Simple coupled-cluster singles and doubles method with perturbative inclusion of triples and explicitly correlated geminals: The $\mathrm{CCSD(T)_{R\bar{1}2}}$ model

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Simple coupled-cluster singles and doubles method with perturbative inclusion of triples and explicitly correlated geminals: The CCSD(T)$_{\overline{R12}}$ model

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To approach the complete basis set limit of the "gold-standard" coupled-cluster singles and doubles plus perturbative triples [CCSD(T)] method, we extend the recently proposed perturbative explicitly correlated coupled-cluster singles and doubles method, CCSD(2)$_{\overline{R12}}$ [E. F. Valeev, Phys. Chem. Chem. Phys. **8**, 106 (2008)], to account for the effect of connected three-electron correlations. The *natural* choice of the zeroth-order Hamiltonian produces a perturbation expansion with rigorously separable second-order energy corrections due to the explicitly correlated geminals and conventional triple and higher excitations. The resulting CCSD(T)$_{\overline{R12}}$ energy is defined as a sum of the standard CCSD(T) energy and an amplitude-dependent geminal correction. The method is technically very simple: Its implementation requires no modification of the standard CCSD(T) program and the formal cost of the geminal correction is small. We investigate the performance of the open-shell version of the CCSD(T)$_{\overline{R12}}$ method as a possible replacement of the standard complete-basis-set CCSD(T) energies in the high accuracy extrapolated *ab initio* thermochemistry model of Stanton *et al.* [J. Chem. Phys. **121**, 11599 (2004)]. Correlation contributions to the heat of formation computed with the new method in an aug-cc-pCVXZ basis set have mean absolute basis set errors of 2.8 and 1.0 kJ/mol when X is T and Q, respectively. The corresponding errors of the standard CCSD(T) method are 9.1, 4.0, and 2.1 kJ/mol when X=T, Q, and 5. Simple two-point basis set extrapolations of standard CCSD(T) energies perform better than the explicitly correlated method for absolute correlation energies and atomization energies, but no such advantage found when computing heats of formation. A simple Schwenke-type two-point extrapolation of the CCSD(T)$_{\overline{R12}}$/aug-cc-pCVXZ energies with X=T,Q yields the most accurate heats of formation found in this work, in error on average by 0.5 kJ/mol and at most by 1.7 kJ/mol. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2939577]

I. INTRODUCTION

The current view of the quantum many-electron problem is that its efficient solution is only possible with the explicit use of the interparticle coordinates r_{ij}.[1,2] Not only can the *Coulomb hole*[3] of the exact wave function be modeled more efficiently in terms of r_{ij} (Ref. 4) but also the Kato–Pack–Brown cusp conditions[5,6] can be emulated. Compared to the standard "r_{ij}-free" wave functions, the explicitly correlated counterparts are unencumbered by the need for empirical extrapolation schemes and can attain much smaller basis set errors. R12 (or F12) methods[7–9] of Kutzelnigg et al. are currently the only viable explicitly correlated approaches generally applicable to systems of chemical interest. Their efficiency stems from the use of the resolution of the identity (RI) to factorize the many-electron integrals that appear in such theories. Thus only up to two-electron integrals need to be evaluated in closed form. The original R12 formulation utilized the orbital (Hartree–Fock) basis to approximate the one-particle identity operator.[8,10] Modern R12 technology uses a separate basis for the RI, either composed of Gaussian orbitals,[11,12] grids,[13] or both.[14]

The most widely studied R12 method is the explicitly correlated second-order Møller–Plesset energy (MP2-R12). Although the MP2 correlation energies lack accuracy needed for many chemical applications, the relative simplicity of the MP2-R12 method stimulated rapid development of the basic R12 methodology to its modern state, including the development of RI (Refs. 11–13) and density fitting techniques,[15–17] investigation of correlation factors,[18–23] ansätze,[13,18,22–24] basis sets,[25–27] and the sundry elaborate but necessary R12 technicalia.[11,13,20,28–30]

Noga *et al.* were first to report[31–33] R12 versions of the coupled-cluster method.[34–38] The CC-R12 method employs the wave operator ansatz that includes the formal double excitations into the geminal pairs in addition to the conventional excitations,

$$\Psi = e^{\hat{T}}|0\rangle \tag{1}$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_\gamma, \tag{2}$$

where we introduced the standard cluster operators,

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$$\hat{T}_1 = t_a^i \tilde{a}_i^a, \quad \hat{T}_2 = \frac{1}{(2!)^2} t_{ab}^{ij} \tilde{a}_{ij}^{ab}, \quad \text{etc.,} \tag{3}$$

as well as the geminal cluster operator,

$$\hat{T}_\gamma = \frac{1}{(2!)^2} t_{xy}^{ij} \tilde{\gamma}_{ij}^{xy}, \tag{4}$$

defined in terms of geminal excitation generators,

$$\tilde{\gamma}_{ij}^{xy} = \frac{1}{2} \bar{R}_{\alpha\beta}^{xy} \tilde{a}_{ij}^{\alpha\beta}. \tag{5}$$

The latter involve a correlation factor $f(r_{12})$ augmented by a strong orthogonality projector $\hat{Q}_{12}$,

$$
\begin{aligned}
R_{\alpha\beta}^{xy} &\equiv \langle \alpha\beta | \hat{Q}_{12} f(r_{12}) | xy \rangle \\
&= \begin{cases} 0, & \text{if both } \alpha \text{ and } \beta \text{ are in the orbital basis} \\ r_{\alpha\beta}^{xy} \equiv \langle \alpha\beta | f(r_{12}) | xy \rangle, & \text{otherwise.} \end{cases}
\end{aligned}
\tag{6}
$$

[In this paper we will denote the occupied spin orbitals as i,j,k,l,m,n, the unoccupied (*virtual*) spin orbitals representable in the Hartree–Fock basis set as a,b,c,d, and any Hartree–Fock orbital as p,q,r,s. $\alpha,\beta,\gamma,\delta$ will stand for *any* virtual orbital and κ,λ,μ,ν will denote any spin orbital. We will denote the virtual spin orbitals not representable in the Hartree–Fock basis as $\alpha',\beta',\gamma',\delta'$. Finally, indices x,y will represent orbitals from the geminal generating set, which in this work will include all active occupied orbitals (this is known as *kl*-ansatz).] The geminal-producing orbital pair xy is usually a product of any occupied orbitals ("*kl*-ansatz"), but any set of orbitals will suffice.[22] Equation (6) corresponds to the definition $\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2$, where $\hat{O}$ and $\hat{V}$ are the projectors on the occupied and virtual orbital spaces. Such choice ensures both strong orthogonality and the orthogonality of the geminal doubles to the conventional double excitations.

The CC-R12 energy is obtained the reference expectation value of the similarity-transformed operator $\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}} = e^{-\hat{T}} (\hat{F} + \hat{W}) e^{\hat{T}}$, where $\hat{F}$ and $\hat{W}$ are the Fock and fluctuation operators, respectively,

$$
\begin{aligned}
E &= \langle 0 | \bar{H} | 0 \rangle \\
&= \langle 0 | \hat{H} | 0 \rangle + \langle 0 | [\hat{F}, \hat{T}] | 0 \rangle + \langle 0 | [\hat{W}, \hat{T}] | 0 \rangle \\
&\quad + \langle 0 | \tfrac{1}{2} [[\hat{W}, \hat{T}], \hat{T}] | 0 \rangle \\
&= E_0 + t_a^i F_i^a + \tfrac{1}{4} t_{ab}^{ij} \bar{g}_{ij}^{ab} + \tfrac{1}{8} t_{xy}^{ij} \bar{R}_{\alpha\beta}^{xy} \bar{g}_{ij}^{\alpha\beta} + \tfrac{1}{2} t_a^i t_b^j \bar{g}_{ij}^{ab}.
\end{aligned}
\tag{7}
$$

Corresponding projections onto singly, doubly, and higher-rank excited determinants,

$$\left| {}_i^a \right\rangle \equiv \tilde{a}_i^a | 0 \rangle, \tag{8}$$

$$\left| {}_{ij}^{ab} \right\rangle \equiv \tilde{a}_{ij}^{ab} | 0 \rangle, \tag{9}$$

etc., as well as the geminal functions produced by the geminal generators [Eq. (5)]

$$\left| {}_{ij}^{xy} \right\rangle \equiv \tilde{\gamma}_{ij}^{xy} | 0 \rangle, \tag{10}$$

determine the conventional amplitudes

$$0 = \left\langle {}_i^a \middle| \bar{H} \middle| 0 \right\rangle, \tag{11}$$

$$0 = \left\langle {}_{ij}^{ab} \middle| \bar{H} \middle| 0 \right\rangle, \tag{12}$$

etc., and the geminal cluster amplitudes,

$$0 = \left\langle {}_{ij}^{xy} \middle| \bar{H} \middle| 0 \right\rangle. \tag{13}$$

Compared to the standard CC methods, the CC-R12 method requires solving the additional set of equations [Eq. (13)] as well as more involved standard amplitude equations due to the geminal terms. Although for high-rank CC methods the addition of the geminal terms does not worsen the formal scaling with the size of the system, the cost estimate for the CCSD-R12 method is significantly greater than that of the standard CCSD counterpart.[39] Nevertheless, Noga *et al.* first implemented a full CCSD-R12 method using the standard approximation[8] (SA) which simplified the theory substantially at the cost of demanding an orbital basis saturated to at least $3L_{occ}$, where L_{occ} is the maximum angular momentum of occupied atomic orbitals. The computational and, especially, programming costs of the unabridged CC-R12 methods are very high. Automated determination of optimized computational pathways for ground and excited-state CC-R12 method will be soon discussed elsewhere by Shiozaki *et al.*[39]

At least for the foreseeable future, its high computational and implementational complexities are likely to limit the full CC-R12 method to benchmark computations on small systems, and the development of simplified CC-R12 methods has been the focus of intense recent activity. First, Klopper and co-workers proposed an approximation to the full CCSD-R12 method, dubbed the CCSD(R12) model.[40–42] The (R12) approximation defines the geminal amplitude equations to contain the fluctuation potential transformed using only the conventional excitation operators (similar approximation is involved in CC*n* models[43]) as well as dropping all terms quadratic in the geminal amplitude from the T_2-amplitude equations. A more radical approximation to the CC-R12 method is the very recent CCSD(T)-F12h group of methods of Adler *et al.*,[44] which can be considered a radically simplified version of the diagonal orbital-invariant CCSD(F12) approach of Tew *et al.*[42]

The common feature of the above methods is that the geminal terms are introduced *a priori* via the CC-R12 wave function ansatz. One of us recently explored an approach in which the geminal terms are included *a posteriori*, as a perturbation to the standard CC wave function.[45,46] This approach is technically attractive since the coupled-cluster amplitude equations are unmodified. The main objective of this paper is to demonstrate how the CCSD(2)$_{R12}$ method can be extended to include the effect of higher excitations, also perturbatively. The result is a perturbative, explicitly correlated version of the highly accurate CCSD(T) method, dubbed the CCSD(T)$_{\overline{R12}}$ approach. We have tested the efficiency of the method by computing the CCSD(T) contributions to the at-

omization energies and heats of formations of the standard high-accuracy extrapolated *ab initio* thermochemistry (HEAT) set of molecules.[47–49]

II. FORMALISM

Consider the matrix representation of the CCSD Hamiltonian, $\bar{H}=e^{-\hat{T}_1-\hat{T}_2}\hat{H}e^{\hat{T}_1+\hat{T}_2}$, in a basis that includes the *reference* and *external* spaces, P and Q,

$$\bar{\mathbf{H}} = \begin{pmatrix} \bar{\mathbf{H}}_{PP} & \bar{\mathbf{H}}_{PQ} \\ \bar{\mathbf{H}}_{QP} & \bar{\mathbf{H}}_{QQ} \end{pmatrix}, \tag{14}$$

where space P includes the reference determinant 0, singles S, and doubles D and space Q may include the explicitly correlated geminal substitutions Γ as well as standard triples T and higher excitations. Perturbation expansion of the exact eigenvalues and eigenvectors of $\bar{H}$ can be constructed straightforwardly by Löwdin partitioning.[50] We first decompose the Hamiltonian into the zeroth- and first-order components,

$$\bar{\mathbf{H}}^{(0)} = \begin{pmatrix} \bar{\mathbf{H}}_{PP} & 0 \\ 0 & \bar{\mathbf{H}}_{QQ}^{(0)} \end{pmatrix}, \tag{15}$$

$$\bar{\mathbf{H}}^{(1)} = \begin{pmatrix} 0 & \bar{\mathbf{H}}_{PQ} \\ \bar{\mathbf{H}}_{QP} & \bar{\mathbf{H}}_{QQ}^{(1)} \end{pmatrix}, \tag{16}$$

where $\bar{\mathbf{H}}_{QQ} = \bar{\mathbf{H}}_{QQ}^{(0)} + \bar{\mathbf{H}}_{QQ}^{(1)}$. The zeroth-order left- and right-hand eigenvectors are defined in terms the ground-state EOM-CCSD eigenvectors, $\mathcal{L}$ and $\mathcal{R}$, as

$$\mathbf{L}^{(0)} = \begin{pmatrix} \mathcal{L} \\ \mathbf{0} \end{pmatrix}, \tag{17}$$

$$\mathbf{R}^{(0)} = \begin{pmatrix} \mathcal{R} \\ \mathbf{0} \end{pmatrix}. \tag{18}$$

The zeroth-order energy is, then, simply the ground-state CCSD energy. The first-order energy vanishes, whereas the second-order energy contribution takes the following form:[45]

$$E^{(2)} = \mathcal{L}^\dagger \bar{\mathbf{H}}_{PQ} (E^{(0)} \mathbf{S}_{QQ} - \bar{\mathbf{H}}_{QQ}^{(0)})^{-1} \bar{\mathbf{H}}_{QP} \mathcal{R}, \tag{19}$$

where we introduced the metric for space Q because the geminal functions as defined in Eq. (10) are not orthonormal. Equation (19) is the common starting point for the most popular coupled-cluster method, CCSD(T), which accounts for the effect of three-electron correlations by defining space Q to contain only the triple excitations.[51] This approach belongs to a broader family of methods that include perturbatively the effects of higher-rank correlations on already correlated reference states.[52–65]. Equation (19) can also account for the basis set incompleteness of the two-electron basis by defining Q to include explicitly correlated geminals [CCSD(2)$_{R12}$ and related methods[45,46]]. In this work we aim to recover both the three-body correlation and the two-electron basis set incompleteness effects. Thus Q will be a union of T and Γ spaces. (More general scenarios, where Q includes also quadruple and higher excitations, can be de-

scribed by trivial extensions of the present formalism. Extensions to higher-rank CC reference states, e.g., CCSDT, are also relatively straightforward.) This definition still leaves us with an infinite number of choices for partitioning the Hamiltonian. As we shall see, the partitioning determines the nature of coupling between the two effects.

A. Coupling between triple and geminal excitations

Although the introduction of geminal terms is intended to correct only the incompleteness of the two-electron basis set, it should also *indirectly* affect the correction due to the three-electron terms. The manner in which the coupling between the two effects is expressed will depend on the partitioning of the Hamiltonian. Here we discuss two limiting cases.

Block-diagonal $\bar{\mathbf{H}}_{QQ}^{(0)}$. Choose $\bar{H}^{(0)}$ such that $\bar{\mathbf{H}}_{T\Gamma}^{(0)}$ and $\bar{\mathbf{H}}_{\Gamma T}^{(0)}$ blocks are zero. Because the overlap matrix $\mathbf{S}_{QQ}$ is also block diagonal,

$$\langle {}^{abc}_{ijk} | {}^{xy}_{mn} \rangle = 0, \tag{20}$$

the result is a separable second-order contribution from the triple and geminal substitutions,

$$E^{(2)} = E_T^{(2)} + E_\Gamma^{(2)}, \tag{21}$$

$$E_T^{(2)} = \mathcal{L}^\dagger \bar{\mathbf{H}}_{PT} (E^{(0)} \mathbf{1}_{TT} - \bar{\mathbf{H}}_{TT}^{(0)})^{-1} \bar{\mathbf{H}}_{TP} \mathcal{R}, \tag{22}$$

$$E_\Gamma^{(2)} = \mathcal{L}^\dagger \bar{\mathbf{H}}_{P\Gamma} (E^{(0)} \mathbf{S}_{\Gamma\Gamma} - \bar{\mathbf{H}}_{\Gamma\Gamma}^{(0)})^{-1} \bar{\mathbf{H}}_{\Gamma P} \mathcal{R}. \tag{23}$$

The coupling between the triples and geminals will appear for the first time in the third-order energy. Introducing the first-order left- and right-hand eigenvectors,

$$\mathbf{L}_Q^{(1)} = \mathcal{L}^\dagger \bar{\mathbf{H}}_{PQ} (E^{(0)} \mathbf{S}_{QQ} - \bar{\mathbf{H}}_{QQ}^{(0)})^{-1}, \tag{24}$$

$$\mathbf{R}_Q^{(1)} = (E^{(0)} \mathbf{S}_{QQ} - \bar{\mathbf{H}}_{QQ}^{(0)})^{-1} \bar{\mathbf{H}}_{QP} \mathcal{R}, \tag{25}$$

the third-order energy becomes

$$E^{(3)} = \mathbf{L}_Q^{(1)} \bar{H}_{QQ}^{(1)} \mathbf{R}_Q^{(1)} = E_T^{(3)} + E_\Gamma^{(3)} + E_{T\Gamma}^{(3)} + E_{\Gamma T}^{(3)}, \tag{26}$$

$$E_T^{(3)} = \mathbf{L}_T^{(1)} \bar{H}_{TT}^{(1)} \mathbf{R}_T^{(1)}, \tag{27}$$

$$E_\Gamma^{(3)} = \mathbf{L}_\Gamma^{(1)} \bar{H}_{\Gamma\Gamma}^{(1)} \mathbf{R}_\Gamma^{(1)}, \tag{28}$$

$$E_{\Gamma T}^{(3)} = \mathbf{L}_\Gamma^{(1)} \bar{H}_{\Gamma T}^{(1)} \mathbf{R}_T^{(1)}, \tag{29}$$

$$E_{T\Gamma}^{(3)} = \mathbf{L}_T^{(1)} \bar{H}_{T\Gamma}^{(1)} \mathbf{R}_\Gamma^{(1)}. \tag{30}$$

Block-diagonal $\bar{\mathbf{H}}_{QQ}^{(1)}$. This can be achieved by including $\bar{\mathbf{H}}_{T\Gamma}$ and $\bar{\mathbf{H}}_{\Gamma T}$ into the zeroth-order Hamiltonian. If, for example, we define the zeroth- and first-order perturbation operators as

$$\bar{H} = \bar{H}^{(0,0)} + \bar{H}^{(1,0)} + \bar{H}^{(0,1)}, \tag{31}$$

$$\bar{H}^{(0,0)} = \hat{P}_P \bar{H} \hat{P}_P + \hat{P}_T \bar{H} \hat{P}_\Gamma + \hat{P}_\Gamma \bar{H} \hat{P}_T + \hat{P}_T \hat{F} \hat{P}_T + \hat{P}_\Gamma \hat{F} \hat{P}_\Gamma, \tag{32}$$

$$\bar{H}^{(1,0)} = \hat{P}_T\bar{H}\hat{P}_P + \hat{P}_P\bar{H}\hat{P}_T + \hat{P}_T(\bar{H}-\hat{F})\hat{P}_T, \tag{33}$$

$$\bar{H}^{(0,1)} = \hat{P}_\Gamma\bar{H}\hat{P}_P + \hat{P}_P\bar{H}\hat{P}_\Gamma + \hat{P}_\Gamma(\bar{H}-\hat{F})\hat{P}_\Gamma, \tag{34}$$

we can formulate a *double perturbation* theory in which the effect of triples and geminals is considered separately. Straightforward manipulations produce the energy corrections to the CCSD energy,

$$E^{(1,0)} = 0, \tag{35}$$

$$E^{(0,1)} = 0, \tag{36}$$

$$E^{(2,0)} = \mathcal{L}^\dagger\bar{\mathbf{H}}_{PT}(E^{(0)}\hat{S} - \bar{H}^{(0)})_{TT}^{-1}\bar{\mathbf{H}}_{TP}\mathcal{R}, \tag{37}$$

$$E^{(1,1)} = \mathcal{L}^\dagger\bar{\mathbf{H}}_{PT}(E^{(0)}\hat{S} - \bar{H}^{(0)})_{TT}^{-1}\bar{\mathbf{H}}_{\Gamma P}\mathcal{R}$$
$$+ \mathcal{L}^\dagger\bar{\mathbf{H}}_{P\Gamma}(E^{(0)}\hat{S} - \bar{H}^{(0)})_{\Gamma T}^{-1}\bar{\mathbf{H}}_{TP}\mathcal{R}, \tag{38}$$

and so on.

The interaction between the geminal and triples perturbation expansions appears in a different manner in the two approaches. While the double perturbation theory allows a finer-grained control of the coupling, the single perturbation theory is technically simpler at the second-order level. The latter advantage is due to the simpler blocked structure of the zeroth-order Hamiltonian that makes the formal matrix inversion in Eq. (19) computationally feasible. There is no other apparent advantage to either method at the second order.

Before we abandon the second partitioning type in favor of the first, we will examine whether the difference between the two approaches is expected to be significant enough for a further investigation. The key difference between the two approaches is how the triples-geminal blocks of the Hamiltonian are treated. Assigning them fully to the zeroth order produces the double perturbation theory variant, whereas designating them fully to the first-order leads to the "block-diagonal" variant. Let us consider the leading orders in the commutator expansion for the matrix elements of these blocks,

$$\langle\,{}^{abc}_{ijk}|\bar{H}|\,{}^{xy}_{mn}\rangle = \langle\,{}^{abc}_{ijk}|\hat{H} + [\hat{H},\hat{T}] + \cdots|\,{}^{xy}_{mn}\rangle, \tag{39a}$$

$$\langle\,{}^{abc}_{ijk}|\hat{H}|\,{}^{xy}_{mn}\rangle = \langle\,{}^{abc}_{ijk}|\hat{W}|\,{}^{xy}_{mn}\rangle$$
$$= -P(mn)C(ijk)C(abc)\delta^i_m\delta^j_n\bar{g}^{k\alpha}_{ab}\bar{R}^{xy}_{c\alpha}, \tag{39b}$$

$$\langle\,{}^{abc}_{ijk}|[\hat{H},\hat{T}]|\,{}^{xy}_{mn}\rangle = \langle\,{}^{abc}_{ijk}|[\hat{F},\hat{T}] + [\hat{W},\hat{T}]|\,{}^{xy}_{mn}\rangle, \tag{39c}$$

$$\langle\,{}^{abc}_{ijk}|[\hat{F},\hat{T}]|\,{}^{xy}_{mn}\rangle = P(mn)C(ijk)C(abc)\delta^i_m\delta^j_n f^\alpha_l t^{kl}_{ab}\bar{R}^{xy}_{c\alpha} \tag{39d}$$

$$\langle\,{}^{abc}_{ijk}|[\hat{W},\hat{T}]|\,{}^{xy}_{mn}\rangle = P(mn)C(ijk)C(abc)$$
$$\times(\delta^i_m\delta^j_n(-P(bc)\,t^l_a\bar{g}^{k\alpha}_{bl}\bar{R}^{xy}_{c\gamma} - t^k_d\bar{g}^{d\alpha}_{ab}\bar{R}^{xy}_{c\gamma}$$
$$+ P(ab)t^{kl}_{ad}\bar{g}^{d\alpha}_{bl}\bar{R}^{xy}_{c\alpha} \tag{39e}$$
$$- \tfrac{1}{2}t^{lo}_{ab}\bar{g}^{k\alpha}_{lo}\bar{R}^{xy}_{c\alpha} + \tfrac{1}{2}t^{kl}_{ab}\bar{g}^{\alpha\beta}_{cl}\bar{R}^{xy}_{\alpha\beta})$$
$$+ P(ij)\delta^i_m t^{jl}_{ab}\bar{g}^{k\alpha}_{nl}\bar{R}^{xy}_{c\alpha} + P(ab)\delta^i_m t^{jk}_{ad}\bar{g}^{d\alpha}_{bn}\bar{R}^{xy}_{c\alpha} \tag{39f}$$
$$+ P(ab)\delta^i_m\delta^j_n t^{kl}_{ad}\bar{g}^{d\alpha}_{bl}\bar{R}^{xy}_{c\alpha}), \tag{39g}$$

$$\langle\,{}^{xy}_{mn}|\bar{H}|\,{}^{abc}_{ijk}\rangle = \langle\,{}^{xy}_{mn}|\hat{H}|\,{}^{abc}_{ijk}\rangle$$
$$= -P(mn)C(ijk)C(abc)\delta^m_i\delta^n_j\bar{g}^{ab}_{k\alpha}\bar{R}^{c\alpha}_{xy}, \tag{39h}$$

where $P(mn)$ produces all permutations of indices m and n, with appropriate parity prefactors, $C(ijk)$ produces all cyclic permutations of indices i, j, and k, etc. Their action is best demonstrated by these examples,

$$P(ij)t^a_it^b_j = t^a_it^b_j - t^a_jt^b_i, \tag{40a}$$

$$C(ijk)t^a_it^b_jt^c_k = t^a_it^b_jt^c_k + t^a_jt^b_kt^c_i + t^a_kt^b_it^c_j. \tag{40b}$$

The non-hermitian character of $\bar{H}$ is manifested in Eqs. (39a)–(39h).

Equations (39a)–(39h) can be evaluated using the R12 technology that uses RI expansion in a basis set sufficiently complete to angular momentum L_{RI}. To determine the sufficient L_{RI}, we consider the partial wave (PW) expansion of Eqs. (39a)–(39h) for the case of an atom. The only expression with nontruncating PW expansion is $\bar{g}^{\alpha\beta}_{cl}\bar{R}^{xy}_{\alpha\beta}$, which is known as the intermediate V in R12 theory,

$$V^{xy}_{pq} \equiv \tfrac{1}{2}\bar{g}^{\alpha\beta}_{pq}\bar{R}^{xy}_{\alpha\beta}. \tag{41}$$

In the kl-ansatz, V can be evaluated "exactly" via RI expansion in a basis complete to $3L_{\mathrm{occ}}$ (L_{occ} is the maximum orbital momentum of the occupied orbitals) according to the usual R12 prescription.[9] Most of the other matrix elements have truncating PW expansions. For example, PW expansion of $\bar{g}^{k\alpha}_{ab}\bar{R}^{xy}_{c\alpha}$ truncates at $\min(l_x+l_y+l_k,l_a+l_b+l_c)$, where l_x is the angular momentum of x, etc. Thus all such matrix elements truncate for the kl-ansatz if the RI basis is complete through $3L_{\mathrm{occ}}$. Another example is $f^\alpha_l\bar{R}^{xy}_{c\alpha}$: Its PW expansion truncates at L_{occ}. Thus, L_{RI} needs to be $\max(3L_{\mathrm{occ}},2L_{\mathrm{occ}}+L_{\mathrm{vir}})$ to evaluate Eqs. (39a)–(39h) accurately.

To estimate the magnitude of the coupling between the geminals and triples, we can consider the same approach used in Ref. 45 to screen out less important terms. The key idea is that the terms that remain in the old R12 approach, standard approximation (SA), are likely to be most important. Only V-intermediate-containing terms survive in the SA,

$$\langle\,{}^{abc}_{ijk}|\bar{H}|\,{}^{xy}_{mn}\rangle \overset{\mathrm{SA}}{=} P(mn)C(ijk)C(abc)\delta^i_m\delta^j_n t^{kl}_{ab}V^{xy}_{cl}, \tag{42}$$

$$\langle \, ^{xy}_{mn}|\bar{H}| \, ^{abc}_{ijk}\rangle \overset{\text{SA}}{=} 0. \tag{43}$$

Although the T-Γ block of $\bar{H}$ does not vanish rigorously under the SA, its matrix elements are second order in the sense of a standard perturbation analysis of the coupled-cluster theory and should be small.

Our analysis suggests that the coupling between the geminals and triples in our perturbation theory should be weak, i.e., $E^{(1,1)}$ in Eq. (38) should be small. It also suggests that the difference between various partitioning schemes should depend weakly on how the geminal-triples and triples-geminals blocks are handled. The weakness of the geminal-triples coupling permits us to choose the partitioning that is simplest from a technical standpoint. In this work we choose the following definition of $\bar{H}^{(0)}$:

$$\bar{H}^{(0)} = \hat{P}_P \bar{H} \hat{P}_P + \hat{P}_Q(\hat{F}_N + E^{(0)})\hat{P}_Q, \tag{44}$$

where we have used the normal-ordered Fock operator $\hat{F}_N \equiv \hat{F} - \langle 0|\hat{F}|0\rangle$. This definition is convenient because it leads to the CCSD(T) family of methods[51,54,55,66] if $Q \equiv T$, and to the CCSD(2)$_{\text{R12}}$ method when $Q \equiv \Gamma$. More importantly, the QQ block zeroth-order operator in Eq. (44) is block diagonal without any need for projection,

$$\langle \, ^{abc}_{ijk}|\hat{F}| \, ^{xy}_{mn}\rangle = 0, \quad \langle \, ^{xy}_{mn}|\hat{F}| \, ^{abc}_{ijk}\rangle = 0. \tag{45}$$

Hence, the geminal and triples contributions to the second-order energy separate [Eq. (21)]. This definition of the zeroth-order Hamiltonian is clearly the most natural and technically simplest.

B. Evaluation of second-order energies

The two contributions to the second-order energy correction, Eqs. (22) and (23), can be evaluated exactly. The resulting method would be denoted as CCSD(2)$_{\text{T,R12}}$ according to the existing convention.[45,59,62] The triples contribution,

$$E_T^{(2)} = - \sum_{klm,cde} \left(\sum_{ia} \lambda_i^a \langle \, ^{a}_{i}|\bar{H}^{(1)}| \, ^{cde}_{klm}\rangle + \sum_{ijab} \lambda_{ij}^{ab} \langle \, ^{ab}_{ij}|\bar{H}^{(1)}| \, ^{cde}_{klm}\rangle \right)$$
$$\times \langle \, ^{cde}_{klm}|\hat{F}_N^{-1}| \, ^{cde}_{klm}\rangle \langle \, ^{cde}_{klm}|\bar{H}^{(1)}|0\rangle, \tag{46}$$

is equivalent to the energy correction in the asymmetric,[54] or Λ,[55] CCSD(T) method. By substitution of the λ amplitudes with their t counterparts we obtain the standard CCSD(T) energy expression,

$$E_T^{(2)} = -\frac{1}{3!^2} \sum_{ijk,abc} \{ C(ijk)C(abc)(t_i^a \bar{g}_{jk}^{bc} + t_{ij}^{ab} F_k^c + t_{il}^{ab} \bar{g}_{jk}^{cl}$$
$$- t_{ij}^{ad} \bar{g}_{kd}^{bc})\} D_{ijk}^{abc} \{ C(ijk)C(abc)(t_{ab}^{il} \bar{g}_{cl}^{jk} - t_{ad}^{ij} \bar{g}_{bc}^{kd})\}, \tag{47}$$

where $D_{ijk}^{abc} \equiv f_a^a + f_b^b + f_c^c - f_i^i - f_j^j - f_k^k$. The second-order geminal energy correction,

$$E_\Gamma^{(2)} = - \sum_{kl,x_1y_1x_2y_2} \left(\langle 0|\bar{H}^{(1)}| \, ^{x_1y_1}_{kl}\rangle + \sum_{ia} \lambda_i^a \langle \, ^{a}_{i}|\bar{H}^{(1)}| \, ^{x_1y_1}_{kl}\rangle \right.$$
$$\left. + \sum_{ijab} \lambda_{ij}^{ab} \langle \, ^{ab}_{ij}|\bar{H}^{(1)}| \, ^{x_1y_1}_{kl}\rangle \right) \langle \, ^{x_1y_1}_{kl}|\hat{F}_N^{-1}| \, ^{x_2y_2}_{kl}\rangle \langle \, ^{x_2y_2}_{kl}|\bar{H}^{(1)}|0\rangle, \tag{48}$$

has appeared in the CCSD(2)$_{\text{R12}}$ method.[45] This expression involves nonfactorizable three-electron integrals in the first-order matrix elements and up to four-electron integrals in the zeroth-order elements. Analytical evaluation of these integrals is, although possible, not practical. These many-electron integrals can be straightforwardly reduced via the R12 technology to at most two-electron integrals. No other approximation is necessary to evaluate Eq. (48) efficiently.

Following Ref. 45, we will utilize additional approximations to screen out the less important (but more complex) terms. Henceforth we refer to these protocols as *screening approximations*.

(1) Lambda amplitudes in Eq. (48) are replaced with their standard t counterparts. This is the same approximation that was involved in evaluating the (T) correction.

(2) Generalized ($f_i^{\alpha'} = 0$) and extended ($f_a^{\alpha'} = 0$) Brillouin conditions are assumed to hold.

(3) Matrix elements of $\bar{H}$ include only those terms that are at most second order in the standard perturbation analysis of the coupled-cluster energy (CCPT).

(4) Matrix elements of $\bar{H}^{(1)}$ include only those terms that do not vanish in the SA.[8]

Application of the above screening approximations to the CCSD(2)$_{\text{R12}}$ method results in the CCSD(2)$_{\overline{\text{R12}}}$ method.[45] The latter is much simpler than its exact counterpart and is very similar to the MP2-R12 method. The CCSD(2)$_{\overline{\text{R12}}}$ method appears to be a dramatic improvement on CCSD (Refs. 45 and 46), and matches performance of more complicated iterative R12 coupled-cluster methods.[67] Thus, the available evidence provides no reason to avoid screening approximations, especially considering their technical merits. In the future it may become necessary to reconsider this position: For example, when near degeneracies are encountered replacement of λ amplitudes with their t counterparts may introduce substantial errors.[54,56] In this work we have limited our analysis to molecules near their equilibrium geometries, hence screening approximations should be appropriate.

The geminal correction within screening approximations becomes

$$E_\Gamma^{(2)} \overset{\text{ScrA}}{=} \frac{1}{4} \widetilde{V}_{ij}^{x_1y_1} t_{x_1y_1}^{ij}, \tag{49a}$$

where

$$-\frac{1}{2}(\widetilde{B}^{(ij)})_{x_1y_1}^{x_2y_2} t_{x_2y_2}^{ij} = \widetilde{V}_{x_1y_1}^{ij}. \tag{49b}$$

Equations (49a) and (49b) involves the familiar intermediates of the MP2-R12 theory,

$$(\widetilde{B}^{(ij)})_{x_1y_1}^{x_2y_2} = B_{x_1y_1}^{x_2y_2} - (f_i^i + f_j^j)X_{x_1y_1}^{x_2y_2}, \tag{50}$$

$$B_{x_1y_1}^{x_2y_2} = \bar{R}_{\alpha\beta}^{x_2y_2} f_\gamma^\beta \bar{R}_{x_1y_1}^{\alpha\gamma}, \tag{51}$$

$$X_{x_1y_1}^{x_2y_2} = \tfrac{1}{2}\bar{R}_{\alpha\beta}^{x_2y_2} \bar{R}_{x_1y_1}^{\alpha\beta}, \tag{52}$$

along with the new first-order interaction matrix,

$$\widetilde{V}_{ij}^{xy} = V_{ij}^{x_1y_1} + t_i^a V_{aj}^{x_1y_1} + t_j^a V_{ia}^{x_1y_1} + \tfrac{1}{2}t_{ij}^{ab} V_{ab}^{x_1y_1}. \tag{53}$$

When a restricted Hartree–Fock (RHF) or unrestricted Hartree–Fock (UHF) reference wave function is used, the t_i^a amplitudes are second order in perturbation, hence the second and third terms on the right-hand side of Eq. (53) are omitted for consistency.

The geminal correction obtained by Eqs. (49a) and (49b) is almost identical to the R12 correction of the MP2-R12 theory. The latter is obtained by replacing intermediate $\widetilde{V}$ with V. As shown in Ref. 45, the presence of the extra T-amplitude-dependent terms in $\widetilde{V}$ allows the R12 correction in CCSD(2)$_{\overline{R12}}$ to account for the interference effect,[68,69] i.e. the difference in the basis set error of MP2 and CCSD energies.[70,71]

Also note that the geminal correction in Eqs. (49a) and (49b) has a symmetric form (i.e., same effective intermediate $\widetilde{V}$ appears in both equations). The original geminal correction of the CCSD(2)$_{\overline{R12}}$ method was, in contrast, asymmetric.[45] The difference between $E_\Gamma^{(2)}$ computed via the two methods is quadratic in T amplitudes and should be small. We recommend using the symmetric form due to its aesthetic appeal.

The current approach has also recently been reformulated[46] in a variational (Lagrangian) form that allows to use fixed geminal first-order coefficients determined according to the prescription of Ten-no.[13] The diagonal fixed-coefficient ansatz can alleviate the problems due to the geminal superposition error[72] at the cost of a small decrease in absolute precision. In this work, however, we fully optimized the geminal amplitudes.

Following the established convention,[45,59,62] we denote the method defined by Eqs. (21), (47), (49a), and (49b) as CCSD(2)$_{\overline{T,R12}}$. We will also use the "CCSD(T)$_{\overline{R12}}$" moniker to emphasize its direct relation to the CCSD(T) method.

III. TECHNICAL DETAILS

Hartree–Fock orbitals were expanded in standard correlation-consistent basis sets of Dunning[73] and Kendall *et al.*[74] The RI basis sets consisted of the primitive $15s9p7d5f$ and $9s7p5d$ sets for C–F and H, respectively, derived by uncontracting the standard cc-pV5Z basis sets and appending extra polarization functions.[75] A Slater-type correlation factor $\exp(-1.3r_{12})$ was represented as a least-squares fit to six Gaussian-type geminals; the optimal exponents and coefficients are (303.393, 54.8852, 14.6991, 4.506 31, 1.360 66, 0.364 39) and (0.051 084 4, 0.081 916, 0.129 811, 0.205 298, 0.299 458, 0.207 455), respectively. All integrals necessary for the explicitly correlated calculations were evaluated using the recurrence relations of Weber and Daul[76] as implemented by an integral code generator LIBINT.[77] The complementary auxiliary basis set (CABS) method in its CABS+ variant[12] was used to factorize the many-electron integrals.

The intermediate B was simplified using approximation C of Kedzuch *et al.*[29,30] The linear system in Eq. (49b) may become ill conditioned, especially if the orbital basis set is large and the molecule includes elements on the right side of the Periodic Table (O, F). We avoid numerical problems due to ill conditioning by using a singular-value decomposition solver (see also Ref. 23 for a discussion of some numerical issues in R12 methods).

All computations were performed with developmental versions of the MPQC (Ref. 78) and PSI3 (Ref. 79) programs. A recent version of MPQC capable of the calculations described in this paper can be accessed anonymously from the main trunk of the code repository at http://mpqc.sourceforge.net/. The necessary PSI3 updates will be included in an upcoming release.

The computational cost of the CCSD(T)$_{\overline{R12}}$ method equals the cost of the CCSD(T) energy plus that of the R12 correction of the CCSD(2)$_{\overline{R12}}$ method. Although the latter involves solving a linear system of o^2 rank for each ij-pair, i.e., an $\mathcal{O}(o^8)$ step, the total cost of this step is negligible compared to the rest of the operations. The worst scaling is therefore the $\mathcal{O}(o^3v^4)$ cost of computing the triples correction. The most expensive operations in the R12 correction algorithm scale as $\mathcal{O}(o^4N^2)$, where N is the size of the auxiliary basis set. The cost of such terms can be further reduced to $\mathcal{O}(o^4nN)$, but this was not done in this work. The current computational implementation of the R12 correction in MPQC is suboptimal for small-scale computational environments: It employs integral-direct algorithms that scale well on modern distributed-memory massively parallel machines but increase the computational cost.[80] Our coupled-cluster program in PSI3, however, can run efficiently on single processors only. Thus the current implementation of the CCSD(T)$_{\overline{R12}}$ method, although of production-level quality, is suboptimal.

IV. RESULTS

The immediate goal of this work is to develop a practical explicitly correlated coupled-cluster method that can be used as a black-box replacement for the standard CCSD(T) method. A natural first target application of such model is computational thermochemistry, for which the basis set error is often a dominant component of the total error. Thus thermochemical computations not only pose a stringent test for the CCSD(T)$_{\overline{R12}}$ method but also can immediately take advantage of the new approach.

The electronic-structure community has developed many robust model chemistries suited for thermochemical computations,[47–49,81–93] most recent of which essentially use the same two features: Basis set extrapolation along the correlation-consistent series and the assumption of additivity of small corrections. In this work we chose the HEAT model for our tests.[47–49] The HEAT model is free of bias toward the experimental data, does not include empirical contributions to the energy, and extends the treatment of electron correlation to the coupled-cluster singles, double, triples, and quadruples (CCSDTQ) level. The HEAT energy at 0 K is defined as a sum,

TABLE I. Statistical analyses of the relative basis set errors (%) of the CCSD(T) correlation energy obtained with the standard, extrapolated, and explicitly correlated methods for the HEAT test set.

Method[a]	X[b]			
	D	T	Q	5
		$\bar{\Delta}$		
CCSD(T)	25.70	8.51	3.37	1.73
$(X-1,X)_{\text{Helgaker}}$	⋯	1.27	−0.38	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	−1.42	−0.23	⋯
CCSD(T)$_{\overline{\text{R12}}}$	6.07	2.12	0.78	⋯
$(X-1,X)_{\overline{\text{R12}}}$	⋯	0.10	−0.06	⋯
		Δ_{std}		
CCSD(T)	3.65	1.39	0.61	0.31
$(X-1,X)_{\text{Helgaker}}$	⋯	0.54	0.13	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	0.44	0.14	⋯
CCSD(T)$_{\overline{\text{R12}}}$	1.11	0.38	0.15	⋯
$(X-1,X)_{\overline{\text{R12}}}$	⋯	0.23	0.07	⋯
		$\bar{\Delta}_{\text{abs}}$		
CCSD(T)	25.70	8.51	3.37	1.73
$(X-1,X)_{\text{Helgaker}}$	⋯	1.32	0.38	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	1.42	0.23	⋯
CCSD(T)$_{\overline{\text{R12}}}$	6.07	2.12	0.78	⋯
$(X-1,X)_{\overline{\text{R12}}}$	⋯	0.17	0.07	⋯
		Δ_{max}		
CCSD(T)	33.45	11.18	4.58	2.34
$(X-1,X)_{\text{Helgaker}}$	⋯	1.91	0.64	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	2.42	0.51	⋯
CCSD(T)$_{\overline{\text{R12}}}$	7.76	2.88	1.09	⋯
$(X-1,X)_{\overline{\text{R12}}}$	⋯	0.84	0.18	⋯

[a]$(X-1,X)_{\text{Helgaker}}$ and $(X-1,X)_{\text{Schwenke}}$ refer to the complete basis set estimates obtained by Helgaker (Ref. 98) or Schwenke (Ref. 101) extrapolations, respectively, of the CCSD(T) energies. $(X-1,X)_{\overline{\text{R12}}}$ is the energy obtained by Schwenke extrapolation of the CCSD(T)$_{\overline{\text{R12}}}$ energies (see text).
[b]The aug-cc-pCVXZ orbital basis set.

TABLE II. Statistical analyses of the CCSD(T) correlation contributions to atomization energies (kJ/mol) obtained with the standard, extrapolated, and explicitly correlated CCSD(T) methods for the molecules in the HEAT test set.

Method[a]	X[b]			
	D	T	Q	5
		$\bar{\Delta}$		
CCSD(T)	55.46	22.12	8.97	4.59
$(X-1,X)_{\text{Helgaker}}$	⋯	8.08	−0.63	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	3.71	−0.27	⋯
CCSD(T)$_{\overline{\text{R12}}}$	26.20	5.65	1.71	⋯
$(X-1,X)_{\overline{\text{R12}}}$	⋯	−4.83	−0.77	⋯
		Δ_{std}		
CCSD(T)	25.72	11.17	4.77	2.44
$(X-1,X)_{\text{Helgaker}}$	⋯	6.16	0.68	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	5.73	0.71	⋯
CCSD(T)$_{\overline{\text{R12}}}$	15.04	3.42	1.18	⋯
$(X-1,X)_{\overline{\text{R12}}}$	⋯	3.08	0.46	⋯
		$\bar{\Delta}_{\text{abs}}$		
CCSD(T)	55.46	22.12	8.97	4.59
$(X-1,X)_{\text{Helgaker}}$	⋯	8.14	0.74	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	5.38	0.61	⋯
CCSD(T)$_{\overline{\text{R12}}}$	26.20	5.65	1.72	⋯
$(X-1,X)_{\overline{\text{R12}}}$	⋯	4.88	0.78	⋯
		Δ_{max}		
CCSD(T)	99.95	44.38	18.52	9.48
$(X-1,X)_{\text{Helgaker}}$	⋯	23.49	1.96	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	17.50	1.38	⋯
CCSD(T)$_{\overline{\text{R12}}}$	54.50	12.01	4.41	⋯
$(X-1,X)_{\overline{\text{R12}}}$	⋯	10.56	1.71	⋯

[a]$(X-1,X)_{\text{Helgaker}}$ and $(X-1,X)_{\text{Schwenke}}$ refer to the complete basis set estimates obtained by Helgaker (Ref. 98) or Schwenke (Ref. 101) extrapolations, respectively, of the CCSD(T) energies. $(X-1,X)_{\overline{\text{R12}}}$ is the energy obtained by Schwenke extrapolation of the CCSD(T)$_{\overline{\text{R12}}}$ energies (see text).
[b]The aug-cc-pCVXZ orbital basis set.

$$E_{\text{HEAT}} = E_{\text{HF}} + E_{\text{CCSD(T)}} + E_{\text{CCSDT}} + E_{\text{CCSDTQ}} + E_{\text{rel}}$$
$$+ E_{\text{ZPE}} + E_{\text{DBOC}} + E_{\text{SO}}, \tag{54}$$

where E_{rel}, E_{ZPE}, E_{DBOC}, and E_{SO} are the scalar relativistic, zero-point, diagonal Born–Oppenheimer, and spin-orbit interaction corrections (see Ref. 47 for complete details). The HEAT model defines two protocols for computing heats of formation at 0 K, one using atomic enthalpies of formation and molecular atomization energies (I) and another referred to as the elemental reaction approach (II) which recalibrates the standard state of carbon to be the CO molecule. The two approaches result in excellent agreement with the experimentally derived values from the Active Thermochemical Tables: Mean absolute errors are only 0.30 and 0.25 kJ/mol, respectively. The corresponding maximum absolute errors (MAEs) are 0.72 and 0.82 kJ/mol. (These values for approach I were taken from Ref. 48, which used updated AcTC values. The errors for approach II were recomputed using the original computed heats of formation from Ref. 47 and the new AcTC data.)

Our focus here is the second component of the HEAT energy, the CCSD(T) correlation energy estimated in the complete basis set limit. We do not attempt to compute the complete basis set limit of the *total* CCSD(T) energy [the sum of the first two terms on RHF of Eq. (54)] because the Hartree–Fock energy can be computed precisely by other means, e.g., basis set extrapolation in polarization-consistent basis sets[94] or, even better, by avoiding global basis sets completely and using adaptive numerical approaches.[95–97]

Although the original HEAT study used wave functions based on spin UHF reference functions, in several cases it was necessary to use a spin-restricted open-shell HF (ROHF) reference. For consistency, all computations in this work used ROHF-based wave functions. Although we used the same molecular geometries as Ref. 47, the CCSD(T) correlation energies computed in this work cannot be compared directly to the original results. The complete-basis-set limits of the CCSD(T) correlation energies were estimated by two-point Helgaker extrapolation[98,99] from the CCSD(T)/aug-cc-pCVXZ energies with $X=Q, 5$.

We evaluated the basis set error of the CCSD(T) correlation energy in three ways: (1) The relative basis set error of the CCSD(T) correlation energy,

TABLE III. Statistical analyses of the CCSD(T) correlation contributions to heats of formation (kJ/mol) obtained with the standard, extrapolated, and explicitly correlated CCSD(T) methods for the HEAT test set. Heats of formation computed using the "elemental reaction" approach of HEAT model chemistry (Ref. 47). Since this method defines H_2, N_2, O_2, F_2, and CO as the "standard states" for elements H, N, O, F, and C, respectively, these molecules were not included in these statistics.

Method[a]	X[b]			
	D	T	Q	5
		$\bar{\Delta}$		
CCSD(T)	11.63	7.08	3.40	1.74
$(X-1,X)_{\text{Helgaker}}$	$\cdots$	5.17	0.71	$\cdots$
$(X-1,X)_{\text{Schwenke}}$	$\cdots$	5.01	0.80	$\cdots$
$\text{CCSD(T)}_{\overline{\text{R12}}}$	8.17	1.82	0.90	$\cdots$
$(X-1,X)_{\overline{\text{R12}}}$	$\cdots$	-1.42	0.32	$\cdots$
		Δ_{std}		
CCSD(T)	18.41	9.58	4.12	2.11
$(X-1,X)_{\text{Helgaker}}$	$\cdots$	6.57	0.60	$\cdots$
$(X-1,X)_{\text{Schwenke}}$	$\cdots$	6.16	0.64	$\cdots$
$\text{CCSD(T)}_{\overline{\text{R12}}}$	15.61	3.15	0.91	$\cdots$
$(X-1,X)_{\overline{\text{R12}}}$	$\cdots$	3.35	0.61	$\cdots$
		$\bar{\Delta}_{\text{abs}}$		
CCSD(T)	16.96	9.10	4.00	2.05
$(X-1,X)_{\text{Helgaker}}$	$\cdots$	6.04	0.74	$\cdots$
$(X-1,X)_{\text{Schwenke}}$	$\cdots$	5.51	0.82	$\cdots$
$\text{CCSD(T)}_{\overline{\text{R12}}}$	14.01	2.83	0.96	$\cdots$
$(X-1,X)_{\overline{\text{R12}}}$	$\cdots$	2.96	0.52	$\cdots$
		Δ_{max}		
CCSD(T)	52.73	25.19	10.72	5.49
$(X-1,X)_{\text{Helgaker}}$	$\cdots$	19.44	2.07	$\cdots$
$(X-1,X)_{\text{Schwenke}}$	$\cdots$	20.87	2.33	$\cdots$
$\text{CCSD(T)}_{\overline{\text{R12}}}$	35.30	7.16	2.38	$\cdots$
$(X-1,X)_{\overline{\text{R12}}}$	$\cdots$	7.59	1.66	$\cdots$

[a]$(X-1,X)_{\text{Helgaker}}$ and $(X-1,X)_{\text{Schwenke}}$ refer to the complete basis set estimates obtained by Helgaker (Ref. 98) or Schwenke (Ref. 101) extrapolations, respectively, of the CCSD(T) energies. $(X-1,X)_{\overline{\text{R12}}}$ is the energy obtained by Schwenke extrapolation of the $\text{CCSD(T)}_{\overline{\text{R12}}}$ energies (see text).
[b]The aug-cc-pCVXZ orbital basis set.

$$\delta_1 = \frac{E_{\text{CBS}} - E}{E_{\text{CBS}}}, \qquad (55)$$

(2) the basis set error of the CCSD(T) correlation contribution to the atomization energy,

$$\delta_2 = E_{\text{CBS}}^{\text{AE}} - E^{\text{AE}}, \qquad (56)$$

and (3) the basis set error of the CCSD(T) correlation contribution to the heat of formation computed using the elemental reaction approach,[47]

$$\delta_3 = E_{\text{CBS}}^f - E^f. \qquad (57)$$

Trivial zero errors (e.g., δ_1 for H) were excluded from the statistical analyses. The results for the CCSD(T) correlation energies are presented in Tables I–III.

The basis set errors of the standard CCSD(T) energies are, as expected, large and very slowly convergent. Even with the largest basis set, aug-cc-pCV5Z, the MAEs of the CCSD(T) contributions to the atomization energies and heats of formations are 4.59 and 2.05 kJ/mol, respectively. These

TABLE IV. Statistical analyses of the basis set errors (%) of the (T) correlation energy contribution relative to the CBS CCSD(T) correlation energy.

Method[a]	X[b]			
	D	T	Q	5
		$\bar{\Delta}$		
CCSD(T)	1.32	0.35	0.15	0.08
$(X-1,X)_{\text{Helgaker}}$	$\cdots$	-0.05	-0.00	$\cdots$
$(X-1,X)_{\text{Schwenke}}$	$\cdots$	-0.03	-0.00	$\cdots$
		Δ_{std}		
CCSD(T)	0.20	0.05	0.02	0.01
$(X-1,X)_{\text{Helgaker}}$	$\cdots$	0.03	0.01	$\cdots$
$(X-1,X)_{\text{Schwenke}}$	$\cdots$	0.02	0.01	$\cdots$
		$\bar{\Delta}_{\text{abs}}$		
CCSD(T)	1.32	0.35	0.15	0.08
$(X-1,X)_{\text{Helgaker}}$	$\cdots$	0.05	0.01	$\cdots$
$(X-1,X)_{\text{Schwenke}}$	$\cdots$	0.03	0.01	$\cdots$
		Δ_{max}		
CCSD(T)	1.59	0.43	0.18	0.10
$(X-1,X)_{\text{Helgaker}}$	$\cdots$	0.10	0.02	$\cdots$
$(X-1,X)_{\text{Schwenke}}$	$\cdots$	0.07	0.02	$\cdots$

[a]$(X-1,X)_{\text{Helgaker}}$ and $(X-1,X)_{\text{Schwenke}}$ refer to the complete basis set estimates obtained by Helgaker (Ref. 98) or Schwenke (Ref. 101) extrapolations, respectively, of the CCSD(T) energies.
[b]The aug-cc-pCVXZ orbital basis set.

values are much larger than the corresponding overall MAEs of the HEAT model, 0.30 and 0.25 kJ/mol. Simple two-point basis set extrapolations reduce the average errors substantially. For example, the errors in $X=$D and $X=$T atomization energy contributions are 55.46 and 22.12 kJ/mol, respectively, whereas Schwenke extrapolation of these data reduces the error to 5.38 kJ/mol, a reduction by a factor of 4.1. As expected, the effectiveness of extrapolation using basis sets with higher X is increased dramatically: The (T,Q) Schwenke extrapolation reduces the error of the atomization contribution from 8.97 to 0.61 kJ/mol (a factor of 14.7 reduction). However, the benefit of extrapolation seems to diminish for the heats of formation. The (D,T) and (T,Q) Schwenke extrapolations reduce the errors of the corresponding unextrapolated results only by factors of 1.7 and 4.9, respectively (see Table III). This effect is somewhat surprising because the number of electron pairs broken up in the atomization process is substantially greater.

Interestingly enough, the benefit of extrapolation for the raw correlation energies (see Table I) seems to mirror that for atomization energies. Therefore, a significant reduction of the basis set error of the correlation energy may translate into only a modest reduction of the error in a relative energy. Although detailed analysis of this phenomenon is outside the scope of this study, we rationalize its origin as follows. As noted before,[100] empirical basis set extrapolations are very good at reducing the average error, but have a difficult time reducing the standard deviation of errors. The ratio of the standard deviation of basis set errors Δ_{std} to the mean error $\bar{\Delta}$ is roughly 0.5 for atomization energies and below 0.2 for absolute correlation energies, *it exceeds 1.0 for heats of formation.* Therefore it seems reasonable that the statistical na-

TABLE V. Statistical analyses of the (T) contribution to atomization energies (kJ/mol) for the molecules in the HEAT test set.

Method[a]	X[b]			
	D	T	Q	5
	$\bar{\Delta}$			
CCSD(T)	8.60	2.07	0.89	0.50
$(X-1,X)_{\text{Helgaker}}$	⋯	−0.68	0.03	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	−0.53	0.03	⋯
	$\bar{\Delta}_{\text{std}}$			
CCSD(T)	4.77	1.18	0.53	0.30
$(X-1,X)_{\text{Helgaker}}$	⋯	0.38	0.08	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	0.30	0.08	⋯
	$\bar{\Delta}_{\text{abs}}$			
CCSD(T)	8.60	2.07	0.89	0.50
$(X-1,X)_{\text{Helgaker}}$	⋯	0.68	0.07	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	0.53	0.07	⋯
	Δ_{max}			
CCSD(T)	19.76	4.81	2.14	1.19
$(X-1,X)_{\text{Helgaker}}$	⋯	1.49	0.19	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	1.16	0.19	⋯

[a]$(X-1,X)_{\text{Helgaker}}$ and $(X-1,X)_{\text{Schwenke}}$ refer to the complete basis set estimates obtained by Helgaker (Ref. 98) or Schwenke (Ref. 101) extrapolations, respectively, of the CCSD(T) energies.
[b]The aug-cc-pCVXZ orbital basis set.

TABLE VI. Statistical analyses of the (T) contributions to heats of formation (kJ/mol) for the HEAT test set. Heats of formation computed using the elemental reaction approach of HEAT model chemistry (Ref. 47). Since this method defines H_2, N_2, O_2, F_2, and CO as the standard states for elements H, N, O, F, and C, respectively, these molecules were not included in these statistics.

Method[a]	X[b]			
	D	T	Q	5
	$\bar{\Delta}$			
CCSD(T)	4.35	1.08	0.52	0.29
$(X-1,X)_{\text{Helgaker}}$	⋯	−0.29	0.10	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	−0.22	0.10	⋯
	$\bar{\Delta}_{\text{std}}$			
CCSD(T)	3.45	0.80	0.36	0.20
$(X-1,X)_{\text{Helgaker}}$	⋯	0.35	0.07	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	0.29	0.07	⋯
	$\bar{\Delta}_{\text{abs}}$			
CCSD(T)	4.48	1.11	0.52	0.29
$(X-1,X)_{\text{Helgaker}}$	⋯	0.37	0.10	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	0.30	0.10	⋯
	Δ_{max}			
CCSD(T)	10.11	2.35	1.15	0.64
$(X-1,X)_{\text{Helgaker}}$	⋯	0.91	0.30	⋯
$(X-1,X)_{\text{Schwenke}}$	⋯	0.74	0.30	⋯

[a]$(X-1,X)_{\text{Helgaker}}$ and $(X-1,X)_{\text{Schwenke}}$ refer to the complete basis set estimates obtained by Helgaker (Ref. 98) or Schwenke (Ref. 101) extrapolations, respectively, of the CCSD(T) energies.
[b]The aug-cc-pCVXZ orbital basis set.

ture of the residual errors resulting from the extrapolation is the culprit behind the (relatively) poor improvement in heats of formation from the basis set extrapolation.

As expected, the performance of the new CCSD(T)$_{\overline{\text{R12}}}$ method is *always* better than that of the standard CCSD(T) method. Although the degree of reduction in MAE due to the explicitly correlated terms is essentially independent of X when we consider the raw correlation energy, at least a triple-zeta basis set should be used with R12 methods if the target is an atomization energy and a heat of formation. For example, introduction of R12 terms decreases the MAE for the heat of formation from 16.96 only to 14.01 kJ/mol with a double-zeta basis. The improvement is much more substantial with triple and quadruple zeta basis sets. Similarly to recent studies,[44,45,67] the basis set errors of the explicitly correlated CC method obtained with a triple-zeta basis are roughly equivalent to those of the standard CC counterpart obtained with a quintuple-zeta basis. This result holds not only for the raw correlation energies but also for the tougher-to-compute atomization energies and heats of formation.

The CCSD(T)$_{\overline{\text{R12}}}$ method also performs well relative to the extrapolation approaches. Although the (T,Q) extrapolation produces smaller MAEs than the CCSD(T)$_{\overline{\text{R12}}}$/aug-cc-pCVQZ method, the (D,T) extrapolation is less accurate on average than the CCSD(T)$_{\overline{\text{R12}}}$/aug-cc-pCVTZ result. This comparison especially favors the explicitly correlated method when considering the heats of formation. For example, the MAE of the CCSD(T)$_{\overline{\text{R12}}}$/aug-cc-pCVTZ heats of formation is roughly twice better than that of the (D,T) extrapolated heats of formation. Given comparable performance, the CCSD(T)$_{\overline{\text{R12}}}$ method should be preferred to the approaches based on basis

set extrapolation because it is less empirical. There is clearly room to improve the performance of R12 methods further by basis set optimization and general R12 methodology improvements, whereas the extrapolation methods are more mature and less likely to be improved further.

We have also experimented with basis set extrapolation of the explicitly correlated energies. We adopted the following Schwenke-type extrapolation expression:

$$E_{X-1,X} = (E_X - E_{X-1})c_{X-1,X} + E_{X-1}. \qquad (58)$$

The unknown coefficient is set such that the average basis set error of extrapolated CCSD(T)$_{\overline{\text{R12}}}$ correlation energies of a set of five molecules (H_2, N_2, O_2, F_2, and CO) is zero. The resulting values are $c_{\text{D,T}}=1.510$ and $c_{\text{T,Q}}=1.630$. Although this extrapolation of the CCSD(T)$_{\overline{\text{R12}}}$ energies seems to improve radically the raw correlation energies (see Table I), its benefit for atomization energies and heats of formation is modest. However, it should be possible to improve upon these preliminary results. For example, it is not clear to what extent reoptimization of the Slater-geminal exponent will change the optimal extrapolation parameters.

Lastly, we investigated whether the basis set incompleteness of the triples is important enough to warrant special treatment. The CCSD(T)$_{\overline{\text{R12}}}$ method only corrects the basis set incompleteness of the two-electron basis set via the introduction of the geminals and includes only the standard (nonexplicitly correlated) (T) energy correction. To this end, we computed the basis set errors of the (T) energy using the
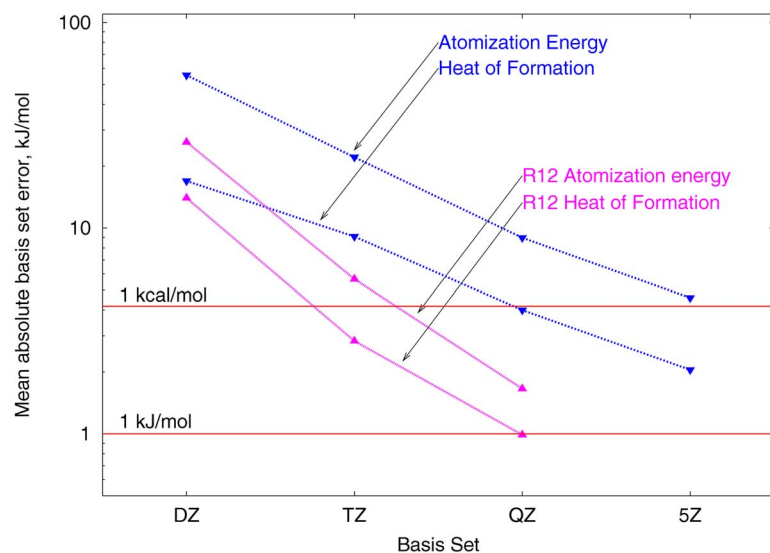
FIG. 1. (Color online) Mean absolute deviations of CCSD(T) contributions to the atomization energies and heats of formation obtained with the standard and explicitly correlated methods.

same three metrics, δ_1, δ_2, and δ_3 used to analyze the CCSD(T) correlation energies. The only difference is that δ_1 was defined relative to the total CCSD(T) correlation energy,

$$\delta_1^{(T)} = \frac{E_{CBS}^{(T)} - E^{(T)}}{E_{CBS}^{CCSD(T)}}. \tag{59}$$

The results are reported in Tables IV–VI.

The main conclusion is that the basis set error of the (T) energy is always significantly smaller than the error of the corresponding CCSD(T)$_{\overline{R12}}$ energy. For example, the mean absolute basis set errors of the X=T and X=Q (T) contributions to the heats of formation are 0.35 and 0.15 kJ/mol, respectively, whereas the errors in the corresponding the CCSD(T)$_{\overline{R12}}$ values are 2.83 and 0.96 kJ/mol. Clearly, there does not seem to be urgent need to tackle the basis set incompleteness of the three-electron basis with these relatively small basis sets. For benchmark calculations, especially on systems where the triples energy correction is substantial, it may be necessary to use explicitly correlated three-electron basis.

V. CONCLUSIONS

We have extended the recently proposed perturbative explicitly correlated coupled-cluster singles and doubles method, CCSD(2)$_{\overline{R12}}$ (Ref. 45) to account for the effect of connected three-electron correlations. The result is a new method, dubbed CCSD(T)$_{\overline{R12}}$, that can be viewed as an explicitly correlated R12 version of the CCSD(T) method. Its correlation energy is a sum of the standard CCSD(T) correlation energy and the explicitly correlated geminal correction defined by Eqs. (49a) and (49b). Evaluation of the geminal correction only requires the standard V, B, and X intermediates of MP2-R12 theory, as well as the converged CCSD t-amplitudes. Technical implementation of the CCSD(T)$_{\overline{R12}}$ method does not involve any modification of an existing CCSD(T) program and relatively simple modification of an MP2-R12 program. We have implemented RHF-, ROHF-, and UHF-based versions of the CCSD(T)$_{\overline{R12}}$ method in developmental versions of the open-source programs MPQC and

PSI3.

We have tested the performance of the CCSD(T)$_{\overline{R12}}$ method as a possible replacement of the standard complete-basis-set CCSD(T) energies in the HEAT model of Stanton *et al.* Correlation contributions to the atomization energies and heats of formation computed with the new explicitly correlated method are much more precise (i.e., have smaller basis set errors) than their standard CCSD(T) counterparts (see Fig. 1). The mean absolute basis set errors for these quantities computed at the CCSD(T)$_{\overline{R12}}$/aug-cc-pCVTZ level are 5.7 and 2.8 kJ/mol, respectively, which is only slightly worse than the 4.6 and 2.1 kJ/mol errors of the more expensive CCSD(T)/aug-cc-pCV5Z energies. Increasing the basis to aug-cc-pCVQZ decreases the MAEs of the CCSD(T)$_{\overline{R12}}$ energies to 1.7 and 1.0 kJ/mol, respectively.

Simple two-point basis set extrapolations of standard CCSD(T) energies perform better than the explicitly correlated method for absolute correlation energies and atomization energies, but we find no such advantage when computing heats of formation. In fact, the (D,T) extrapolation of CCSD(T) energies produces heats of formation that are roughly a factor of 2 less precise than the directly computed CCSD(T)$_{\overline{R12}}$/aug-cc-pCVTZ energy.

We have also investigated whether simple extrapolation can improve the explicitly correlated energies computed with small basis sets even further. Although the absolute energies were improved substantially, relative energies, such as atomization energies and heats of formation, benefit little. Nevertheless, a simple Schwenke-type two-point extrapolation of the CCSD(T)$_{\overline{R12}}$/aug-cc-pCVXZ energies with X=T,Q yields the most accurate heats of formation found in this work, in error on average by 0.5 kJ/mol and at most by 1.7 kJ/mol. These errors are already comparable to the uncertainty in the CBS CCSD(T) energies of the HEAT approach: Bomble *et al.* reported that including X=6 energies in extrapolation can change the CCSD(T) contributions to heat of formation by 0.38 kJ/mol for CO and 0.64 kJ/mol for CN.[48] Therefore any additional effort will be counterproductive until we establish unequivocally (e.g., to 0.1 kJ/mol precision) the CBS CCSD(T) limits for the HEAT model. We

believe that an explicitly correlated method such as $CCSD(T)_{\overline{R12}}$ is the only means to attain that goal.

We found no evidence for the importance of incompleteness of the three-electron basis. The basis set error of the (T) energy in our tests was significantly smaller than the residual basis error of CCSD(T), $CCSD(T)_{\overline{R12}}$, or extrapolated energies.

The overall conclusion of this work is that the $CCSD(T)_{\overline{R12}}$ method is a simple-to-implement, robust, first-principles explicitly correlated variant of the CCSD(T) method. It should be immediately useful in computational thermochemistry as an alternative to empirical basis set extrapolation.

ACKNOWLEDGMENTS

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