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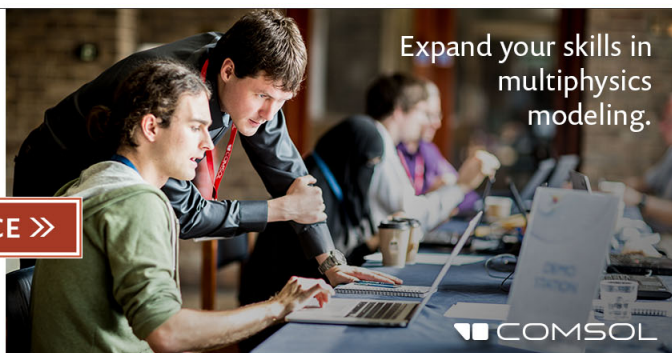
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Explicitly correlated coupled-cluster singles and doubles method based on complete diagrammatic equations

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The explicitly correlated coupled-cluster singles and doubles (CCSD-R12) and related methods—its linearized approximation CCSD(R12) and explicitly correlated second-order Møller–Plesset perturbation method—have been implemented into efficient computer codes that take into account point-group symmetry. The implementation has been largely automated by the computerized symbolic algebra SMITH that can handle complex index permutation symmetry of intermediate tensors that occur in the explicitly correlated methods. Unlike prior implementations that invoke the standard approximation or the generalized or extended Brillouin condition, our CCSD-R12 implementation is based on the nontruncated formalisms [T. Shiozaki *et al.*, Phys. Chem. Chem. Phys. **10**, 3358 (2008)] in which every diagrammatic term that arises from the modified *Ansatz 2* is evaluated either analytically or by the resolution-of-the-identity insertion with the complementary auxiliary basis set. The CCSD-R12 correlation energies presented here for selected systems using the Slater-type correlation function can, therefore, serve as benchmarks for rigorous assessment of other approximate CC-R12 methods. Two recently introduced methods, CCSD(R12) and CCSD(2)_{RTZ}, are shown to be remarkably accurate approximations to CCSD-R12. © 2008 American Institute of Physics. [DOI: 10.1063/1.2967181]

While the importance of the explicit inclusion of the interelectronic degrees of freedom (r_{12}) in the wave function expansion was realized by Hylleraas¹ as early as in 1929, only recently such expansions have become applicable to general polyelectron wave functions.² The methods pioneered by Kutzelnigg,^{3,4} referred simply as the R12 methods (the term which we use, in this work, for both the R12 methods with linear correlation factors and the F12 methods with nonlinear correlation functions because they can be handled identically by our algorithms given appropriate molecular integrals) are among the most practical such methods primarily by virtue of the use of the resolution-of-the-identity (RI) approximation to evaluate many-electron molecular integrals.⁵ Until recently, the development of the R12 methods has concentrated largely on the second-order Møller–Plesset perturbation method (MP2-R12), which has also been the first to adopt the Slater-type correlation function⁶ and the separate basis sets for orbital expansions and the RI insertion.^{7–9} With these techniques, MP2-R12 typically recovers 99% of the MP2 correlation energy in the complete basis set (CBS) limit using as small as a triple- ζ correlation-consistent orbital basis set (OBS).^{4,10,11} Since the majority of the error in MP2-R12 is ascribed to the higher-order electron-correlation effects rather than those from the basis set incompleteness, the R12 technique should be combined

with more sophisticated electron-correlation treatments such as the coupled-cluster (CC) method.

The explicitly correlated CC methods (CC-R12) have been first studied by Noga *et al.*^{12–16} within the so-called standard approximation (SA). The SA uses the same basis set for the orbital expansion and the RI insertion and simplifies the equations dramatically, but it requires a large primitive basis to achieve satisfactory accuracy. To alleviate this shortcoming, Klopper and co-workers^{17–20} have introduced an approximation to CC-R12 with singles and doubles (CCSD-R12) called CCSD(R12) and implemented it without the SA. Adler *et al.*²¹ have proposed an even simpler method. Alternatively, Valeev and co-workers^{22–24} introduced CCSD(2)_{R12} and CCSD(2)_{RTZ} methods, which treat r_{12} -dependent terms through Löwdin perturbation theory and do not depend on the SA. A further simplification can be made by holding the geminal t amplitudes fixed at their limiting values suggested by the first-order cusp conditions,^{23,25,26} as in Ten-no's^{9,27} diagonal orbital-invariant MP2-R12 approach.

The performance of the aforementioned simplifications can be assessed rigorously by the comparison with an unabridged implementation of CCSD-R12 that does not rely on a drastic truncation of diagrammatic equations such as the SA, generalized and extended Brillouin conditions (GBC and EBC),⁵ or other approximations mentioned above. To this date, however, an implementation of unabridged CCSD-R12 equations, let alone its higher-ranked analogs, has not been reported due to the immense complexity of such undertak-

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ings. In this Communication, we present an efficient implementation of CCSD-R12 based on nontruncated equations and computational sequences reported by us recently,²⁸ which retain all diagrammatic contributions that arise from the modified *Ansatz* 2 and are evaluated either analytically or by invoking the RI insertion using a complementary auxiliary basis set (CABS). We employ the computerized, automated approach to implementing the exceedingly complicated computational sequences of CCSD-R12 and also its related methods, i.e., MP2-R12 and CCSD(R12), and arrive at computer codes that take advantage of point-group symmetry and are applicable to closed- and open-shell systems. With this, we document the benchmark correlation energies of CCSD-R12 for selected atomic and molecular systems with various OBS and CABS, which we use to demonstrate the remarkable accuracy of two of the approximate treatments, i.e., CCSD(R12) of Fliegl *et al.*²⁰ and CCSD(2)_{RI2} of Valeev.⁸

The similarity-transformed Hamiltonian of CCSD-R12 is defined as

$$\bar{H} = \exp(-\hat{S})\hat{H}_N \exp(\hat{S}) = [\hat{H}_N \exp(\hat{S})]_C, \quad (1)$$

$$\hat{H}_N = f_{\lambda}^{\kappa}\{\kappa^{\dagger}\lambda\} + \frac{1}{4}v_{\mu\nu}^{\kappa\lambda}\{\kappa^{\dagger}\lambda^{\dagger}\nu\mu\}, \quad (2)$$

where \hat{H}_N is the usual normal-ordered Hamiltonian, and f and v denote Fock and antisymmetrized two-electron integral matrices, respectively. The following index notation is used: a and b label unoccupied orbitals in the OBS, i, j, k , and l label occupied orbitals in the OBS, p and q label any orbitals in the OBS, α, β, γ , and δ label unoccupied orbitals in the CBS, α' labels unoccupied orbitals in the CBS but not in the OBS, and $\kappa, \lambda, \mu, \nu$ label any orbitals in the CBS. The bracket “[$\cdot\cdot\cdot$]_C” designates the diagrammatic connectedness of the operators in it, and the curly brackets indicate that the creation and annihilation operators are in the normal order. In Eq. (2) and hereafter, repeated indices imply the summation over them without any restrictions. The cluster excitation operator \hat{S} in Eq. (1) is

$$\hat{S} = t_i^a\{a^{\dagger}i\} + \frac{1}{4}t_{ij}^{ab}\{a^{\dagger}b^{\dagger}ji\} + \frac{1}{8}F_{kl}^{\alpha\beta}t_{ij}^{kl}\{\alpha^{\dagger}\beta^{\dagger}ji\}, \quad (3)$$

with

$$F_{kl}^{\alpha\beta} = \begin{cases} r_{kl}^{\alpha\beta} & \text{if } \phi_{\alpha} \in \{\phi_a\} \text{ or } \phi_{\beta} \in \{\phi_a\} \\ 0 & \text{otherwise,} \end{cases} \quad (4)$$

where $r_{kl}^{\alpha\beta} \equiv \langle \phi_{\alpha}\phi_{\beta} | F_{12} | \phi_k\phi_l \rangle$ is an antisymmetrized integral of the correlation factor (F_{12}) and the strong orthogonality projector of the modified *Ansatz* 2 introduced by Valeev⁸ is implicit in Eq. (4).

The correlation energy E_0 and unknown amplitudes in Eq. (3) are determined by solving what correspond to the usual energy and amplitude equations of CCSD and the so-called geminal t amplitude equation, which is unique to CCSD-R12. SMITH derives these equations and optimized programmable computational sequences using the three-step procedure that has been described in detail in Ref. 28. Here we will only point out the two essential details that distinguish SMITH from its predecessors such as TCE.²⁹ First, the

following “special” intermediate tensor quantities (intermediates):

$$V_{ij}^{pq} = \frac{1}{2}v_{\alpha\beta}^{pq}F_{ij}^{\alpha\beta}, \quad (5)$$

$$X_{ij}^{kl} = \frac{1}{2}F_{\alpha\beta}^{kl*}F_{ij}^{\alpha\beta}, \quad (6)$$

$$B_{ij}^{kl} = F_{\alpha\beta}^{kl*}f_{\gamma}^{\alpha\beta}F_{ij}^{\beta\gamma}, \quad (7)$$

$$P_{ij}^{kl} = \frac{1}{4}F_{\alpha\beta}^{kl*}v_{\gamma\delta}^{\alpha\beta}F_{ij}^{\gamma\delta}, \quad (8)$$

require special handling because their evaluation involves integration of several nonstandard two-electron operators. Some of these integrals exact the *analytical* compensation of the $1/r_{12}$ singularity in the Hamiltonian by the correlation factor F_{12} , which is the reason for the accelerated basis set convergence of the CCSD-R12 correlation energy. Second, sums over indices (α, β , etc.) that span infinite ranges are approximated by sums over the corresponding CABS indices of finite ranges. This step is called the RI insertion with the CABS and yields programmable expressions involving tensors with finite index ranges only.

All input tensors, i.e., intermediates in Eqs. (5)–(8) along with ordinary integrals of the correlation factor F , Fock f , and Coulomb v operators, and the spin and spatial symmetry of spin orbitals are furnished by the MPQC program of Janssen *et al.*³⁰ In this program, intermediate B is evaluated in the so-called approximation C of Kedzuch *et al.*,³¹ which does not rely on GBC or EBC, and intermediates V and X by the methods described elsewhere.^{4,8} Intermediate P does not appear in MP2-R12 or various approximate CCSD-R12 methods implemented previously, but it does in the nontruncated CCSD-R12 method (as well as in the CI-R12 and MP n -R12 methods³²). We have added a computer code to MPQC that evaluates P using the CABS approach as follows:

$$P_{ij}^{kl} = \left(\frac{F_{12}^2}{r_{12}} \right)_{ij}^{kl} - \frac{1}{2} \left(\frac{F_{12}}{r_{12}} \right)_{pq}^{kl} r_{ij}^{pq} - \left(\frac{F_{12}}{r_{12}} \right)_{\alpha\alpha'}^{kl} r_{ij}^{\alpha\alpha'} - \frac{1}{2} v_{pq}^{kl} r_{ij}^{pq} - v_{\alpha\alpha'}^{kl} r_{ij}^{\alpha\alpha'}. \quad (9)$$

We have also developed a code that performs an automated code synthesis of the computational sequences of CC-R12, which involve intermediates with more complicated index permutation symmetry than those found in conventional CC. Unlike its predecessor TCE, which can only handle certain limited *Ansätze* and restricted orders of tensor contractions that lead to intermediates with *a priori* known high index permutation symmetry,^{29,33,34} SMITH can accommodate virtually any *Ansätze* defined by expectation values of any number of excitation, de-excitation, and interaction operators in a Slater determinant. The index permutation symmetry of an intermediate is determined on a case-by-case basis by SMITH by analyzing the definition of the intermediate as a product of input tensors and applying the general rules given in Ref. 28. SMITH uses this information to determine the optimal data layout and contraction algorithms individually for each intermediate and its contraction. The synthesized codes are compiled with NWChem,³⁵ reusing some of the algo-

TABLE I. MP2 and CCSD valence correlation energies (E_{corr}) of Ne in mE_h . The Slater geminal with $\gamma=1.5$ has been used.

OBS/CABS	MP2		MP2-R12		CCSD		CCSD(2) $_{\text{RT}2}$ ^a		CCSD(R12)		CCSD-R12	
	E_{corr}	%	E_{corr}	%	E_{corr}	%	E_{corr}	%	E_{corr}	%	E_{corr}	%
aug-cc-pVDZ/K2	-206.87	64.6	-312.72	97.7	-210.15	66.6	-311.31	98.6	-306.22	97.0	-306.10	97.0
aug-cc-pVTZ/K2	-272.52	85.1	-316.54	98.9	-274.09	86.8	-310.32	98.3	-311.64	98.7	-311.15	98.6
aug-cc-pVQZ/K2	-297.24	92.8	-318.60	99.5	-297.76	94.3	-313.54	99.3	-314.37	99.6	-313.79	99.4
aug-cc-pV5Z/K2	-307.97	96.2	-319.65	99.8	-306.79	97.2	-315.32	99.9	-315.26	99.9	-314.75	99.7
aug-cc-pV6Z/K2	-312.87	97.7	-319.87	99.9	-310.61	98.4	-315.47	99.9	-315.54	99.9	-315.31	99.9
aug-cc-pVDZ/K3	-206.87	64.6	-312.68	97.7	-210.15	66.6	-311.31	98.6	-306.19	97.0	-306.52	97.1
aug-cc-pVTZ/K3	-272.52	85.1	-316.56	98.9	-274.09	86.8	-310.32	98.3	-311.66	98.7	-311.52	98.7
aug-cc-pVQZ/K3	-297.24	92.8	-318.62	99.5	-297.76	94.3	-313.56	99.3	-314.42	99.6	-314.10	99.5
aug-cc-pV5Z/K3	-307.97	96.2	-319.50	99.8	-306.79	97.2	-315.18	99.8	-315.27	99.9	-314.99	99.8
aug-cc-pV6Z/K3	-312.87	97.7	-319.93	99.9	-310.61	98.4	-315.59	100.0	-315.55	100.0	-315.27	99.9
aug-cc-pVDZ/K4	-206.87	64.6	-312.64	97.6	-210.15	66.6	-311.28	98.6	-306.15	97.0	-306.57	97.1
aug-cc-pVTZ/K4	-272.52	85.1	-316.54	98.9	-274.09	86.8	-310.33	98.3	-311.65	98.7	-311.57	98.7
aug-cc-pVQZ/K4	-297.24	92.8	-318.62	99.5	-297.76	94.3	-313.56	99.3	-314.42	99.6	-314.15	99.5
CBS limit	-320.2 ^b	100.0			-315.7 ^b	100.0						

^aComputed by MPQC (Ref. 30) and PS13 (Ref. 36) using the approach of Ref. 24.^bTaken from Ref. 22.

rithms and software interface of TCE (Ref. 29) and retrieving the tensors supplied by MPQC via a disk-based interface.

With SMITH, we have implemented the CCSD-R12 method that can exploit spin, real Abelian point-group symmetry and is applicable to closed- and open-shell molecules. Its computational cost exhibits the correct $O(n^6)$ dependence on the number of orbitals n . We have also implemented CCSD(R12) of Fliegl *et al.*,²⁰ which is a linearized approximation of CCSD-R12. The results of CCSD(2) $_{\text{RT}2}$ have been obtained by using a separate hand-coded implementation^{22–24} based on MPQC (Ref. 30) and PS13.³⁶ The CCSD-R12 equations are derived assuming neither GBC nor EBC,⁵ which is consistent with the way the special intermediate B (*vide supra*) is evaluated. CCSD(R12) is based on GBC according to its original definition by Fliegl *et al.*,²⁰ and CCSD(2) $_{\text{RT}2}$ uses both GBC and EBC. Although the effect of GBC is always marginal, that of EBC can be large³⁷ and the correlation energies obtained with EBC and nonlinear correlation factor are sometimes exceedingly low when a very small OBS is used.

In the iterative solution of conventional CC equations, t amplitudes are updated usually by the combination of standard Jacobi relaxation and the DIIS (direct inversion in the

iterative subspace) extrapolation.^{38,39} For the geminal t amplitude equation of CCSD-R12, we employ the following Jacobi relaxation:

$$\delta_{ij}^{kl} = [X_{kl}^{mn}(f_i^j + f_j^i) - B_{kl}^{mn}]^{-1} \delta_{ij}^{mn}, \quad (10)$$

which suggests an incremental change (δ_{ij}^{kl}) to the geminal amplitudes (t_{ij}^{kl}) from the residual (δ_{ij}^{mn}) in the geminal t amplitude equation. The inversion requires $O(n_h^8)$ arithmetic operations with n_h as the number of occupied spin orbitals, but its prefactor is so small that this step is in practice negligible in the overall computation. The benchmark valence electron-correlation energies of Ne, H₂O, and F₂ obtained by MP2, CCSD, and their R12 variants are compiled in Tables I and II. Geometries for H₂O and F₂ were taken from Ref. 22. Dunning's correlation-consistent basis sets, aug-cc-pVnZ ($n = \text{D, T, Q, 5, and 6}$), were used for OBS.⁴⁰ CABS were constructed from the 15s9p7d5f3g1h/9s6p4d3f2g, and 32s24p18d15f12g9h6i auxiliary basis sets^{7,41} (abbreviated by K2, K3, and K4, respectively) using the CABS+ approach.⁸ For the correlation factor in Eq. (4), we selected one Slater-type geminal,⁶ $F_{12} = \exp(-\gamma r_{12})$ with $\gamma = 1.5a_0^{-1}$,

TABLE II. MP2 and CCSD valence correlation energies (E_{corr}) of H₂O and F₂ in mE_h . The Slater geminal with $\gamma=1.5$ has been used.

OBS/CABS	MP2		MP2-R12		CCSD		CCSD(2) $_{\text{RT}2}$ ^a		CCSD(R12)		CCSD-R12		
	E_{corr}	%	E_{corr}	%	E_{corr}	%	E_{corr}	%	E_{corr}	%	E_{corr}	%	
H ₂ O	aug-cc-pVDZ/K3	-219.34	73.0	-294.38	98.0	-227.11	76.2	-291.51	97.9	-290.33	97.5	-289.86	97.3
	aug-cc-pVTZ/K3	-268.35	89.3	-298.31	99.3	-273.05	91.7	-295.42	99.2	-295.81	99.3	-295.40	99.2
	aug-cc-pVQZ/K3	-285.91	95.2	-299.72	99.8	-288.21	96.7	-297.40	99.8	-297.54	99.9	-297.23	99.8
	CBS limit	-300.4 ^b	100.0			-297.9 ^b	100.0						
F ₂	aug-cc-pVDZ/K3	-428.00	70.0	-599.89	98.1	-435.39	72.5	-592.20	98.5	-585.07	97.3	-584.83	97.3
	aug-cc-pVTZ/K3	-536.06	87.7	-606.43	99.2	-538.91	89.7	-594.54	98.9	-595.52	99.1	-594.98	99.0
	aug-cc-pVQZ/K3	-575.78	94.2	-609.54	99.7	-575.10	95.7	-598.94	99.7	-599.69	99.8	-599.01	99.7
	CBS limit	-611.4 ^b	100.0			-601.0 ^b	100.0						

^aComputed by MPQC (Ref. 30) and PS13 (Ref. 36) using the approach of Ref. 24.^bTaken from Ref. 22.

approximated by a linear combination of six Gaussian functions.²²

An analysis of the benchmark data reveals that the CCSD-R12 method recovers typically 97%, 99%, and virtually 100% of the CBS CCSD correlation energies with aug-cc-pVDZ, TZ, and QZ, respectively. They are a radical improvement over the corresponding figures in conventional CCSD (roughly 70%, 90%, and 95%, respectively) and only slightly worse than their MP2-R12 counterparts. In all cases the CCSD-R12 correlation energy approaches the CBS limit from above as the OBS is increased. Although even the non-truncated CCSD-R12 method is not strictly variational due to the use of the RI approximation, in practice it provides an upper bound to the exact CCSD energy even with the smallest CABS. In contrast, the CCSD-R12 method using SA can produce energies below the CBS limit when the OBS is too small.¹⁶

The accuracy of the RI approximation was tested for Ne by expanding the CABS basis toward completeness. It can be seen that the CCSD-R12 energies are marginally more sensitive to the size of the CABS than CCSD(R12), CCSD(2)_{RI2}, or MP2-R12 because certain terms in CCSD-R12 geminal amplitude equations require as many as four insertions of CABS compared to only three in the simpler methods. Nevertheless, the error due to the RI approximation is always significantly smaller than the residual basis set error of the CCSD-R12 energy even when the smallest CABS (K2) is used. This is encouraging because CCSD-R12 involves the arithmetic operations that increase as cubic power of the number of CABS. While the operation costs of CCSD and CCSD-R12 both exhibit the $O(n^6)$ dependence on the size of the OBS, the cubic dependence of the cost on the CABS size makes CCSD-R12 at least an order of magnitude more costly than CCSD with the same OBS. However, CCSD-R12 with aug-cc-pVDZ and TZ can recover nearly the same proportion of CBS correlation energies as CCSD with aug-cc-pV5Z and 6Z, respectively, and the vastly superior cost performance of CCSD-R12 over CCSD is evident.

CCSD-R12 is also the rigorous benchmark to gauge the performance of the more approximate CC-R12 methods. The comparison between CCSD-R12 and CCSD(R12) confirms that the latter works remarkably well, yielding correlation energies typically within $1 mE_h$ of the corresponding CCSD-R12 values at a small fraction of the computational cost of CCSD-R12. An even less expensive, perturbative approximation to CCSD-R12, CCSD(2)_{RI2},²² is also extremely accurate, particularly when aug-cc-pVTZ or a larger OBS is used. The nonessential assumption of EBC in CCSD(2)_{RI2} tends to make the correlation energies obtained with the aug-cc-pVDZ basis artificially too low.

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