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# Canonical transcorrelated theory with projected Slater-type geminals

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An effective Hamiltonian perturbed with explicit interelectronic correlation is derived from similarity transformation of Hamiltonian using a unitary operator with Slater-type geminals. The Slater-type geminal is projected onto the excitation (and deexcitation) component as in the F12 theory. Simplification is made by truncating higher-body operators, resulting in a correlated Hamiltonian which is Hermitian and has exactly the same complexity as the original Hamiltonian in the second quantized form. It can thus be easily combined with arbitrary correlation models proposed to date. The present approach constructs a singularity-free Hamiltonian *a priori*, similarly to the so-called transcorrelated theory, while the use of the canonical transformation assures that the effective Hamiltonian is two-body and Hermite. Our theory is naturally extensible to multireference calculations on the basis of the generalized normal ordering. The construction of the effective Hamiltonian is non-iterative. The numerical assessments demonstrate that the present scheme improves the basis set convergence of the post-mean-field calculations at a similar rate to the explicitly correlated methods proposed by others that couple geminals and conventional excitations. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3688225>]

## I. INTRODUCTION

Explicit correlation methods, which include functions explicitly dependent on the interelectronic coordinate  $f(r_{ij})$  into trial wave functions, have been developed to overcome the slow convergence of energies and properties with basis size in post-mean-field quantum chemical calculations. The improved convergence is ascribed to the proper description of cusped wave functions around electron–electron coalescence. The so-called F12 methods originating from the seminal work of Kutzelnigg<sup>1</sup> have been extensively studied in the last decade using a Slater-type correlation factor of Ten-no<sup>2</sup> (see Refs. 2–46).

In this work, we propose a new class of explicitly correlated theories using an effective Hamiltonian approach with the so-called canonical transformation (CT). The CT theory has been developed by Yanai, Chan, Neuscamman, and co-workers,<sup>47–54</sup> in which dynamic electron correlation is described by a similarity transformation of the Hamiltonian  $\hat{H}$  using a unitary operator  $e^{\hat{A}}$  with an operator  $\hat{A} = -\hat{A}^\dagger$ . The central idea is to use the operator and cumulant decompositions to define a two-body effective Hamiltonian through an approximate Baker–Campbell–Hausdorff (BCH) expansion,

$$\begin{aligned} \hat{H} &= e^{\hat{A}^\dagger} \hat{H} e^{\hat{A}} \\ &\approx \hat{H} + [\hat{H}, \hat{A}]_{1,2} + \frac{1}{2!} [[\hat{H}, \hat{A}]_{1,2}, \hat{A}]_{1,2} + \dots, \quad (1) \end{aligned}$$

which can be evaluated recursively (see also Ref. 55). Here  $[\dots]_{1,2}$  denotes that a commutator is approximated by an operator that contains only one- and two-body operators in the sense of the generalized normal ordering of Mukherjee

and Kutzelnigg.<sup>56–58</sup> The CT is closely related to Kutzelnigg and Mukherjee’s general unitary transformation methods,<sup>58–66</sup> which encompass a rigorous formulation. In this work, we generalize this approach to explicitly correlated theories by introducing a unitary operator ( $\hat{A}$ ) that depends on the interelectronic distances.

Our approach bears close relation to analytic similarity transformations suggested by Hirschfelder and by Jankowski in as early as 1960s,<sup>67–69</sup> which Boys and Handy have further studied and referred to as a “transcorrelated” Hamiltonian.<sup>70–75</sup> Note that the transcorrelated Hamiltonian is a three-body non-Hermite operator. Ten-no has introduced a frozen Gaussian geminal<sup>76,77</sup> in the transcorrelated methods and applied post-mean-field correlation methods.<sup>78,79</sup> The transcorrelated scheme for periodic solids has been studied by Tsuneyuki *et al.*<sup>80</sup> Imamura and Scuseria have developed a correlation functional in density functional theory from transcorrelated Hamiltonians.<sup>81</sup> The obstacle in the transcorrelated approaches has nonetheless been the non-Hermicity of the transcorrelated Hamiltonian,<sup>82</sup> leading to numerical instability. Recently Luo has proposed a variational variant<sup>83,84</sup> by neglecting the non-Hermite terms.

Along these lines, the standard CC-F12 theory<sup>10</sup> can also be seen as a similarity transformation that yields up to six-body operators, as noted previously.<sup>15</sup> The success of the F12 theory should be ascribed to the use of projection that retains only the excitation part of a Slater-type geminal [ $f(r_{12}) = -\gamma^{-1} \exp(-\gamma r_{12})$ ]. Our canonical transcorrelated theory uses the same projection to the Slater-type geminals, and the associated amplitudes are determined by the first-order cusp condition as Ten-no proposed in the F12 theory (SP or “fixed” Ansatz),<sup>15</sup> so that the  $\hat{A}$  is given *a priori*. The present theory can, therefore, be viewed as a transcorrelation method

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with a unitary transformation using projected Slater-type geminals.

The effective Hamiltonian approach with  $\hat{H}$  has the following features: (1) The complexity of explicit correlation is transferred from the wave function to the Hamiltonian; (2) Bare electrons are transformed into weakly correlated one-particle elements, i.e., quasi-particles dressed in a field of the explicitly correlated interaction; (3) The high-rank perturbative correlation is all averaged to pair-wise interactions by recursively removing three-body connected cumulant terms; and (4) The Slater-type geminal acting on Hamiltonian effectively regularizes (or smoothes) the interelectronic Coulomb singularity in the original Hamiltonian ( $1/r_{12}$ ). This *perturb-then-diagonalize* approach has been also used in conventional (or, non-F12) methods in a slightly different context such as Van Vleck's perturbation theory, Freed's effective valence Hamiltonian theory,<sup>85</sup> Kirtman's<sup>86</sup> and Hoffmann's<sup>87,88</sup> generalized Van Vleck theory, the symmetry-adapted cluster configuration interaction theory,<sup>89</sup> the equation-of-motion coupled cluster (CC) theory,<sup>90</sup> the flow-renormalization group by Wegner<sup>91</sup> and by Glazek and Wilson<sup>92</sup> (see also Ref. 93) and White's canonical diagonalization theory.<sup>94</sup>

Since the effective Hamiltonian  $\hat{H}$  remains Hermitian and has the same quartic complexity as the original Hamiltonian, we can directly use the existing electronic structure methods to solve the Schrödinger equation based on the *a priori* perturbatively correlated  $\hat{H}$  for the determination of correlated wave functions (and density matrices).

The present formalism is connected to multireference (MR) electronic structure theories through Mukherjee and Kutzelnigg's generalized normal ordering,<sup>56–58</sup> with which we approximate commutators  $[\dots]_{1,2}$  using one- and two-body reduced density matrices (RDMs) of an active-space MR wave function accounting for static correlation. The explicitly correlated MR approaches have been recently studied by a number of groups. Gdanitz has reported the first explicitly correlated MR method quite long time ago, combining a linear R12 correlation factor with the MR configuration interaction (MRCI) approaches.<sup>95,96</sup> A major improvement was brought by Ten-no, who has introduced the internally contracted geminal excitations in conjunction with a nonlinear F12 factor and the fixed amplitude ansatz using the MR Møller–Plesset perturbation method.<sup>19</sup> An *a posteriori* F12 approach for arbitrary correlation models using the RDMs of the underlying models has been proposed by Torheyden and Valeev.<sup>38</sup> There has been also an attempt to combine the F12 theory with the complete active space self-consistent field (CASSCF) by Varganov and Martínez.<sup>97</sup> Shiozaki and Werner have developed an efficient and accurate internally contracted explicitly correlated multireference perturbation method (CASPT2-F12),<sup>43</sup> and then extended their formalism to MRCI-F12 and multireference averaged coupled pair functional (MRACPF-F12).<sup>44,45</sup> Kedžuch *et al.* have studied an explicitly correlated variant of the MR Brillouin–Wigner coupled cluster method.<sup>46</sup> We will present a comparison of our method and some of these methods.

This paper is organized as follows. Section II defines the F12-dressed Hamiltonian, which entails several approximations that significantly reduce its complexity. This

Hamiltonian can be plugged into any quantum chemical solvers. Section III demonstrates several single-reference dynamic correlation methods as well as the linearized CT singles and doubles theory based on the F12-dressed Hamiltonian. Finally, the summary is made in Sec. IV. Abbreviations are listed in Appendix.

## II. THEORY

### A. Notation

We use the following notation for indices.  $\{p, q, r, s, t, u\}$  label any functions in the orbital basis set (OBS) spanned by a finite one-electron atomic-orbital basis, and  $\{\mu, \nu, \lambda, \kappa\}$  label functions in an infinite, complete orbital basis space. The doubly and partially occupied orbitals in the reference functions are both labeled by  $\{i, j, k, l\}$ . In addition,  $\{\alpha, \beta, \gamma\}$  denotes external unoccupied orbitals in the complete orbital space,  $\{a, b\}$  those in the finite orbital space, and  $\{x, y\}$  those in the space spanned by the complementary auxiliary orbital basis set (CABS) of Valeev.<sup>14</sup> All the orbitals are assumed to be orthonormal and spatial (i.e., spin-independent). Index notation is schematically summarized in Fig. 1.

The molecular Hamiltonian is written as

$$\hat{H} = h_v^\mu \hat{E}_\mu^v + \frac{1}{2} g_{\nu\kappa}^{\mu\lambda} \hat{E}_{\mu\lambda}^{\nu\kappa}, \quad (2)$$

where  $h_v^\mu$  and  $g_{\nu\kappa}^{\mu\lambda}$  are one- and two-electron elements (or, integrals), respectively. Hereafter, with the Einstein summation convention, repeated indices are always implicitly summed. We introduce the standard spin-summed excitation operators,

$$\hat{E}_v^\mu = \sum_{\sigma=\alpha,\beta} \hat{a}_{\mu\sigma}^\dagger \hat{a}_{v\sigma}, \quad (3)$$

$$\hat{E}_{\nu\kappa}^{\mu\lambda} = \sum_{\sigma\tau=\alpha,\beta} \hat{a}_{\mu\sigma}^\dagger \hat{a}_{\lambda\tau}^\dagger \hat{a}_{\kappa\tau} \hat{a}_{\nu\sigma}, \quad (4)$$

and the corresponding RDMs,

$$D_v^\mu = \langle \Psi_0 | \hat{E}_v^\mu | \Psi_0 \rangle, \quad (5)$$

$$D_{\nu\kappa}^{\mu\lambda} = \langle \Psi_0 | \hat{E}_{\nu\kappa}^{\mu\lambda} | \Psi_0 \rangle. \quad (6)$$

$|\Psi_0\rangle$  is generally an active-space multi-determinant reference wave function. Note that, in single reference closed-shell

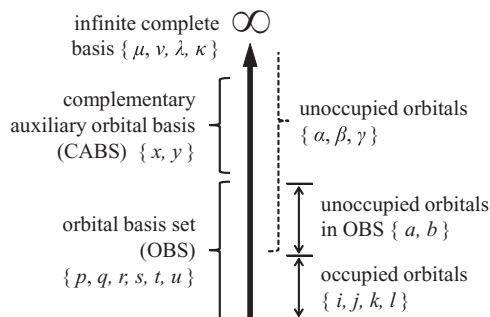


FIG. 1. Schematic specification of notation for orbital indices in the defined orbital spaces.

cases, the RDMs are simply  $D_j^i = 2\delta_j^i$  and  $D_{ji}^{ik} = 4\delta_j^i\delta_l^k - 2\delta_l^i\delta_j^k$  where  $\delta$  refers to Kronecker's delta. The Fock operator is

$$\hat{F} = f_v^\mu \hat{E}_\mu^v, \quad (7)$$

in which the generalized Fock matrix  $f_v^\mu$  is defined by

$$f_v^\mu = h_v^\mu + D_\kappa^\lambda \left( g_{\nu\kappa}^{\mu\lambda} - \frac{1}{2} g_{\kappa\nu}^{\mu\lambda} \right). \quad (8)$$

In single reference cases,  $f_q^p$  in the canonical orbital basis becomes a diagonal matrix, whose diagonal elements are the orbital energies.

## B. Canonical transcorrelated Hamiltonian

In this study, we propose a canonical transcorrelated Hamiltonian with the F12 operator:

$$\hat{H}^{\text{F12}} \equiv \hat{H} + [\hat{H}, \hat{A}^{\text{F12}}]_{1,2} + \frac{1}{2} [[\hat{F}, \hat{A}^{\text{F12}}]_{1,2}, \hat{A}^{\text{F12}}]_{1,2}, \quad (9)$$

which is derived by approximating Eq. (1) in two ways: (i) terminating the expansion at the second order and (ii) replacing  $\hat{H}$  at the second order term (i.e., the double commutator) by the Fock operator  $\hat{F}$ . Note that  $\hat{F}$  is the effective one-particle approximation to  $\hat{H}$ . This truncation of the infinite expansion is correct through the second order in perturbation.<sup>65,66</sup> Similar considerations are made in approximate CC-F12 models.<sup>41</sup> The approximated Hamiltonian [Eq. (9)] covers all the terms that arise in the MP2-F12 theory, and the CCSD method based on this Hamiltonian is similar to the CCSD(F12) theory.<sup>16</sup> The terms associated with the double commutator  $[[\frac{1}{2}g_{\nu\kappa}^{\mu\lambda}\hat{E}_{\mu\lambda}^{\nu\kappa}, \hat{A}^{\text{F12}}], \hat{A}^{\text{F12}}]$ , which have been included only in the full CC-F12 theory,<sup>11,26</sup> are neglected in Eq. (9). We use an anti-Hermitian generator with projected geminal functions to make  $\hat{H}^{\text{F12}}$  Hermitic:

$$\hat{A}^{\text{F12}} = \frac{1}{2} G_{ij}^{\alpha\beta} (\hat{E}_{ij}^{\alpha\beta} - \hat{E}_{\alpha\beta}^{ij}), \quad (10)$$

$$G_{ij}^{\alpha\beta} = \frac{3}{8} \langle \alpha\beta | \hat{Q}_{12} F_{12} | ij \rangle + \frac{1}{8} \langle \alpha\beta | \hat{Q}_{12} F_{12} | ji \rangle, \quad (11)$$

$$F_{12} = -\gamma^{-1} \exp(-\gamma r_{12}), \quad (12)$$

in which we have fixed the amplitudes by those determined by the first-order cusp condition.<sup>15</sup>  $\hat{Q}_{12}$  is the so-called strong orthogonality projector,

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2, \quad (13)$$

where  $\hat{O}_1$  and  $\hat{V}_1$  are projectors to the space spanned by occupied ( $i, j$ ) and unoccupied ( $a, b$ ) orbitals represented by the orbital basis set (OBS), respectively. This projector ensures  $\langle ab | \hat{Q}_{12} F_{12} | ij \rangle = 0$ . Note that at the complete basis set limit  $\hat{Q}_{12}$  is a projector to the null space, and hence  $\exp(\hat{A}^{\text{F12}})$  is one (i.e.,  $\hat{1}$ ).

Inserting  $\hat{A}^{\text{F12}}$  [Eq. (10)] into  $\hat{H}^{\text{F12}}$  [Eq. (9)], one obtains an explicit formula for the transformed Hamiltonian in terms

of tensor products as follows. Let us write the transformed Hamiltonian as

$$\hat{H}^{\text{F12}} = \bar{h}_q^p \hat{E}_p^q + \frac{1}{2} \bar{g}_{qs}^{pr} \hat{E}_{pr}^{qs}. \quad (14)$$

One- and two-body perturbed elements ( $\bar{h}_q^p$  and  $\bar{g}_{qs}^{pr}$ ) are given by

$$\bar{h}_q^p = h_q^p + \frac{1}{2} (\bar{C}_{1q}^p + \bar{C}_{1p}^q), \quad (15)$$

$$\bar{g}_{qs}^{pr} = g_{qs}^{pr} + \frac{1}{4} (\bar{C}_{2qs}^{pr} + \bar{C}_{2sq}^{rp} + \bar{C}_{2pr}^{qs} + \bar{C}_{2rp}^{sq}), \quad (16)$$

in which the one-body perturbed elements ( $\bar{C}_{1q}^p$ ) are

$$\bar{C}_{1q}^p = \bar{c}'_{1q}^p + \bar{c}''_{1q}^p, \quad (17)$$

where the intermediates  $\bar{c}'_{1q}^p$  and  $\bar{c}''_{1q}^p$  are expressed as

$$\bar{c}'_{1q}^p = \bar{D}_{ij}^{tr} \mathcal{U}_{ija}^{trq} \delta_{pq}^{aq} - \bar{D}_{is}^{tr} (2\mathcal{U}_{ija}^{trs} - \mathcal{U}_{jia}^{trs}) \delta_{pq}^{aj}, \quad (18)$$

$$\bar{c}''_{1q}^p = \frac{1}{2} \bar{D}_{ij}^{kl} \mathcal{S}_{ija}^{klb} \delta_{pq}^{ab}. \quad (19)$$

The two-body perturbed elements  $\{\bar{C}_{2qs}^{pr}\}$  are given by

$$\begin{aligned} \bar{C}_{2qs}^{pr} = & 4h_x^p G_{ij}^{xb} \delta_{pqrs}^{pijb} + 2V_{ij}^{pr} \delta_{pqrs}^{pirj} - 2X_{ij}^{kl} f_k^p \delta_{pqrs}^{pilj} \\ & + B_{ij}^{kl} \delta_{pqrs}^{klij} + \bar{c}'_{2qs}^{pr} + \bar{c}''_{2qs}^{pr} \end{aligned} \quad (20)$$

with the intermediates  $\bar{c}'_{2qs}^{pr}$  and  $\bar{c}''_{2qs}^{pr}$  written as

$$\begin{aligned} \bar{c}'_{2qs}^{pr} = & D_i^t (4\mathcal{U}_{ija}^{trs} - 2\mathcal{U}_{jia}^{trs} - 2\mathcal{U}_{ija}^{rts}) \delta_{pqrs}^{ajrs} \\ & + D_u^t (4\mathcal{U}_{ija}^{ptu} - 2\mathcal{U}_{ija}^{tpu}) \delta_{pqrs}^{piaj} - 2D_j^t \mathcal{U}_{ija}^{pts} \delta_{pqrs}^{pias}, \end{aligned} \quad (21)$$

$$\bar{c}''_{2qs}^{pr} = \mathcal{S}_{ija}^{klb} (2D_i^k \delta_{pqrs}^{lbaj} - D_j^k \delta_{pqrs}^{lbai} - D_i^l \delta_{pqrs}^{kbaj} - D_j^l \delta_{pqrs}^{kiab}), \quad (22)$$

The analytic removals of singularities are accounted for by the F12 intermediates:

$$V_{ij}^{pq} = g_{\alpha\beta}^{pq} G_{ij}^{\alpha\beta}, \quad (23)$$

$$X_{ij}^{kl} = G_{ij}^{\alpha\beta} G_{kl}^{\alpha\beta}, \quad (24)$$

$$B_{ij}^{kl} = G_{ij}^{\alpha\beta} f_\gamma^\alpha G_{kl}^{\gamma\beta} + G_{ij}^{\alpha\beta} f_\gamma^\beta G_{kl}^{\alpha\gamma}, \quad (25)$$

which also appear in the MP2-F12 theory. The  $X$  and  $B$  terms arise from  $[[\hat{F}, \hat{A}^{\text{F12}}], \hat{A}^{\text{F12}}]$  in Eq. (9). The other intermediates are defined by

$$\mathcal{U}_{ijb}^{prs} = g_{xs}^{pr} G_{ij}^{xb}, \quad (26)$$

$$\mathcal{S}_{ija}^{klb} = \frac{1}{2} G_{ij}^{xa} G_{kl}^{yb} [f_y^x + \delta_y^x (f_a^a - f_i^i - f_j^j)], \quad (27)$$

$$\bar{D}_{qs}^{pr} = 2 \left( D_q^p D_s^r - \frac{1}{2} D_s^p D_q^r \right) - D_{qs}^{pr}, \quad (28)$$

$$\delta_{pq}^{\bar{p}\bar{q}} = \delta_p^{\bar{p}} \delta_q^{\bar{q}}, \quad (29)$$

$$\delta_{pqrs}^{\bar{p}\bar{q}\bar{r}\bar{s}} = \delta_p^{\bar{p}} \delta_q^{\bar{q}} \delta_r^{\bar{r}} \delta_s^{\bar{s}}. \quad (30)$$

All the F12 integrals [e.g., Eq. (11)] are computed by the Rys-like quadrature scheme<sup>98–100</sup> on the basis of Ten-no’s formula.<sup>2,20</sup> The  $B$  intermediate [Eq. (25)] is computed using the so-called Approximation C of Kedřuch *et al.*<sup>17</sup> The auxiliary basis set is used for the resolution of the identity approximation.<sup>12,14</sup>

It should be mentioned that the two-body elements  $\bar{v}_{qs}^{pr}$  have a four-fold permutation symmetry,  $\bar{v}_{qs}^{pr} = \bar{v}_{sq}^{rp} = \bar{v}_{pr}^{qs} = \bar{v}_{rp}^{sq}$ , while the other symmetry  $\bar{v}_{qs}^{pr} = \bar{v}_{qs}^{rp}$  is not generally maintained, in contrast to the original Hamiltonian. It is also noted that most contributions to the perturbed four-index elements  $\bar{C}_{2qs}^{pr}$  [Eq. (20)] are at most two-external quantity, except for a small three-external contribution  $\bar{c}_{2qs}^{pr}$  [Eq. (21)].

### III. RESULTS AND DISCUSSIONS

#### A. Multireference benchmark: Singlet-triplet separation of methylene

The performance of the canonical transcorrelated theory in MR applications is assessed in this section. In our MR calculations, we first determine a zeroth-order MR wave function  $|\Psi_0\rangle$  from a CASSCF calculation based on the uncorrelated Hamiltonian  $\hat{H}$ . The resulting RDMs of the CASSCF wave function are then used to construct the canonical transcorrelated Hamiltonian  $\hat{H}^{\text{F12}}$  [Eq. (14)]. Starting from the MR  $|\Psi_0\rangle$  and  $\hat{H}^{\text{F12}}$ , we perform canonical transformation with singles and doubles (CTSD)<sup>47–54</sup> leading to a *further* transformed Hamiltonian,

$$\hat{H}^{\text{F12-CT}} = e^{\hat{A}^{\text{CT}}} \hat{H}^{\text{F12}} e^{\hat{A}^{\text{CT}}}. \quad (31)$$

The definition of the CTSD amplitude  $\hat{A}^{\text{CT}}$  does not differ from that of the past implementation represented in the finite OBS,

$$\hat{A}^{\text{CT}} = A_i^{a'} (\hat{E}_i^{a'} - \hat{E}_i^i) + \frac{1}{2} A_{ij}^{a'b'} (\hat{E}_{ij}^{a'b'} - \hat{E}_{ij}^{ij}), \quad (32)$$

where  $a'$  and  $b'$  run over active and unoccupied orbitals. The CTSD stationary equation to determine  $\hat{A}^{\text{CT}}$  and the energy expression were evaluated using  $\hat{H}^{\text{F12}}$ , instead of the uncorrelated  $\hat{H}$  (see Refs. 47–54 for more details on the CTSD model). The transformation with  $e^{\hat{A}^{\text{CT}}}$  introduces dynamic correlation that maps a MR reference wave function onto the target wave function  $|\Psi\rangle$  as  $e^{\hat{A}^{\text{CT}}} |\Psi_0\rangle$ . Substantial portions of dynamic correlation energies associated with electron–electron cusps are recovered in  $\hat{H}^{\text{F12}}$ , while the remaining correlation is described by CTSD, which are both essential to chemical applications. Note that the strong orthogonality projector  $\hat{Q}_{12}$  [Eq. (13)] in  $\hat{H}^{\text{F12}}$  avoid double counting of orbital correlation.

We have applied our MR F12 scheme to a benchmark calculation of the adiabatic  $^1A_1 - ^3B_1$  separation of methylene ( $\text{CH}_2$ ). Peterson’s correlation consistent F12 basis sets<sup>101,102</sup> [cc-pVXZ-F12 for OBS and cc-pVXZ-F12/OptRI for CABS,

denoted hereafter as VXZ-F12,  $X = \text{D}(\text{double-}\zeta)$ ,  $\text{T}(\text{triple-}\zeta)$ , and  $\text{Q}(\text{quadruple-}\zeta)$ ] were used. We used the full valence active space CAS(6e, 6o), correlating six electrons in three  $a_1$ , two  $b_2$ , and one  $b_1$  orbitals. Each state was calculated at the same molecular geometries as in the earlier CASPT2-F12<sup>43</sup> and MRCI-F12<sup>44,45</sup> studies of Shiozaki *et al.* using the same basis sets, active space, and  $\gamma$  as just described, in order to compare directly. We note however that we have not included semi-internal geminal excitations so far, unlike the MRCI-F12 of Shiozaki *et al.*, which might change the results but only slightly for basis functions larger than double- $\zeta$ .<sup>19</sup> For comparison, we performed conventional CTSD calculations with aug-cc-pVXZ basis<sup>103,104</sup> with  $X = \text{D}, \text{T}, \text{Q}, 5$ , which is abbreviated as aXZ in the following.

The total energies of the singlet and triplet states of  $\text{CH}_2$  are shown in Table I together with the singlet–triplet separation energies. These energies do not include the CABS singles correction for the CASSCF energies.<sup>45,105</sup> The experimental value for the singlet–triplet splitting is  $9.1 \pm 0.2$  kcal/mol.<sup>106</sup> The singlet–triplet energy gap from CTSD using  $\hat{H}^{\text{F12}}$ , denoted F12-CTSD, was in best agreement with the experimental value among the VTZ-F12 basis calculations we performed; the deviations from the observed were approximately 0.2, 3.6, and 0.5 kcal/mol for F12-CTSD, CASPT2-F12, and MRCI-F12, respectively. Although the VTZ-F12 and aTZ basis sets are of similar size (89 and 92 basis functions, respectively) and have functions of angular momentum functions up to  $f$ -type function, the F12-CTSD/VTZ-F12 energies were much more accurate than the CTSD/aTZ results. The computational costs of these two

TABLE I. Total energies of the singlet ( $E(^1A_1)$ ) and triplet ( $E(^3B_1)$ ) methylene  $\text{CH}_2$  in  $E_h$  and the singlet-triplet separation in kcal/mol. CAS (6e, 6o) for all the methods. The CABS singles correction is not included.

	OBS	$E(^1A_1)$	$E(^3B_1)$	S-T gap
CASSCF				
aDZ		−38.94438	−38.96129	10.61
aTZ		−38.95523	−38.97127	10.06
aQZ		−38.95762	−38.97361	10.04
a5Z		−38.95816	−38.97416	10.04
CTSD				
aDZ		−39.03490	−39.05121	10.24
aTZ		−39.08113	−39.09635	9.55
aQZ		−39.10124	−39.11590	9.20
a5Z		−39.10962	−39.12414	9.11
F12-CTSD (present)				
VDZ-F12		−39.11832	−39.13321	9.34
VTZ-F12		−39.13005	−39.14433	8.96
CASPT2-F12 (Shiozaki <i>et al.</i> ) <sup>a</sup>				
VDZ-F12		−39.05913	−39.07986	13.01
VTZ-F12		−39.06374	−39.08404	12.74
VQZ-F12		−39.06478	−39.08509	12.74
MRCI+Q-F12 (Shiozaki <i>et al.</i> ) <sup>b</sup>				
VDZ-F12		−39.06987	−39.08474	9.33
VTZ-F12		−39.07651	−39.09026	8.63
VQZ-F12		−39.07813	−39.09173	8.53

<sup>a</sup>Reference 43.

<sup>b</sup>Reference 44.

CTSD calculations (starting from  $\hat{H}$  and  $\hat{H}^{F12}$ ) were virtually identical. Our current pilot implementation of generating canonical transcorrelated Hamiltonian ( $\hat{H}^{F12}$ ) relies on in-core memory to store all integrals and intermediates, whose sizes are  $O(N^4)$ , from which the F12-CTSD calculations are so far limited to small basis sets (e.g., VTZ-F12). This limitation will be lifted in the future; the CTSD calculation itself is capable of handling large basis functions since we have recently implemented an efficient parallelized code.

## B. Single-reference case: Higher-order perturbation and coupled-cluster theory

Our theory can be combined with arbitrary single reference (SR) many-electron theory, with which we have benchmarked its performance on capturing dynamic correlation due to electron–electron cusps. We solve the Schrödinger equation  $\hat{H}^{F12}\hat{\Omega}|\Psi_{SR}\rangle = E\hat{\Omega}|\Psi_{SR}\rangle$  based on the perturbed one- and two-electron integrals (Hamiltonian elements  $\bar{h}_q^p$  and  $\bar{v}_{qs}^{pr}$  of  $\hat{H}^{F12}$  [Eq. (14)]) where  $\hat{\Omega}$  refers to the wave operator. In this way, we can simply reuse existing computer implementations of high-level SR correlation methods<sup>107–110</sup> to investigate the performance of the F12 approach towards the limits of complete dynamic correlation. Here we have interfaced our correlated Hamiltonian to the TCE module<sup>107,108,111,112</sup>

available in UTCHEM program package,<sup>113</sup> in which high-level many-body algorithms [such as Møller–Plesset perturbation theory with up to fourth order (MP4) and the coupled cluster theory with up to quadruples (CCSDTQ)] have been implemented into a massively parallelized software through automatic derivation and computer-aided implementation. Automated implementation approaches to the development of F12 methods in conjunction with higher-order many-body models have been reported by Shiozaki *et al.* with the generator SMITH<sup>26,31–33</sup> and Köhn *et al.* with GECCO.<sup>30,34,35</sup>

Generally speaking, it is convenient to assume the Brillouin condition in the many electron theories (especially for MP $n$  methods). Therefore, just as  $\hat{F}$  given by Eq. (7), we introduce  $\hat{F}^{F12}$  as a Fock operator whose Hamiltonian elements are replaced by those of  $\hat{H}^{F12}$ . With the F12-correlated Fock matrix elements  $F^{F12}_{pq} = \langle \phi_p | \hat{F}^{F12} | \phi_q \rangle$ , we define the Brillouin condition and canonical Hartree–Fock (HF) equation for the canonical transcorrelated theory as  $F^{F12}_{ia} = 0$  and  $F^{F12}_{pq} = \epsilon_p \delta_q^p$ , respectively. Note that the conventional and F12-correlated canonical orbitals are not identical. To obtain the canonical orbitals for  $\hat{F}^{F12}$ , we iteratively diagonalize the F12-correlated Fock matrix  $F^{F12}_{pq}$  until the self-consistency is satisfied. In addition, since the TCE module assumes the eight-fold permutation symmetry, the two-particle elements of  $\hat{H}^{F12}$  have been explicitly symmetrized  $[(\bar{v}_{qs}^{pr} + \bar{v}_{qs}^{rp})/2]$

TABLE II. Valence correlation energies (in  $E_h$ ) of the Ne atom with aug-cc-pVXZ for OBS and aug-cc-pVXZ/OptRI for CABS as denoted by aXZ. A Slater geminal with  $\gamma = 1.5$  a.u. has been used.

Method	aDZ	aTZ	aQZ	a5Z	a6Z	CBS
Original uncorrelated Hamiltonian						
HF total energy	−128.49635	−128.53327	−128.54376	−128.54679	−128.54706	
MP2	−0.20687	−0.27252	−0.29724	−0.30797	−0.31287	−0.31961
MP3	−0.20842	−0.27273	−0.29684	−0.30610	−0.30996	−0.31526
MP4	−0.21411	−0.28052	−0.30490	−0.31425	−0.31817	−0.32355
CCSD	−0.21015	−0.27409	−0.29776	−0.30680	−0.31061	−0.31584
QCISD	−0.21078	−0.27452	−0.29811	−0.30713	−0.31092	−0.31614
CCSD(T)	−0.21294	−0.27938	−0.30370	−0.31305	−0.31697	−0.32236
CCSD[T]	−0.21341	−0.27966	−0.30395	−0.31328	−0.31719	−0.32257
LCCSD	−0.21216	−0.27702	−0.30110			
CCSDT	−0.21307	−0.27939	−0.30367			
CCSDTQ	−0.21312	−0.27946				
Canonical transcorrelated Hamiltonian (present)						
F12-HF	−0.11148	−0.04356	−0.02025			
F12-MP2	−0.31411	−0.31171	−0.31478			
F12-MP3	−0.31623	−0.31226	−0.31450			
F12-MP4	−0.32142	−0.31970	−0.32244			
F12-CCSD	−0.31783	−0.31356	−0.31542			
F12-QCISD	−0.31838	−0.31395	−0.31577			
F12-CCSD(T)	−0.32044	−0.31867	−0.32129			
F12-CCSD[T]	−0.32084	−0.31894	−0.32153			
F12-LCCSD	−0.31968	−0.31634	−0.31868			
F12-CCSDT	−0.32055	−0.31870	−0.32126			
F12-CCSDTQ	−0.32062	−0.31876				
Shiozaki <i>et al.</i> <sup>a</sup>						
CCSD-F12	−0.30652	−0.31152	−0.31410	−0.31499		
CCSDT-F12	−0.30896	−0.31664	−0.31994	−0.32113		
CCSDTQ-F12	−0.30905	−0.31670	−0.32004			

<sup>a</sup>Reference 32.

TABLE III. Reaction energies (in  $E_h$ ) of the dissociation  $C_2H_2 + 3H_2 \rightarrow 2CH_4$  computed by CCSD(T), F12-CCSD(T), and CCSD(T)(F12\*).

OBS	HF	MP2	CCSD	CCSD(T)
aDZ	0.18514	0.17465	0.17988	0.17638
aTZ	0.17906	0.16979	0.17579	0.17177
aQZ	0.17861	0.16886	0.17505	0.17094
a5Z	0.17864	0.16848	0.17485	0.17067
a6Z	0.17864	0.16829	0.17478	0.17058
	F12-HF	F12-MP2	F12-CCSD	F12-CCSD(T)
aDZ	0.17844	0.17035	0.17523	0.17226
aTZ	0.17672	0.16910	0.17452	0.17087
	HF(CS)	MP2-F12	CCSD(F12*)	CCSD(T)(F12*)
aDZ	0.17875	0.16927	0.17570	0.16688
aTZ	0.17806	0.16828	0.17490	0.17078

$\rightarrow \bar{v}_{qs}^{pr}$ ]. The transcorrelated Hamiltonian  $\hat{H}^{F12}$  with such optimized orbitals were then used in *a posteriori* TCE calculations. We have tested a variety of SR models: MP2, MP3, MP4, CCSD, CCSDT, CCSDTQ, two variants of CCSD with perturbative triples, CCSD(T), CCSD[T], the quadratic configuration interaction with singles and doubles (QCISD), and the linearized CCSD (LCCSD).

As a benchmark, we have computed the valence correlation energy of Ne as shown in Table II, where a canonical transcorrelated method with SR model X is denoted as F12-X. Dunning’s augmented correlation-consistent basis sets (aXZ) were used for OBS and the corresponding CABS functions by Peterson and co-workers (aug-cc-pVXZ/OptRI)<sup>114</sup> for the F12 intermediates. Table II also compiles the HF and valence correlation energies obtained by the conventional TCE calculations as well as those reported by Shiozaki *et al.*<sup>32</sup> (the CCSD-F12, CCSDT-F12, and CCSDTQ-F12 models with the same F12 correlation factor as in our calculations  $\gamma = 1.5$  a.u.). For comparison, we have also used  $\gamma = 1.5$  a.u. in this example. It has been shown that the canonical transcorrelation method gives a significant improvement in correlation energies for all the tested SR models, approaching the complete basis set (CBS) values (obtained by extrapolation from a5Z

and a6Z energies) within 2–6  $mE_h$  for the aDZ basis set. As the basis set size increases, the correlation energies converge to the CBS limits, whereas the F12-HF model (neglecting the orbital correlation) to the HF basis limit. The F12-X correlation energies for the aDZ basis set has been found closer to the basis set limit compared to those for the aTZ basis set due to fortuitous error cancellation. The F12-CCSD, F12-CCSDT, and F12-CCSDTQ methods seem to have captured a larger portion of the correlation energy of Ne than the corresponding CC-F12 methods.

### C. CCSD(T) with canonical transcorrelated Hamiltonian

The CCSD(T) method is widely used as a highly accurate method that is well balanced between efficiency and accuracy, sometimes referred to as the “gold standard.” Several approximate models to CCSD(T)-F12 have been proposed<sup>16,23,25,29,36,40</sup> to efficiently achieve near CBS limit CCSD(T) accuracy with small to medium-sized basis sets. In this section, the performance of our F12-CCSD(T) theory is presented for thermochemical applications to calculate energy differences and bonding potentials.

TABLE IV. Equilibrium bond length  $R_e$  (Å) and harmonic vibrational constant  $\omega_e$  ( $cm^{-1}$ ) of  $N_2$  computed by CCSD(T), F12-CCSD(T), and CCSD(T)(F12\*).

OBS	HF		MP2		CCSD		CCSD(T)			
	$R_e$	$\omega_e$	$R_e$	$\omega_e$	$R_e$	$\omega_e$	$R_e$	$\omega_e$	$R_e$	$\omega_e$
aDZ	1.0783	2735.0	1.1318	2156.1	1.1143	2391.0	1.1209	2317.6		
aTZ	1.0670	2726.0	1.1141	2185.2	1.0967	2417.2	1.1040	2337.8		
aQZ	1.0656	2728.5	1.1107	2200.0	1.0932	2432.9	1.1005	2352.9		
a5Z	1.0654	2729.9	1.1098	2204.6	1.0923	2438.1	1.0995	2357.8		
a6Z	1.0654	2730.1	1.1096	2205.8	1.0920	2439.6	1.0993	2359.0		
	F12-HF		F12-MP2		F12-CCSD		F12-CCSD(T)		CCSD(T)(F12*)	
	$R_e$	$\omega_e$	$R_e$	$\omega_e$	$R_e$	$\omega_e$	$R_e$	$\omega_e$	$R_e$	$\omega_e$
aDZ	1.0624	2750.7	1.1082	2247.8	1.0944	2440.7	1.0997	2379.7	1.0994	2364.3
aTZ	1.0638	2739.0	1.1081	2226.4	1.0922	2442.5	1.0989	2368.1	1.0989	2364.4
aQZ	1.0644	2735.7	1.1085	2218.4	1.0916	2444.1	1.0986	2366.3	1.0988	2363.6

Table III shows the reaction energies computed by the explicitly correlated CCSD(T) methods with aXZ basis sets and  $\gamma = 1.0$  a.u. for the dissociation  $\text{C}_2\text{H}_2 + 3\text{H}_2 \rightarrow 2\text{CH}_4$ . The molecular geometries used were  $r_{\text{CC}}=6.2991$  a.u. and  $r_{\text{CH}} = 2.0094$  a.u. for  $\text{C}_2\text{H}_2$ ,  $r_{\text{CH}} = 2.0552$  a.u. for  $\text{CH}_4$ , and  $r_{\text{HH}} = 1.4034$  a.u. for  $\text{H}_2$ . The CABS singles (CS) correction was included in the energies of the F12 calculations. Here, we compare the results obtained with the CCSD(F12\*) and CCSD(T)(F12\*) models, developed by Hättig, Tew, and Köhn.<sup>40–42</sup> With the aTZ basis set, the F12-CCSD(T) calculation has reproduced the CCSD(T)(F12\*) results within  $0.1 mE_h$ , while it is away from the basis set limit by approximately  $0.3 mE_h$ .

We have also applied F12-CCSD(T) to the equilibrium bond length ( $R_e$ ) and harmonic vibrational frequency ( $\omega_e$ ) of the  $\text{N}_2$  molecule (Table IV). The CCSD(T)(F12\*) reference data are taken from literature.<sup>115</sup> These F12 calculations have taken into account the CABS singles correction. A close agreement was again found between the F12-CCSD(T) and CCSD(T)(F12\*) results with errors of  $0.0003 \text{ \AA}$  and  $2.7 \text{ cm}^{-1}$  for  $R_e$  and  $\omega_e$ , respectively. The deviation of the CBS limits of the CCSD(T) values from the experimentally observed ( $R_e = 1.0977 \text{ \AA}$  and  $\omega_e = 2359 \text{ cm}^{-1}$ ) was seen in the previous studies (e.g., Ref. 116).

#### IV. CONCLUSIONS

In this study, a canonical transcorrelated Hamiltonian has been proposed as an effective Hamiltonian approach. The explicit electron correlation with the projected Slater-type geminals is built into a Hamiltonian through the canonical transformation. The present approach provides a formulation to effectively remove high-energy orbital components by using the F12 factor as a regulator for renormalizing them into the smaller-size orbital space. The features of the canonical transcorrelated theory are: (1) The resulting effective Hamiltonian is already perturbed with a considerable amount of the dynamic correlation associated with the interelectronic Coulomb singularity; (2) It remains Hermitian and has exactly the same size, dimension, and quartic complexity as the bare Hamiltonian; (3) There is no adjustable parameter in the geminal excitations with Ten-no's fixed amplitude ansatz,<sup>15</sup> since the F12 amplitudes for the present transformation are predetermined and calculated in a non-iterative manner; (4) The theory is extensible to multireference models on the basis of the generalized normal ordering of Mukherjee and Kutzelnigg; (5) In contrast to the standard F12 theories which couple the F12 and conventional excitations in the amplitude equations<sup>3,4,6,7</sup> or Valeev's *a posteriori* F12 corrections,<sup>24,27,29,38</sup> we have introduced an *a priori* F12 transformed Hamiltonian that can be readily used in conjunction with arbitrary correlation models to describe the remaining orbital correlation.

We have demonstrated its applications to various solvers in quantum chemical methods, such as CCSD(T), QCISD, MP4, CCSDT, CCSDTQ, and so forth. The benchmarks on small molecules have revealed that the numerical performance of our explicit correlation scheme is comparable to that of other F12 theories. In our method, the F12 correction and

the orbital correlation are treated separately at different steps, and thus it is indicated that they are more or less additively separable.

In comparison to the standard F12 methods, the present approach is particularly useful for explicit correlation in complicated theories such as *ab initio* density matrix renormalization group (DMRG),<sup>117–121</sup> DMRG-CT,<sup>122,123</sup> DMRG-CASPT2,<sup>124</sup> and tensor-network strong correlation methods.<sup>125–127</sup> The method can be also readily applied to determinant-based quantum Monte Carlo,<sup>128,129</sup> perfect pairing and other valence-bond, geminal-type theories,<sup>130,131</sup> and others, where direct coupling between the multireference wave functions and the F12 factor can be cumbersome.

There remain some questions to be addressed in the future, e.g., regarding errors that arise from the truncation of the BCH expansion of  $\hat{H}^{\text{F12}}$  at the second order [Eq. (9)] as well as the neglect of semi-internal excitations in the F12 amplitudes [Eq. (10)] for the multireference case. They are currently under investigation and will be reported elsewhere.

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#### APPENDIX: ABBREVIATIONS

The abbreviations used in this article are summarized in Table V.

TABLE V. List of abbreviations.

aXZ	Augmented correlation-consistent basis sets: aug-cc-pVXZ (X=D,T,Q,5,6)
CABS	Complementary auxiliary orbital basis set
CAS	Complete active space
CASSCF	CAS self-consistent field
CASPT2	CAS second-order perturbation theory
CBS	Complete basis set
CC	Coupled cluster theory
CCSD(T)	CC with single, double, and perturbative triples
CCSDTQ	CC with singles, doubles, triples, and quadruples
CS	CABS singles correlation
CT	Canonical transformation
CTSD	CT with singles and doubles
HF	Hartree-Fock
LCCSD	Linearized CCSD
MP $n$	$n$ -th order Møller-Plesset perturbation theory ( $n = 2, 3, 4$ )
MP2-F12	Explicitly correlated MP2 with Slater-type geminals
MR	Multireference
MRCI	MR configuration interaction
MRCI+Q	MRCI with the Davidson correction
OBS	Orbital basis set
QCISD	Quadratic configuration interaction with singles and doubles
RDM	Reduced density matrices
SR	Single reference



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