

Coupled-cluster methods with perturbative inclusion of explicitly correlated terms: a preliminary investigation

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Received 12th September 2007, Accepted 19th October 2007

First published as an Advance Article on the web 13th November 2007

DOI: 10.1039/b713938a

We propose to account for the large basis-set error of a conventional coupled-cluster energy and wave function by a simple perturbative correction. The perturbation expansion is constructed by Löwdin partitioning of the similarity-transformed Hamiltonian in a space that includes explicitly correlated basis functions. To test this idea, we investigate the second-order explicitly correlated correction to the coupled-cluster singles and doubles (CCSD) energy, denoted here as the CCSD(2)_{R12} method. The proposed perturbation expansion presents a systematic and easy-to-interpret picture of the “interference” between the basis-set and correlation hierarchies in the many-body electronic-structure theory. The leading-order term in the energy correction is the amplitude-independent R12 correction from the standard second-order Møller–Plesset R12 method. The cluster amplitudes appear in the higher-order terms and their effect is to decrease the basis-set correction, in accordance with the usual experience. In addition to the use of the standard R12 technology which simplifies all matrix elements to at most two-electron integrals, we propose several optional approximations to select only the most important terms in the energy correction. For a limited test set, the valence CCSD energies computed with the approximate method, termed CCSD(2)_{R12}, are on average precise to (1.9, 1.4, 0.5 and 0.1%) when computed with Dunning’s aug-cc-pVXZ basis sets [X = (D, T, Q, 5)] accompanied by a single Slater-type correlation factor. This precision is a roughly an order of magnitude improvement over the standard CCSD method, whose respective average basis-set errors are (28.2, 10.6, 4.4 and 2.1%). Performance of the CCSD(2)_{R12} method is almost identical to that of the more complex iterative counterpart, CCSD(R12). The proposed approach to explicitly correlated coupled-cluster methods is technically appealing since no modification of the coupled-cluster equations is necessary and the standard Møller–Plesset R12 machinery can be reused.

1. Introduction

A low-rank coupled-cluster (CC) ansatz^{1–4} has sufficient accuracy for confident quantitative description of molecular structure, properties and reactivity.⁵ Unfortunately, large one-electron basis sets are required to reach the quantitative threshold of precision. The problem is the determinantal *n*-electron basis, which differs qualitatively from the exact wave function at short interelectronic distances *r_{ij}* where the Coulomb repulsion dominates. Terms with explicit dependence on *r_{ij}* can model the Coulomb hole more directly and efficiently⁶ and, therefore, dramatically reduce the basis-set error of the correlation energy. The Achilles heel of the explicitly correlated methods is the appearance of nonfactorizable many-electron integrals. Although such integrals can be

evaluated in closed form,⁷ the high computational cost of even three-electron integrals makes such methods non-competitive in the “chemical” accuracy regime with the basis-set extrapolation. The R12 (or F12[†]) methods^{8–10} are the most practical of modern explicitly correlated techniques because the many-electron integrals are ingeniously reduced to two-electron integrals only.

The R12 version of the second-order Møller–Plesset energy (MP2) method has been most studied because it is technically the simplest. Several types of three- and four-electron integrals appear in the MP2-R12 methods, but all can be reduced,⁹ although tediously, to at most two-electron integrals with controlled and negligible error.¹¹ The MP2-R12 method becomes competitive with extrapolation schemes when combined with a Slater-type correlation factor, suggested by Ten-no,¹² which is more appropriate for modeling the Coulomb hole than the linear term. A precision of 1–2% can typically be achieved on average for valence correlation contributions to electronic energies, reaction enthalpies, and atomization energies with only a triple-zeta orbital basis set accompanied by a single Slater-type geminal correlation factor.^{13–16} Use of several Gaussian-type correlation factors can result in a slightly higher precision.¹⁴

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[†] The R12 methods that use nonlinear correlation factors are often called F12 in the literature to distinguish them from the methods with the linear *r₁₂* factor. The F12 method is formally identical to the R12 method, and, furthermore, the F12 notation does not uniquely identify the method because the correlation factor must be fully specified. Hence, we use the name “R12” here, except when referring to previously published data.

It is difficult to translate the high precision of the MP2-R12 method to predictive chemical applications because the MP2 method generally lacks the necessary accuracy. One possible solution is to use the MP2-R12 method to correct the basis-set incompleteness of the energy in the context of additive model chemistries, such as Gaussian- n (Gn) methods,^{17–19} Weizmann- n (Wn) methods,^{20,21} the “focal point” framework,^{22,23} or the correlation-consistent composite approach²⁴ among many. Unfortunately, because of the “interference effects”^{25,26} between the correlation and basis-set hierarchies, the basis-set incompleteness at the MP2 level is usually larger than that of higher-order correlated methods.^{27,28} Such interference effects are accounted for in the complete basis-set (CBS) model chemistry of Petersson *et al.*^{29,30} *via* an empirical formula, and in principle such an approach could lead to a model chemistry based on an MP2-R12 method. It is, however, desirable to exploit the high precision of the state-of-the-art R12 methodology by *directly* combining it with methods of comparable accuracy.

The rigorous R12 version of the coupled-cluster method using the modern R12 technology, marked by the use of a separate basis for the resolution-of-the-identity (RI) approximation, is technically very demanding compared to the MP2-R12 method. Numerous new three-, four-, and five-electron integrals appear in the CC-R12 amplitude equations and make implementation of such methods difficult. The CC-R12 methods through CCSD(T)-R12 have been explored by Noga *et al.*,^{31–35} but only using the “old” R12 technology. The old approach simplified the equations but required the use of a very large Hartree–Fock basis and therefore was aimed at benchmark-accuracy applications for rather small systems. Fliegler and co-workers introduced the “(R12)” approximation^{36–38} to the CC-R12 method, with the coupling between the standard and explicitly correlated amplitudes drastically simplified *à la* CC n methods.³⁹ The amplitudes of the R12 terms in the CC(R12) method are optimized iteratively (or could be simply kept fixed, as in the rational generator variant⁴⁰ of the MP2-R12 method, to satisfy the cusp conditions for the exact wave function). The authors found that the (R12) approach closely tracks the results of the rigorous one-basis CC-R12 method at a much lower computational cost. The overall performance of the recent extension of the CC(R12) method to nonlinear correlation factors has been very promising: correlation energies and reaction enthalpies computed with a triple-zeta basis are precise to better than 2%, on a par with the conventional quintuple-zeta result.⁴¹

Here we consider a new way to introduce the explicitly correlated terms into the coupled-cluster method. Instead of making approximations to the CC-R12 equations, as is done in the CC(R12) method, our approach introduces the explicitly correlated terms by perturbing the standard coupled-cluster wave function *via* Löwdin partitioning⁴² of the similarity-transformed Hamiltonian. This experiment is motivated by the argument for the R12 method itself, *i.e.* the standard low-rank determinantal expansion can effectively recover a significant portion (>80%) of the correlation energy and the rest can be handled with few explicitly correlated terms. The coupling between the standard and explicitly correlated amplitudes is weak in the MP2-R12 method, and, therefore, the

same can be assumed in general. This coupling should be well described by a low-order perturbation theory and not require the infinite-order treatment of CC-R12 or CC(R12) methods.

Development of perturbation expansions for the eigenvalues and eigenvectors of the similarity-transformed coupled-cluster Hamiltonian by Löwdin partitioning is not a new idea. The formalism in its current form was suggested by Stanton and Gauss⁴³ as a way to correct EOMIP-CCSD energies to account for higher-order excitations. A related approach was used earlier by Head-Gordon *et al.* to correct configuration-interaction single-excitation energies for the effect of double excitations,⁴⁴ as well as later to develop the “(2)” corrections for coupled-cluster energies.^{45,46} Notably, Stanton used this route to “derive” the celebrated CCSD(T) method by treating triple excitations *via* a perturbation expansion defined with respect to the zeroth-order CCSD wave function.⁴⁷ The asymmetric,⁴⁸ or Λ ,⁴⁹ (T) correction naturally follows from such treatment. The general approach has since been used in many related disguises.^{50–56} The common theme is that, until now, the use of explicitly correlated basis functions has never been considered in such perturbative approaches.

Our main hypothesis is that the effect of the explicitly correlated terms on the coupled-cluster energy and wave function can be recovered accurately with only a low-order perturbation treatment. The immediate goal of this work is strictly to examine this hypothesis and lay the groundwork for a more thorough study. Thus this work will be limited to the coupled-cluster singles and doubles model corrected up to second-order for the explicitly correlated terms (corrections due to triple and higher conventional excitations will be incorporated in a future study). Furthermore, only the dominant terms will be included here to simplify the equations.

2. Methodology

The present approach begins with the similarity-transformed Hamiltonian of the standard CC method, $\bar{H} = e^{-T}\hat{H}e^T$. In this work, \hat{T} will be limited to one- and two-electron excitations:

$$\hat{T}_1 = T_a^i \bar{a}_i^a, \quad (1)$$

$$\hat{T}_2 = \frac{1}{4} T_{ab}^{ij} \bar{a}_{ij}^{ab}, \quad (2)$$

where we used the standard tensor notation.^{9,32,57} The T -amplitudes in eqn (1) and (2) are obtained from the standard CCSD method. Matrix representation of \bar{H} will be constructed in a basis that spans a “reference” space \mathbf{P} , comprised of Slater determinants up to the same rank as the excitation operator (vacuum $\mathbf{0}$, singles \mathbf{S} , and doubles \mathbf{D}), and an “external space” \mathbf{Q} , including the explicitly correlated double substitutions $\mathbf{\Gamma}$:

$$\bar{\mathbf{H}} = \begin{pmatrix} \bar{\mathbf{H}}_{\mathbf{PP}} & \bar{\mathbf{H}}_{\mathbf{PQ}} \\ \bar{\mathbf{H}}_{\mathbf{PQ}} & \bar{\mathbf{H}}_{\mathbf{QQ}} \end{pmatrix} \quad (3)$$

The explicitly correlated basis functions are defined as usual:

$$|\Gamma_{ij}^{xy}\rangle \equiv \frac{1}{2} \bar{R}_{z\beta}^{xy} a_{ij}^{z\beta} |0\rangle, \quad (4)$$

where the choice of orbitals \mathbf{x} and \mathbf{y} that “generate” the geminal space is flexible (such orbital pairs will be typeset in bold³³). In this work \mathbf{x} and \mathbf{y} will be occupied orbitals (this is known as the *kl*-ansatz), but other choices have also been considered.⁵⁸ To ensure *strong orthogonality*, the geminal integrals in eqn (5) are defined as in ref. 9.‡

$$\bar{R}_{z\beta}^{xy} = \begin{cases} 0, & \text{if both } \alpha \text{ and } \beta \text{ are in the orbital basis} \\ \bar{r}_{z\beta}^{xy}, & \text{otherwise} \end{cases} \quad (5)$$

This ansatz ensures that space Γ , despite the non-unit metric $\mathbf{S}_{\Gamma\Gamma}$, is orthogonal to \mathbf{D} . The integral r_{pq}^{rs} is over a correlation function $f(r_{12})$, which can be any well-behaved function.

Note that the Hamiltonian in eqn (3) is not identical to the matrix that would be used in the EOM-CCSD-R12 method because in the latter the full excitation operator (including excitations into Γ block) would be used for the similarity transformation. Therefore the $\bar{\mathbf{H}}_{\mathbf{PP}}$ block is the similarity-transformed Hamiltonian used in the EOM-CCSD method. Its left and right-hand ground-state eigenvectors,

$$\mathcal{L} = \begin{pmatrix} 1 \\ \Lambda_{\mathbf{S}} \\ \Lambda_{\mathbf{D}} \end{pmatrix} \mathcal{R} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad (6)$$

can be considered a good approximation to the left- and right-hand eigenvectors, \mathbf{L} and \mathbf{R} , of the full matrix in eqn (3).§

Löwdin partitioning⁴² of the Hamiltonian matrix expresses the exact eigenvalue E of the full matrix in terms of sub-blocks $\mathbf{L}_{\mathbf{P}}$ and $\mathbf{R}_{\mathbf{P}}$ of the exact eigenvectors:

$$E \mathbf{L}_{\mathbf{P}}^{\dagger} \mathbf{R}_{\mathbf{P}} = \mathbf{L}_{\mathbf{P}}^{\dagger} \bar{\mathbf{H}}_{\mathbf{PP}} \mathbf{R}_{\mathbf{P}} + \mathbf{L}_{\mathbf{P}}^{\dagger} \bar{\mathbf{H}}_{\mathbf{PQ}} (E \mathbf{S}_{\mathbf{QQ}} - \bar{\mathbf{H}}_{\mathbf{QQ}})^{-1} \bar{\mathbf{H}}_{\mathbf{QP}} \mathbf{R}_{\mathbf{P}}, \quad (7)$$

where \mathbf{S} is the overlap matrix. Rayleigh–Schrödinger perturbation theory can then be straightforwardly applied to this expression. We define the zeroth-order eigenvectors in terms of the EOM-CCSD eigenvectors as

$$\mathbf{L}^{(0)} \equiv \begin{pmatrix} \mathbf{L}_{\mathbf{P}}^{(0)} \\ \mathbf{L}_{\mathbf{Q}}^{(0)} \end{pmatrix} = \begin{pmatrix} \mathcal{L} \\ \mathbf{0} \end{pmatrix} \quad (8)$$

$$\mathbf{R}^{(0)} \equiv \begin{pmatrix} \mathbf{R}_{\mathbf{P}}^{(0)} \\ \mathbf{R}_{\mathbf{Q}}^{(0)} \end{pmatrix} = \begin{pmatrix} \mathcal{R} \\ \mathbf{0} \end{pmatrix} \quad (9)$$

whereas the zeroth- and first-order Hamiltonians will be defined as follows:

$$\bar{\mathbf{H}}^{(0)} = \begin{pmatrix} \bar{\mathbf{H}}_{\mathbf{PP}} & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{H}}_{\mathbf{QQ}}^{(0)} \end{pmatrix} \quad (10)$$

$$\bar{\mathbf{H}}^{(1)} = \begin{pmatrix} \mathbf{0} & \bar{\mathbf{H}}_{\mathbf{PQ}} \\ \bar{\mathbf{H}}_{\mathbf{PQ}} & \bar{\mathbf{H}}_{\mathbf{QQ}}^{(1)} \end{pmatrix} \quad (11)$$

‡ Werner *et al.* recently referred to this choice as Ansatz.¹⁵

§ Λ amplitudes are the standard lambda-amplitudes of the ground-state coupled-cluster theory,² also known as the Lagrange multipliers in the variational formulation of the coupled-cluster method.⁵

The zeroth-order energy is the ground-state CCSD energy:

$$E^{(0)} = (\mathbf{L}^{(0)})^{\dagger} \bar{\mathbf{H}}^{(0)} \mathbf{R}^{(0)} = \mathcal{L}^{\dagger} \bar{\mathbf{H}}_{\mathbf{PP}}^{(0)} \mathcal{R} \equiv E_{\text{CCSD}}. \quad (12)$$

The first-order energy correction vanishes whereas the second-order energy is

$$E^{(2)} = \mathcal{L}^{\dagger} \bar{\mathbf{H}}_{\mathbf{PQ}} (E^{(0)} \mathbf{S}_{\mathbf{QQ}} - \bar{\mathbf{H}}_{\mathbf{QQ}}^{(0)})^{-1} \bar{\mathbf{H}}_{\mathbf{QP}} \mathcal{R}, \quad (13)$$

or, in terms of spaces $\mathbf{0}$, \mathbf{S} , \mathbf{D} , and Γ ,

$$E^{(2)} = \bar{\mathbf{H}}_{\mathbf{0}\Gamma} (E^{(0)} \mathbf{S}_{\Gamma\Gamma} - \bar{\mathbf{H}}_{\Gamma\Gamma}^{(0)})^{-1} \bar{\mathbf{H}}_{\Gamma\mathbf{0}} + \Lambda_{\mathbf{S}}^{\dagger} \bar{\mathbf{H}}_{\mathbf{S}\Gamma} (E^{(0)} \mathbf{S}_{\Gamma\Gamma} - \bar{\mathbf{H}}_{\Gamma\Gamma}^{(0)})^{-1} \bar{\mathbf{H}}_{\Gamma\mathbf{0}} + \Lambda_{\mathbf{D}}^{\dagger} \bar{\mathbf{H}}_{\mathbf{D}\Gamma} (E^{(0)} \mathbf{S}_{\Gamma\Gamma} - \bar{\mathbf{H}}_{\Gamma\Gamma}^{(0)})^{-1} \bar{\mathbf{H}}_{\Gamma\mathbf{0}} \quad (14)$$

To evaluate eqn (14) we must define $\bar{\mathbf{H}}_{\Gamma\Gamma}^{(0)}$. Before doing so, note that the explicitly correlated correction of the MP2-R12 theory can be derived using the same approach if the bare electronic Hamiltonian \hat{H} is used in place of \bar{H} and the “reference” space only includes the vacuum. Then the energy correction has the form of the first term on the right-hand side of eqn (14):

$$E_{\text{MP}}^{(2)} = \mathbf{H}_{\mathbf{0}\Gamma} (E_{\text{MP}}^{(0)} \mathbf{S}_{\Gamma\Gamma} - \mathbf{H}_{\Gamma\Gamma}^{(0)})^{-1} \mathbf{H}_{\Gamma\mathbf{0}} \quad (15)$$

The standard MP2-R12 expression is obtained if the Fock operator is chosen as the zeroth-order Hamiltonian, or $\hat{H}_{\text{MP}}^{(0)} = E_{\text{MP}}^{(0)} + \hat{F}_N$ in the normal-ordered form. To maximize the resemblance to the MP2-R12 method, we will choose the zeroth-order Hamiltonian as

$$\bar{H}^{(0)} = \hat{P}_{\mathbf{P}} \bar{H} \hat{P}_{\mathbf{P}} + \hat{P}_{\mathbf{Q}} (E^{(0)} + \hat{F}_N) \hat{P}_{\mathbf{Q}}, \quad (16)$$

with normal-ordered Fock operator \hat{F}_N . In this formulation the $E^{(0)} \mathbf{S}_{\Gamma\Gamma} - \bar{\mathbf{H}}_{\Gamma\Gamma}^{(0)}$ matrix of eqn (14) is independent of T -amplitudes and identical to the $E^{(0)} \mathbf{S}_{\Gamma\Gamma} - \mathbf{H}_{\Gamma\Gamma}^{(0)}$ matrix of eqn (15). Its evaluation has been discussed elsewhere^{9,10,15,59,60}.

Eqn (14) and (16) correspond to the method that we term CCSD(2)_{R12}, by analogy with the established convention.⁵² All remaining matrices in eqn (14) include up to three-electron integrals and have truncating partial wave expansions (it was not the case for the matrix elements of the exchange operator in the $\mathbf{H}_{\Gamma\Gamma}^{(0)}$ matrix^{8,9}). They can be evaluated straightforwardly using the standard approximation of the R12 method (full details will be given elsewhere). To judge the performance of the proposed method, here we are only interested in computing the dominant contributions to each matrix. Thus we propose several approximations, which, while not mandatory, will simplify the equations drastically:

1. Each term can be classified according to the standard CC perturbation theory defined with respect to the Hartree–Fock reference, in which the one-electron Hamiltonian elements are zeroth-order, T_2 -amplitudes have a leading first-order contribution, *etc.* For example, $\bar{\mathbf{H}}_{\mathbf{0}\Gamma}$ matrix elements,

$$\langle 0 | \bar{H} | \Gamma_{ij}^{xy} \rangle = V_{ij}^{xy}, \quad (17)$$

are purely first-order. The $\bar{\mathbf{H}}_{\Gamma\mathbf{0}}$ matrix is more complicated: in addition to the same first-order term identical to $\bar{\mathbf{H}}_{\mathbf{0}\Gamma}^{\dagger}$, it

contains second and higher-order terms:

$$\langle \Gamma_{ij}^{\text{xy}} | \bar{H} | 0 \rangle = V_{\text{xy}}^{ij} + \frac{1}{2} V_{\text{xy}}^{ab} T_{ab}^{ij} + \dots \quad (18)$$

In this work we will include up to third-order contributions to the energy and up to second-order terms in the matrix elements.

2. Most many-electron integrals that appear in matrices $\bar{\mathbf{H}}_{\mathbf{R0}}$, $\bar{\mathbf{H}}_{\mathbf{0R}}$, $\bar{\mathbf{H}}_{\mathbf{SR}}$ and $\bar{\mathbf{H}}_{\mathbf{DR}}$ vanish if the Hartree–Fock basis is used to resolve the identity (such an approach was used in the original R12 method). In this work we will keep only the integrals that do not vanish under such an approximation: namely, the V intermediate of the R12 theory.

3. Although the left-hand eigenvector is not necessary to compute the reference energy, it is needed to evaluate the energy correction. To avoid having to solve Λ -equations, we can simply replace them with the corresponding T -amplitudes (they have the same leading-order term). The motivation for such replacement can be found in the argument for the standard (T) correction to the CCSD energy.

4. Extended (EBC) and generalized Brillouin conditions (GBC)^{9,11} will be assumed in this work. While the effect of the generalized Brillouin condition is always small,¹¹ its extended counterpart usually affects the MP2-R12 energies appreciably, especially if only a double-zeta basis is used. If EBC is not assumed, the coupling term between the doubles and geminals functions appears in the zeroth-order operator.[¶]^{10,59} In the current method the coupling between doubles and geminals blocks only appears in the first-order (see eqn (10) and (11)). For consistent comparison with the MP2-R12 results, we will postpone this issue until later and simply assume EBC here.

The CCSD(2)_{R12} method using these approximations will be termed CCSD(2)_{R12}. Its energy correction is extremely simple:

$$E^{(2)} = \bar{\mathbf{H}}_{\mathbf{0R}} (E^{(0)} \mathbf{S}_{\mathbf{R}\Gamma} - \bar{\mathbf{H}}_{\mathbf{R}\Gamma}^{(0)})^{-1} (\bar{\mathbf{H}}_{\mathbf{R0}} + \bar{\mathbf{H}}_{\mathbf{DR}}^{\dagger} \mathcal{T}_{\mathbf{D}}), \quad (19)$$

where $\mathcal{T}_{\mathbf{D}}$ is a vector of T_2 amplitudes. Furthermore, the elements of matrices $\mathbf{H}_{\mathbf{0R}}$, $\mathbf{H}_{\mathbf{R0}}$ and $\mathbf{H}_{\mathbf{DR}}$ become, respectively,

$$\langle 0 | \bar{H} | \Gamma_{ij}^{\text{xy}} \rangle = V_{ij}^{\text{xy}} \quad (20)$$

$$\langle \Gamma_{ij}^{\text{xy}} | \bar{H} | 0 \rangle \approx V_{\text{xy}}^{ij} + \frac{1}{2} V_{\text{xy}}^{ab} T_{ab}^{ij} \quad (21)$$

$$\langle \tilde{a}_{kl}^{ab} | \bar{H} | \Gamma_{ij}^{\text{xy}} \rangle \approx (\delta_i^k \delta_j^l - \delta_j^k \delta_i^l) V_{\text{xy}}^{ab}. \quad (22)$$

The final energy correction $E^{(2)}$ is a sum of pair contributions

$$E^{(2)} = \frac{1}{2} \sum_{ij} \varepsilon_{ij}^{(2)} = \frac{1}{4} T_{ij}^{\text{xy}} \tilde{V}_{\text{xy}}^{ij}, \quad (23)$$

computed from the “dressed” interaction matrix,

$$\tilde{V}_{\text{xy}}^{ij} = V_{\text{xy}}^{ij} + V_{\text{xy}}^{ab} T_{ab}^{ij}, \quad (24)$$

and the geminal amplitudes T_{ij}^{xy} determined from the linear system,

$$V_{ij}^{\text{xy}} = -T_{ij}^{\text{wz}} (\tilde{B}^{(ij)})_{\text{wz}}^{\text{xy}}. \quad (25)$$

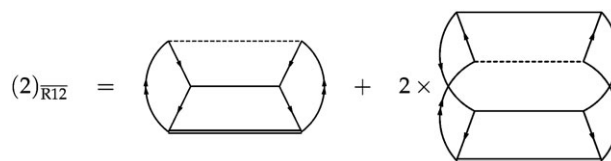


Fig. 1 A diagrammatic illustration of the $(2)_{\text{R12}}$ correction. The T amplitudes, the two-electron component of the Hamiltonian and the correlation factor are denoted as single lines, dashed lines and double lines respectively.

The zeroth-order matrix in eqn (25) is expressed in terms of the standard B and X intermediates of the MP2-R12 method^{9,59} as:

$$(\tilde{B}^{(ij)})_{\text{wz}}^{\text{xy}} = B_{\text{wz}}^{\text{xy}} - (\varepsilon_i + \varepsilon_j) X_{\text{wz}}^{\text{xy}} \quad (26)$$

A diagrammatic representation for the $(2)_{\text{R12}}$ correction is shown in Fig. 1.

It is immediately clear that the pair energy correction in eqn (23) becomes identical to its MP2-R12 counterpart if the dressed interaction \tilde{V} is replaced with the standard interaction V . Since the second term on the r.h.s. of eqn (24) has the second-order leading contribution according to the standard Hartree–Fock-based CCPT, it should be small compared to the first. The MP2 basis-set incompleteness error (BSIE) is, therefore, the leading-order contribution to the CCSD BSIE, whereas the dependence on T -amplitudes only appears in the next order. This next-order term can be understood as the source of *interference effects*, identified by Petersson and Nyden^{25,26} as responsible for lower BSIE of infinite-order theories, like CI and CC, compared to the MP2 counterpart. We must note that Petersson and Nyden also exploited a perturbation expansion of a *correlated* wave function to develop an empirical correction for the interference effect. It is striking that the current non-empirical picture of the interference effect is not only reminiscent of these pioneering efforts, but was also obtained from a similar mathematical approach.

The computational implementation of the proposed method is very straightforward. Converged coupled-cluster amplitudes from a coupled-cluster code and the standard MP2-R12 intermediates V , B , and X are all that is needed to evaluate the energy correction. The expressions for the intermediate B in standard approximations B or C involve two-electron integrals with 2 indices from the complementary auxiliary basis set (CABS) space; however, such terms may be ignored^{15,62} (this was not done in this work). The computation of the intermediates formally scales with the sixth power of the size of the system, *i.e.* the same as the cost of the CCSD procedure. Although the cost of solving the linear system in eqn (25) scales with the eighth power of the system size, the prefactor is so small that this step has a negligible cost (the scaling of this step can be reduced to the sixth power if the linear system is solved iteratively). The extra cost of the explicitly correlated correction can be decreased by the use of density-fitting techniques⁶³ and/or their combination with the resolution-of-the-identity method.⁶⁴

¶ Such coupling is zero if the less-efficient Ansatz $\mathbf{I}^{59,61}$ is used.

3. Computational details

Geometries for H₂O and F₂ were fixed at their experimental equilibrium values: $r_{\text{OH}} = 95.72$ pm,⁶⁵ $\alpha_{\text{HOH}} = 104.52^\circ$,⁶⁵ $r_{\text{FF}} = 141.193$ pm.⁶⁶

Hartree–Fock orbitals were expanded in standard correlation-consistent basis sets of Dunning and co-workers.^{67,68} The RI basis sets consisted of the primitive 19s14p8d6f4g3h2i and 9s6p4d3f2g sets of spherical harmonic Gaussians for Ne/O/F and H respectively.⁵⁹

The Slater-type correlation factor $\exp(-1.5r_{12})$ was represented as a least-squares fit to 6 Gaussian-type geminals (the optimal exponents and coefficients are (303.393, 54.8852, 14.6991, 4.50631, 1.36066, 0.36439) and (0.0510844, 0.081916, 0.129811, 0.205298, 0.299458, 0.207455) respectively). All integrals necessary for the explicitly correlated calculations were evaluated using the recurrence relations of Valeev and Schaefer⁶⁹ and Weber and Daul⁷⁰ as implemented by an integrals code generator LIBINT.⁷¹ The complementary auxiliary basis set (CABS) method in its CABS+ variant⁷² was used to reduce the many-electron integrals. The geminal–geminal block of the zeroth-order Hamiltonian was treated using standard approximation C of Kedzuch *et al.*⁶⁰ Since approximation C does not assume either extended or generalized Brillouin conditions, it is slightly inconsistent to assume such conditions elsewhere (in matrices \mathbf{H}_{T0} , and \mathbf{H}_{DR}). However, the effect of these conditions on the zeroth-order Hamiltonian matrix is negligible: we recomputed Ne correlation energies with the linear correlation factor using standard approximation B, in which EBC and GBC were avoided, and the energy changed by less than 0.05 mE_h.

All computations were performed with the developers' versions of MPQC⁷³ and PSI3⁷⁴ programs. The massively-parallel implementation of the MP2-R12 method in MPQC⁷⁵ is used to compute intermediates V , B , and X in a fully integral-direct fashion. These intermediates are then combined with the converged CCSD amplitudes obtained from PSI3. Both programs were made to adhere to the recently-developed Common Components Architecture standard for the molecular integrals⁷⁶ to enable data exchange between the programs. Snapshots of the MPQC and PSI3 source codes can be obtained from the respective code repositories using tags libint2-branch-ccsd-pt2r12 and 3499.

Table 1 Valence MP2 and CCSD correlation energies for the neon atom, in mE_h. The explicitly correlated values were obtained with the r_{12} correlation factor

Basis set ^a	MP2		MP2-R12		CCSD		CCSD(2) _{RI2}			
	E	%	δ^b	E	%	E	%	δ^c	E	%
<i>sp</i>	−146.38	45.7	−114.57	−260.92	81.5	−145.25	46.0	−109.75	−254.97	80.8
<i>spd</i>	−259.24	81.0	−55.56	−314.81	98.3	−258.97	82.0	−47.67	−306.61	97.1
<i>spdf</i>	−294.08	91.8	−25.50	−319.54	99.8	−294.03	93.1	−19.74	−313.74	99.4
<i>spdfg</i>	−307.93	96.2	−12.11	−320.04	100.0	−306.78	97.2	−8.59	−315.37	99.9
<i>spdfgh</i>	−313.19	97.8	−6.92	−320.11	100.0	−310.90	98.5	−4.68	−315.59	100.0
Complete	−320.2 ^d	100	0	−320.2 ^d	100	−315.7 ^e	100	0	−315.7 ^e	100

^a Subsets of the 20s14p11d9f7g5h3i basis set from ref. 59. ^b $E(\text{MP2-R12}) - E(\text{MP2})$. ^c $E(\text{CCSD}(2)_{\text{RI2}}) - E(\text{CCSD})$. ^d MP2-R12 20s14p11d9f7g5h3i energy from ref. 59. ^e The CCSD-R12 19s14p8d6f4g3h energy from ref. 78 including the residual basis-set error correction estimated as the difference between the MP2-R12 20s14p11d9f7g5h3i energy from ref. 59 and the MP2-R12 19s14p8d6f4g3h energy from ref. 78.

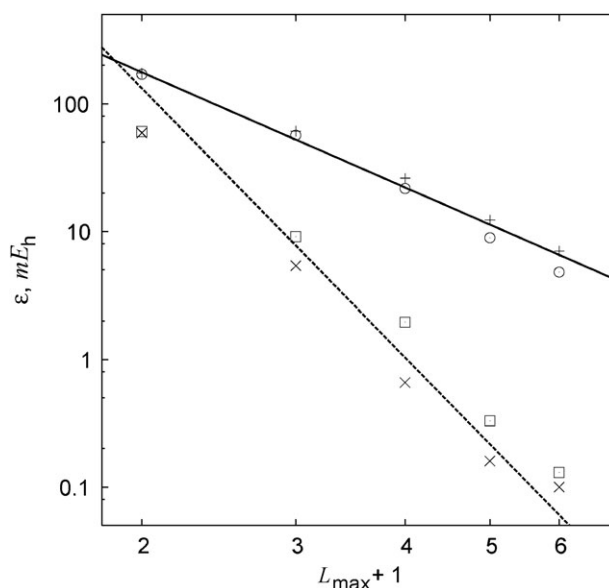


Fig. 2 Convergence of the basis-set error in standard and explicitly correlated valence correlation energies for the Ne atom (see Table 1). A $(L + 1)^{-3}$ fit to the average error of the standard MP2 (+) and CCSD (O) energies is shown with the solid line. The dashed line shows a $(L + 1)^{-7}$ fit to the average error of the MP2-R12 (x) and CCSD(2)_{RI2} (□) energies.

4. Results

Table 1 lists MP2 and CCSD valence correlation energies for the neon atom computed with a “partial wave”-style basis set accompanied by a linear correlation factor. Convergence of the standard and explicitly correlated energies is expected to follow the established (at least for the MP2 case²⁷) $\mathcal{O}[(L_{\text{max}} + 1)^{-3}]$ and $\mathcal{O}[(L_{\text{max}} + 1)^{-7}]$ asymptotics. The basis-set incompleteness errors plotted in Fig. 2 indeed follow these trends. With every basis set, precision of the CCSD(2)_{RI2} energy is close to that of the MP2-R12 energy. The explicitly correlated energies computed with the largest basis set are at most 0.1 mE_h removed from their CBS estimates. We conclude that the approximations introduced in this work do not seem to affect the convergence in the asymptotic regime. However, a more complete study is still warranted.

It is clear that the T -dependent contribution to the basis-set incompleteness is non-negligible even with the largest basis set.

Table 2 Valence MP2 and CCSD correlation energies for the neon atom, in mE_h . The explicitly correlated values were obtained with the $\exp(-1.5r_{12})$ correlation factor

Basis set	MP2		MP2-R12		CCSD		CCSD(2) $_{\overline{R12}}$			
	E	%	δ^a	E	%	E	%	δ^b	E	%
aug-cc-pVDZ	-206.87	64.6	-112.44	-319.31	99.7	-210.15	66.6	-100.78	-310.93	98.5
aug-cc-pVTZ	-272.52	85.1	-43.71	-316.22	98.8	-274.09	86.8	-35.83	-309.93	98.2
aug-cc-pVQZ	-297.24	92.8	-20.51	-317.75	99.2	-297.76	94.3	-15.47	-313.23	99.2
aug-cc-pV5Z	-307.97	96.2	-11.37	-319.34	99.7	-306.79	97.2	-8.14	-314.94	99.8
aug-cc-pV6Z	-312.87	97.7	-6.98	-319.85	99.9	-310.61	98.4	-4.81	-315.41	99.9
Complete	-320.2 ^c	100	0	-320.2 ^c	100	-315.7 ^d	100	0	-315.7 ^d	100

^a $E(\text{MP2-R12}) - E(\text{MP2})$. ^b $E(\text{CCSD}(2)_{\overline{R12}}) - E(\text{CCSD})$. ^c MP2-R12 20s14p11d9f7g5h3i energy from ref. 59. ^d The CCSD-R12 19s14p8d6f4g3h energy from ref. 78 including the residual basis-set error correction estimated as the difference between the MP2-R12 20s14p11d9f7g5h3i energy from ref. 59 and the MP2-R12 19s14p8d6f4g3h energy from ref. 78.

Table 3 Valence MP2 and CCSD correlation energies for the water molecule, in mE_h . The MP2-R12 and CCSD(2) $_{\overline{R12}}$ values were obtained with the $\exp(-1.5r_{12})$ correlation factor

Basis set	MP2		MP2-R12		CCSD		CCSD(2) $_{\overline{R12}}$		CCSD(F12) ^a	
	E	%	E	%	E	%	E	%	E	%
aug-cc-pVDZ	-219.34	73.0	-297.34	99.0	-227.11	76.2	-290.72	97.6	-284.79	95.4
aug-cc-pVTZ	-268.35	89.3	-298.72	99.4	-273.05	91.7	-294.75	98.9	-295.02	98.9
aug-cc-pVQZ	-285.91	95.2	-299.59	99.7	-288.21	96.7	-296.93	99.7	-297.49	99.7
aug-cc-pV5Z	-292.90	97.5	-300.18	99.9	-293.65	98.6	-297.65	99.9	-298.10	99.9
Complete	-300.4 ^b	100	-300.4 ^b	100	-297.9 ^b	100	-297.9 ^b	100	-298.4 ^c	100

^a See ref. 41. These values were computed with the $\exp(-1.3r_{12})$ correlation factor at the optimized MP2(fc)/aug-cc-pVTZ geometry. ^b Estimate from ref. 78. ^c Obtained from the CCSD/aug-cc-pVXZ data (X = Q, 5) of ref. 41 using a Schwenke extrapolation scheme.⁷⁹

Table 4 Valence MP2 and CCSD correlation energies for the fluorine molecule, in mE_h . The MP2-R12 and CCSD(2) $_{\overline{R12}}$ values were obtained with the $\exp(-1.5r_{12})$ correlation factor

Basis set	MP2		MP2-R12		CCSD		CCSD(2) $_{\overline{R12}}$		CCSD(F12) ^a	
	E	%	E	%	E	%	E	%	E	%
aug-cc-pVDZ	-428.06	70.0	-608.52	99.5	-435.45	72.5	-591.02	98.3	-568.58	94.8
aug-cc-pVTZ	-536.12	87.7	-606.56	99.2	-538.96	89.7	-593.59	98.8	-592.01	98.7
aug-cc-pVQZ	-575.84	94.2	-608.58	99.5	-575.16	95.7	-598.20	99.5	-597.57	99.6
aug-cc-pV5Z	-592.78	97.0	-610.79	99.9	-588.57	97.9	-600.50	99.9	-599.43	99.9
Complete	-611.4 ^b	100	-611.4 ^b	100	-601.0 ^b	100	-601.0 ^b	100	-599.9 ^c	100

^a See ref. 41. These values were computed with the $\exp(-1.3r_{12})$ correlation factor at the optimized MP2(fc)/aug-cc-pVTZ geometry. ^b Estimate from ref. 78. ^c Obtained from the CCSD/aug-cc-pVXZ data (X = Q, 5) of ref. 41 using a Schwenke extrapolation scheme.⁷⁹

Whereas the explicitly correlated corrections at the MP2 and coupled-cluster levels differ by less than 5 mE_h with the smallest basis set, they still differ by more than 2 mE_h when computed with the largest basis set. The assumption of additivity, often employed to approximate the CBS limit of a coupled-cluster method by combining the CBS limit at the MP2 level and a small basis CC energy,^{22,77} does not seem to work well for absolute electronic energies.²⁸ For example, if it were applied to estimate the CCSD CBS limit from the MP2-R12/*spdfgh* energy (precise to 0.1 mE_h) and the CCSD/*spdfgh* energy, the predicted energy would be -317.81 mE_h , certainly more than 2 mE_h below the actual CCSD CBS limit. The interference effects,^{25,26} which are responsible for this discrepancy, seem to be quantitatively described by the CCSD(2) $_{\overline{R12}}$ method.

Use of more practical correlation-consistent basis sets calls for short-range nonlinear correlation factors, such as a Slater-

type geminal. The results for Ne, presented in Table 2, are essentially similar to those from Table 1. Errors smaller than 2% are achieved with all basis sets with both MP2-R12 and CCSD(2) $_{\overline{R12}}$ methods (the double-zeta energies are, in all likelihood, artificially precise because of the fortuitous effect of assuming the extended Brillouin condition). With the largest, sextuple-zeta basis set, the MP2-R12 and CCSD(2) $_{\overline{R12}}$ energies are within a few tenths of a millihartree of the CBS-limit estimates. As with the r_{12} results in Table 1, the T -dependent contribution to the BSIE is also unequivocally important here.

Molecular MP2 and CCSD valence correlation energies, presented in Tables 3 and 4, fully support the above analysis. For the molecules we are also able to compare the CCSD(2) $_{\overline{R12}}$ energies to those obtained with the CCSD(F12) method of Klopper *et al.*⁴¹ Although the latter values were evaluated at geometries different from ours, the apparent

differences in the CBS limits are small. We found that the CCSD(2) $_{\overline{R12}}$ and CCSD(F12) methods perform almost identically to each other unless the aug-cc-pVDZ basis is used. The likely issue with the latter is, again, the assumption of EBC in our method. Assuming EBC has little effect on the explicitly correlated energies for larger basis sets, the two methods can be compared directly. Even disregarding the geometrical differences, the CCSD(2) $_{\overline{R12}}$ and CCSD(F12) energies differ by less than 0.6 mE_h for H₂O and less than 1.6 mE_h for F₂. If we subtract the difference in the CBS limit, the two methods agree to within 0.2 and 0.5 mE_h respectively. Although the CCSD(F12) method couples the standard and explicitly correlated amplitudes iteratively, it appears that this coupling is very weak and can be confidently treated using our perturbative approach.

5. Conclusions and perspective

Here we outlined a simple perturbative approach to coupled-cluster R12 methods and explored the second-order explicitly correlated correction to the coupled-cluster singles and doubles energy, dubbed CCSD(2) $_{\overline{R12}}$. Although the formalism does not require use of any approximations other than the resolution of the identity for the many-electron integrals, we introduced a simplified method, CCSD(2) $_{\overline{R12}}$, with several additional approximations that maximally truncated the working equations without apparent negative impact. In the future we will test these approximations in more detail as well as explore various partitioning of the similarity-transformed Hamiltonian.

The proposed perturbation expansion is a systematic, easy-to-interpret view of the “interference” between the basis-set and correlation hierarchies in the many-body electronic-structure theory. The leading-order term in the second-order energy expression in the CCSD(2) $_{\overline{R12}}$ method is simply the R12 correction of the MP2-R12 method and does not depend on the coupled-cluster amplitudes (hence it is the same for any CC method). The next-order term includes coupled-cluster amplitudes linearly and makes the correction dependent on the particular coupled-cluster method used. This term is responsible for the interference effects^{25,26} and its effect is to lower the magnitude of the correction compared to the MP2-R12 method, in accordance with the usual experience.

Performance of the CCSD(2) $_{\overline{R12}}$ method is (unexpectedly) good. It is remarkable that, despite several approximations, a simple non-iterative correction can be used to compute the CCSD energy of a Ne atom precise to a few tenths of a millihartree, *i.e.* much better than 0.1%. With a single Slater-type geminal as a correlation factor, the CCSD valence correlation energy can be computed to better than 2% precision with only a triple-zeta basis set. We also found that the CCSD(2) $_{\overline{R12}}$ method performed almost identically to the more expensive, iterative CCSD(F12) method of Klopper *et al.*^{36–38,41}

Another virtue of the CCSD(2) $_{\overline{R12}}$ is its technical simplicity: no modification of a standard coupled-cluster program is required and an MP2-R12 energy program has to be changed very little. The computational cost of the second-order energy correction is virtually identical to that of the MP2-R12 energy,

the dominant contribution of which scales with the sixth power of the size of the system. Therefore, the presented method can be applied to systems of the same size as the underlying coupled-cluster method. The idea of the presented approach is very general and should be widely applicable, for example, to accurate computation of excited-state energies and properties, or in combination with multireference coupled-cluster methods.

Acknowledgements

I would like to thank Daniel Crawford for helpful discussions and recognize his long-time development of the coupled-cluster codes in PSI3. Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research *via* grant 46811-G6.

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