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Variational solution of the congruently transformed Hamiltonian for many-electron systems using a full-configuration-interaction calculation

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The congruent transformation of the electronic Hamiltonian is developed to address the electron correlation problem in many-electron systems. The central strategy presented in this method is to perform transformation on the electronic Hamiltonian for the approximate removal of the Coulomb singularity. The principle difference between the present method and the transcorrelated method of Handy and Boys [Proc. R. Soc. London, Ser. A **310**, 43 (1969)] is that the congruent transformation preserves the Hermitian property of the Hamiltonian. The congruent transformation is carried out using explicitly correlated functions and the optimum correlated transform Hamiltonian is obtained by performing a search over a set of transformation functions. The ansatz of the transformation function is selected to facilitate analytical evaluation of all the resulting integrals. The ground-state energy is obtained variationally by performing a full-configuration-interaction (FCI) calculation on the congruently transformed Hamiltonian. Computed results on well-studied benchmark systems show that for identical basis functions, the energy from the congruently transformed Hamiltonian is significantly lower than that from the conventional FCI calculation. Since the number of configuration state functions in the FCI calculation increases rapidly with the size of the one-particle basis set, the results indicate that the congruently transformed Hamiltonian provides a viable alternative to obtain FCI quality energy using a smaller underlying one-particle basis set.

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I. INTRODUCTION

The form of the many-electron wave function in the proximity of the electron-electron and electron-nuclear coalescence points plays a critical role in accurate determination of the ground-state and excited-state energies. Although, the precise structure of the many-electron wave function continues to be elusive, the form of the exact wave function at the coalescence point is well understood and is given by the Kato cusp condition [1–4]. In the many-electron wave function, the electron-nuclear cusp condition can be incorporated by using Slater-type orbitals (STOs). For calculations involving Gaussian-type orbitals (GTOs), one-electron basis can be improved iteratively by adding GTOs with increasing angular momentum quantum number [5]. The subject of convergence of the single-particle basis has been analyzed extensively using both analytical and numerical techniques [6–8]. The electron-electron cusp has been the focus of intense research because of its direct relation to the electron correlation problem and the accurate description of the Coulomb and Fermi holes [9–13]. However, unlike the electron-nuclear cusp, atom-centered basis functions are not ideal for the accurate description of the many-electron wave function near the electron-electron cusp [14–16]. Indeed it has been shown that the slow convergence of a full-configuration-interaction (FCI) calculation with respect to the one-particle basis is related to the inadequate treatment of the electron-electron cusp [15]. The solution is to include explicit r_{12} dependence in the form of the wave function, and there is a large assortment of quantum chemical methods that have incorporated this approach. For example, in the variational Monte Carlo (VMC) method, the Jastrow function is used for including explicit r_{12} terms in the trial wave function [2,4]. The form of the Jastrow function is chosen to ensure that the electron-electron and electron-nuclear Kato cusp conditions are satisfied. The parameters in the Jastrow function are obtained by minimizing the linear combination of energy and its variance. Because of the complicated mathematical form of the Jastrow function it is not possible to evaluate the integral over the electronic coordinates analytically, and a stochastic numerical method is used for computation of the energy. Recently, Morales *et al.* [17] performed highly accurate multideterminant VMC calculations on water. Detailed reviews of various applications of quantum Monte Carlo (QMC) methods in physics and chemistry can be found in Refs. [18–20]. Explicitly correlated methods have also been developed for post Hartree-Fock schemes such as perturbation theory (MP2-R12), coupled-cluster methods (CC-R12), and multireference configuration-interaction schemes (R12-MRCI). These methods introduce the electron-electron interparticle distance directly into the calculation in order to increase the accuracy of the calculations. The field of explicitly correlated methods for electronic structure calculation has been reviewed and a detailed description of various methods can be found in Refs. [14,15,21]. A common feature of the R12 and F12 methods discussed above is that they all involve analytical computation of the r_{12} correlation function. Recently, Chinnamsetty and co-workers [22] have presented an interesting study that compares and contrasts QMC with various F12 methods.

A different strategy known as the transcorrelated method was developed by Handy and Boys in 1969 [23]. The basic idea of the transcorrelated method is to remove the electron-electron Coulomb singularity by performing similarity transformation on the Hamiltonian using an explicitly correlated function. The method was later extended by Ten-no to treat the electron-electron cusp using Guassian geminal functions and

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was applied to chemical systems [8,24]. The transcorrelated method has also been combined with other methods such as QMC [25] and coupled-cluster theory [26] and has been used to study electron correlation in periodic systems [27]. One of the defining characteristics of this method is that the transcorrelated Hamiltonian is not Hermitian and therefore is not required to be bounded from below by the exact ground-state energy. The correlation function can be obtained either by minimizing the energy variance of the transcorrelated Hamiltonian [28,29] or by requiring the correlation function to satisfy the electron-electron cusp condition.

The focus of the present work is to address the non-Hermitian property of the transcorrelated Hamiltonian by replacing the similarity transformation with congruent transformation [30–32]. By performing congruent transformation, we preserve the Hermitian property of the electronic Hamiltonian which allows us to use a standard electronic structure methods such as the configuration-interaction method to minimize the total energy. The remainder of the paper describes the theoretical development and the implementation details of the method. The derivation of the congruently transformed Hamiltonian is presented in Sec. II. The details of performing FCI calculations using the congruently transformed Hamiltonian and interfacing it with existing FCI methods are presented in Secs. II A and II B. Benchmark calculations using the congruently transformed Hamiltonian are presented in Sec. III. The analysis of the results and the conclusions are presented in Sec. IV.

II. CONGRUENTLY TRANSFORMED HAMILTONIAN

The congruently transformed (CT) Hamiltonian $\tilde{H}$ is defined by performing the following transformation [30–32]:

$$\tilde{H} = G^{\dagger} H G, \tag{1}$$

where G is an explicitly correlated function which will be defined later. The expectation value of the CT Hamiltonian with respect to any trial wave function is given as

$$\tilde{E}_{\mathrm{T}}[\Psi_{\mathrm{T}}, G] = \frac{\langle \Psi_{\mathrm{T}} | \tilde{H} | \Psi_{\mathrm{T}} \rangle}{\langle \Psi_{\mathrm{T}} | \tilde{1} | \Psi_{\mathrm{T}} \rangle}, \tag{2}$$

where $\tilde{1} = G^{\dagger} 1 G$. The above expression is mathematically equivalent to calculating the expectation value of the electronic Hamiltonian using a correlated wave function and is bounded from below by the exact ground-state energy $E_{\mathrm{exact}} \leqslant \tilde{E}_{\mathrm{T}}$. The optimized energy associated with the CT Hamiltonian is obtained by performing a minimization with respect to the trial wave function and the explicitly correlated function:

$$E_{\mathrm{CT}} = \min_{\Psi_{\mathrm{T}}} \min_{G} \tilde{E}_{\mathrm{T}}[\Psi_{\mathrm{T}}, G]. \tag{3}$$

The optimization of the correlation function G and the trial wave function Ψ_{T} is conducted in two steps. In the first step, the form of the trial function is kept fixed to a single Slater determinant and the parameters of the geminal functions are determined by minimizing the geminal parameters and the molecular orbitals. In the second step, the minimized geminal function G_{min} is kept fixed and the trial wave function Ψ_{T} is minimized. The steps involved are described by the following equations:

$$\tilde{E}[G_{\mathrm{min}}] = \min_{G, \Phi_{\mathrm{SD}}} \tilde{E}_{\mathrm{T}}[\Phi_{\mathrm{SD}}, G], \tag{4}$$

$$E_{\mathrm{CT}} = \min_{\Psi_{\mathrm{T}}} \tilde{E}_{\mathrm{T}}[\Psi_{\mathrm{T}}, G_{\mathrm{min}}]. \tag{5}$$

The optimization of the correlation function and the trial wave function are described in the following subsections.

A. Optimization of the correlation function

The choice of the correlation function G plays an important part in the implementation of the method for practical applications. In principle, a variety of correlated functions such as two- and three-body Jastrow functions can be used. However, the matrix elements associated with these functions cannot be integrated analytically and one has to use numerical techniques such as the VMC method to calculate the integrals. In the present work, Gaussian-type geminal (GTG) functions are used for the correlated functions. The GTG functions were introduced by Boys [33,34] and Singer [35] and have been used extensively in explicitly correlated methods [36–41]. Slater determinants augmented with GTG functions have been used to study electron-electron and electron-proton systems. Explicit correlation has also been included in the multiconfiguration self consistent field (MCSCF) wave function by augmenting it with the geminal correlation function [42]. The integrals involving GTG functions with GTOs can be performed analytically and have been derived earlier [33,34,43,44]. The form of the correlated function used in the following calculations is defined as

$$G = \sum_{i<j}^{N} g(i,j), \tag{6}$$

$$g(i,j) = \sum_{k=1}^{N_{\mathrm{g}}} b_k e^{-\gamma_k r_{ij}^2}, \tag{7}$$

where N is number of electrons and N_{g} is the number of Gaussian functions. The geminal coefficients $\{b_k, \gamma_k\}$ in the GTG function are determined variationally. In the limit of $G \to 1$, the energy $\tilde{E}[G_{\mathrm{min}}]$ becomes equal to the Hartree-Fock (HF) energy:

$$E_{\mathrm{HF}} = \lim_{G \to 1} \tilde{E}[G_{\mathrm{min}}]. \tag{8}$$

As a consequence, the HF energy is the upper bound to the geminal minimization process:

$$\tilde{E}[G_{\mathrm{min}}] \leqslant E_{\mathrm{HF}}. \tag{9}$$

The transformed Hamiltonian is expanded as the sum of two- to six-particle operators as shown below:

$$\tilde{H} = \sum_{i<j} \sum_{k} \sum_{m<n} g(m,n) h_1(k) g(i,j)$$
$$+ \sum_{i<j} \sum_{k<l} \sum_{m<n} g(i,j) r_{kl}^{-1} g(m,n), \tag{10}$$
$$= O_2 + O_3 + O_4 + O_5 + O_6, \tag{11}$$

where the operators $\{O_n,\ n = 2, \ldots, 6\}$ are defined by collecting all two-, three-, four-, five-, and six-particle operators obtained by expanding the summation in Eq. (10).

Specifically,

$$O_2 = \sum_{i<j} h_2(i,j), \tag{12}$$

$$O_3 = \sum_{i<j<k} h_3(i,j,k), \tag{13}$$

$$O_4 = \sum_{i<j<k<l} h_4(i,j,k,l), \tag{14}$$

$$O_5 = \sum_{i<j<k<l<m} h_5(i,j,k,l,m), \tag{15}$$

$$O_6 = \sum_{i<j<k<l<m<n} h_6(i,j,k,l,m,n). \tag{16}$$

The exact forms of the operators $\{h_n, n = 2,\ldots,6\}$ have been derived earlier and are not duplicated here [45]. It should be emphasized that the operators $\{h_n, n = 2,\ldots,6\}$ are defined so that they are completely symmetric with respect to all $n!$ permutation of the indices:

$$\mathcal{P}_k h_n = h_n, \quad \text{where} \quad \mathcal{P}_k \in S_n. \tag{17}$$

The operator $\mathcal{P}_k$ is the permutation operator that belongs to the complete symmetric group S_n. An important feature of this method is the availability of the analytical gradients of the total energy with respect to the geminal parameters. The gradients can be computed analytically and are given by the following expressions:

$$\frac{\partial g(1,2)}{\partial b_k} = e^{-\gamma_k r_{12}^2}, \tag{18}$$

$$\frac{\partial g(1,2)}{\partial \gamma_k} = -b_k r_{12}^2 e^{-\gamma_k r_{12}^2}. \tag{19}$$

The atomic orbital (AO) integrals involving the gradients of the GTG functions are performed analytically and are computed with other AO integrals.

B. Optimization of the trial wave function

The optimization of the trial wave function Ψ_T is performed by performing a FCI calculation on the CT Hamiltonian. The FCI wave function is constructed by performing all possible excitations from the reference wave function [46]. This can be represented by the following expression,

$$\Psi_\mathrm{FCI} = C_0\Phi + \sum_{a}^{N_\mathrm{occ}}\sum_{p}^{N_\mathrm{vir}} C_a^p \Phi_a^p + \sum_{a<b}^{N_\mathrm{occ}}\sum_{p<q}^{N_\mathrm{vir}} C_{ab}^{pq}\Phi_{ab}^{pq} + \sum_{a<b<c}^{N_\mathrm{occ}}\sum_{p<q<r}^{N_\mathrm{vir}} C_{abc}^{pqr}\Phi_{abc}^{pqr} + \cdots, \tag{20}$$

where we have retained N_vir in the expression to emphasize that only a finite number of terms are evaluated. This point is a subject of discussion later in the derivation. The occupied and virtual orbitals are represented by $(a,b,c,\ldots)$ and $(p,q,r,\ldots)$, respectively, and the CI coefficients are represented by $(C_a^p,\ldots)$ and are obtained variationally by minimizing the total energy. The construction of the full set of excitations and the determination of the CI coefficients are the two principle computational challenges associated with the FCI method. For very small molecules, the CI matrix can be explicitly constructed and diagonalized; however, this simple approach becomes prohibitively expensive as the system size increases. Currently, there are various computational techniques for efficient calculation of the expansion coefficients [12,47–51]. The calculation requires matrix elements involving the operators $\{\langle\Phi_k|O_\alpha|\Phi_{k'}\rangle, \alpha = 2,\ldots,6\}$ which are derived below.

The matrix elements involving the two-particle operators are evaluated as

$$\langle\Phi_0|O_2|\Phi_0\rangle = \frac{1}{2!}\sum_{k=1}^{2!}\sum_{i_1i_2}^{N_\mathrm{occ}}(-1)^{p_k}\langle i_1i_2|h_2|P_k i_1i_2\rangle, \tag{21}$$

$$\langle\Phi_0|O_2|\Phi_a^p\rangle = \frac{1}{1!}\sum_{k=1}^{2!}\sum_{i_1}^{N_\mathrm{occ}}(-1)^{p_k}\langle ai_1|h_2|P_k pi_1\rangle, \tag{22}$$

$$\langle\Phi_0|O_2|\Phi_{ab}^{pq}\rangle = \sum_{k=1}^{2!}(-1)^{p_k}\langle ab|h_2|P_k pq\rangle. \tag{23}$$

The matrix elements involving the three-particle operators are evaluated as

$$\langle\Phi_0|O_3|\Phi_0\rangle = \frac{1}{3!}\sum_{k=1}^{3!}\sum_{i_1i_2i_3}^{N_\mathrm{occ}}(-1)^{p_k}\langle i_1i_2i_3|h_3|P_k i_1i_2i_3\rangle, \tag{24}$$

$$\langle\Phi_0|O_3|\Phi_a^p\rangle = \frac{1}{2!}\sum_{k=1}^{3!}\sum_{i_1i_2}^{N_\mathrm{occ}}(-1)^{p_k}\langle ai_1i_2|h_3|P_k pi_1i_2\rangle, \tag{25}$$

$$\langle\Phi_0|O_3|\Phi_{ab}^{pq}\rangle = \sum_{k=1}^{3!}\sum_{i_1}^{N_\mathrm{occ}}(-1)^{p_k}\langle abi_1|h_3|P_k pqi_1\rangle, \tag{26}$$

$$\langle\Phi_0|O_3|\Phi_{abc}^{pqr}\rangle = \sum_{k=1}^{3!}(-1)^{p_k}\langle abc|h_3|P_k pqr\rangle. \tag{27}$$

The matrix elements involving the four-particle operators are evaluated as

$$\langle\Phi_0|O_4|\Phi_0\rangle = \frac{1}{4!}\sum_{k=1}^{4!}\sum_{i_1i_2i_3i_4}^{N_\mathrm{occ}}(-1)^{p_k}\langle i_1i_2i_3i_4|h_4|P_k i_1i_2i_3i_4\rangle, \tag{28}$$

$$\langle\Phi_0|O_4|\Phi_a^p\rangle = \frac{1}{3!}\sum_{k=1}^{4!}\sum_{i_1i_2i_3}^{N_\mathrm{occ}}(-1)^{p_k}\langle ai_1i_2i_3|h_4|P_k pi_1i_2i_3\rangle, \tag{29}$$

$$\langle\Phi_0|O_4|\Phi_{ab}^{pq}\rangle = \frac{1}{2!}\sum_{k=1}^{4!}\sum_{i_1i_2}^{N_\mathrm{occ}}(-1)^{p_k}\langle abi_1i_2|h_4|P_k pqi_1i_2\rangle, \tag{30}$$

$$\langle\Phi_0|O_4|\Phi_{abc}^{pqr}\rangle = \sum_{k=1}^{4!}\sum_{i_1}^{N_\mathrm{occ}}(-1)^{p_k}\langle abci_1|h_4|P_k pqri_1\rangle, \tag{31}$$

$$\langle\Phi_0|O_4|\Phi_{abcd}^{pqrs}\rangle = \sum_{k=1}^{4!}(-1)^{p_k}\langle abcd|h_4|P_k pqrs\rangle. \tag{32}$$

The matrix elements involving the five-particle operators are evaluated as

$$\langle\Phi_0|O_5|\Phi_0\rangle = \frac{1}{5!}\sum_{k=1}^{5!}\sum_{i_1i_2i_3i_4i_5}^{N_\mathrm{occ}}(-1)^{p_k}\langle i_1i_2i_3i_4i_5|h_5|P_k i_1i_2i_3i_4i_5\rangle, \tag{33}$$

$$\langle\Phi_0|O_5|\Phi_a^p\rangle = \frac{1}{4!}\sum_{k=1}^{5!}\sum_{i_1i_2i_3i_4}^{N_\mathrm{occ}}(-1)^{p_k}\langle ai_1i_2i_3i_4|h_5|P_k pi_1i_2i_3i_4\rangle, \tag{34}$$

$$\langle \Phi_0 | O_5 | \Phi^{pq}_{ab} \rangle = \frac{1}{3!} \sum_{k=1}^{5!} \sum_{i_1 i_2 i_3}^{N_{\rm occ}} (-1)^{p_k} \langle a b i_1 i_2 i_3 | h_5 | P_k p q i_1 i_2 i_3 \rangle, \tag{35}$$

$$\langle \Phi_0 | O_5 | \Phi^{pqr}_{abc} \rangle = \frac{1}{2!} \sum_{k=1}^{5!} \sum_{i_1 i_2}^{N_{\rm occ}} (-1)^{p_k} \langle a b c i_1 i_2 | h_5 | P_k p q r i_1 i_2 \rangle, \tag{36}$$

$$\langle \Phi_0 | O_5 | \Phi^{pqrs}_{abcd} \rangle = \sum_{k=1}^{5!} \sum_{i_1}^{N_{\rm occ}} (-1)^{p_k} \langle a b c d i_1 | h_5 | P_k p q r s i_1 \rangle, \tag{37}$$

$$\langle \Phi_0 | O_5 | \Phi^{pqrst}_{abcde} \rangle = \sum_{k=1}^{5!} \langle a b c d e | h_5 | P_k p q r s t \rangle. \tag{38}$$

The matrix elements involving the six-particle operators are evaluated as

$$\langle \Phi_0 | O_6 | \Phi_0 \rangle = \frac{1}{6!} \sum_{k=1}^{6!} \sum_{i_1 i_2 i_3 i_4 i_5 i_6}^{N_{\rm occ}} (-1)^{p_k} \langle i_1 i_2 i_3 i_4 i_5 i_6 | h_6 | P_k i_1 i_2 i_3 i_4 i_5 i_6 \rangle, \tag{39}$$

$$\langle \Phi_0 | O_6 | \Phi^{p}_{a} \rangle = \frac{1}{5!} \sum_{k=1}^{6!} \sum_{i_1 i_2 i_3 i_4 i_5}^{N_{\rm occ}} (-1)^{p_k} \langle a i_1 i_2 i_3 i_4 i_5 | h_6 | P_k p i_1 i_2 i_3 i_4 i_5 \rangle, \tag{40}$$

$$\langle \Phi_0 | O_6 | \Phi^{pq}_{ab} \rangle = \frac{1}{4!} \sum_{k=1}^{6!} \sum_{i_1 i_2 i_3 i_4}^{N_{\rm occ}} (-1)^{p_k} \langle a b i_1 i_2 i_3 i_4 | h_6 | P_k p q i_1 i_2 i_3 i_4 \rangle, \tag{41}$$

$$\langle \Phi_0 | O_6 | \Phi^{pqr}_{abc} \rangle = \frac{1}{3!} \sum_{k=1}^{6!} \sum_{i_1 i_2 i_3}^{N_{\rm occ}} (-1)^{p_k} \langle a b c i_1 i_2 i_3 | h_6 | P_k p q r i_1 i_2 i_3 \rangle, \tag{42}$$

$$\langle \Phi_0 | O_6 | \Phi^{pqrs}_{abcd} \rangle = \frac{1}{2!} \sum_{k=1}^{6!} \sum_{i_1 i_2}^{N_{\rm occ}} (-1)^{p_k} \langle a b c d i_1 i_2 | h_6 | P_k p q r s i_1 i_2 \rangle, \tag{43}$$

$$\langle \Phi_0 | O_6 | \Phi^{pqrst}_{abcde} \rangle = \sum_{k=1}^{6!} \sum_{i_1}^{N_{\rm occ}} \langle a b c d e i_1 | h_6 | P_k p q r s t i_1 \rangle, \tag{44}$$

$$\langle \Phi_0 | O_6 | \Phi^{pqrstu}_{abcdef} \rangle = \sum_{k=1}^{6!} \langle a b c d e f | h_6 | P_k p q r s t u \rangle. \tag{45}$$

The computation of matrix elements in the above expressions require atomic orbital integrals involving the GTG functions. One of the advantages of using the GTG functions is that all the AO integrals needed for the CT Hamiltonian (CTH) calculation can be computed analytically. Boys and Singer have derived the integrals involving GTG functions with s-type GTOs. Persson and Taylor [44] have extended the method for higher angular momentum by using the Hermite-Gaussian expansion approach. Recently, Höfener and co-workers [52] have also derived the geminal integrals by extending the Obara-Saika techniques for calculating the GTG integrals.

The solution for the CI coefficients requires diagonalization of the CI Hamiltonian matrix. However, the lowest eigenvalue and eigenfunction can be obtained without explicit construction and storage of the CI matrix. There are various efficient methods such as the Davidson diagonalization to perform this task [53]. Recently, Alavi *et al.* [54–58] have developed the FCI-QMC method which allows very efficient evaluation of the FCI wave function.

In the present calculation, the FCI eigenvector was obtained by performing Nesbet's update scheme [59] and was selected because of its ease of implementation. In the Nesbet method, an expansion coefficient c_μ is updated by Δc_μ:

$$c_\mu = c_\mu + \Delta c_\mu, \tag{46}$$

where the update is calculated as

$$\Delta c_\mu = \frac{\sigma_\mu}{E \tilde{1}_{\mu\mu} - \tilde{H}_{\mu\mu}}, \tag{47}$$

$$\sigma_\mu = \sum_i \tilde{H}_{\mu i} c_i - E \sum_i \tilde{1}_{\mu i} c_i. \tag{48}$$

The energy is updated at each step using

$$\Delta E = \frac{\sigma_\mu \Delta c_\mu}{D + \Delta D}, \tag{49}$$

$$\Delta D = \Delta c_\mu \left[2 \sum_i S_{\mu i} c_i + S_{\mu\mu} \Delta c_\mu \right]. \tag{50}$$

The FCI energy can be recovered from the CT calculation by setting $G = 1$:

$$E_{\rm FCI} = \lim_{G \to 1} E_{\rm CT}. \tag{51}$$

From the above relationship, we expect that the CTH energy calculated with $G_{\rm min}$ will be lower than the FCI results. In the following section, we perform CTH calculations on well-studied two-electron systems and compare calculated energies with reported benchmark values.

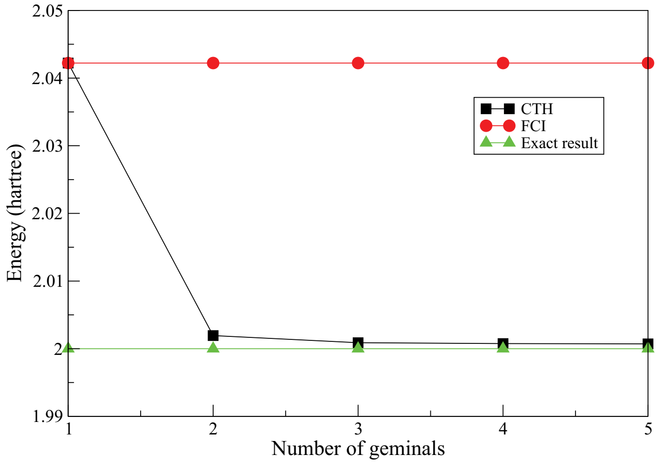

FIG. 1. (Color online) Comparison of the exact ground-state energy of the Hooke's atom with the results from CTH and FCI calculations.

TABLE I. Geminal parameters for Hooke's atom using the 6-311G basis set.

Number	b_k	γ_k
1	1.0000	0.0000
2	−0.6090	0.1050
3	−0.0709	2.350
4	0.0216	0.175
5	−0.0132	1.120

III. CALCULATIONS AND RESULTS OF BENCHMARK SYSTEMS

The Hooke's atom is one of the few correlated two-electron systems for which the Schrödinger equation can be solved analytically. This feature has made it a testing ground for a wide variety of methods [60–63]. The Hooke's atom consists of two electrons in a parabolic potential. The Hamiltonian of that system can be written as

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{2}kr_1^2 + \frac{1}{2}kr_2^2 + \frac{1}{r_{12}}, \tag{52}$$

where all the quantities are expressed in atomic units. The interaction between an electron and the nucleus is described with the harmonic potential. For $k = 0.5$ a.u., the Schrödinger equation can be solved exactly and the ground-state energy is equal to 2.0 hartrees [64]. The Hooke's atom provides an ideal ground for testing the CTH method. The CTH calculations were performed using the 6-311G basis and the geminal parameters were obtained variationally from the solution of Eq. (4). The energy was converged with respect to the number of geminal parameters N_g, and the results are presented in Fig. 1. It is seen that the energy was converged after the addition of four geminal parameters and the optimized geminal parameters are listed in Table I. Comparing the energy with the exact result of 2.0 hartrees, it is seen that the $\tilde{E}[G_{\mathrm{min}}]$ is slightly higher by 0.770 mhartrees (or 0.483 kcal/mol). The optimized Slater determinant Φ obtained in the previous step is used as the reference wave function for the CTH calculations and the results are summarized in Fig. 1. For $G = 1$, the CTH energy is identical to the FCI energy. However, inclusion of additional geminal terms makes the CTH energy lower than the energy from the FCI calculation. It is seen that the CTH energy is in good agreement with the exact analytical results and is higher by 0.000 296 hartrees; these results are provided in Table II.

The CTH calculations were also carried out for the helium atom and the results are presented in Fig. 2. The calculations were performed using different basis functions, and the results were compared with HF and FCI values. It is seen that for small basis sets, the $\tilde{E}$ energy is lower than the FCI energy. We expect this because of the inclusion of the optimized geminal terms. The key result from Fig. 2 is that for small basis sets the CTH method provides a substantial lowering of energy with respect to the corresponding FCI values. The CTH calculations with respect to a small basis provide a wave function that is comparable to the FCI wave function at much larger basis functions. Since the cost of the FCI expansion increases sharply with the size of the underlying one-particle basis, the CTH method provides an appealing alternative for obtaining accurate results when an FCI calculation is prohibitively expensive. The dependence of the CTH energies on the number of geminal parameters is shown in Fig. 3 and the optimized geminal parameters for the helium atom are listed in Table III.

TABLE II. Difference between exact and calculated energy of the Hooke's atom using the CTH method.

Hartree	kcal/mol	kJ/mol	eV	cm^{-1}
0.000 296	0.186	0.777	0.008 05	65.0

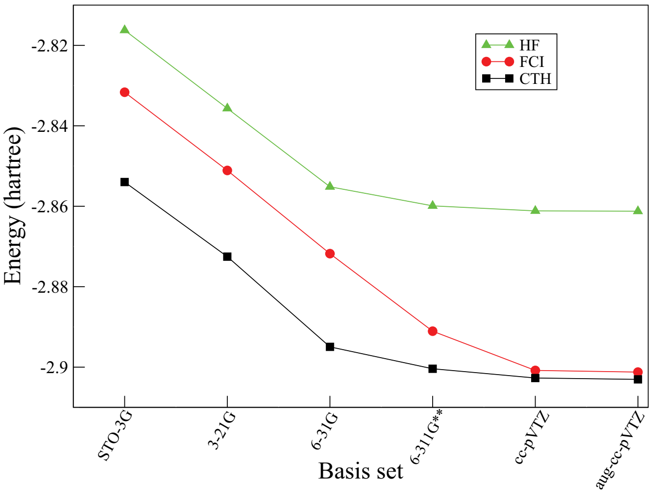

FIG. 2. (Color online) Effect of basis set on the ground-state energy of helium for HF, FCI, and CTH methods.

IV. DISCUSSION AND CONCLUSIONS

The first geminal parameter is always set to $b_1 = 1$ and $\gamma_1 = 0$ and is never optimized during the calculations. When all the other $N_g - 1$ geminal parameters are set to zero, these values of b_1 and γ_1 represent the $G = 1$ limit. Geminal

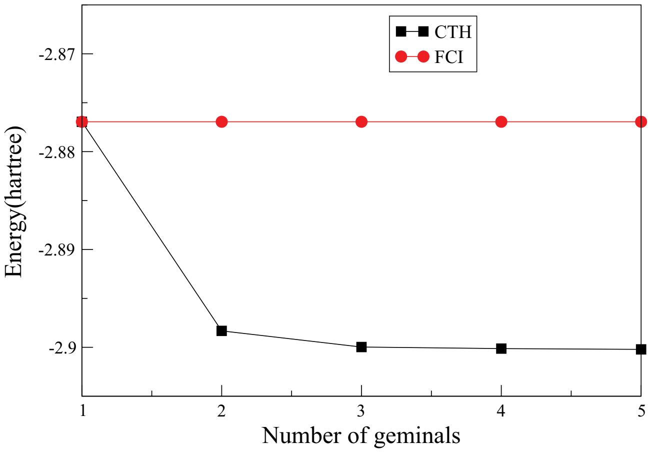

FIG. 3. (Color online) Convergence of the CT Hamiltonian energy of the helium atom with respect to the number of geminal functions. The calculations were performed with the 6-311G basis set.

TABLE III. Geminal parameters for the helium atom using 6-311G.

Number	b_k	γ_k
1	1.000 000	0.000 00
2	−0.320 260	0.578 16
3	−0.063 365	10.3760
4	0.020 918	0.835 36
5	−0.029 282	0.087 99

parameters from $b_2,\ldots,b_{N_g}$ and $\gamma_2,\ldots,\gamma_{N_g}$ are optimized to obtain $G_{\min}$ as described in Eq. (4). This procedure ensures that the optimized energy is always bounded from above by the HF energy. Figures 1 and 2 show the effect of inclusion of additional geminal parameters and it is seen that the second geminal parameter lowers the energy significantly. This is an important result and clearly indicates the importance of the geminal function in construction of the CTH. The set of $\{b_k\}$ was optimized without any constraint and it is seen from Tables I and III that the overall geminal parameter is negative. This is an expected result and is in agreement with previous work on explicitly correlated methods [52,65,66]. The negative values of geminal parameters indicate the role of the geminal function in providing a better description of the Coulomb hole.

The analytical forms of the GTG functions are inherently approximate and are not capable of describing the cusp correctly because their first derivative vanishes in the limit of $r_{ee} = 0$:

$$\left(\frac{\partial G}{\partial r_{ee}}\right)_{r_{ee}=0} = 0. \tag{53}$$

To assess the quality of the CTH energy, it is important to estimate how much of an error this feature introduces in the calculated energy. For the Hooke's atom this can be done in a a straightforward manner since the analytical solution of the Schrödinger equation is known. From Table II, it is seen that the CTH energy is close to the exact ground-state energy and is higher by 0.296 mhartrees or 0.186 kcal/mol. This difference between the CTH and the exact energy represents the upper bound in the error that one can expect for this system by approximating the cusp with GTG functions. For the helium atom, the situation is less straightforward because we do not have access to the exact solution. Instead, we compared the CTH energies with other high-level methods from previous studies [67–75] that include the exact cusp condition in the wave function. In order to achieve the best CTH energy, the calculation was performed with an aug-cc-pVTZ basis set and geminal parameters were optimized with respect to the aug-cc-pVTZ basis. Comparing the CTH method with the highly accurate iterative complement interaction (ICI) method by Nakashima and Nakatsuji [70,71], it is seen that CTH energy is higher than the ICI energy by 0.429 kcal/mol. A comparison of the CTH calculation to the ICI method and other highly accurate results can be seen in Table IV. The impact of the electron-electron cusp on ground-state energy was investigated in detail by Prendergast and co-workers [12] using CI and QMC methods. Their study concluded that one can still expect to get a mhartree level of accuracy even in situations where the exact cusp condition is not satisfied. Our study using GTG functions also confirms this observation. The use of GTG functions in the CTH method represents a trade-off between the implementation of the exact cusp condition and analytical expression for computing Gaussian-type geminal integrals.

One of the objectives of the CTH method is to address the factorial scaling of the FCI calculation with respect to the basis size. As discussed above, the CTH method can give results that are comparable to FCI calculations at larger basis functions. As the system size increases, the computation cost of the CTH method is dominated by the calculation and storage of the many-particle integrals. Therefore, additional optimization techniques must be used for efficient implementation of the CTH method. Some of the many-particle integrals can be factorized as products of lower-dimensional integrals. For example, five- and six-particle integrals of the form

$$\begin{aligned}&\langle i_1 i_2 i_3 i_4 i_5 i_6 | g(1,2) r_{34}^{-1} g(5,6) | j_1 j_2 j_3 j_4 j_5 j_6 \rangle \\ &\quad = \langle i_1 i_2 | g(1,2) | j_1 j_2 \rangle \langle i_3 i_4 | r_{34}^{-1} | j_3 j_4 \rangle \\ &\quad\quad \times \langle i_5 i_6 | g(5,6) | j_5 j_6 \rangle\end{aligned} \tag{54}$$

can be factored exactly in term to lower-dimensional integrals. The many-particle integrals that cannot be factorized exactly into lower-dimensional integrals can be approximately factorized by using the resolution of identity (RI) approach that has been used extensively in R12 and F12 methods [77–80]. The RI scheme not only reduces the complexity of evaluating the integrals but also helps in reducing the memory requirement for storing the integrals. We have implemented the RI-CTH method and have performed calculations on a series of ten isoelectronic systems. However, the implementation details are beyond the present discussion and are presented in a separate article [81].

In addition to the RI extension, the CTH method can also be used for computation of excited-state energies. One of the key aspects of the correlation function used in the congruent transformation is that it is a completely symmetric operator and belongs to the A_1 irreducible representation. The CTH and identity operators retain their A_1 symmetry. Consequently, eigenfunctions of different symmetries are orthogonal to each other and the CTH method can be used for computation of excited states with symmetry different than that of the ground-state wave function. Excited states that are of the same

TABLE IV. Comparison of ground-state energy (in hartrees) of the helium atom.

E	Function	Ref.
−2.900233	FCI	[76]
−2.903041	CTH	This work
−2.903 724 377 034 119 598 311 592 245 194 404 446 696 9	Free ICI	[70,71]

symmetry as the ground-state pose additional challenges and will be investigated in future studies.

In conclusion, the congruent transformation of the electronic Hamiltonian using a Gaussian-type geminal function is presented as a general method for calculating accurate ground-state energy. The form of the CTH can be systematically improved by using the geminal function. It was found that a small number of geminal functions are needed to converge the energy. Furthermore, the addition of just one geminal parameter results in a substantial improvement in the accuracy of the wave function. For a given finite basis set the CTH energy was found to be lower that the FCI calculation on an untransformed Hamiltonian. The results indicate that the CTH provides a viable alternative for obtaining FCI quality energy using a smaller underlying one-particle basis set.

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