HTML ABSTRACT + LINKS

Coupled-cluster theory with simplified linear-r_{12} corrections: The CCSD(R12) model

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(Received 10 November 2004; accepted 29 November 2004; published online 16 February 2005)

A simplified singles-and-doubles linear-r_{12} corrected coupled-cluster model, denoted CCSD(R12), is proposed and compared with the complete singles-and-doubles linear-r_{12} coupled-cluster method CCSD-R12. An orthonormal auxiliary basis set is used for the resolution-of-the-identity approximation to calculate three-electron integrals needed in the linear-r_{12} Ansatz. Basis-set convergence is investigated for a selected set of atoms and small molecules. In a large basis, the CCSD(R12) model provides an excellent approximation to the full linear-r_{12} energy contribution, whereas the magnitude of this contribution is significantly overestimated at the level of second-order perturbation theory. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1850094]

I. INTRODUCTION

The very slow convergence of ground-state energies with increasing one-electron basis set and the corresponding increase in computational costs are great disadvantages of coupled-cluster calculations. However, the slow basis-set convergence typical for coupled-cluster calculations can be improved significantly by combining the coupled-cluster model with the linear-r_{12} Ansatz of Kutzelnigg,[1] to obtain the explicitly correlated linear-r_{12} corrected coupled-cluster (CC-R12) models.[2–7] Unfortunately, calculations with these CC-R12 models are computationally demanding due to the large basis sets that are required, and therefore restricted to rather small molecules (with up to five atoms).[8,9] For calculations of larger molecules with, for example, up to 20 atoms, it is necessary to develop approximate CC-R12 models with (ideally) the same accuracy but against much reduced computational cost.

The use of auxiliary basis sets, completeness insertions, and density-fitting techniques open up possibilities to achieve this objective, as shown for the MP2-R12 model, that is, second-order Møller–Plesset perturbation theory with the linear-r_{12} Ansatz.[10–16] All these approaches aim at improving on the calculation of the necessary many-electron integrals. In the present work, however, we aim at constructing a simplified coupled-cluster model in an attempt to extend the application range of CC-R12 calculations. We are in this paper not concerned with the integrals.

In coupled-cluster calculations with the linear-r_{12} Ansatz, the linear-r_{12} terms are treated similar to the regular double excitations. Hence, in the amplitude equations, terms occur that are linear or quadratic in the amplitudes of the linear-r_{12} terms. It is the purpose of the present article to identify those (linear and quadratic) terms in the amplitude equations that can be safely neglected in CC-R12 calculations, in particular, in high-quality basis sets (e.g., quadruple-zeta quality or better). Indeed, such terms can be identified and omitted without significant loss in accuracy. Omitting these terms leads to an approach, denoted CCSD(R12), which was proposed in earlier work.[17]

This CCSD(R12) method has now been implemented in the DALTON program package[18] in the framework of an integral-direct implementation. An orthonormal auxiliary basis set can be used for the resolution-of-the-identity approximation to calculate the three-electron integrals needed in the theory.

The CCSD(R12) model is discussed in Sec. II. Then, in Sec. III, computational details such as employed basis sets, geometries, and programs are given. Numerical results are presented in Sec. IV, and the article is concluded in Sec. V.

II. THEORY

A. The CCSD-R12 model

We start from the coupled-cluster wave function

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

where the reference state is the Hartree–Fock wave function. Since we are interested in single-and-double excitations, the operator $\hat{S}$ is defined as

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

For a closed-shell reference state $|\mathrm{HF}\rangle$, the excitation operators are

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

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TABLE I. Calculated ground-state energies in E_h and energy differences ΔR12 in mE_h.

		SCF	MP2	ΔR12(MP2)[a]	CCSD	ΔR12(CCSD(R12))[b]	ΔR12(CCSD-R12)[c]
Ne	aug-cc-pVDZ	−128.496 350	−128.703 223	−94.714	−128.706 504	−84.974	−110.250
	aug-cc-pVTZ	−128.533 273	−128.805 792	−32.934	−128.807 368	−27.147	−33.741
	aug-cc-pVQZ	−128.543 756	−128.840 999	−15.273	−128.841 514	−11.557	−12.675
	aug-cc-pV5Z	−128.546 786	−128.854 755	−8.657	−128.853 584	−6.191	−6.417
	aug-cc-pV6Z	−128.547 062	−128.859 935	−5.665	−128.857 669	−3.914	−3.886
F^-	aug-cc-pVDZ	−99.428 282	−99.665 948	−70.608	−99.662 690	−61.350	−77.673
	aug-cc-pVTZ	−99.450 807	−99.745 879	−23.500	−99.739 301	−18.437	−21.998
	aug-cc-pVQZ	−99.457 462	−99.774 407	−10.427	−99.765 819	−7.296	−8.666
	aug-cc-pV5Z	−99.459 261	−99.785 557	−6.290	−99.774 889	−4.082	−4.455
	aug-cc-pV6Z	−99.459 430	−99.789 971	−3.798	−99.778 066	−2.363	−2.543

[a]ΔR12(MP2)=MP2-R12−MP2.
[b]ΔR12(CCSD(R12))=CCSD(R12)−CCSD.
[c]ΔR12(CCSD-R12)=CCSD-R12−CCSD.

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

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

with

$$r_{\alpha k\beta l} = \langle \phi_\alpha(1)\phi_\beta(2)|r_{12}|\phi_k(1)\phi_l(2)\rangle. \tag{6}$$

We have used the usual convention that i, j, … denote active (i.e., correlated) occupied, and a, b, … unoccupied (virtual) orbitals. The indices α, β, … are used to denote 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,[19]

$$(1-\hat{P}_1)(1-\hat{P}_2)r_{12}|\phi_k(1)\phi_l(2)\rangle, \tag{7}$$

which can be expressed with the help of a complementary orbital subspace $\{\phi_\alpha\}$ as in Eqs. (5) and (6). For Ansatz 1 of R12 theory, with which we are concerned in this paper, 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 $\{\phi_p\}$ form together a complete basis for the one-electron Hilbert space. The projection operator $\hat{P}_1$ onto the finite one-electron orbital basis is defined as

$$\hat{P}_1 = \sum_p |\phi_p(1)\langle\phi_p(1)|. \tag{8}$$

Note that for Ansatz 1 the R12 contributions vanish in the basis-set limit. This is not the case for Ansatz 2 (for details, see Ref. 15). For our purposes, it is therefore necessary to

TABLE II. Calculated ground-state energies in E_h and energy differences ΔR12 in mE_h.

		SCF	MP2	ΔR12(MP2)[a]	CCSD	ΔR12(CCSD(R12))[b]	ΔR12(CCSD-R12)[c]
BH	aug-cc-pVDZ	−25.126 427	−25.188 800	−11.882	−25.216 240	−7.809	−10.130
	aug-cc-pVTZ	−25.130 201	−25.204 590	−4.165	−25.229 381	−2.143	−2.592
	aug-cc-pVQZ	−25.131 371	−25.210 004	−2.004	−25.233 103	−0.788	−0.825
	aug-cc-pV5Z	−25.131 597	−25.211 809	−1.224	−25.234 054	−0.426	−0.423
	aug-cc-pV6Z	−25.131 630	−25.212 557	−0.815	−25.234 365	−0.265	−0.258
HF	aug-cc-pVDZ	−100.033 466	−100.255 737	−76.612	−100.259 446	−66.485	−86.390
	aug-cc-pVTZ	−100.061 069	−100.340 865	−26.893	−100.342 043	−20.966	−25.315
	aug-cc-pVQZ	−100.068 559	−100.369 758	−12.308	−100.369 101	−8.676	−9.480
	aug-cc-pV5Z	−100.070 573	−100.380 557	−7.004	−100.378 040	−4.644	−4.754
	aug-cc-pV6Z	−100.070 770	−100.384 701	−4.550	−100.381 087	−2.907	−2.880
N_2	aug-cc-pVDZ	−108.960 650	−109.214 291	−136.280	−109.280 460	−60.882	−82.316
	aug-cc-pVTZ	−108.984 698	−109.364 163	−24.017	−109.361 574	−17.306	−22.644
	aug-cc-pVQZ	−108.991 558	−109.393 288	−11.244	−109.386 793	−6.950	−7.682
	aug-cc-pV5Z	−108.992 959	−109.403 739	−6.524	−109.394 586	−3.741	−3.801
	aug-cc-pV6Z	−108.993 135	−109.407 910	−4.432	−109.397 297	−2.421	−2.390
CO	aug-cc-pVDZ	−112.754 691	−113.053 968	−74.152	−113.060 979	−62.301	−81.893
	aug-cc-pVTZ	−112.781 433	−113.142 172	−26.125	−113.144 520	−19.169	−23.372
	aug-cc-pVQZ	−112.789 036	−113.172 824	−12.177	−113.171 610	−7.772	−8.361
	aug-cc-pV5Z	−112.790 658	−113.183 877	−7.059	−113.180 060	−4.176	−4.207
	aug-cc-pV6Z	−112.790 848	−113.188 297	−4.630	−113.183 008	−2.614	−2.580

[a]ΔR12(MP2)=MP2-R12−MP2.
[b]ΔR12(CCSD(R12))=CCSD(R12)−CCSD.
[c]ΔR12(CCSD-R12)=CCSD-R12−CCSD.

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TABLE III. Calculated ground-state energies in E_h and energy differences ΔR12 in mE_h.

		SCF	MP2	ΔR12(MP2)[a]	CCSD	ΔR12(CCSD(R12))[b]	ΔR12(CCSD-R12)[c]
H_2O	aug-cc-pVDZ	−76.041 428	−76.260 765	−60.493	−76.268 534	−50.559	−65.058
	aug-cc-pVTZ	−76.060 613	−76.328 958	−20.991	−76.333 665	−15.362	−17.877
	aug-cc-pVQZ	−76.066 001	−76.351 913	−9.651	−76.354 214	−6.278	−6.670
	aug-cc-pV5Z	−76.067 321	−76.360 225	−5.412	−76.360 648	−3.295	−3.318
	aug-cc-pV6Z	−76.067 462	−76.363 417	−3.514	−76.362 813	−2.058	−2.032
NH_3	aug-cc-pVDZ	−56.205 440	−56.404 695	−46.418	−56.419 711	−37.357	−48.294
	aug-cc-pVTZ	−56.220 384	−56.460 537	−15.367	−56.472 206	−10.444	−11.864
	aug-cc-pVQZ	−56.224 035	−56.477 772	−7.156	−56.486 781	−4.246	−4.405
	aug-cc-pV5Z	−56.224 917	−56.483 825	−4.020	−56.490 314	−3.042	−3.032
	aug-cc-pV6Z	−56.225 022	−56.486 175	−2.644	−56.492 044	−1.950	−1.922
CH_4	aug-cc-pVDZ	−40.199 598	−40.367 327	−35.547	−40.390 626	−27.477	−35.980
	aug-cc-pVTZ	−40.213 666	−40.414 459	−11.206	−40.434 357	−7.051	−8.119
	aug-cc-pVQZ	−40.216 298	−40.427 402	−5.145	−40.444 722	−2.787	−2.908
	aug-cc-pV5Z	−40.217 005	−40.431 896	−2.956	−40.447 765	−1.489	−1.474

[a]ΔR12(MP2)=MP2-R12−MP2.
[b]ΔR12(CCSD(R12))=CCSD(R12)−CCSD.
[c]ΔR12(CCSD-R12)=CCSD-R12−CCSD.

introduce a modified Ansatz 2 where the R12 amplitudes are orthogonal to the conventional coupled-cluster excitation manifold. Hence, we define for Ansatz 2 the correlated pair function as recently proposed by Valeev,[10]

$$[(1-\hat{O}_1)(1-\hat{O}_2)-\hat{V}_1\hat{V}_2]r_{12}|\phi_k(1)\phi_l(2)\rangle. \tag{9}$$

Using this modified Ansatz 2, the R12 contributions vanish in the basis-set limit, as is the case for Ansatz 1. $\hat{O}_1$ is a projection operator onto the subspace of all occupied molecular orbitals (active and frozen), while $\hat{V}_1$ is a projection operator onto the space spanned by the virtual orbitals,

$$\hat{O}_1=\sum_i |\phi_i(1)\langle\phi_i(1)|, \tag{10}$$

$$\hat{V}_1=\sum_a |\phi_a(1)\langle\phi_a(1)|. \tag{11}$$

B. Similarity-transformed operators

We assume canonical Hartree–Fock orbitals and partition the Hamiltonian into the many-electron Fock operator $\hat{f}$, the fluctuation potential $\hat{\Phi}$, and the nuclear repulsion term h_{nuc},

$$\hat{H}=\hat{f}+\hat{\Phi}+h_{\mathrm{nuc}}. \tag{12}$$

A similarity transformation of these operators then yields

$$\hat{H}^S=\exp(-\hat{S})\hat{H}\exp(\hat{S})=\hat{f}^S+\hat{\Phi}^S+h_{\mathrm{nuc}}, \tag{13}$$

$$\hat{f}^S=\exp(-\hat{S})\hat{f}\exp(\hat{S})=\sum_m \varepsilon_{\mu_m}t_{\mu_m}\hat{\tau}_{\mu_m}+[\hat{f},\hat{T}_{2'}]+\hat{f}, \tag{14}$$

$$\hat{\Phi}^S=\exp(-\hat{S})\hat{\Phi}\exp(\hat{S}). \tag{15}$$

Energy differences between the occupied and virtual orbitals are denoted as ε_{μ_m}, and the coupled-cluster amplitudes are written as t_{μ_m}. For future use (*vide infra*), we also introduce the operator $\bar{\hat{\Phi}}$,

TABLE IV. Calculated ground-state energy contributions from $\hat{T}_1$, $\hat{T}_2$, and $\hat{T}_{2'}$ in mE_h.

		CCSD(R12)			CCSD-(R12)			
		$E(\hat{T}_1,\hat{T}_2)$	$E(\hat{T}_{2'})$	ΔR12	$E(\hat{T}_1,\hat{T}_2)$	$E(\hat{T}_{2'})$	ΔR12	$E_{\mathrm{CCSD}}-E_{\mathrm{SCF}}$
Ne	aug-cc-pVDZ	−204.693	−90.435	−84.974	−202.910	−117.494	−110.250	−210.154
	aug-cc-pVTZ	−271.103	−30.138	−27.147	−270.346	−37.489	−33.741	−274.095
	aug-cc-pVQZ	−295.924	−13.391	−11.557	−295.752	−14.681	−12.675	−297.758
	aug-cc-pV5Z	−305.614	−7.376	−6.191	−305.573	−7.644	−6.417	−306.799
	aug-cc-pV6Z	−309.777	−4.744	−3.914	−309.784	−4.709	−3.886	−310.607
F^-	aug-cc-pVDZ	−229.019	−66.739	−61.350	−227.444	−84.636	−77.673	−234.408
	aug-cc-pVTZ	−285.832	−21.099	−18.437	−285.284	−25.209	−21.998	−288.494
	aug-cc-pVQZ	−306.817	−8.836	−7.296	−306.534	−10.490	−8.666	−308.357
	aug-cc-pV5Z	−314.575	−5.134	−4.082	−314.481	−5.602	−4.455	−315.628
	aug-cc-pV6Z	−317.966	−3.032	−2.363	−317.915	−3.264	−2.543	−318.636

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TABLE V. Calculated ground-state energy contributions from $\hat{T}_1$, $\hat{T}_2$, and $\hat{T}_{2'}$ in mE_h.

		CCSD(R12)			CCSD-R12			
		$E(\hat{T}_1,\hat{T}_2)$	$E(\hat{T}_{2'})$	ΔR12	$E(\hat{T}_1,\hat{T}_2)$	$E(\hat{T}_{2'})$	ΔR12	$E_{CCSD}-E_{SCF}$
BH	aug-cc-pVDZ	−87.678	−9.944	−7.809	−87.107	−12.836	−10.130	−89.813
	aug-cc-pVTZ	−98.262	−3.060	−2.143	−98.076	−3.696	−2.592	−99.180
	aug-cc-pVQZ	−101.236	−1.284	−0.788	−101.216	−1.341	−0.825	−101.733
	aug-cc-pV5Z	−102.146	−0.737	−0.426	−102.148	−0.732	−0.423	−102.457
	aug-cc-pV6Z	−102.258	−0.474	−0.265	−102.532	−0.461	−0.258	−102.735
HF	aug-cc-pVDZ	−220.264	−72.201	−66.485	−218.383	−93.987	−86.390	−225.980
	aug-cc-pVTZ	−277.929	−24.012	−20.966	−277.276	−29.013	−25.315	−280.974
	aug-cc-pVQZ	−298.773	−10.446	−8.676	−298.614	−11.408	−9.480	−300.542
	aug-cc-pV5Z	−306.348	−5.763	−4.644	−306.324	−5.897	−4.754	−307.467
	aug-cc-pV6Z	−309.549	−8.674	−2.907	−309.557	−3.639	−2.880	−310.316
N_2	aug-cc-pVDZ	−312.546	−68.146	−60.882	−310.007	−92.119	−82.316	−319.810
	aug-cc-pVTZ	−373.360	−20.822	−17.306	−372.286	−27.234	−22.644	−376.876
	aug-cc-pVQZ	−393.165	−9.020	−6.950	−392.952	−9.965	−7.682	−395.235
	aug-cc-pV5Z	−400.331	−5.037	−3.741	−400.313	−5.115	−3.801	−401.627
	aug-cc-pV6Z	−403.243	−3.339	−2.421	−403.257	−3.294	−2.390	−404.161
CO	aug-cc-pVDZ	−299.236	−69.353	−62.301	−297.011	−91.170	−81.893	−306.288
	aug-cc-pVTZ	−359.487	−22.769	−19.169	−358.724	−27.735	−23.372	−363.087
	aug-cc-pVQZ	−380.465	−9.881	−7.772	−380.317	−10.618	−8.361	−382.573
	aug-cc-pV5Z	−388.068	−5.510	−4.176	−388.062	−5.547	−4.207	−389.402
	aug-cc-pV6Z	−391.244	−3.529	−2.614	−391.259	−3.480	−2.580	−392.159

$$\bar{\hat{\Phi}} = \exp(-\hat{T}_1 - \hat{T}_2)\hat{\Phi}\exp(\hat{T}_1 + \hat{T}_2), \tag{16}$$

which is obtained from a similarity transformation of the fluctuation potential, but restricted to the conventional single-and-double excitation operators $\hat{T}_1$ and $\hat{T}_2$.

C. CCSD-R12 equations

In Secs. II A and II B we have presented the fundamental equations of CC-R12 theory. We shall now have a closer look at the CCSD-R12 model in order to arrive at the CCSD(R12) equations.

As common in coupled-cluster theory, we employ a projection technique to solve the Schrödinger equation. In terms of the similarity-transformed Hamiltonian $\hat{H}^S$ defined in Sec. II B, the full linear-r_{12} singles-and-doubles coupled-cluster equations, denoted CCSD-R12, take the following form:

$$E = \langle \mathrm{HF}|\hat{H}^S|\mathrm{HF}\rangle \tag{17}$$

for the energy, and

$$\langle \mu_1|\hat{H}^S|\mathrm{HF}\rangle = \varepsilon_{\mu_1} t_{\mu_1} + \langle \mu_1|\hat{\Phi}^S|\mathrm{HF}\rangle = 0, \tag{18}$$

$$\langle \mu_2|\hat{H}^S|\mathrm{HF}\rangle = \varepsilon_{\mu_2} t_{\mu_2} + \langle \mu_2|\hat{\Phi}^S|\mathrm{HF}\rangle = 0, \tag{19}$$

TABLE VI. Calculated ground-state energy contributions from $\hat{T}_1$, $\hat{T}_2$, and $\hat{T}_{2'}$ in mE_h.

		CCSD(R12)			CCSD-R12			
		$E(\hat{T}_1,\hat{T}_2)$	$E(\hat{T}_{2'})$	ΔR12	$E(\hat{T}_1,\hat{T}_2)$	$E(\hat{T}_{2'})$	ΔR12	$E_{CCSD}-E_{SCF}$
H_2O	aug-cc-pVDZ	−221.481	−56.184	−50.559	−219.735	−72.430	−65.058	−227.106
	aug-cc-pVTZ	−270.192	−18.222	−15.362	−269.714	−21.215	−17.877	−273.052
	aug-cc-pVQZ	−286.597	−7.895	−6.278	−286.500	−8.383	−6.670	−288.213
	aug-cc-pV5Z	−292.341	−4.281	−3.295	−292.336	−4.309	−3.318	−293.328
	aug-cc-pV6Z	−294.683	−2.726	−2.058	−294.692	−2.691	−2.032	−295.350
NH_3	aug-cc-pVDZ	−209.154	−42.474	−37.357	−207.565	−54.999	−48.294	−214.271
	aug-cc-pVTZ	−249.370	−12.895	−10.444	−249.036	−14.650	−11.864	−251.822
	aug-cc-pVQZ	−261.386	−5.607	−4.246	−261.339	−5.813	−4.405	−262.746
	aug-cc-pV5Z	−265.397	−3.042	−3.042	−265.402	−3.026	−3.032	−265.397
	aug-cc-pV6Z	−267.011	−1.961	−1.950	−267.022	−1.922	−1.922	−267.022
CH_4	aug-cc-pVDZ	−186.548	−31.957	−27.477	−185.122	−41.886	−35.980	−191.028
	aug-cc-pVTZ	−218.684	−9.057	−7.051	−218.375	−10.435	−8.119	−220.691
	aug-cc-pVQZ	−227.358	−3.853	−2.787	−227.315	−4.018	−2.908	−228.425
	aug-cc-pV5Z	−230.114	−2.134	−1.489	−230.122	−2.112	−1.474	−230.760

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TABLE VII. Calculated ground-state energies in E_h and energy differences in mE_h using a 19*s*14*p*8*d*6*f*4*g*3*h*2*i* basis (9*s*6*p*4*d*3*f*2*g* for H).

	SCF	MP2	ΔR12(MP2)[a]	CCSD	ΔR12(CCSD(R12))[b]	ΔR12(CCSD-R12)[c]
HF	−100.070 779	−100.385 261	−5.208	−100.381 539	−3.291	−3.226
H_2O	−76.067 391	−76.363 531	−4.330	−76.362 936	−2.515	−2.457
CH_2	−100.070 779	−39.049 673	−2.177	−39.070 636	−0.968	−0.939
F_2	−198.773 806	−199.375 405	−9.617	−199.368 727	−6.076	−5.968
N_2	−108.992 934	−109.408 683	−5.279	−109.397 732	−2.875	−2.804
CH_4	−198.773 806	−40.433 215	−2.802	−40.448 575	−1.365	−1.323
HCN	−92.915 579	−93.297 521	−4.794	−93.292 702	−2.484	−2.412
HNC	−92.900 156	−93.269 223	−4.770	−93.269 609	−2.475	−2.404
NH	−92.915 579	−56.485 916	−3.480	−56.492 476	−1.849	−1.802
CO	−112.790 636	−113.189 124	−5.515	−113.183 500	−3.092	−3.017
CO_2	−187.725 049	−188.401 612	−9.537	−188.378 721	−5.557	−5.429
C_2H_2	−112.790 636	−77.196 391	−4.250	−77.200 098	−2.074	−2.008

[a]ΔR12(MP2)=MP2-R12−MP2.
[b]ΔR12(CCSD(R12))=CCSD(R12)−CCSD.
[c]ΔR12(CCSD-R12)=CCSD-R12−CCSD.

$$\langle \mu_{2'} | \hat{H}^S | \mathrm{HF} \rangle = \langle \mu_{2'} | [\hat{f}, \hat{T}_{2'}] + \hat{\Phi}^S | \mathrm{HF} \rangle = 0 \tag{20}$$

for the amplitude equations. μ_1 and μ_2 are the conventional single-and-double excitations in the Hartree–Fock space (for details, see Ref. 20), while the double excitations in the R12-space are defined as

$$\langle \mu_{2'} | = \sum_{\alpha\beta} r_{k\alpha l\beta} \left\langle \overline{{}^{\alpha\beta}_{ij}} \right|, \tag{21}$$

with the projection manifold[20]

$$\left\langle \overline{{}^{\alpha\beta}_{ij}} \right| = \tfrac{1}{3} \left\langle {}^{\alpha\beta}_{ij} \right| + \tfrac{1}{6} \left\langle {}^{\alpha\beta}_{ji} \right|, \tag{22}$$

$$\left\langle {}^{\alpha\beta}_{ij} \right| = \langle \mathrm{HF} | E^\dagger_{\alpha i} E^\dagger_{\beta j}. \tag{23}$$

Note that no approximations or truncations are invoked up to this point, except that we restrict the operator $\hat{S}$ to contain only single-and-double excitations.

D. The CCSD(R12) model

We shall now derive the CCSD(R12) model. Our motivation is to avoid terms in the amplitude equations which are of higher order in $\hat{T}_{2'}$ and contribute only very little to the energy, and whose integrals can only—unless a very large basis is used—be computed in an inaccurate, crude manner by inserting various completeness relations. Thus, for Ansatz 1, we do not change the projections onto the standard excitation manifold of singles and doubles, but focus on the projection onto the R12 doubles. The projection onto the R12 doubles of Ansatz 1, given by Eq. (20), is

$$\langle \mu_{2'} | [\hat{f}, \hat{T}_{2'}] + \hat{\Phi}^S | \mathrm{HF} \rangle = 0. \tag{24}$$

In analogy to the CC*n* models [e.g., CC2 (Ref. 21) and CC3 (Refs. 22 and 23)], we simplify this equation by restricting the similarity transformation of the fluctuation potential to the standard single-and-double excitations. In Eq. (24), the fluctuation potential is transformed with the standard singles and doubles *as well as* the R12 doubles. In the CCSD(R12) model, we omit the R12 doubles in this transformation, because we regard the R12 doubles as being of higher order than the standard singles and doubles. Hence, the CCSD(R12) model is obtained by replacing the operator $\hat{\Phi}^S$

TABLE VIII. Calculated ground-state energies in E_h and energy differences in mE_h using a 19*s*14*p*8*d*6*f*4*g*3*h*2*i* basis (9*s*6*p*4*d*3*f*2*g* for H).

	CCSD[T]	ΔR12(CCSD[T](R12))[a]	ΔR12(CCSD[T]-R12)[b]	CCSD(T)	ΔR12(CCSD(T)(R12))[c]	ΔR12(CCSD(T)-R12)[d]
HF	−100.390 605	−3.253	−3.189	−100.390 267	−3.259	−3.194
H_2O	−76.372 998	−2.477	−2.421	−76.372 703	−2.480	−2.424
CH_2	−39.076 365	−0.947	−0.919	−39.076 255	−0.947	−0.919
F_2	−199.392 197	−5.990	−5.884	−199.391 333	−5.996	−5.890
N_2	−109.419 799	−2.810	−2.741	−109.418 895	−2.809	−2.740
CH_4	−40.456 007	−1.344	−1.304	−40.455 763	−1.342	−1.302
HCN	−93.313 789	−2.420	−2.351	−93.312 928	−2.420	−2.351
HNC	−93.290 147	−2.412	−2.343	−93.289 213	−2.414	−2.345
NH	−56.501 961	−1.819	−1.773	−56.501 712	−1.818	−1.772
CO	−113.204 364	−3.022	−2.949	−113.202 965	−3.031	−2.958
CO_2	−188.413 821	−5.440	−5.316	−188.411 613	−5.453	−5.328
C_2H_2	−77.219 171	−2.018	−1.954	−77.218 507	−2.017	−1.953

[a]ΔR12(CCSD[T](R12))=CCSD[T](R12)−CCSD[T].
[b]ΔR12(CCSD[T]-R12)=CCSD[T]-R12−CCSD[T].
[c]ΔR12(CCSD(T)R12)=CCSD(T)R12−CCSD(T).
[d]ΔR12(CCSD(T)-R12)=CCSD(T)-R12−CCSD(T).

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TABLE IX. Calculated ΔR12 contributions in mE_h using a 19*s*14*p*8*d*6*f*4*g*3*h*2*i* auxiliary basis.

		ΔR12(MP2)[a]	ΔR12(CCSD(R12))[b]
Ne	aug-cc-pVDZ	−45.753	−38.618
	aug-cc-pVTZ	−20.423	−15.784
	aug-cc-pVQZ	−10.051	−7.326
	aug-cc-pV5Z	−7.551	−5.305
	aug-cc-pV6Z	−6.363	−4.376
F^-	aug-cc-pVDZ	−35.008	−27.324
	aug-cc-pVTZ	−14.665	−10.291
	aug-cc-pVQZ	−8.223	−5.416
	aug-cc-pV5Z	−5.591	−3.538
	aug-cc-pV6Z	−4.411	−2.724

[a]ΔR12(MP2)=MP2-R12−MP2.
[b]ΔR12(CCSD(R12))=CCSD(R12)−CCSD.

TABLE XI. Calculated ΔR12 contributions in mE_h using a 19*s*14*p*8*d*6*f*4*g*3*h*2*i* auxiliary basis (9*s*6*p*4*d*3*f*2*g* for H).

		ΔR12(MP2)[a]	ΔR12(CCSD(R12))[b]
H_2O	aug-cc-pVDZ	−31.688	−23.968
	aug-cc-pVTZ	−14.175	−9.551
	aug-cc-pVQZ	−7.237	−4.521
	aug-cc-pV5Z	−5.000	−2.988
NH_3	aug-cc-pVDZ	−26.459	−18.747
	aug-cc-pVTZ	−11.464	−7.085
	aug-cc-pVQZ	−5.854	−3.331
CH_4	aug-cc-pVDZ	−23.057	−15.248
	aug-cc-pVTZ	−9.308	−5.241
	aug-cc-pVQZ	−4.751	−2.460

[a]ΔR12(MP2)=MP2-R12−MP2.
[b]ΔR12(CCSD(R12))=CCSD(R12)−CCSD.

in Eq. (24) by the operator $\bar{\hat{\Phi}}$ that was defined previously [Eq. (16), *vide supra*]. This yields

$$\langle \mu_{2'} | [\hat{f}, \hat{T}_{2'}] + \bar{\hat{\Phi}} | \mathrm{HF} \rangle = 0. \tag{25}$$

If we rewrite Eq. (24) using the operator $\bar{\hat{\Phi}}$, it takes the form

$$\langle \mu_{2'} | [\hat{f}, \hat{T}_{2'}] + \bar{\hat{\Phi}} + [\bar{\hat{\Phi}}, \hat{T}_{2'}] + \tfrac{1}{2}[[\bar{\hat{\Phi}}, \hat{T}_{2'}], \hat{T}_{2'}] | \mathrm{HF} \rangle = 0, \tag{26}$$

thereby revealing the commutators $[\bar{\hat{\Phi}}, \hat{T}_{2'}]$ and $[[\bar{\hat{\Phi}}, \hat{T}_{2'}], \hat{T}_{2'}]$ that are omitted. As these are commutators, the size extensivity of the explicitly correlated coupled-cluster model is conserved. The neglected terms contribute, respectively, in $\mathcal{O}(\hat{T}_{2'}^2)$ and $\mathcal{O}(\hat{T}_{2'}^3)$ to the energy. In reasonably large orbital basis sets these corrections should be negligible. Note that with Ansatz 1, and also with Ansatz 2 as defined in Eq. (9), the R12 corrections to the energy and the R12 part of the wave function vanish in the limit of a complete orbital basis set.

A comment is in order concerning the (modified) Ansatz 2. In this Ansatz, a term quadratic in $\hat{T}_{2'}$ contributes in the full CCSD-R12 approach to the standard doubles equations,

$$\langle \mu_2 | [[\hat{H}, \hat{T}_{2'}], \hat{T}_{2'}] | \mathrm{HF} \rangle \neq 0. \tag{27}$$

We suggest to neglect this term, which is quadratic in the R12 doubles $\hat{T}_{2'}$, in the CCSD(R12) model, in addition to those terms skipped in the R12 doubles equations. Concerning noniterative corrections for connected triples, such as in the CCSD(T) and CCSD[T] models, we note at this point that there are no R12 contributions to the triples in Ansatz 1. Hence, the calculation of the triples correction can be performed using the standard singles and doubles amplitudes. Ansatz 2 is more complicated, because in this case the $\hat{T}_{2'}$ amplitudes contribute to the equations defining the triples amplitudes. In CCSD(T)-R12, for instance,

$$\langle \mu_3 | [\hat{f}, \hat{T}_3] + [\hat{\Phi}, \hat{T}_2] + [\hat{\Phi}, \hat{T}_{2'}] | \mathrm{HF} \rangle = 0. \tag{28}$$

We propose to neglect the contribution of $[\hat{\Phi}, \hat{T}_{2'}]$ to the triples amplitude equations in CCSD(T)(R12), since this term is expected to contribute little to the correlation energy but would considerably increase the computational costs.

TABLE X. Calculated ΔR12 contributions in mE_h using a 19*s*14*p*8*d*6*f*4*g*3*h*2*i* auxiliary basis (9*s*6*p*4*d*3*f*2*g* for H).

		ΔR12(MP2)[a]	ΔR12(CCSD(R12))[b]
BH	aug-cc-pVDZ	−9.141	−4.251
	aug-cc-pVTZ	−4.077	−1.563
	aug-cc-pVQZ	−2.183	−0.748
	aug-cc-pV5Z	−1.385	−0.453
	aug-cc-pV6Z	−1.279	−0.416
HF	aug-cc-pVDZ	−38.409	−30.815
	aug-cc-pVTZ	−17.229	−12.503
	aug-cc-pVQZ	−8.630	−5.853
	aug-cc-pV5Z	−6.249	−4.066
	aug-cc-pV6Z	−5.446	−3.436
N_2	aug-cc-pVDZ	−101.520	−27.809
	aug-cc-pVTZ	−17.527	−11.244
	aug-cc-pVQZ	−8.875	−5.207
	aug-cc-pV5Z	−6.400	−3.596
CO	aug-cc-pVDZ	−40.264	−29.795
	aug-cc-pVTZ	−18.627	−12.223
	aug-cc-pVQZ	−9.657	−5.833
	aug-cc-pV5Z	−6.820	−3.947

[a]ΔR12(MP2)=MP2-R12−MP2.
[b]ΔR12(CCSD(R12))=CCSD(R12)−CCSD.

III. COMPUTATIONAL DETAILS

All CC-R12 calculations were carried out with Ansatz 1 and in the standard approximation *B* of R12 theory. The CCSD(R12) results presented in Tables I–III were obtained with the DALTON[18] or DIRCCR12-OS program[24] using aug-cc-pVXZ basis sets.[25–27] Note that in these calculations, the same aug-cc-pVXZ basis was used both as orbital basis and as auxiliary basis. This was done to be able to compare the CCSD(R12) results with the results from the full CCSD-R12 model as implemented in the DIRCCR12-OS program.[24] It is not possible to use an auxiliary basis in the DIRCCR12-OS program. The geometries of the molecules investigated in Tables I–III correspond to experimental data. See Ref. 28 for N_2, BH, HF, and CO; see Ref. 29 for H_2O, Ref. 30 for NH_3;

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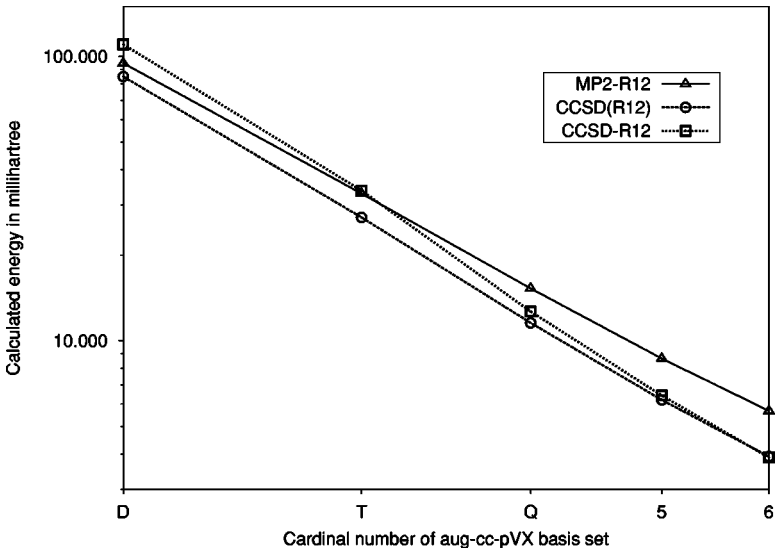


FIG. 1. Calculated ΔR12 contributions for Ne in mE_h, plotted using a double logarithmic scale.

and Ref. 31 for CH_4. Only the valence electrons were correlated. The calculated contributions from the coupled-cluster amplitudes denoted as $E(\hat{T}_1,\hat{T}_2)$ and $E(\hat{T}_{2'})$ are listed in Tables IV–VI.

For the results presented in Tables VII and VIII, the geometries of the investigated molecules were optimized[32] at the CCSD(T)-R12 level by computing a number of grid points (at least five per degree of freedom) around the analytically optimized CCSD(T)/cc-pV6Z equilibrium geometries taken from Ref. 33. Again, only the valence electrons were correlated. All data in Tables VII and VIII were computed with the DIRCCR12-OS program[24] in the 19*s*14*p*8*d*6*f*4*g*3*h*2*i* basis (9*s*6*p*4*d*3*f*2*g* for H) of Ref. 15.

The CCSD(R12) results using the auxiliary basis set (19*s*14*p*8*d*6*f*4*g*3*h*2*i*/9*s*6*p*4*d*3*f*2*g*) of Ref. 15 are presented in Tables IX–XI. These were carried out with the DALTON program.[18]

CCSD(R12) calculations are carried out as follows. Prior to iteratively solving the CCSD(R12) equations, we compute and transform integrals in $\mathcal{O}(nN^4)$ and $\mathcal{O}(n^2N^4)$ floating-point operations, where n is the number of occupied orbitals and N the size of the orbital (or auxiliary) basis. Then, in each CCSD(R12) iteration, computational work related to the R12 part is done that depends either only on the number of occupied orbitals or that scales not worse than n^4N^2.

The full CCSD-R12 approach is computationally more demanding than CCSD(R12). For example, an intermediate called $\mathcal{Z}_{kl;o}^{mn;a}$ is precomputed in the DIRCCR12-OS program in $\mathcal{O}(n^3N^4)$ operations. We note, however, the following: First, Noga and Valiron[5] have pointed out that this noniterative $\mathcal{O}(n^3N^4)$ step can be avoided by recomputing the corresponding contributions in each iteration in $\mathcal{O}(n^3N^3)$ operations, or by neglecting those quadratic terms in the R12 doubles equations that depend on both $\hat{T}_1$ and $\hat{T}_{2'}$. In Ref. 5, the neglect of these terms was denoted approximation B'. Second, in typical accurate CC-R12 calculations, the orbital and auxiliary basis sets are much larger than the number of occupied orbitals, and under such circumstances, the work in each iteration related to the R12 terms is negligible compared with the standard CCSD work, which scales as n^2N^4 (and n^3N^3). This applies to our CCSD(R12) model as well as to the full CCSD-R12 approach. The most important advantage of the CCSD(R12) model is not so much the direct savings in computing time but rather the fact that fewer and

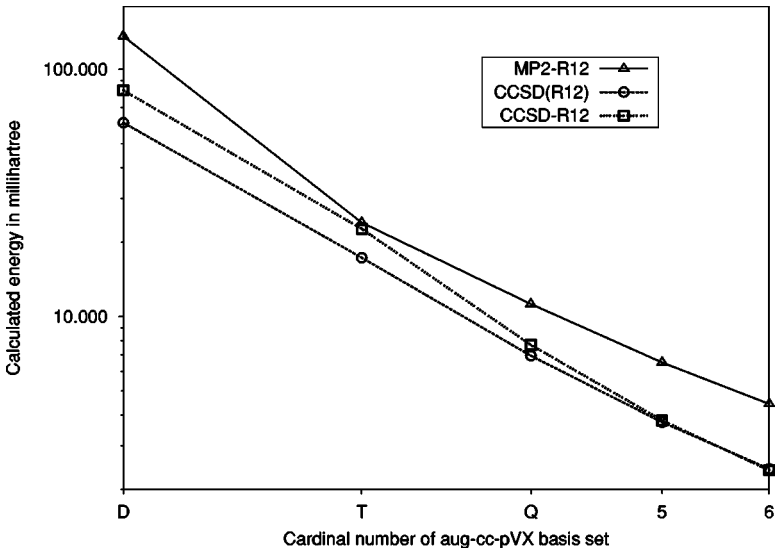


FIG. 2. Calculated ΔR12 contributions for N_2 in mE_h, plotted using a double logarithmic scale.

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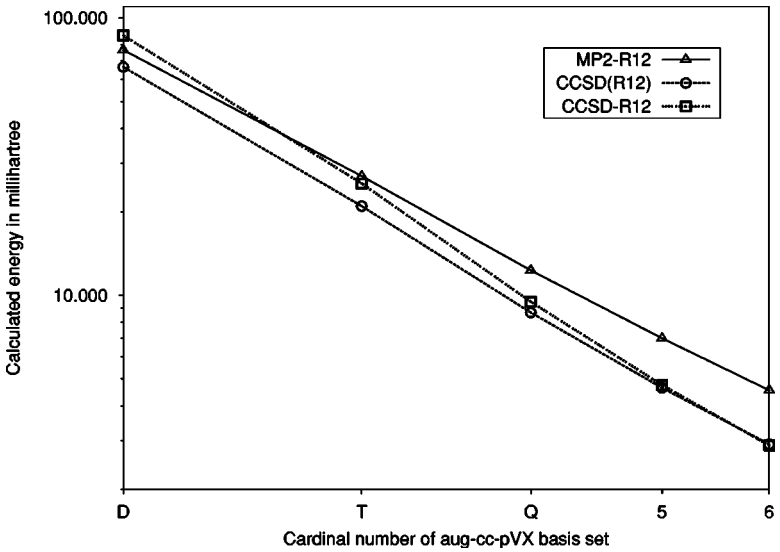


FIG. 3. Calculated ΔR12 contributions for HF in mE_h, plotted using a double logarithmic scale.

less problematic insertions of the resolution of the identity are required than for the full CCSD-R12 approach. The CCSD(R12) model therefore holds promise for significant savings in computing time, because the (auxiliary) basis sets can be chosen smaller than for the CCSD-R12 approach.

IV. RESULTS AND DISCUSSION

For a selected set of atoms and molecules, we first investigate the performance of the CCSD(R12) and CCSD-R12 models in aug-cc-pVXZ basis sets with X=D, T, Q, 5, and 6. The corresponding results are presented in Tables I–III. The general trends, observed for all systems, are depicted in Figs. 1–3.

The improved convergence with R12 terms in comparison with the conventional CCSD model is clearly seen. For basis sets of triple-zeta quality or lower, the results of the CCSD(R12) model are significantly different from those of the CCSD-R12 model. The omitted terms are not negligible in a small basis. Nevertheless, the CCSD(R12) correlation energies are in any case lower than those of the conventional CCSD approach. In basis sets of quadruple-zeta quality or higher, the differences between the CCSD(R12) and CCSD-R12 models decrease rapidly. As anticipated, the commutators $[\bar{\hat{\Phi}},\hat{T}_{2'}]$ and $[[\bar{\hat{\Phi}},\hat{T}_{2'}],\hat{T}_{2'}]$ can be neglected in a basis set of this quality for the investigated atoms and molecules.

In Tables I–III, the ΔR12 contributions are listed. These are the energy differences between the conventional models and the corresponding R12 models. Generally, the ΔR12(CCSD-R12) contribution is larger than ΔR12(CCSD(R12)), but the opposite is observed for the aug-cc-pV6Z basis. It seems that the simplified CCSD(R12) model overestimates somewhat the magnitude of the R12 contributions close to the basis-set limit.

Next, we compare the R12 correction as obtained at the CCSD(R12) level with the corresponding correction at the MP2-R12 level. In previous work, we have proposed the so-called MP2-limit correction, which consists of adding R12 corrections as obtained at the MP2-R12 level to conventional coupled-cluster energies.[34] We observe in the present work that this MP2-limit correction seems appropriate in small basis sets but inappropriate in larger sets. At the MP2-R12 level, the magnitude of the basis-set incompleteness cor-

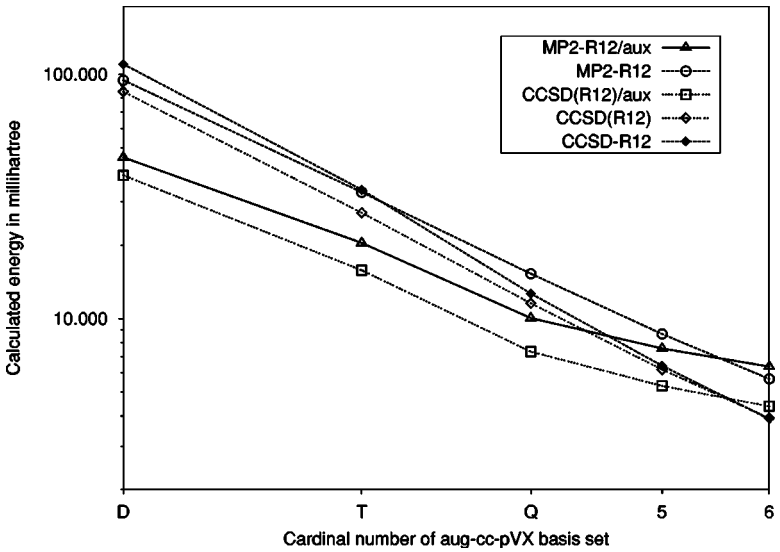


FIG. 4. Calculated ΔR12 contributions for Ne in mE_h, using a 19*s*14*p*8*d*6*f*4*g*3*h*2*i* basis as auxiliary basis, plotted using a double logarithmic scale.

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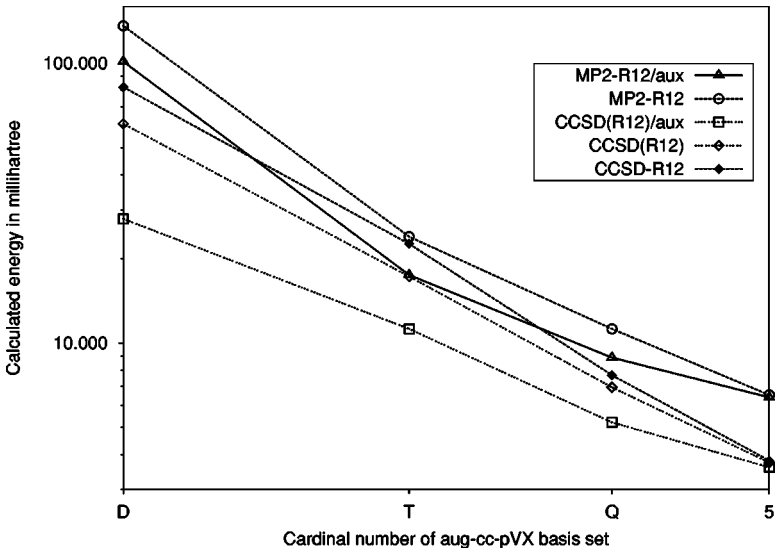


FIG. 5. Calculated ΔR12 contributions for N_2 in mE_h, using a 19*s*14*p*8*d*6*f*4*g*3*h*2*i* basis as auxiliary basis, plotted using a double logarithmic scale.

rection is overestimated significantly in a large basis. In particular in the highly accurate aug-cc-pV5Z and aug-cc-pV6Z basis sets, ΔR12(MP2-R12) is often more than a factor of 2 larger than the R12 correction calculated by the CCSD(R12) or CCSD-R12 aproaches. Since the R12 correction is a measure for the basis-set error in a conventional coupled-cluster calculation, these results imply that the basis-set error of highly correlated methods [e.g., CCSD or CCSD(T)] can be approximated by an MP2-correction only for small basis sets (up to about triple-zeta quality), but that such estimates will fail completely for more accurate basis sets. This observation supports the use of different extrapolation formulas for MP2 and coupled-cluster calculations.[35]

A comparison between the energy contributions from the $\hat{T}_1$ and $\hat{T}_2$ **(**$E(\hat{T}_1,\hat{T}_2)$**)** and the $\hat{T}_{2'}$ amplitudes **(**$E(\hat{T}_{2'})$**)** is given in Tables IV–VI, together with the ΔR12 contributions of the CCSD(R12) and CCSD-R12 models. The conventional CCSD correlation energy is given as $E_{\mathrm{CCSD}}-E_{\mathrm{SCF}}$. The results for $E(\hat{T}_1,\hat{T}_2)$ are not identical with the conventional correlation energy. They are smaller due to the coupling with $\hat{T}_{2'}$. $E(\hat{T}_{2'})$ is consistently larger than ΔR12 for both models, but the differences are not systematic. The results get closer to $E_{\mathrm{CCSD}}-E_{\mathrm{SCF}}$ with increasing basis sets. Starting with quadruple-zeta basis sets, the $E(\hat{T}_1,\hat{T}_2)$ contributions of the CCSD(R12) model are nearly identical with those of the CCSD-R12 model. $E(\hat{T}_{2'})$ decreases rapidly for larger basis sets for all investigated cases. For quadruple-zeta basis sets, the differences between CCSD(R12) and CCSD-R12 are below one mE_h for the investigated molecules, and they decrease quickly with inceasing quality of the orbital basis.

In Tables VII and VIII, a comparison of ground-state energies of different molecules and models close to the basis-set limit is presented. Here, the behavior of the approximate (R12) treatment of the R12 doubles is investigated in connection with perturbative corrections for connected triple excitations. As expected, the total energies obtained with the approximate (R12) models are below those of the -R12 methods. The differences are in the order of one mE_h, that is, negligible.

In Tables IX–XI, the same set of molecules as in Tables

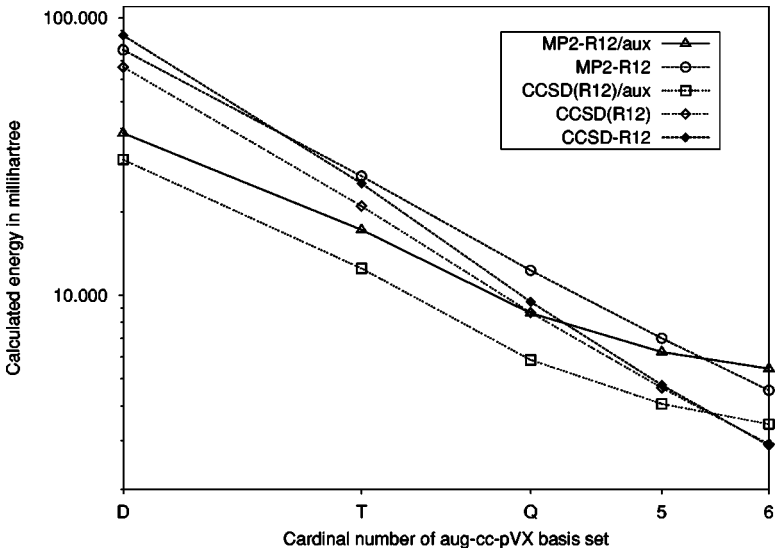


FIG. 6. Calculated ΔR12 contributions for HF in mE_h, using a 19*s*14*p*8*d*6*f*4*g*3*h*2*i* basis (9*s*6*p*4*d*3*f*2*g* for H) as auxiliary basis, plotted using a double logarithmic scale.

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I–III is investigated using a 19*s*14*p*8*d*6*f*4*g*3*h*2*i* basis (9*s*6*p*4*d*3*f*2*g* for H) as auxiliary basis. Since it is not possible to perform the same calculations with the DIRCCR12-OS program, we cannot compare these results with the full CCSD-R12 model. However, if we compare with the results from Tables I–III, it appears that the ΔR12 contributions from the MP2-R12 and the CCSD(R12) calculations are considerably smaller than those contributions that were obtained in calculations where the orbital basis was used as auxiliary basis. Thus, by virtue of error cancellation, the CCSD(R12) method without auxiliary basis yields lower correlation energies than the corresponding method that utilizes an auxiliary basis. This trend is illustrated in Figs. 4–6.

V. CONCLUSIONS

A linear-r_{12} coupled-cluster model, denoted CCSD(R12), has been proposed. A comparison with the full CCSD-R12 approach shows that in a large basis (quadruple-zeta quality or better) the differences between the CCSD(R12) and CCSD-R12 methods are insignificant. In a small basis (triple-zeta quality or less) the differences are larger, but also in these basis sets we prefer the CCSD(R12) model over the original CCSD-R12 method, because the implementation of the CCSD(R12) equations involves less completeness insertions than the CCSD-R12 model. In a small basis, these completeness insertions may be inaccurate, and should be avoided if possible. In large basis sets, we have obtained CCSD(R12) energies that are slightly lower than the energies from the CCSD-R12 model.

For smaller basis sets, one might wish to estimate the CCSD-R12 energy by adding the ΔR12(MP2-R12) correction to the conventional CCSD result. However, this approach, denoted MP2-limit correction in the literature,[34] overestimates the magnitude of the R12 correction in larger basis sets, starting with the quadruple-zeta level. Adding MP2 basis-set corrections to conventional CCSD results can fail completely. It is much more reliable and accurate to perform a CCSD(R12) calculation instead.

Perturbative corrections for connected triple excitations can be computed as usual from the standard singles and doubles amplitudes. Hence, CCSD(T)(R12) and CCSD[T](R12) computations can be performed in exactly the same manner (at least for Ansatz 1) as the corresponding CCSD(T)-R12 and CCSD[T]-R12 calculations.

ACKNOWLEDGMENTS

This research has been supported by the Deutsche Forschungsgemeinschaft (DFG) through the Center for Functional Nanostructures (CFN, Project No. C2.3). The authors thank Jozef Noga for making possible the CCSD(R12) calculations with the DIRCCR12-OS program.

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