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Infinite-order diagrammatic summation approach to the explicitly correlated congruent transformed Hamiltonian

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We present the development of a real-space and projected congruent transformation method for treating electron correlation in chemical systems. This method uses an explicitly correlated function for performing congruent transformation on the electronic Hamiltonian. As a result of this transformation, the electronic Hamiltonian is transformed into a sum of two-, three-, four-, five-, and six-particle operators. Efficient computational implementation of these many-particle operators continues to be challenging for application of the congruent transformation approach for many-electron systems. In this work, we present a projected congruent transformed Hamiltonian (PCTH) approach to avoid computation of integrals involving operators that couple more than two particles. The projected congruent transformation becomes identical to the real-space congruent transformation in the limit of infinite basis size. However, for practical calculations, the projection is always performed on a finite-dimensional space. We show that after representing the contributing expressions of the PCTH in terms of diagrams, it is possible to identify a subset of diagrams that can be summed up to infinite order. This technique, denoted as partial infinite-order summation (PIOS), partly alleviates the limitation from the finite-basis representation of the PCTH method. The PCTH and PCTH-PIOS methods were applied to an isoelectronic series of 10-electron systems (Ne, HF, H_2O, NH_3, CH_4) and results were compared with configuration interaction (CISD) calculations. The results indicate that the PCTH-PIOS method can treat electron-electron correlations while avoiding explicit construction and diagonalization of the Hamiltonian matrix.

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I. INTRODUCTION

The form of the many-electron wave function at small electron-electron separation plays an important role in the accurate determination of the ground-state energy. The relationship between the Coulomb singularity in the electronic Hamiltonian and form of the many-electron wave function at the electron-electron coalescence point is well known and is given by the Kato cusp condition [1–4]. Explicitly correlated methods improve the form of the many-electron wave function near the electron-electron coalescence point by incorporating explicit r_{12} dependence in the form of the wave function. The inclusion of the r_{12} term was shown to be indispensable for high-precision calculations of ground- and excited-state energies in atoms and molecules and has been implemented in various methods including quantum Monte Carlo (QMC) [2–9], perturbation theory (R12-MP2) [10–13], coupled-cluster (R12-CC) [14–21], configuration interaction, transcorrelated Hamiltonian [22–28], geminal augmented MCSCF [29], the correlation operator approach [30], and in explicitly correlated Gaussians [31–33]. One of the main challenges in efficient implementation of explicitly correlated methods is the analytical evaluation of integrals involving the r_{12} term. The electronic Hamiltonian has only one- and two-particle operators; however, because of the r_{12} term in the wave function, integrals involving the Hamiltonian and explicitly correlated wave functions often involve three-particle and higher terms. The resolution of identity (RI) approach has been successfully applied for efficient evaluation of many-particle integrals and has been widely adopted for implementing faster, more efficient R12-MP2 [34–38] and R12-CC methods [39].

In this article, we introduce the projected version of the explicitly correlated congruent transformed Hamiltonian (CTH) method [40]. In the CTH method, an explicitly correlated function is used to perform congruent transformation [41,42] on the electronic Hamiltonian. This approach is similar to the transcorrelated Hamiltonian method where a similarity transformation is performed on the Hamiltonian [22,23]. However, one of the advantages of the CTH method is that the transformation preserves the Hermitian property of the Hamiltonian. Consequently, the transformed Hamiltonian is amenable to standard variational procedures for obtaining the ground-state energy [40]. The transformed Hamiltonian involves up to six-particle operators and efficient implementation of these many-particle operators is crucial for application of the CTH method. To address the limitations of the CTH method for many-electron systems, we have developed the projected congruent transformed Hamiltonian (PCTH) method. The PCTH method is formulated by projecting the CT Hamiltonian on a finite-dimensional space spanned by N-particle orthonormal basis functions. The PCTH method is identical to the CTH method in the limit of an infinite number of basis functions; however, practical implementation of the PCTH is always approximate because of the truncation of the basis. Here, we present a diagrammatic summation approach to include infinite-order contributions to the finite-basis implementation of the PCTH method. We have used diagrammatic notation that is commonly used in the perturbation theory and coupled-cluster equations to represent the terms in the PCTH expansion [43]. After that, we show that certain classes of diagrams can be summed up to infinite order and the result can be expressed

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as an analytical expression of a renormalized two-particle operator. Because the method in its current form is applicable only to selected (as opposed to all) classes of diagrams, it is denoted as a partial infinite-order summation (PIOS) method. The details of the derivation of the PIOS method are presented in the following section. The PIOS method was used for calculating the ground-state energy of isoelectronic 10-electron systems (Ne,HF,H_2O,NH_3,CH_4) and the results are presented in Sec. III.

II. THEORY AND COMPUTATIONAL DETAILS

A. Real-space formulation of congruent transformed Hamiltonian

The first step in the construction of the CTH is to define an explicitly correlated two-body operator as shown below:

$$G(1,\ldots,N) = \sum_{i<j}^{N} g(r_{ij}) = \sum_{i<j}^{N} g(i,j), \tag{1}$$

where N is the number of electrons in the system. The derivation presented here is independent of the choice of the two-body explicitly correlated function $g(1,2)$. The specific form used in the present calculation will be discussed in Sec. II D. The congruent transformed operators are defined as

$$\tilde{H} = G^{\dagger} H G, \tag{2}$$

$$\tilde{S} = G^{\dagger} \mathbf{1} G, \tag{3}$$

where the transformed Hamiltonian contains up to six-particle operators [40,44]. For a given trial wave function Ψ_T, the CTH energy is defined as

$$E[\Psi_T,G] = \frac{\langle \Psi_T | \tilde{H} | \Psi_T \rangle}{\langle \Psi_T | \tilde{S} | \Psi_T \rangle}. \tag{4}$$

The congruent transformation preserves the Hermitian property of the electronic Hamiltonian and by construction the CTH energy is an upper bound to the exact ground-state energy

$$E_{\text{exact}} \leqslant \min_{\Psi_T,G} E[\Psi_T,G] \leqslant \min_{\Psi_T} E[\Psi_T,G=1]. \tag{5}$$

As a consequence of the above relationship, the CTH energy is amenable to standard variational procedure and can be minimized with respect to both the trial wave function Ψ_T and the explicitly correlated function G. In the limit of $G = 1$, the CTH energy is equivalent to the expectation value of the electronic Hamiltonian with respect to the trial wave function Ψ_T. The congruent transformed Hamiltonian can be expressed as the sum of two-, three-, four-, five-, and six-particle operators as shown below:

$$\tilde{H} = \left[\sum_{i<j} g(i,j) \right] \left[\sum_{i} h_i + \sum_{i<j} r_{ij}^{-1} \right] \left[\sum_{i<j} g(i,j) \right] \tag{6}$$

$$= \Omega_2 + \Omega_3 + \Omega_4 + \Omega_5 + \Omega_6, \tag{7}$$

where the m-particle operator $\Omega_m(1,\ldots,N)$ for the N electron system is defined as

$$\Omega_m = \frac{1}{m!} \sum_{i_1 \neq i_2 \cdots \neq i_m}^{N} \omega_m(i_1,\ldots,i_m), \tag{8}$$

and the exact expression for ω_m is given in Ref. [45]. It is important to note that ω_m is constructed such that it is completely symmetric with respect to all the m electronic coordinates as shown by the following equation:

$$\mathcal{P}_k \omega_m(1,\ldots,m) = \omega_m(1,\ldots,m). \tag{9}$$

In the above equation, $\mathcal{P}_k$ is a permutation operator of the symmetric S_m group with m symbols. The matrix element of the CTH with Slater determinant Φ_0 can be expressed as the sum of the matrix elements of the individual Ω_i operators:

$$\langle \Phi_0 | \tilde{H} | \Phi_0 \rangle = \langle \Phi_0 | \Omega_2 | \Phi_0 \rangle + \cdots + \langle \Phi_0 | \Omega_6 | \Phi_0 \rangle. \tag{10}$$

The individual component can be calculated from integrals involving only the occupied molecular orbitals

$$\langle \Phi_0 | \Omega_m | \Phi_0 \rangle = \frac{1}{m!} \sum_{i_1,\ldots,i_n}^{N_{\text{occ}}} \langle i_1 \ldots i_m | \omega_m \sum_{\mathcal{P}_k \in S_m}^{m!} (-1)^{p_k} \mathcal{P}_k | i_1 \ldots i_m \rangle, \tag{11}$$

where $\mathcal{P}_k$ is the permutation operator of the symmetry group S_m and p_k is the parity associated with the permutation. We introduce the following compact notation for the antisymmetrized sum:

$$\langle \Phi_0 | \Omega_m | \Phi_0 \rangle = \frac{1}{m!} \sum_{i_1,\ldots,i_n}^{N_{\text{occ}}} \langle i_1 \ldots i_m | \omega_m | i_1 \ldots i_m \rangle_A, \tag{12}$$

where the subscript A denotes that the matrix element is antisymmetrized. The matrix element of the overlap $\langle \Phi_0 | \tilde{S} | \Phi_0 \rangle$ can be obtained using a similar procedure. The operator $\tilde{S}$ is written as

$$\langle \Phi_0 | \tilde{S} | \Phi_0 \rangle = \langle \Phi_0 | \Omega_2^{\text{S}} | \Phi_0 \rangle + \cdots + \langle \Phi_0 | \Omega_4^{\text{S}} | \Phi_0 \rangle. \tag{13}$$

The superscript in the Ω_m^{S} denotes that the operator is related to the transformed overlap operator. The total energy can be written as

$$E_{\text{CTH}} = \frac{\langle \Phi_0 | \Omega_2 | \Phi_0 \rangle + \cdots + \langle \Phi_0 | \Omega_6 | \Phi_0 \rangle}{\langle \Phi_0 | \Omega_2^{\text{S}} | \Phi_0 \rangle + \cdots + \langle \Phi_0 | \Omega_4^{\text{S}} | \Phi_0 \rangle}. \tag{14}$$

The main bottleneck in application of the above energy expression is that the computational cost is dominated by the Ω_5 and Ω_6 terms. Therefore, it is desirable to introduce approximations to the above expression that will reduce the computational effort of the CTH method. The projected congruent transformed Hamiltonian (PCTH) is one such approach and is described in the following section.

B. Projected congruent transformed Hamiltonian

The correlation operator G can be expanded into a complete set of Slater determinants. For the present derivation, we are only interested in application of the correlation operator on the Hartree-Fock reference state Φ_0 as shown below:

$$G|\Phi_0\rangle = \sum_{k}^{\infty} \langle \Phi_k|G|\Phi_0\rangle |\Phi_k\rangle. \tag{15}$$

Because the correlation operator G is a two-particle operator, the expansion in Eq. (15) can be substantially reduced by using the Slater-Condon rule that G will only connect singly and doubly excited determinants. Consequently, triples and higher excited states are excluded from the expansion as shown in the following equation:

$$G|\Phi_0\rangle = \sum_{k \in 0,S,D}^{\infty} \langle \Phi_k|G|\Phi_0\rangle |\Phi_k\rangle \tag{16}$$

$$= \langle \Phi_0|G|\Phi_0\rangle |\Phi_0\rangle + \sum_{i}^{N_{\text{occ}}} \sum_{a>N_{\text{occ}}}^{\infty} \big\langle \Phi_i^a \big| G|\Phi_0\rangle \big|\Phi_i^a\big\rangle + \frac{1}{4} \sum_{ij}^{N_{\text{occ}}} \sum_{ab>N_{\text{occ}}}^{\infty} \big\langle \Phi_{ij}^{ab} \big| G|\Phi_0\rangle \big|\Phi_{ij}^{ab}\big\rangle. \tag{17}$$

In the above expression, we have used the following convention [43] for indexing the molecular orbitals. Occupied states are labeled by $i,j,k,l,\ldots$, and unoccupied states are labeled by $a,b,c,d,\ldots$. States that can be both occupied and unoccupied are labeled as p,q,r,s. For practical implementation, we are also interested in defining the finite-basis representation of the correlation operator. This is denoted as $G^{(M)}$ and is defined as

$$G^{(M)} = P^{(M)} G P^{(M)}, \tag{18}$$

where $P^{(M)}$ is the projector onto the M-dimensional subspace. The matrix element of $G^{(M)}$ between any two arbitrary Slater determinants is given by the expression

$$\big\langle \Phi_{ijk\ldots}^{abc\ldots} \big| G^{(M)} \big| \Phi_{i'j'k'\ldots}^{a'b'c'\ldots} \big\rangle = \begin{cases} \big\langle \Phi_{ijk\ldots}^{abc\ldots} \big| G \big| \Phi_{i'j'k'\ldots}^{a'b'c'\ldots} \big\rangle & \text{for} \quad \max(ijk,abc,i'j'k',a'b'c'\ldots) \leqslant M, \\ 0 & \text{for} \quad \max(ijk,abc,i'j'k',a'b'c'\ldots) > M. \end{cases} \tag{19}$$

As seen from the above equation, $G^{(M)}$ coincides with the correlation operator G only for finite basis. In the limit of a complete basis, $G^{(M)}$ becomes identical to the G

$$G = \lim_{M \to \infty} G^{(M)}. \tag{20}$$

Operation of $G^{(M)}$ on the reference state Φ_0 is given by the expression

$$G^{(M)}|\Phi_0\rangle = \langle \Phi_0|G|\Phi_0\rangle|\Phi_0\rangle + \sum_{i}^{N_{\text{occ}}} \sum_{a>N_{\text{occ}}}^{M} \big\langle \Phi_i^a \big| G|\Phi_0\rangle \big|\Phi_i^a\big\rangle + \frac{1}{4} \sum_{ij}^{N_{\text{occ}}} \sum_{ab>N_{\text{occ}}}^{M} \big\langle \Phi_{ij}^{ab} \big| G|\Phi_0\rangle \big|\Phi_{ij}^{ab}\big\rangle, \tag{21}$$

where explicit dependence on M is highlighted. To write the above expression in a compact representation, we will introduce the single- and double-excitation operators which are defined in the following equations:

$$T_0 = \langle \Phi_0|G|\Phi_0\rangle, \tag{22}$$

$$T_1^{(M)} = \sum_{i}^{N_{\text{occ}}} \sum_{a>N_{\text{occ}}}^{M} \big\langle \Phi_i^a \big| G|\Phi_0\rangle \hat{X}_i^a, \tag{23}$$

$$T_2^{(M)} = \frac{1}{4} \sum_{ij}^{N_{\text{occ}}} \sum_{ab>N_{\text{occ}}}^{M} \big\langle \Phi_{ij}^{ab} \big| G|\Phi_0\rangle \hat{X}_{ij}^{ab}. \tag{24}$$

These expressions can be simplified as

$$T_0 = \frac{1}{2} \sum_{ij} \langle ij|g|ij\rangle_{\text{A}}, \tag{25}$$

$$T_1^{(M)} = \sum_{ij}^{N_{\text{occ}}} \sum_{a}^{M} \langle ij|g|aj\rangle_{\text{A}} \hat{X}_i^a, \tag{26}$$

$$T_2^{(M)} = \frac{1}{4} \sum_{ij}^{N_{\text{occ}}} \sum_{ab}^{M} \langle ij|g|ab\rangle_{\text{A}} \hat{X}_{ij}^{ab}. \tag{27}$$

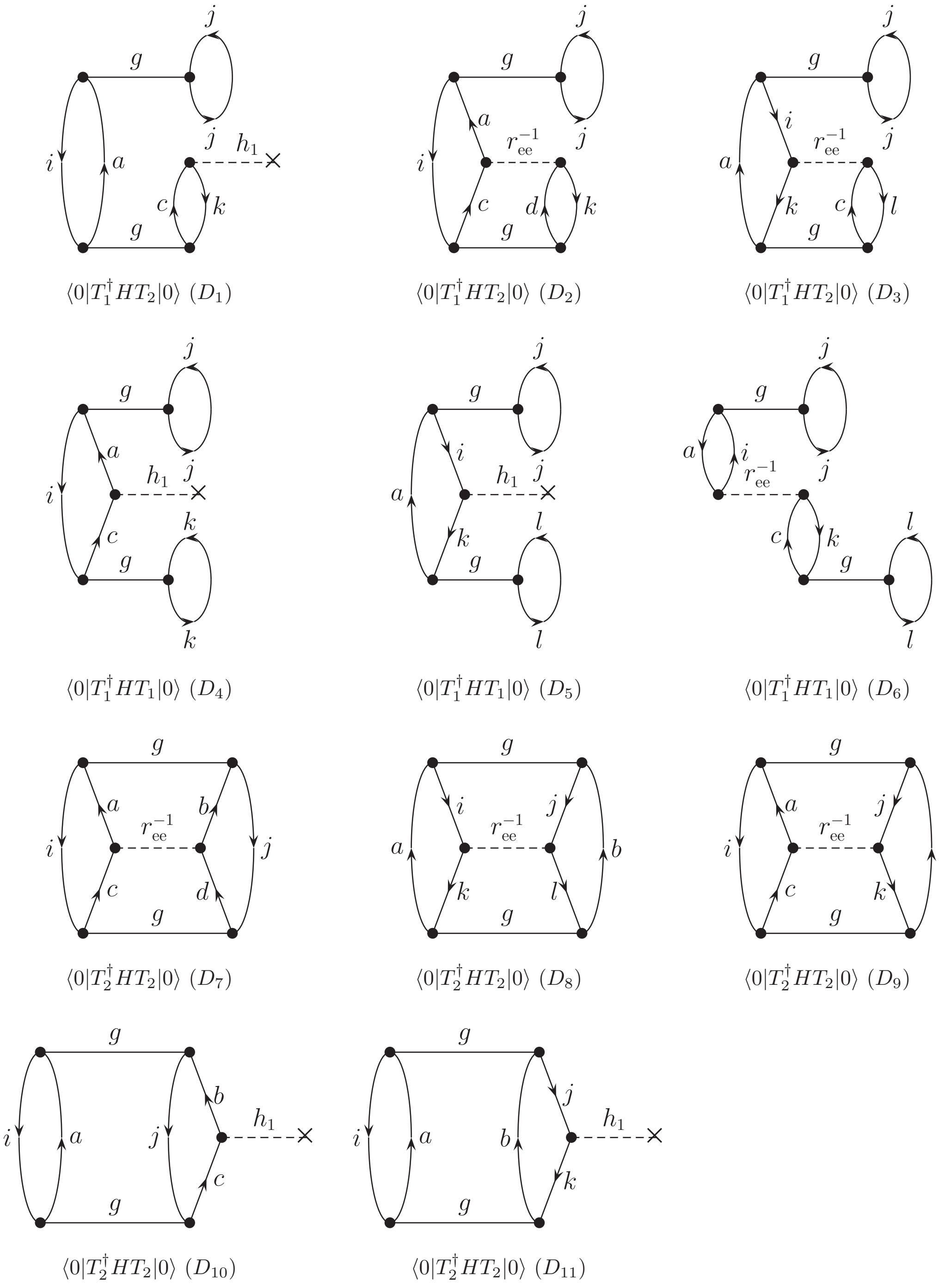
Substituting $T_1^{(M)}$ and $T_2^{(M)}$ we get

$$\langle \Phi_0|G^{(M)} H G^{(M)}|\Phi_0\rangle = \langle \Phi_0|\big(T_0 + T_1^{(M)} + T_2^{(M)}\big)^{\dagger} \times H\big(T_0 + T_1^{(M)} + T_2^{(M)}\big)|\Phi_0\rangle. \tag{28}$$

The matrix elements involving $T_0^{(M)}$ as one of the components can be obtained easily and are presented below:

$$\langle \Phi_0|T_0^{\dagger} H T_0|\Phi_0\rangle = \langle \Phi_0|G|\Phi_0\rangle\langle \Phi_0|H|\Phi_0\rangle\langle \Phi_0|G|\Phi_0\rangle \tag{29}$$

$$= \left(\frac{1}{2}\sum_{ij}\langle ij|g|ij\rangle_{\text{A}}\right)^2 \times \left(\sum_{i}\langle i|h_1|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|r_{12}^{-1}|ij\rangle_{\text{A}}\right), \tag{30}$$



$\langle 0|T_1^\dagger H T_2|0\rangle$ (D_1) $\langle 0|T_1^\dagger H T_2|0\rangle$ (D_2) $\langle 0|T_1^\dagger H T_2|0\rangle$ (D_3)

$\langle 0|T_1^\dagger H T_1|0\rangle$ (D_4) $\langle 0|T_1^\dagger H T_1|0\rangle$ (D_5) $\langle 0|T_1^\dagger H T_1|0\rangle$ (D_6)

$\langle 0|T_2^\dagger H T_2|0\rangle$ (D_7) $\langle 0|T_2^\dagger H T_2|0\rangle$ (D_8) $\langle 0|T_2^\dagger H T_2|0\rangle$ (D_9)

$\langle 0|T_2^\dagger H T_2|0\rangle$ (D_{10}) $\langle 0|T_2^\dagger H T_2|0\rangle$ (D_{11})

FIG. 1. Diagrams for the diagrammatic representation of a congruent transformed Hamiltonian.

$$\begin{aligned}\langle\Phi_0|T_0^\dagger H T_1^{(M)}|\Phi_0\rangle &= \langle\Phi_0|G|\Phi_0\rangle\langle\Phi_0|H T_1^{(M)}|\Phi_0\rangle\\ &= 0 \quad \text{(Brillouin's theorem)},\end{aligned} \tag{31}$$

$$\begin{aligned}&\langle\Phi_0|T_0^\dagger H T_2^{(M)}|\Phi_0\rangle\\ &\quad = \frac{1}{8}\left(\sum_{ij}\langle ij|g|ij\rangle_{\mathrm{A}}\right)\left(\sum_{ij}\sum_{ab}^{M}\langle ij|g|ab\rangle_{\mathrm{A}}\langle ij|r_{12}^{-1}|ab\rangle_{\mathrm{A}}\right).\end{aligned} \tag{32}$$

The analytical expressions of matrix elements $\langle\Phi_0|T_1^{(M)\dagger} H T_1^{(M)}|\Phi_0\rangle$, $\langle\Phi_0|T_1^{(M)\dagger} H T_2^{(M)}|\Phi_0\rangle$, and $\langle\Phi_0|T_2^{(M)\dagger} H T_2^{(M)}|\Phi_0\rangle$ that involve both the excitation operators require more involved algebraic manipulation. Efficient computer implementation of these expressions are generally achieved using the α-β string representation of the Slater determinant [46]. The analytical expression of the matrix elements can be obtained by using the generalized Wick's theorem [43] and enumerating all possible contractions. However, for the present derivation, we use the diagrammatic representation to write the resulting expressions. The representative diagrams for the matrix elements are shown in Fig. 1 and are summarized in the following equations:

$$\langle \Phi_0 | T_1^{(M)\dagger} H T_2^{(M)} | \Phi_0 \rangle = D_1 + D_2 + D_3 + \cdots \tag{33}$$

$$\langle \Phi_0 | T_1^{(M)\dagger} H T_1^{(M)} | \Phi_0 \rangle = D_4 + D_5 + D_6 + \cdots \tag{34}$$

$$\langle \Phi_0 | T_2^{(M)\dagger} H T_2^{(M)} | \Phi_0 \rangle = D_7 + D_8 + D_9 + D_{10} + D_{11} \cdots . \tag{35}$$

The finite-basis representation of the CTH energy is given as

$$E_{\mathrm{PCTH}}^{(M)} = \frac{\langle \Phi_0 | G^{(M)\dagger} H G^{(M)} | \Phi_0 \rangle}{\langle \Phi_0 | G^{(M)\dagger} G^{(M)} | \Phi_0 \rangle}. \tag{36}$$

The finite-basis energy is related to the CTH energy by the limiting condition

$$E_{\mathrm{CTH}} = \frac{\lim_{M\to\infty} \langle \Phi_0 | G^{(M)\dagger} H G^{(M)} | \Phi_0 \rangle}{\lim_{M\to\infty} \langle \Phi_0 | G^{(M)\dagger} G^{(M)} | \Phi_0 \rangle}. \tag{37}$$

C. Infinite-order summation of diagrams

In this section, we will develop the partial infinite-order summation approach. The central ideal of this method is to select a subset of diagrams from the $\langle \Phi_0 | G^{(M)} H G^{(M)} | \Phi_0 \rangle$ expansion and perform the $M \to \infty$ limit analytically for those diagrams. Because we are interested in infinite-order summation of selected diagrams (as opposed to all the diagrams) we denote this technique as the partial infinite-order summation (PIOS) method. For a compact representation, we label the set of diagrams that will be used for the PIOS method by $\mathcal{S}_{\mathrm{PIOS}}$.

One of the important issues associated with the PIOS method is the selection diagrams in the set $\mathcal{S}_{\mathrm{PIOS}}$. The success of the PIOS method relies on the existence of the analytical solution of the $M \to \infty$ limit, therefore only sets of diagrams whose infinite-order summation can be expressed analytically should be considered for $\mathcal{S}_{\mathrm{PIOS}}$. Moreover, even if the analytical expression for the $M \to \infty$ limit exists, the implementation and evaluation of the expression may be computationally demanding. Because of these reasons, the set of diagrams that can be selected in $\mathcal{S}_{\mathrm{PIOS}}$ is limited.

For the present work, we focused on diagrams related to the $g r_{\mathrm{ee}}^{-1} g$ expression. The set $\mathcal{S}_{\mathrm{PIOS}}$ consisted of all closed diagrams that connected matrix elements $\langle ij | g | **\rangle_{\mathrm{A}}$ and $\langle ** | g | ij \rangle_{\mathrm{A}}$ with $\langle ** | r_{\mathrm{ee}}^{-1} | ** \rangle_{\mathrm{A}}$, where the asterisks denote place holders for particle and hole lines. Figures 2 and 3 list all the diagrams that were included in the $\mathcal{S}_{\mathrm{PIOS}}$ set where $\{i,j\}$ represent hole lines and $\{p,q,r,s\}$ can be either hole or particle lines $\{\uparrow,\downarrow\}$

$$\mathcal{S}_{\mathrm{PIOS}} = \{D_{14}, \ldots, D_{27}\}. \tag{38}$$

In the next step the $M \to \infty$ limit of the summation of all the diagrams in set $\mathcal{S}_{\mathrm{PIOS}}$ were performed and the result is shown in the following equation:

$$\lim_{M\to\infty} \{D_{14} + \cdots + D_{27}\} = \sum_{pqrs}^{\infty} \langle ij | g | pq \rangle_{\mathrm{A}} \langle pq | r_{\mathrm{ee}}^{-1} | rs \rangle_{\mathrm{A}} \langle rs | g | ij \rangle_{\mathrm{A}}, \tag{39}$$

where the subscript A denotes that the matrix elements are antisymmetric. Substituting the explicit expression of the antisymmetrizer, we get

$$\lim_{M\to\infty} \{D_{14} + \cdots + D_{27}\} = \sum_{pqrs}^{\infty} \langle ij | g(1 - P_{12}) | pq \rangle \langle pq | r_{\mathrm{ee}}^{-1} (1 - P_{12}) | rs \rangle \times \langle rs | g(1 - P_{12}) | ij \rangle. \tag{40}$$

Using the idempotent property of the antisymmetrizer,

$$(1 - P_{12})^2 = 2(1 - P_{12}), \tag{41}$$

we can obtain the following expression:

$$\lim_{M\to\infty} \{D_{14} + \cdots + D_{27}\} = \frac{1}{4} \sum_{pqrs}^{\infty} \langle ij | g(1 - P_{12}) | pq \rangle \langle pq | (1 - P_{12}) r_{\mathrm{ee}}^{-1} \times (1 - P_{12}) | rs \rangle \langle rs | (1 - P_{12}) g (1 - P_{12}) | ij \rangle. \tag{42}$$

The expression $(1 - P_{12}) | pq \rangle$ represents a set of Slater determinants for a two-electron system and satisfies the following closure relationship:

$$1 = \frac{1}{4} \sum_{pq}^{\infty} (1 - P_{12}) | pq \rangle \langle pq | (1 - P_{12}). \tag{43}$$

Substituting the identity operator in Eq. (43) into Eq. (42),

$$\lim_{M\to\infty} \{D_{14} + \cdots + D_{27}\} = 4 \langle ij | g r_{\mathrm{ee}}^{-1} g (1 - P_{12}) | ij \rangle \tag{44}$$

$$= 4 \langle ij | g r_{\mathrm{ee}}^{-1} g | ij \rangle_{\mathrm{A}} \tag{45}$$

$$= 4 D_{28}, \tag{46}$$

where the diagram D_{28} is shown in Fig. 4. The diagram D_{28} is related to the expectation value of the following two-particle operator:

$$\Omega_2^{\mathrm{ee}} = \sum_{i<j} g(i,j) r_{ij}^{-1} g(i,j). \tag{47}$$

Combining the results from Eqs. (46) and (47), we obtain

$$\langle \Phi_0 | \Omega_2^{\mathrm{ee}} | \Phi_0 \rangle = \langle \Phi_0 | \sum_{i<j} g(i,j) r_{ij}^{-1} g(i,j) | \Phi_0 \rangle \tag{48}$$

$$= \frac{1}{2} D_{28} \tag{49}$$

$$= \frac{1}{8} \lim_{M\to\infty} \{D_{14} + \cdots + D_{27}\} \tag{50}$$

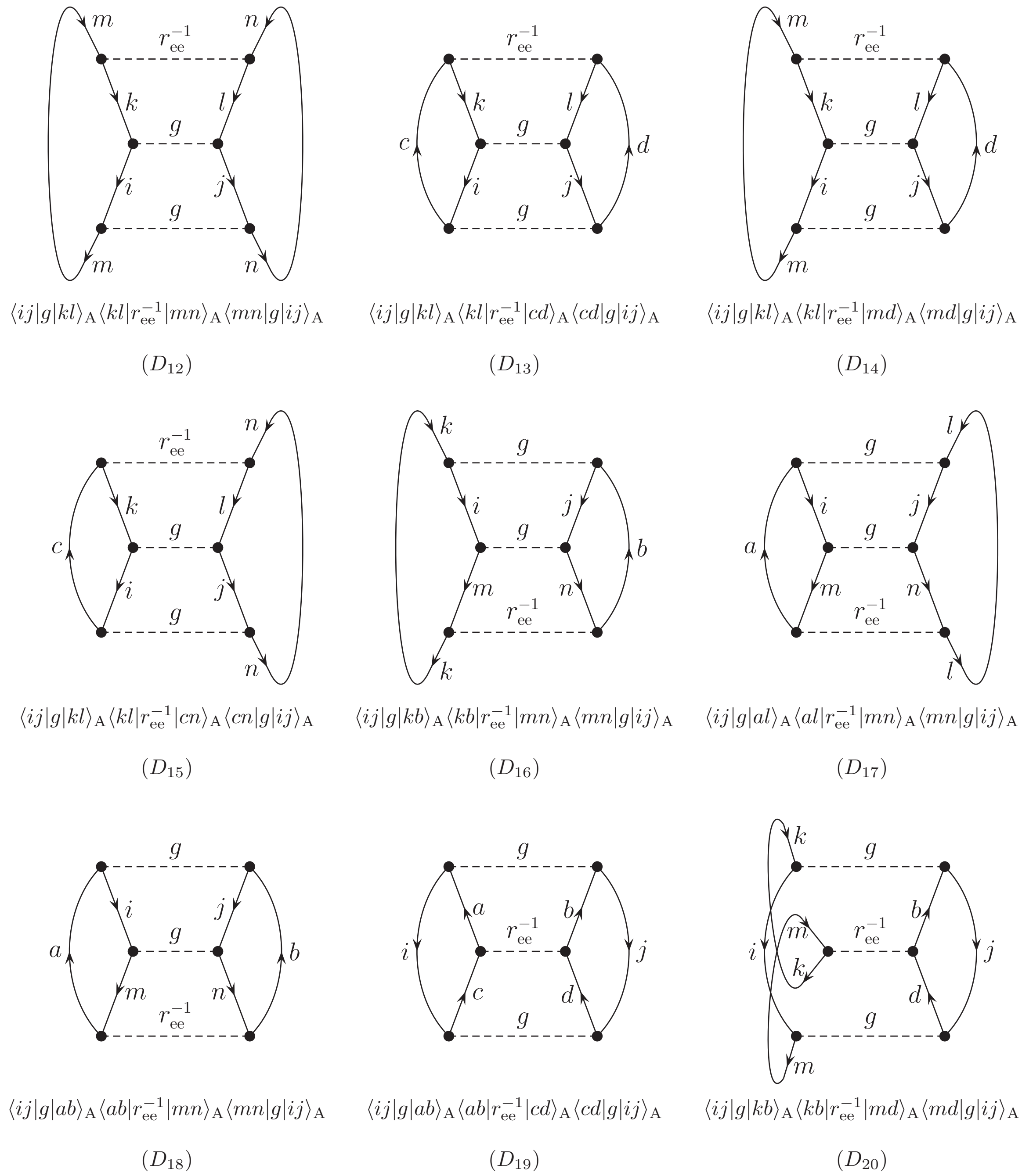
$$= \lim_{M\to\infty} \langle \Phi_0 | \Omega_2^{\mathrm{ee}} | \Phi_0 \rangle^{(M)}, \tag{51}$$

where we have used the compact notation

$$\langle \Phi_0 | \Omega_2^{\mathrm{ee}} | \Phi_0 \rangle^{(M)} = \tfrac{1}{8} \{D_{14} + \cdots + D_{27}\}. \tag{52}$$

The relationship expressed in Eq. (51) is one of the key results of the PIOS derivation.

In addition to the $g r_{\mathrm{ee}}^{-1} g$ term, the calculation of the PIOS energy also requires diagrammatic summation of the overlap term gg. The derivation for gg is identical to the derivation



$\langle ij|g|kl\rangle_{\rm A}\langle kl|r_{\rm ee}^{-1}|mn\rangle_{\rm A}\langle mn|g|ij\rangle_{\rm A}$

(D_{12})

$\langle ij|g|kl\rangle_{\rm A}\langle kl|r_{\rm ee}^{-1}|cd\rangle_{\rm A}\langle cd|g|ij\rangle_{\rm A}$

(D_{13})

$\langle ij|g|kl\rangle_{\rm A}\langle kl|r_{\rm ee}^{-1}|md\rangle_{\rm A}\langle md|g|ij\rangle_{\rm A}$

(D_{14})

$\langle ij|g|kl\rangle_{\rm A}\langle kl|r_{\rm ee}^{-1}|cn\rangle_{\rm A}\langle cn|g|ij\rangle_{\rm A}$

(D_{15})

$\langle ij|g|kb\rangle_{\rm A}\langle kb|r_{\rm ee}^{-1}|mn\rangle_{\rm A}\langle mn|g|ij\rangle_{\rm A}$

(D_{16})

$\langle ij|g|al\rangle_{\rm A}\langle al|r_{\rm ee}^{-1}|mn\rangle_{\rm A}\langle mn|g|ij\rangle_{\rm A}$

(D_{17})

$\langle ij|g|ab\rangle_{\rm A}\langle ab|r_{\rm ee}^{-1}|mn\rangle_{\rm A}\langle mn|g|ij\rangle_{\rm A}$

(D_{18})

$\langle ij|g|ab\rangle_{\rm A}\langle ab|r_{\rm ee}^{-1}|cd\rangle_{\rm A}\langle cd|g|ij\rangle_{\rm A}$

(D_{19})

$\langle ij|g|kb\rangle_{\rm A}\langle kb|r_{\rm ee}^{-1}|md\rangle_{\rm A}\langle md|g|ij\rangle_{\rm A}$

(D_{20})

FIG. 2. Diagrams for partial infinite-order summation.

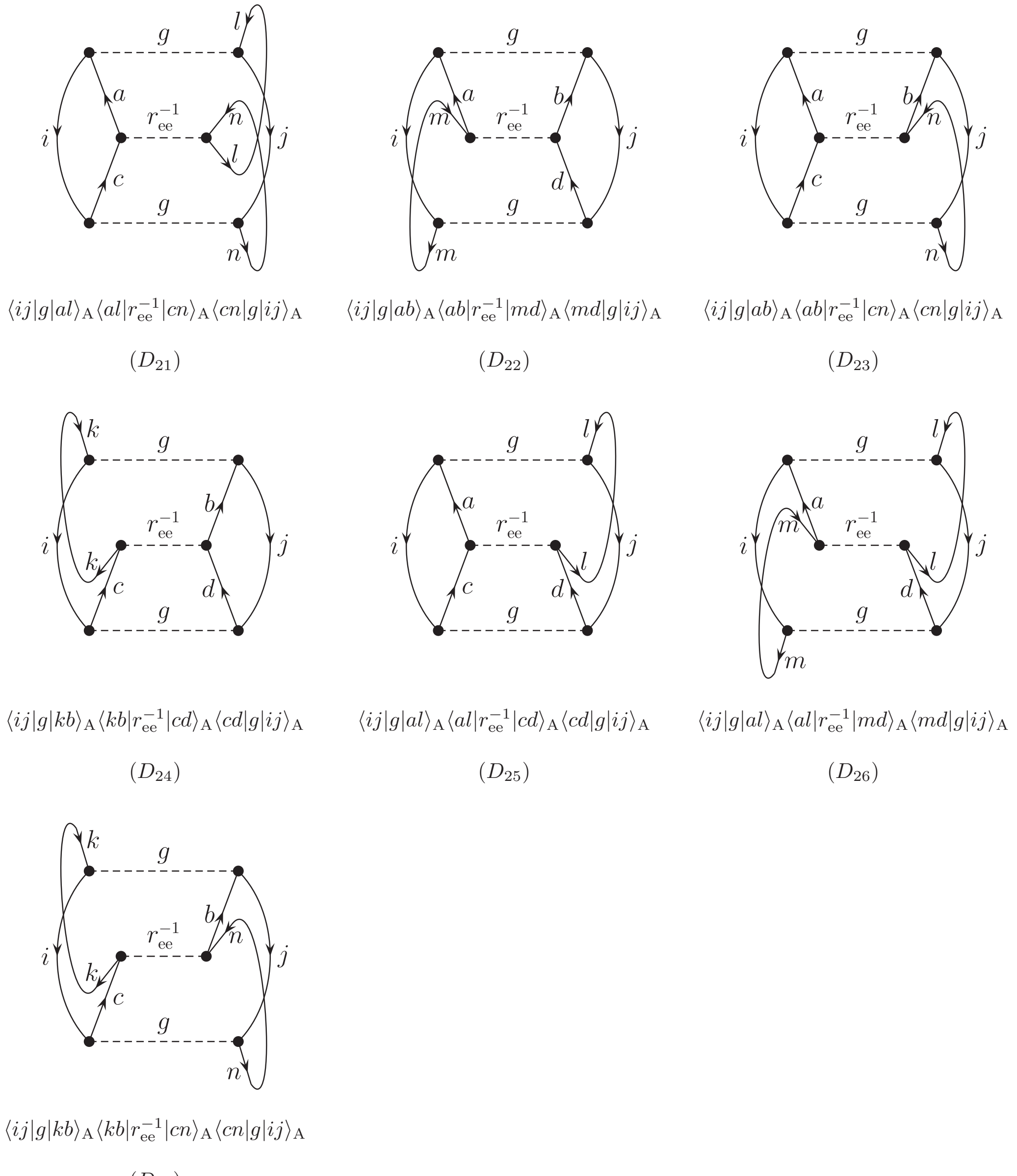
presented above for $gr_{\rm ee}^{-1}g$ and is not presented here to avoid repetition. Analogous to $\Omega_2^{\rm ee}$, we define the following terms for the overlap operator $\Omega_2^{\rm S}$:

$$\langle\Phi_0|\Omega_2^{\rm S}|\Phi_0\rangle = \lim_{M\to\infty}\langle\Phi_0|\Omega_2^{\rm S}|\Phi_0\rangle^{(M)}, \tag{53}$$

$$\Omega_2^{\rm S} = \sum_{i<j} g(i,j)g(i,j). \tag{54}$$

Using the results from Eqs. (51) and (53), we define the PCTH-PIOS energy expression as

$$E_{\rm PCTH-PIOS} = \frac{\langle\Phi_0|G^{(M)\dagger}HG^{(M)}|\Phi_0\rangle - \langle\Phi_0|\Omega_2^{\rm ee}|\Phi_0\rangle^{(M)} + \langle\Phi_0|\Omega_2^{\rm ee}|\Phi_0\rangle}{\langle\Phi_0|G^{(M)\dagger}G^{(M)}|\Phi_0\rangle - \langle\Phi_0|\Omega_2^{\rm S}|\Phi_0\rangle^{(M)} + \langle\Phi_0|\Omega_2^{\rm S}|\Phi_0\rangle}. \tag{55}$$



$\langle ij|g|al\rangle_{\rm A}\langle al|r_{\rm ee}^{-1}|cn\rangle_{\rm A}\langle cn|g|ij\rangle_{\rm A}$

(D_{21})

$\langle ij|g|ab\rangle_{\rm A}\langle ab|r_{\rm ee}^{-1}|md\rangle_{\rm A}\langle md|g|ij\rangle_{\rm A}$

(D_{22})

$\langle ij|g|ab\rangle_{\rm A}\langle ab|r_{\rm ee}^{-1}|cn\rangle_{\rm A}\langle cn|g|ij\rangle_{\rm A}$

(D_{23})

$\langle ij|g|kb\rangle_{\rm A}\langle kb|r_{\rm ee}^{-1}|cd\rangle_{\rm A}\langle cd|g|ij\rangle_{\rm A}$

(D_{24})

$\langle ij|g|al\rangle_{\rm A}\langle al|r_{\rm ee}^{-1}|cd\rangle_{\rm A}\langle cd|g|ij\rangle_{\rm A}$

(D_{25})

$\langle ij|g|al\rangle_{\rm A}\langle al|r_{\rm ee}^{-1}|md\rangle_{\rm A}\langle md|g|ij\rangle_{\rm A}$

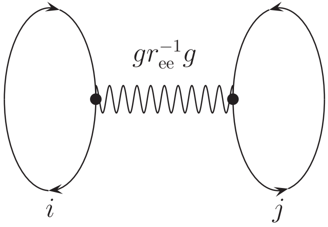
(D_{26})

$\langle ij|g|kb\rangle_{\rm A}\langle kb|r_{\rm ee}^{-1}|cn\rangle_{\rm A}\langle cn|g|ij\rangle_{\rm A}$

(D_{27})

FIG. 3. More diagrams for partial infinite-order summation.

Equation (55) illustrates the conceptual structure of the PIOS method. Starting with the finite-basis expression of the congruent transformed Hamiltonian, the partial infinite-order summation technique allows us to remove the finite-basis approximation for one of the components ($\Omega_2^{\rm ee}$ in this case) of the energy expression. The term ($\langle\Phi_0|\Omega_2^{\rm ee}|\Phi_0\rangle - \langle\Phi_0|\Omega_2^{\rm ee}|\Phi_0\rangle^{(M)}$) represents the missing piece in the PCTH energy expression because of the finite size of the projected space.



$\langle ij|gr_{\rm ee}^{-1}g|ij\rangle_{\rm A}$

(D_{28})

FIG. 4. Diagram for the $gr_{\rm ee}^{-1}g$ integral.

D. Form of the correlation function

Although the expression in Eq. (55) is valid for any form of $g(1,2)$, the computational cost and ease of implementation depend on the specific choice of $g(1,2)$. In this work, we have used Gaussian-type geminal (GTG) functions [11,12,16,24,25,29,47–51] for representing the two-body correlation function

$$g(r_{12}) = \sum_{k=1}^{N_{\rm g}} b_k e^{-r_{12}^2/d_k^2}, \tag{56}$$

where b_k, d_k are the geminal parameters that completely define the GTG function. There are mainly two different techniques for determining the geminal parameters. In the first method, the parameters are determined variationally by minimizing the total energy. Although this approach is very accurate, it becomes computationally expensive because it involves multidimensional minimization and recomputation of the atomic orbital (AO) integrals. The second approach is to have a set of precomputed values of the geminal parameters. This approach is computationally fast; however, the challenge is to find a transferable set of parameters that can be applied to different molecules. In this work, we have developed a mixed approach where the linear geminal parameters b_k are variationally optimized by minimizing the PIOS energy and the nonlinear geminal parameters d_k are precomputed before the start of the geminal optimization.

The strategy for determining the nonlinear parameters developed in this work is to use an appropriate characteristic length scale associated with the molecule for calculating the d_k parameters. We have used the average electron-electron separation distance as the characteristic system-dependent quantity for calculating the geminal parameters. Using the reference Slater determinant Φ_0, we define the average electron-electron distance as

$$\langle r_{12}^2 \rangle_0 = \frac{2}{N(N-1)} \langle \Phi_0 | \sum_{i<j} r_{ij}^2 | \Phi_0 \rangle. \tag{57}$$

The d_k parameters are selected from a set of numbers obtained by scaling $\langle r_{12}^2 \rangle_0$

$$d_k^2 \in \left[\frac{1}{n} \langle r_{12}^2 \rangle_0, \ldots \frac{1}{2} \langle r_{12}^2 \rangle_0, \langle r_{12}^2 \rangle_0, 2 \langle r_{12}^2 \rangle_0, \ldots n \langle r_{12}^2 \rangle_0 \right]. \tag{58}$$

The choice of $\langle r_{12}^2 \rangle_0$ over $\langle r_{12} \rangle_0$ was made purely for computational convenience. The integral involving r_{12}^2 is separable in x, y, and z components and can be integrated easily with Cartesian Gaussian-type orbitals (GTOs). Similar separation is not possible for $\langle r_{12} \rangle_0$. The above procedure provides a fast and physically intuitive method for obtaining the nonlinear geminal parameters.

One of the advantages of the GTG function is that the AO integrals involving the GTG functions are analytical and can be expressed in a closed form. Analytical expressions for integrals involving s-type GTOs are known and were derived by Boys [52]. An analytical form for the higher angular momentum GTOs using the McMurchie-Davidson algorithm was derived by Persson and Taylor [47]. Because of the availability of fast analytical integral routines, Gaussian-type geminal functions have found widespread application in a large number of explicitly correlated calculations [11,12,16,24,25,29,40,44,47–51]. As seen in Eq. (55), the geminal integrals needed for computation of the energy expression is of the form G_{0k}. These geminal integrals are known as the overlap integrals and are especially efficient to compute because they can be written as a product of three one-dimensional integrals

$$[\mu\nu | e^{-r_{12}^2/d_k^2} | \lambda\sigma] = I_x I_y I_z. \tag{59}$$

The exact expression for the integrals can be found in Refs. [47,52].

III. RESULTS AND CONCLUSION

The implementation of the PCTH-PIOS method was tested by performing the ground-state energy of the isoelectronic 10-electron systems Ne, HF, H_2O, NH_3, and CH_4. All the calculations were performed using $N_g = 2$ with two Gaussian-type geminal functions. The first set of geminal parameters were fixed at $b_1 = 1$ and $d_1^2 = \infty$. The resulting expression for g used in the calculation is given by

$$g(1,2) = 1 + b_2 \, e^{-r_{12}^2/d_2^2}. \tag{60}$$

This choice of parameters ensured that the PCTH energy is always bounded from the top by the Hartree-Fock (HF) energy. The PCTH energy is bounded from below by the energy derived by the configuration interaction (CI) method that is limited to single and double excitations (the CISD energy). This is because the energy expression of the PCTH method is identical to the CISD energy where the CI coefficients are constrained to $c_k = \langle \Phi_k | G | \Phi_0 \rangle$. The upper and lower bounds of the PCTH energy calculated using the HF reference wave function is given by the expression

$$E_{\text{CISD}} < E_{\text{PCTH}} < E_{\text{HF}}. \tag{61}$$

The Hartree-Fock calculation was performed, and $\langle r_{12}^2 \rangle_0$ was evaluated and used to construct the following trial set for the selection of the d_2 parameter:

$$d_{\text{trial}}^2 \in \tfrac{1}{3} \langle r_{12}^2 \rangle_0, \tfrac{1}{2} \langle r_{12}^2 \rangle_0, \langle r_{12}^2 \rangle_0, 2 \langle r_{12}^2 \rangle_0, 3 \langle r_{12}^2 \rangle_0. \tag{62}$$

The b_2 parameter was optimized for each trial d_2^2, and the $b_{2,\text{opt}}$ and $d_{2,\text{opt}}^2$ were obtained by finding the lowest PCTH energy in the trial set. The change in the energy as a function of the trial nonlinear parameter is presented in Fig. 5. Interestingly, the optimum expression for d_2 in all the systems was found to be $d_2^2 = \langle r_{12}^2 \rangle_0 / 2$. This result shows that although the numerical value of the d_2 parameter is different for each chemical system, the relationship between d_2 and the average electron-electron separation distance is conserved. The PCTH-PIOS calculations were performed using the optimized geminal parameters. The correlation energies obtained from the PCTH-PIOS method are compared with other methods (CISD, MP2,

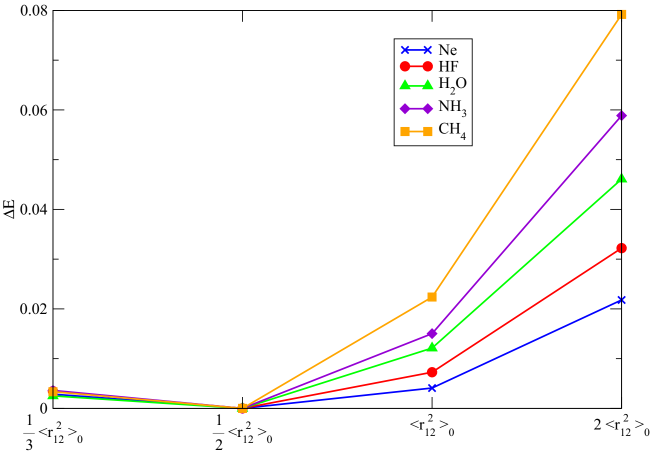


FIG. 5. (Color online) $\Delta E = \frac{E_{\text{min}} - E}{E_{\text{min}}} \times 100$, where E_{min} is the E_{PCTH} energy obtained using $\frac{1}{2} \langle r_{12}^2 \rangle_0$.

TABLE I. Correlation energies for isoelectronic 10-electron systems. All values are reported in a.u.

Method	Ne	HF	H_2O	NH_3	CH_4
PCTH/6-31G*	−0.130603	−0.151003	−0.155345	−0.143408	−0.118838
PCTH-PIOS/6-31G*	−0.160906	−0.269057	−0.300579	−0.257571	−0.192598
MP2/6-31G*	−0.150315	−0.179777	−0.186849	−0.170397	−0.137732
CCSD/6-31G*	−0.152327	−0.184207	−0.195842	−0.185705	−0.158185
CISD/6-31G*	−0.148933	−0.178315	−0.188207	−0.178082	−0.152076
CISD/cc-pVTZ	−0.320384	−0.322179	−0.305133	−0.272034	−0.227915

and CCSD) and the results are presented in Table I. Comparing the PCTH energies with the CISD/6-31G* results, it is seen that the PCTH energies are higher than the CISD energies. As discussed in Eq. (61), this is an expected result because the PCTH energy is bounded from below by CISD energy. However, the PCTH-PIOS energies in all cases are lower than the CISD/6-13G* results. We attribute this lowering of energy to the additions of diagrams in the PCTH-PIOS method. Comparing PCTH-PIOS/6-31G* and CISD/cc-pVTZ results we see that the PCTH-PIOS energies are bounded from below by the exact ground-state energy. These results indicate the relevance of the infinite-order diagrammatic summation approach of the PCTH-PIOS method.

In conclusion, we have presented the development of the projected congruent transformed Hamiltonian method for many-electron systems. The congruent transformation of the many-electron Hamiltonian was performed using Gaussian-type geminal functions. The challenge of efficient optimization of the geminal function was addressed by using different strategies for optimizing linear and nonlinear parameters. The linear geminal parameters were obtained variationally by minimizing the PCTH energy. The expectation value of the square of the electron-electron separation distance was used as the characteristic length scale for construction of the nonlinear geminal parameters. One of the key results in this work is the development and application of the partial infinite-order summation method. The PCTH-PIOS method is based on performing infinite-order summation for a subset of diagrams in the PCTH energy expression. The closed-shell version of the PCTH-PIOS method was implemented and the method was applied to a series of 10-electron systems. The correlation energies computed using the PCTH-PIOS method were found to be in good agreement with CISD calculations. This is an interesting result because unlike the CISD method, the PCTH-PIOS method avoids construction and diagonalization of the CI Hamiltonian. The results indicate that PCTH-PIOS can be used for treating electron correlation in many-electron systems.

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