 kJ/mol for the quadruple-zeta basis (at the MP2-R12 level). Also, for reactions 1, 2, 6, 11, and 12, the MP2-R12 results deviate from the experimental values by about 24 kJ/mol in the triple-zeta and 28 kJ/mol in the quadruple-zeta basis, which

TABLE I

Investigated reactions and experimental reaction energies in kJ/mol.

No.	Reaction	Exp.[a]
1	$CS_2 + 2\,H_2O \rightarrow CO_2 + 2\,H_2S$	−46.6
2	$CO + Cl_2 \rightarrow COCl_2$	−115.4
3	$NH_3 + 4\,H_2O_2 \rightarrow HNO_3 + 5\,H_2O$	−741.2
4	$C_2H_2 + H_2 \rightarrow C_2H_4$	−202.7
5	$CO + H_2 \rightarrow H_2CO$	−20.8
6	$H_2O_2 + H_2 \rightarrow 2\,H_2O$	−363.5
7	$H_2CO + H_2 \rightarrow CH_3OH$	−122.7
8	$C_2H_6 + H_2 \rightarrow 2\,CH_4$	−78.0
9	$C_2H_4 + H_2 \rightarrow C_2H_6$	−164.1
10	$CH_4 + 4\,H_2O_2 \rightarrow CO_2 + 6\,H_2O$	−1211.3
11	$SO_2 + H_2O_2 \rightarrow SO_3 + H_2O$	−204.4
12	$CO + H_2O_2 \rightarrow CO_2 + H_2O$	−392.4
13	$CH_2CO + H_2CO \rightarrow C_2H_4O + CO$	−14.8
14	$CO + NH_3 \rightarrow HCONH_2$	−39.0
15	$C_2H_2 + H_2O \rightarrow CH_3CHO$	−160.8

[a] All experimental data are corrected for zero-point vibrational energy and finite temperature contributions. The experimental accuracy is about ±4 kJ/mol.

TABLE II

Calculated aug-cc-pV(T + d)Z ground-state energies (in E_h) in Ansatz 1 and approximation B in comparison with the conventional MP2, CCSD, and CCSD(T) models.

Molecule	SCF	MP2	MP2-R12	CCSD	CCSD(R12)	CCSD(T)	CCSD(T)(R12)
H_2	−1.133049	−1.165023	−1.166677	−1.172615	−1.173360	−1.172615	−1.173360
H_2O	−76.060282	−76.328992	−76.341823	−76.333657	−76.342266	−76.342326	−76.350836
CO	−112.779889	−113.142411	−113.158916	−113.144289	−113.155040	−113.162175	−113.172729
CH_4	−40.213658	−40.414459	−40.423407	−40.434361	−40.439388	−40.440895	−40.445847
CO_2	−187.706875	−188.321641	−188.350497	−188.310245	−188.329801	−188.340554	−188.359767
SO_2	−547.302286	−547.979803	−548.011338	−547.969333	−547.990137	−548.006119	−548.026481
H_2O_2	−150.838805	−151.347987	−151.371413	−151.354041	−151.369787	−151.374261	−151.389782
SO_3	−622.166862	−623.083228	−623.127194	−623.065402	−623.095163	−623.112128	−623.141329
$HCONH_2$	−169.004547	−169.620770	−169.649129	−169.629481	−169.647957	−169.657002	−169.675166
CH_2CO	−151.785470	−152.334603	−152.358938	−152.341535	−152.357084	−152.369087	−152.384336
C_2H_4O	−152.928164	−153.514045	−153.540288	−153.531102	−153.547656	−153.556582	−153.572863
CH_3OH	−115.092039	−115.529008	−115.549591	−115.546487	−115.559654	−115.562357	−115.575347

TABLE III

Calculated aug-cc-pV(T + d)Z ground-state energies (in E_h) in Ansatz 1 and approximation B in comparison with the conventional MP2, CCSD, and CCSD(T) models.

Molecule	SCF	MP2	MP2-R12	CCSD	CCSD(R12)	CCSD(T)	CCSD(T)(R12)
H_2S	−398.715993	−398.911014	−398.921152	−398.934920	−398.940526	−398.943591	−398.949085
NH_3	−56.220324	−56.460541	−56.471485	−56.472209	−56.478963	−56.480543	−56.487197
H_2CO	−113.913144	−114.316410	−114.334927	−114.325357	−114.337294	−114.342922	−114.354665
CS_2	−832.971927	−833.475430	−833.499278	−833.486658	−833.500464	−833.523291	−833.536636
HNO_3	−279.561077	−280.514329	−280.556591	−280.496843	−280.525555	−280.545011	−280.573207
C_2H_2	−76.849103	−77.164057	−77.176963	−77.175090	−77.182581	−77.192183	−77.199483
C_2H_4	−78.064694	−78.404529	−78.418577	−78.428217	−78.436299	−78.443714	−78.451637
C_2H_6	−79.260379	−79.635368	−79.651677	−79.665951	−79.675291	−79.679886	−79.689073
$COCl_2$	−1031.804169	−1032.585458	−1032.628427	−1032.607359	−1032.634851	−1032.648634	−1032.675566
Cl_2	−919.002357	−919.390544	−919.416517	−919.423204	−919.439204	−919.442727	−919.458393
CH_3CHO	−152.974287	−153.552446	−153.578813	−153.571232	−153.587855	−153.596596	−153.612936

TABLE IV

Calculated aug-cc-pV(Q + d)Z ground-state energies (in E_h) in Ansatz 1 and approximation B in comparison with the conventional MP2, CCSD, and CCSD(T) models.

Molecule	SCF	MP2	MP2-R12	CCSD	CCSD(R12)	CCSD(T)	CCSD(T)(R12)
H_2	−1.133499	−1.166739	−1.167521	−1.173854	−1.174175	−1.173854	−1.174175
H_2O	−76.065649	−76.351907	−76.359404	−76.354162	−76.358869	−76.363576	−76.368223
CO	−112.787390	−113.172893	−113.182859	−113.171183	−113.177217	−113.190262	−113.196179
CH_4	−40.216289	−40.427399	−40.432036	−40.444724	−40.447132	−40.451718	−40.454088
CO_2	−187.719442	−188.373789	−188.390969	−188.357091	−188.367922	−188.389399	−188.400028
SO_2	−547.316925	−548.039627	−548.059340	−548.023161	−548.035233	−548.062663	−548.074456
H_2O_2	−150.848728	−151.391022	−151.405089	−151.392474	−151.401312	−151.414289	−151.422991
SO_3	−622.187562	−623.166383	−623.193694	−623.141078	−623.158230	−623.191338	−623.208138
$HCONH_2$	−169.015402	−169.669316	−169.685621	−169.671923	−169.681784	−169.701352	−169.711034
CH_2CO	−151.795017	−152.377023	−152.391138	−152.378274	−152.386651	−152.407591	−152.415796
C_2H_4O	−152.937493	−153.557910	−153.572843	−153.568710	−153.577498	−153.596009	−153.604641
CH_3OH	−115.099534	−115.563094	−115.574704	−115.576062	−115.583007	−115.593170	−115.600014

TABLE V

Calculated aug-cc-pV(Q + d)Z ground-state energies (in E_h) in Ansatz 1 and approximation B in comparison with the conventional MP2, CCSD, and CCSD(T) models.

Molecule	SCF	MP2	MP2-R12	CCSD	CCSD(R12)	CCSD(T)	CCSD(T)(R12)
H_2S	−398.719393	−398.927952	−398.933604	−398.949371	−398.952267	−398.958971	−398.961804
NH_3	−56.223971	−56.477766	−56.483660	−56.486775	−56.490152	−56.495730	−56.499053
H_2CO	−113.920514	−114.348647	−114.359480	−114.353525	−114.360044	−114.372338	−114.378742
CS_2	−832.980361	−833.517090	−833.530956	−833.522171	−833.529550	−833.561389	−833.568510
HNO_3	−279.579953	−280.592867	−280.618256	−280.567141	−280.583240	−280.618440	−280.634232
C_2H_2	−76.853475	−77.185720	−77.193077	−77.192837	−77.196744	−77.210940	−77.214740
C_2H_4	−78.069387	−78.427679	−78.435454	−78.447094	−78.451223	−78.463579	−78.467618
C_2H_6	−79.265305	−79.659733	−79.668387	−79.685633	−79.690227	−79.700523	−79.705036
$COCl_2$	−1031.818254	−1032.657463	−1032.683039	−1032.672632	−1032.687764	−1032.717768	−1032.732570
Cl_2	−919.009096	−919.431713	−919.447480	−919.461168	−919.470130	−919.483312	−919.492071
CH_3CHO	−152.983904	−153.596179	−153.611149	−153.608807	−153.617610	−153.635922	−153.644564

TABLE VI

Calculated aug-cc-pV(5 + d)Z ground-state energies (in E_h) for the conventional MP2, CCSD, and CCSD(T) models.*

Molecule	SCF	MP2	CCSD	CCSD(T)
H_2	−1.133637	−1.167366	−1.174241	−1.174241
H_2O	−76.066965	−76.360211	−76.360587	−76.370281
CO	−112.789001	−113.183909	−113.179589	−113.199138
CH_4	−40.216996	−40.431893	−40.447765	−40.454897
CO_2	−187.722229	−188.392734	−188.371839	−188.404923
SO_2	−547.320762	−548.062805	−548.041211	−548.081757
H_2O_2	−150.851223	−151.406905	−151.404812	−151.427239
SO_3	NA	NA	NA	NA
$HCONH_2$	−169.017847	−169.686647	−169.684933	−169.715051
CH_2CO	−151.797166	−152.392105	−152.389476	−152.419427
C_2H_4O	−152.939741	−153.573642	−153.580322	−153.608257
CH_3OH	−115.101404	−115.575327	−115.585209	−115.602751

*NA, not available.

TABLE VII

Calculated aug-cc-pV(5 + d)Z ground-state energies (in E_h) for the conventional MP2, CCSD, and CCSD(T) models.*

Molecule	SCF	MP2	CCSD	CCSD(T)
H_2S	−398.720057	−398.934533	−398.953753	−398.963687
NH_3	−56.224852	−56.483816	−56.491120	−56.500282
H_2CO	−113.922239	−114.360286	−114.362299	−114.381574
CS_2	−832.981847	−833.533400	−833.533309	−833.573505
HNO_3	NA	NA	NA	NA
C_2H_2	−76.854438	−77.193201	−77.197955	−77.216398
C_2H_4	−78.070486	−78.435578	−78.452501	−78.469301
C_2H_6	−79.266545	−79.668200	−79.691414	−79.706596
$COCl_2$	−1031.820947	−1032.684673	−1032.692657	−1032.739238
Cl_2	−919.010376	−919.448117	−919.472969	−919.496110
CH_3CHO	NA	NA	NA	NA

*NA, not available.

TABLE VIII

Reaction energy differences ($\Delta H_{calc} - \Delta H_{exp}$) between aug-cc-pV(T + d)Z and experimental data in kJ/mol.

No.	ΔMP2	ΔMP2-R12	ΔCCSD	ΔCCSD(R12)	ΔCCSD(T)	ΔCCSD(T)(R12)
1	19.7	20.7	−22.0	−21.3	−5.4	−4.9
2	−22.4	−23.7	10.7	8.8	0.6	−1.3
3	−64.3	−69.0	14.6	9.3	8.5	3.3
4	4.6	6.0	−8.7	−8.3	−4.5	−4.2
5	−2.8	−3.7	−1.4	−2.6	−0.6	−1.7
6	−17.1	−18.7	−5.8	−7.7	1.8	−0.2
7	−2.2	−3.3	−4.7	−6.0	−0.2	−1.5
8	3.1	3.3	−1.2	−1.1	1.1	1.2
9	−8.7	−10.3	−6.9	−8.2	−2.8	−4.1
10	−73.1	−81.4	−0.8	−9.2	12.6	4.1
11	−17.3	−22.1	5.7	0.9	9.9	5.1
12	−28.3	−32.9	10.2	5.8	7.9	3.6
13	0.5	0.8	−7.5	−7.0	−2.9	−2.5
14	−7.8	−10.2	4.9	2.4	1.5	−1.0
15	4.9	3.2	−3.3	−4.6	−2.2	−3.6

TABLE IX

Calculated errors (kJ/mol) at the aug-cc-pV(T + d)Z level.

	MP2	CCSD	CCSD(T)	MP2-R12	CCSD(R12)	CCSD(T)(R12)
Mean error	−14.1	−1.1	1.7	−16.1	−3.3	−0.5
Mean absolute error	26.1	7.2	4.2	20.6	6.9	2.8
Standard deviation	25.3	9.3	5.5	27.7	8.0	3.3
Maximum absolute error	73.1	22.0	12.6	81.4	21.3	5.1

TABLE X

Reaction energy differences ($\Delta H_{calc} - \Delta H_{exp}$) between aug-cc-pV(Q + d)Z and experimental data in kJ/mol.

No.	ΔMP2	ΔMP2-R12	ΔCCSD	ΔCCSD(R12)	ΔCCSD(T)	ΔCCSD(T)(R12)
1	23.5	24.5	−19.9	−19.5	−2.8	−2.4
2	−23.4	−23.0	9.6	9.3	−0.6	−1.0
3	−74.1	−76.0	2.7	0.3	−3.0	−5.3
4	5.2	6.2	−8.4	−8.1	−4.1	−3.9
5	−2.9	−3.1	−1.5	−1.9	−0.8	−1.2
6	−20.0	−20.3	−9.3	−10.0	−1.5	−2.2
7	−2.6	−2.5	−5.1	−5.4	−0.6	−1.0
8	3.6	4.1	−0.7	−0.4	1.7	2.0
9	−7.4	−7.6	−5.7	−6.1	−1.5	−1.9
10	−85.0	−88.3	−16.0	−19.4	−1.6	−5.1
11	−25.7	−28.4	−4.6	−7.1	−0.3	−2.8
12	−32.4	−34.0	4.9	3.1	2.7	1.0
13	1.3	1.5	−6.5	−6.3	−1.9	−1.7
14	−10.0	−11.2	2.3	1.2	−1.3	−2.5
15	7.1	6.8	−1.5	−2.0	−0.4	−0.9

TABLE XI

Calculated errors (kJ/mol) at the aug-cc-pV(Q + d)Z level.

	MP2	CCSD	CCSD(T)	MP2-R12	CCSD(R12)	CCSD(T)(R12)
Mean error	−16.2	−4.0	−1.1	−16.8	−4.8	−1.9
Mean absolute error	21.6	6.6	1.7	22.5	6.7	2.3
Standard deviation	29.6	7.7	1.7	30.7	7.7	2.0
Maximum absolute error	85.0	19.9	4.1	88.3	19.5	5.3

is seven times larger than the experimental error bar (≈4 kJ/mol). The conventional MP2 deviations are in the same range as those for MP2-R12. Compared with the experimental values, the deviations of the MP2 and MP2-R12 energies in the triple-zeta basis are coincidentally smaller than for the quadruple-zeta basis.

Beyond MP2-R12, the CCSD(R12) model leads to much more accurate reaction energies, with a maximum deviation from the experimental value of 21 kJ/mol for reaction 1 in the triple-zeta basis and 20 kJ/mol in the quadruple-zeta basis. Similar results are obtained for the conventional CCSD model. At this level, the errors due to the truncation of the *n*-electron space are larger than the errors due to the truncation of the one-particle basis set. An exception is reaction 10 in the triple-zeta basis, where the CCSD error (0.8 kJ/mol) is surprisingly small. The corresponding CCSD(R12) error is 9.2 kJ/mol, but we note that in the quadruple-zeta basis, the conventional CCSD error is also large (16.0 kJ/mol). The small CCSD/aug-cc-pV(T + d)Z error is the result of a fortuitous error cancellation.

After adding the (T) triples corrections, we find a maximum deviation of 5.1 kJ/mol for reaction 11 at the CCSD(T)(R12)/aug-cc-pV(T + d)Z level. Deviations of >4 kJ/mol are only found for reactions 1, 4, 9, 10, and 11. A maximum deviation of 5.3 kJ/mol is found for reaction 3 in the aug-cc-pV(Q + d)Z basis, while deviations of >3 kJ/mol are otherwise only found for reactions 4 and 10. When comparing the CCSD(T) and CCSD(T)(R12) models in the aug-cc-pV(T + d)Z basis set, it appears that the values of the R12 model are either in the same range (within 1.5 kJ/mol) as the conventional model or closer to the experiment. At the aug-cc-pV(Q + d)Z level, we observe only small differences of ≤2.5 kJ/mol between the CCSD(T) and CCSD(T)(R12) results. Keeping in mind that the experimental accuracy is about ±4 kJ/mol, a comparison with experimental data is not very meaningful, since the errors of both models are smaller than the experimental uncertainty.

The error analyses for both basis sets are listed for all investigated models in Tables IX and XI. The errors and standard deviations for the conventional

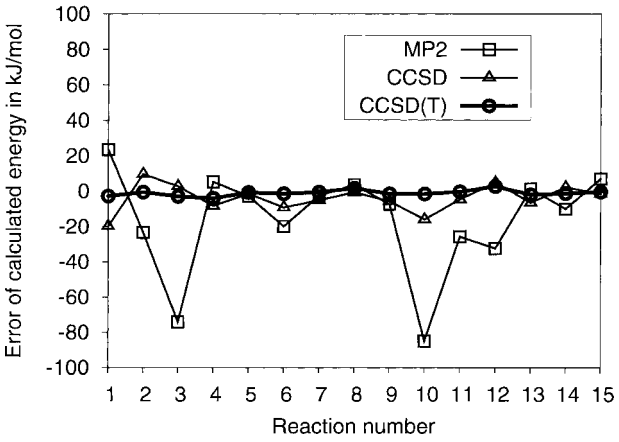


FIGURE 1. Deviations from experimental data ($\Delta H_{calc} - \Delta H_{exp}$, in kJ/mol) of calculated reaction energies at the conventional coupled-cluster level in the aug-cc-pV(Q + d)Z basis.

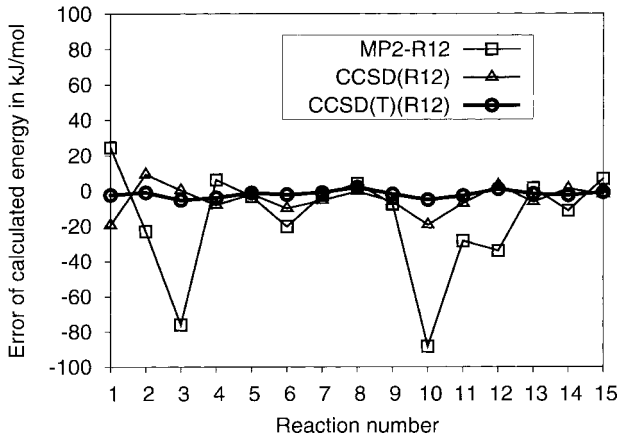


FIGURE 2. Deviations from experimental data ($\Delta H_{calc} - \Delta H_{exp}$, in kJ/mol) of calculated reaction energies at the linear-r_{12} coupled-cluster level in the aug-cc-pV(Q + d)Z basis.

TABLE XII

Reaction energy differences ($\Delta H_{calc} - \Delta H_{exp}$) between CCSD(T) and experimental data in kJ/mol using different aug-cc-pV(X + d)Z basis sets.

No.	TZ	QZ	TZ/QZ	5Z	QZ/5Z	TZ(R12)	QZ(R12)
1	−5.4	−2.8	−0.5	−1.3	0.3	−4.9	−2.4
2	0.6	−0.6	−1.8	−0.1	−0.1	−1.3	−1.0
3	8.5	−3.0	−6.8	—	—	3.3	−5.3
4	−4.5	−4.1	−4.1	−3.8	−3.5	−4.2	−3.9
5	−0.6	−0.8	−2.1	−0.7	−0.7	−1.7	−1.2
6	1.8	−1.5	−3.1	−1.7	−1.9	−0.2	−2.2
7	−0.2	−0.6	−1.6	−0.5	−0.4	−1.5	−1.0
8	1.1	1.7	1.9	2.0	2.3	1.2	2.0
9	−2.8	−1.5	−1.1	−1.4	−1.3	−4.1	−1.9
10	12.6	−1.6	−7.3	−3.7	−5.8	4.1	−5.1
11	9.9	−0.3	−4.9	—	—	5.1	−2.8
12	7.9	2.7	−0.1	1.7	0.5	3.6	1.0
13	−2.9	−1.9	−1.2	−2.0	−2.2	−2.5	−1.7
14	1.5	−1.3	−3.9	−2.0	−2.9	−1.0	−2.5
15	−2.2	−0.4	0.7	—	—	−3.6	−0.9

MP2, CCSD, and CCSD(T) models are all in the same range as their R12 counterparts MP2-R12, CCSD(R12), and CCSD(T)(R12). For the aug-cc-pV(Q + d)Z basis set, the mean absolute error and the standard deviation decrease from 22.5 and 30.7 kJ/mol (MP2-R12) over 6.7 and 7.7 kJ/mol (CCSD(R12)) to 2.3 and 2.0 kJ/mol (CCSD(T)(R12)). For each step, this is a reduction of the mean absolute error by a factor of 3 and for the standard deviation a reduction by a factor of 4. For the CCSD(T)(R12) model, the mean absolute error for both investigated basis sets is smaller than the experimental uncertainty of about ±4 kJ/mol. Thus, the CCSD(T)(R12) model leads to accurate results for the investigated reactions.

A comparison between the CCSD(T) and CCSD(T)(R12) results obtained in various basis sets, including basis-set extrapolation, is given in Table XII. The corresponding error analysis is presented in Table XIII. As expected, the CCSD(T) results for the aug-cc-pV(5+d)Z basis set and the aug-cc-pV(Q+d)Z/aug-cc-pV(5 + d)Z extrapolated values, denoted QZ/5Z, give the best results for the 12 reactions investigated. It appears that CCSD(T)/aug-cc-pV(Q + d)Z calculations lead to the best description as compared with the experimental data, and CCSD(T)/aug-cc-pV(T+d)Z calculations to the poorest. In view of the experimental uncertainty of ±4 kJ/mol, we can only conclude that both CCSD(T) and CCSD(T)(R12) calculations in the investigated basis sets lead to very accurate reaction energies.

A better estimate of the quality of the different CCSD(T) calculations can be obtained by comparing them with QZ/5Z extrapolated reaction energies, which can be considered to be close to the basis-set limit. The CCSD(T) and CCSD(T)(R12) models are compared for a variety of basis sets in Table XIV. The corresponding error analysis is presented in Table XV. These results are depicted in Figure 3, where the difference between the calculated reaction energy and the extrapolated basis-set limit is plotted for a subset of 12 reactions.

We observe that CCSD(T)/aug-cc-pV(T + d)Z calculations are not sufficient to obtain accurate

TABLE XIII

Error analysis for the CCSD(T) model with and without (R12) contribution in different basis sets (kJ/mol).*

CCSD(T)	$\bar{\Delta}$	$\bar{\Delta}_{abs}$	Δ_{std}	Δ_{max}
aug-cc-pV(T + d)Z	1.7	4.2	5.5	12.6
aug-cc-pV(Q + d)Z	−1.1	1.7	1.7	4.1
Extrapolated (TZ/QZ)	−2.4	2.7	2.6	7.3
aug-cc-pV(5 + d)Z	−0.9	1.4	1.6	3.8
Extrapolated (QZ/5Z)	−1.0	1.5	2.0	5.8
aug-cc-pV(T + d)Z (R12)	−0.5	2.8	3.3	5.1
aug-cc-pV(Q + d)Z (R12)	−1.9	2.3	2.0	5.3

*Experimental data were used as reference values. Note that the 5Z and the extrapolated QZ/5Z values are only calculated for 12 reactions. $\bar{\Delta}$ = mean error, $\bar{\Delta}_{abs}$ = mean absolute error, Δ_{std} = standard deviation, Δ_{max} = maximum absolute error.

TABLE XIV

Reaction energy differences ($\Delta H_{calc} - \Delta H_{ref}$) between calculated CCSD(T) and extrapolated QZ/5Z data in kJ/mol using different aug-cc-pV(X + d)Z basis sets.

No.	TZ	QZ	TZ/QZ	5Z	TZ(R12)	QZ(R12)
1	−5.7	−3.1	−0.8	−1.6	−5.2	−2.7
2	0.7	−0.5	−1.7	0.0	−1.2	−0.9
4	−1.0	−0.6	−0.6	−0.3	−0.7	−0.4
5	0.1	−0.1	−1.4	0.0	−1.0	−0.5
6	3.7	0.4	−1.2	0.2	1.7	−0.3
7	0.2	−0.2	−1.2	−0.1	−1.1	−0.6
8	−1.2	−0.6	−0.4	−0.3	−1.1	−0.3
9	−1.5	−0.2	0.2	−0.1	−2.8	−0.6
10	18.4	4.2	−1.5	2.1	9.9	0.7
12	7.4	2.2	−0.6	1.2	3.1	0.5
13	−0.7	0.3	1.0	0.2	−0.3	0.5
14	4.4	1.6	−1.0	0.9	1.9	0.4

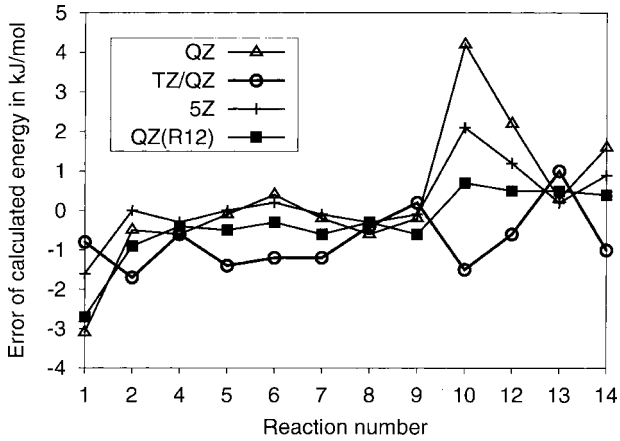


FIGURE 3. Deviations from extrapolated QZ/5Z data ($\Delta H_{calc} - \Delta H_{ref}$, in kJ/mol) of calculated reaction energies at the CCSD(T) coupled-cluster level with and without linear-r_{12} contributions in different basis sets.

results. Rather, we recommend that a CCSD(T)(R12) calculation be performed in this basis, because all errors are reduced with respect to the conventional model. Moreover, we note that the remaining errors in the CCSD(T)(R12)/aug-cc-pV(T + d)Z calculation are partly due to deficiencies in the HF treatment. For example, the relatively large error of 9.9 kJ/mol for reaction 10 at the CCSD(T)(R12)/aug-cc-pV(T + d)Z level is reduced to only 3.5 kJ/mol if the HF part of the CCSD(T)(R12)/aug-cc-pV(T + d)Z calculation is replaced by the HF result obtained in the aug-cc-pV(5 + d)Z basis. At the aug-cc-pV(Q + d)Z level, the HF results have practically converged.

The CCSD(T)/aug-cc-pV(5 + d)Z calculation leads to the most accurate results. Unfortunately, these calculations were not practical for the larger molecules (for technical reasons). The aug-cc-pV(T + d)Z/aug-cc-pV(Q + d)Z extrapolation, denoted TZ/QZ, improves the results for most reactions but not for the reactions 2, 5, 6, 7, and 13 with respect to the CCSD(T)/aug-cc-pV(Q + d)Z values. It is rewarding to see that the basis-set limit for the reaction energies (represented by the QZ/5Z extrapolation) has almost been reached at the CCSD(T)(R12)/aug-cc-pV(Q + d)Z level.

TABLE XV

Error analysis for the CCSD(T) model with and without (R12) contribution in different basis sets (kJ/mol).*

CCSD(T)	$\bar{\Delta}$	$\bar{\Delta}_{abs}$	Δ_{std}	Δ_{max}
aug-cc-pV(T + d)Z	1.7	3.0	5.5	18.4
aug-cc-pV(Q + d)Z	0.2	0.9	1.6	4.2
Extrapolated (TZ/QZ)	−0.6	0.8	0.8	1.7
aug-cc-pV(5 + d)Z	0.1	0.5	0.8	2.1
aug-cc-pV(T + d)Z (R12)	0.2	2.0	3.3	9.9
aug-cc-pV(Q + d)Z (R12)	−0.3	0.6	0.8	2.7

*Extrapolated QZ/5Z data were used as reference values. Note that only 12 reactions were investigated. $\bar{\Delta}$ = mean error, $\bar{\Delta}_{abs}$ = mean absolute error, Δ_{std} = standard deviation, Δ_{max} = maximum absolute error.

Conclusions

The perturbative (T) triples correction of the CCSD(T) model was included into the CCSD(R12) model. The resulting model is denoted CCSD(T)(R12) and has been made available in the Dalton program package. The performance of the new CCSD(T)(R12) model was assessed by calculating a series of chemical reaction energies for a set of 15 chemical reactions involving 23 small molecules. The MP2-R12, CCSD(R12), and CCSD(T)(R12) results were compared with experimental data that were corrected for ZPVE and finite temperature effects. Results for the conventional MP2, CCSD, and CCSD(T) models obtained in the same aug-cc-pV(T + d)Z and aug-cc-pV(Q + d)Z basis sets were also included. An error analysis showed that for the reactions studied, the CCSD(T)(R12) and CCSD(T) models yield accurate results with deviations from the experimental values within the experimental uncertainty.

Because the CCSD(T)/aug-cc-pV(Q + d)Z level yields already calculated energies of reaction that are accurate to within the experimental error bars, the improved basis-set convergence of the R12 models could not be revealed by the comparison with experimental data. Therefore, CCSD(T)/aug-cc-pV(5+d)Z calculations were performed for a subset of 12 reactions to obtain an estimate of the basis-set limit from aug-cc-pV(Q+d)Z/aug-cc-pV(5+d)Z extrapolations.

Results close to the basis-set limit were obtained by the CCSD(T) aug-cc-pV(T + d)Z/aug-cc-pV(Q + d)Z extrapolation, but compared with directly computed CCSD(T)/aug-cc-pV(Q + d)Z results, the TZ/QZ extrapolation was not always an improvement. It was observed that the CCSD(T)(R12)/aug-cc-pV(Q + d)Z results had almost reached the basis-set limit, whereas the conventional CCSD(T)/aug-cc-pV(Q + d)Z calculations showed a few relatively large deviations. The CCSD(T)(R12)/aug-cc-pV(Q + d)Z calculation did not cost significantly more than a CCSD(T)/aug-cc-pV(Q + d)Z calculation but yielded nearly as accurate results as the (more time-consuming) CCSD(T)/aug-cc-pV (5 + d)Z calculation.

We note that in terms of accuracy and computation time, the CCSD(T)(R12)/aug-cc-pV(Q + d)Z level is competing with the TZ/QZ extrapolation, which is less time-consuming and almost as accurate (cf. Tables XIV and XV). However, we expect that one may reach the CCSD(T)/aug-cc-pV(5 + d)Z quality already at the aug-cc-pV(T + d)Z level if one uses correlation factors such as Slater-type geminals in place of the linear-r_{12} terms [24]. Such correlation factors have recently been implemented in the Dalton program at the MP2 level [25]; work is in progress to make the new correlation factors available at the CCSD(T) level as well. Furthermore, we note that the basis sets used in the present work had been optimized for use in conventional electron-correlation calculations and extrapolations based on such calculations. CCSD(T)(R12) calculations, in particular with the new correlation factors, would gain significantly in terms of accuracy by reoptimizing the basis sets for use in this type of calculations [25]. To summarize these considerations, the best strategy for highly accurate calculations of reaction energies in future work might be to perform separate HF and CCSD(T)(R12) calculations in different basis sets, for instance, the former in an aug-cc-pV(Q + d)Z basis and the latter in a reoptimized cc-pV(T + d)Z basis using Slater-type geminals.

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