Kobe University Repository : Kernel

PDF issue: 2025-12-05

Nonunitary projective transcorrelation theory inspired by the F12 ansatz

Ten-no, L. Seiichiro

(Citation)
Journal of Chemical Physics,159(17):171103

(Issue Date)
2023-11-07

(Resource Type)
journal article

(Version)
Version of Record

(Rights)
This article may be downloaded for personal use only. Any other use requires prior permission of the author and AIP Publishing. This article appeared in J. Chem. Phys. 159(17), 171103 (2023) and may be found at https://doi.org/10.1063/5.0175337

(URL)
https://hdl.handle.net/20.500.14094/0100488746

The Journal of Chemical Physics

RAPID COMMUNICATION | NOVEMBER 03 2023

Nonunitary projective transcorrelation theory inspired by the F12 ansatz FREE

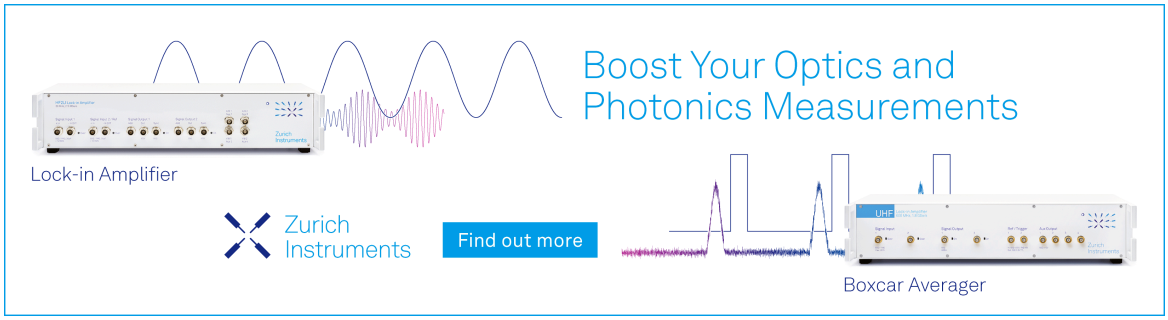
Seiichiro L. Ten-no

Check for updates

J. Chem. Phys. 159, 171103 (2023)
https://doi.org/10.1063/5.0175337

View Online
Export Citation

23 April 2024 04:34:50



AIP Publishing

The Journal of Chemical Physics

COMMUNICATION

pubs.aip.org/aip/jcp

Nonunitary projective transcorrelation theory inspired by the F12 ansatz

Cite as: J. Chem. Phys. 159, 171103 (2023); doi: 10.1063/5.0175337
Submitted: 6 September 2023 • Accepted: 16 October 2023 •
Published Online: 3 November 2023

View Online Export Citation CrossMark

Seiichiro L. Ten-no[a)]

AFFILIATIONS

Graduate School of System Informatics, Kobe University, Nada-ku, Kobe 657-8501, Japan

[a)]Author to whom correspondence should be addressed: tenno@garnet.kobe-u.ac.jp

ABSTRACT

An alternative nonunitary transcorrelation, inspired by the F12 ansatz, is investigated. In contrast to the Jastrow transcorrelation of Boys-Handy, the effective Hamiltonian of this projective transcorrelation features: 1. a series terminating formally at four-body interactions. 2. no spin-contamination within the non-relativistic framework. 3. simultaneous satisfaction of the singlet and triplet first-order cusp conditions. 4. arbitrary choices of pairs for correlation including frozen-core approximations. We discuss the connection between the projective transcorrelation and F12 theory with applications to small molecules, to show that the cusp conditions play an important role to reduce the uncertainty arising from the nonunitary transformation.

Published under an exclusive license by AIP Publishing. https://doi.org/10.1063/5.0175337

23 April 2024 04:34:50

I. INTRODUCTION

Computing electronic structures in high accuracy is one of the most significant challenges in quantum chemistry and physics. However, the exponential growth in the size of the Hilbert space, as the number of correlated electrons and orbitals increases, poses a hindrance to the application of wavefunction theory to large molecules. A major obstacle lies in the cusp behavior that emerges at the coalescence of the exact wavefunction due to the Coulomb singularity, which requires the utilization of expensive orbital space. Explicitly correlated electronic structure theory has alleviated this issue by incorporating ansätze that explicitly involve inter-electronic distances. Particularly, F12 theory, building on the R12 technology initiated by the seminal work of Kuzelnigg,[1] circumvents the explicit calculation of many-electron integrals. Over the last two decades, it has rapidly evolved and grown. Thanks to fundamental advancements, along with its integration with local correlation methods and high-performance computing, F12 theory has become a widely adopted standard tool, offering an accurate and robust treatment of complex systems. Readers interested in the advancements of F12/R12 methods can refer to various review articles.[2–10]

Another explicitly correlated approach is based on the similarity-transformed Hamiltonian

$$\hat{H}_{\mathrm{TC}} = e^{-J}\hat{H}e^{J}, \tag{1}$$

with a Jastrow-type correlator $J = \sum_{i>j}^{N} j(\mathbf{x}_i, \mathbf{x}_j)$ generally as a function of spatial-spin coordinates $\{\mathbf{x}_i\}$. As j is commutable with $\hat{H}$ except for the kinetic energy operators $\hat{t}_i$, the expansion of $\hat{H}_{\mathrm{TC}}$ terminates at the double commutator involving the three-body operator $[[\hat{t}_i, j_{ij}], j_{ik}]$. Hirshfelder advocated that the choice of $\exp(j_{ij}) = 1 + \frac{1}{2}r_{ij}\exp(-\alpha r_{ij})$ removes the Coulomb pole $1/r_{ij}$ in the original Hamiltonian,[11] in accord with Kato's cusp condition.[12] The transcorrelated (TC) method of Boys and Handy follows this idea.[13–15] One of the major difficulties arising from $\hat{H}_{\mathrm{TC}}$ is that the nonhermiticity sacrifices the variational upper-bound. In other words, the obtained energy is not a measure to judge the accuracy of the solution. Since the 2000s, there have been some developments in TC. Practical perturbation and coupled-cluster theories with TC were proposed for polyatomic molecules, using frozen Gaussian geminals and the resolution of the identity (RI) approximation for three-electron integrals.[16–19] TC has been applied to homogeneous electron gas.[20–22] Applications to solids have been intensively studied by Tsuneyuki and co-workers.[23–26]

While F12 theory remains the predominant method for accurate molecular electronic structures, there has been a recent resurgence in the interest of TC primarily driven by two objectives. The first objective is to combine TC with approximate full configuration interaction (FCI) solvers like density matrix renormalization group, selected CI, and quantum Monte Carlo methods.[27–34] The second is to reduce the number of qubits in quantum simulations by downfolding the high-energy contribution of the Hamiltonian.[35,36]

Published under an exclusive license by AIP Publishing

For the latter purpose, the F12 canonical transcorrelation (F12-CT) approach of Yanai and Shiozaki[37] is an alternative choice.[38–40] F12-CT employs the unitary transformation based on the F12 ansatz inheriting all the advantages of F12 theory over methods employing Jastrow factors. Especially, the flexibility of the formulation in the orbital space allows to use the singlet and triplet cusp conditions,[12,41,42] which cannot be satisfied simultaneously by Jastrow factors. However, on the negative side, the unitary transformation in F12-CT results in a nonterminating series, necessitating a drastic approximation to truncate the effective Hamiltonian expansion.

The objective of this paper is to investigate a nonunitary projective transcorrelation (pTC) in a terminating series. The pTC formulation along with the connection to F12 theory will be presented in Sec. II. A numerical analysis of pTC is performed perturbatively using small molecules in Sec. III, followed by conclusions in Sec. IV.

II. THEORY

A. Formulation of pTC

Throughout this paper, we use the conventions for orbital indices and projection operators in Table I, along with the Einstein summation convention unless indicated. Let us consider the generator,

$$\hat{\mathcal{G}} = \frac{1}{2}\langle\kappa\lambda|\hat{\mathcal{Q}}_{12}\hat{\mathcal{R}}_{12}|rs\rangle\hat{E}^{\kappa\lambda}_{rs}, \tag{2}$$

where $\hat{\mathcal{Q}}_{12}$ is a suitable orthogonalization operator to project out the geminal contributions representable by the given basis set (GBS) from those in the complete basis set (CBS),

$$\hat{\mathcal{Q}}_{12} = (1-\hat{P}_1\hat{P}_2)\hat{\mathcal{S}}_{12}, \tag{3}$$

$\hat{\mathcal{S}}_{12}$ is a supplementary operator, $\hat{\mathcal{R}}_{12}$ is the rational generator,[43]

$$\hat{\mathcal{R}}_{12} = \{g^{(d)}(\mathbf{r}_1,\mathbf{r}_2) + g^{(x)}(\mathbf{r}_1,\mathbf{r}_2)\hat{\mathcal{P}}_{12}\}, \tag{4}$$

with a permutation operator $\hat{\mathcal{P}}_{12}$ to interchange the spatial functions, e.g. $\hat{\mathcal{P}}_{12}|pq\rangle = |qp\rangle$, and $\hat{E}^{\kappa\lambda\cdots}_{\mu\nu\cdots} = \hat{a}^\dagger_{\kappa\sigma_1}\hat{a}^\dagger_{\lambda\sigma_2}\cdots\hat{a}_{\nu\sigma_2}\hat{a}_{\mu\sigma_1}$ are spin-free orbital replacement operators. Unlike the Jastrow factor, the rational generator with the asymptotic behaviors,

$$g^{(d)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{3}{8}r_{12} + O(r_{12}^2) \tag{5}$$

$$g^{(x)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{8}r_{12} + O(r_{12}^2), \tag{6}$$

satisfies the s- and p-wave cusp conditions simultaneously.[43] The simplest variant, the so-called SP or fixed amplitudes (FIX) ansatz,

$$\hat{\mathcal{R}}_{12} = f(r_{12})\left(\frac{3}{8} + \frac{1}{8}\hat{\mathcal{P}}_{12}\right), \tag{7}$$

in combination with the Slater-type correlation factor,[44]

$$f(r_{12}) = -\frac{1}{\gamma}\exp(-\gamma r_{12}), \tag{8}$$

is diagonal orbital invariant (DOI), without linear dependencies, free from geminal superposition errors,[45] and has facilitated the popularity of F12 theory.

TABLE I. Convention of orbital indices and projectors.

Indices	Type of orbitals	Projector
$p,q,\ldots$	Orbitals in the GBS	$\hat{P}_n$
$\alpha,\beta,\ldots$	Orthogonal complement to GBS	$\hat{Q}_n$
$\kappa,\lambda,\ldots$	Orbitals in the CBS	$1 = \hat{P}_n + \hat{Q}_n$
$i,j,\ldots$	Occupied orbitals	$\hat{O}_n$
$a,b,\ldots$	Virtual orbitals	$\hat{V}_n$
$i',j',\ldots$	Core orbitals in the occupied space	$\hat{O}'_n$
$v',w',\ldots$	Valence orbitals in the occupied space	$\hat{O}_n - \hat{O}'_n$

The rational generator $\hat{\mathcal{R}}_{12}$ commutes with any potentials in the Hamiltonian as Jastrow factors do; however, the similarity transformation $e^{-\hat{\mathcal{R}}}\hat{H}e^{\hat{\mathcal{R}}}$ becomes nonterminating due to $\hat{\mathcal{P}}_{12}$.[43] Thus, the projector form in Eq. (3) is essential to realize a terminating expression of pTC. If a partitioning between occupied and virtual orbitals is clear in GBS as in the single reference (SR) case, the natural choice of $\hat{\mathcal{S}}_{12}$ is the strong-orthogonality (SO) projector,[46]

$$\hat{\mathcal{S}}^{(\mathrm{SO})}_{12} = (1-\hat{O}_1)(1-\hat{O}_2), \tag{9}$$

$$\hat{\mathcal{Q}}^{(\mathrm{SO})}_{12} = 1 - \hat{O}_1\hat{Q}_2 - \hat{Q}_1\hat{O}_2 - \hat{P}_1\hat{P}_2, \tag{10}$$

sometimes called modified ansatz 2 (or ansatz 3)[47] ensuring the orthogonality within the Hilbert space spanned by GBS, $\langle\Phi_I|\hat{\mathcal{G}}|\Phi_J\rangle = 0$, and those between the reference determinant Φ and all singles in the complementary space, $\langle\hat{E}^\alpha_i\Phi|\hat{\mathcal{G}}|\Phi\rangle = 0$. The resulting $\mathcal{G}$ resembles the extended SP ansatz of Köhn for response properties.[48] The same projector was also employed in the multireference (MR) framework for the F12 treatment of external excitations.[49,50] However, SO is not suitable when the occupied space cannot be defined uniquely. Another choice is the universal (U) projector that just excludes the contribution of core orbitals,

$$\hat{\mathcal{S}}^{(\mathrm{U})}_{12} = (1-\hat{O}'_1)(1-\hat{O}'_2), \tag{11}$$

$$\hat{\mathcal{Q}}^{(\mathrm{U})}_{12} = 1 - \hat{O}'_1\hat{Q}_2 - \hat{Q}_1\hat{O}'_2 - \hat{P}_1\hat{P}_2. \tag{12}$$

For all-electron correlation, this reduces to $\hat{\mathcal{Q}}^{(\mathrm{U})}_{12} = 1 - \hat{P}_1\hat{P}_2$, initially introduced to approximate SO within the standard approximation (SA),[51] and later employed by Torheyden and Valeev for a universal F12 perturbative correction.[52] We do not introduce any normal ordering to $\hat{\mathcal{G}}$ for the sake of universality of pTC. In this case, $\hat{\mathcal{Q}}^{(\mathrm{U})}_{12}$ also ensures the orthogonality within GBS, $\langle\Phi_I|\hat{\mathcal{G}}|\Phi_J\rangle = 0$, but not for complementary singles, $\langle\hat{E}^\alpha_{v'}\Phi|\hat{\mathcal{G}}|\Phi\rangle \neq 0$. However, this contribution is considered to vanish quickly with the size of GBS, e.g. the angular momentum of α for nonzero $\langle\hat{E}^\alpha_{v'}\Phi|\hat{\mathcal{G}}|\Phi\rangle \neq 0$ is bound at most at $3L_{\mathrm{occ.}}$ for the maximum angular momentum of the occupied orbitals $L_{\mathrm{occ.}}$ in Φ.

We now define the pTC Hamiltonian as the similarity transformation with $\hat{\mathcal{G}}$,

$$\hat{\mathcal{H}}_{\mathrm{pTC}} = \mathcal{B}\{e^{-\hat{\mathcal{G}}}\hat{H}e^{\hat{\mathcal{G}}}\}, \tag{13}$$

23 April 2024 04:34:50

Published under an exclusive license by AIP Publishing

where $\mathcal{B}\{\ldots\}$ denotes the second quantized representation within GBS. $\hat{\mathcal{G}}$ contains at least one creation operator in the complementary space, which should be contracted with $\hat{H}$ via $\hat{Q}_n$ for nonzero contributions to $\hat{\mathcal{H}}_{\mathrm{pTC}}$. The $\hat{\mathcal{H}}_{\mathrm{pTC}}$ then terminates at the double commutator,

$$\begin{aligned}\hat{\mathcal{H}}_{\mathrm{pTC}} &= \mathcal{B}\left\{\hat{H} + [\hat{H}, \hat{\mathcal{G}}] + \frac{1}{2}[[\hat{H}, \hat{\mathcal{G}}], \hat{\mathcal{G}}]\right\} \\ &= \hat{\mathcal{H}} + \hat{\mathcal{H}}_{2\mathrm{h}} + \hat{\mathcal{H}}_{2\mathrm{w}} + \hat{\mathcal{H}}_{3\mathrm{l}} + \hat{\mathcal{H}}_{3\mathrm{q}} + \hat{\mathcal{H}}_4, \end{aligned} \tag{14}$$

where $\hat{\mathcal{H}} = \mathcal{B}\{\hat{H}\}$, and the contractions through four-body operators in skeleton forms are

$$\hat{\mathcal{H}}_{2\mathrm{h}} = \mathcal{B}\{\hat{H}_1\hat{\mathcal{G}}\} = \langle \hat{h}_1 \hat{Q}_1 \hat{\mathcal{S}}_{12} \hat{\mathcal{R}}_{12}\rangle_{pq}^{rs} \hat{E}_{rs}^{pq} \tag{15}$$

$$\hat{\mathcal{H}}_{2\mathrm{w}} = \mathcal{B}\{\hat{H}_2\hat{\mathcal{G}}\} = \frac{1}{2}\langle r_{12}^{-1} \hat{\mathcal{Q}}_{12} \hat{\mathcal{R}}_{12}\rangle_{pq}^{rs} \hat{E}_{rs}^{pq} \tag{16}$$

$$\hat{\mathcal{H}}_{3\mathrm{l}} = \mathcal{B}\{\hat{H}_2\hat{\mathcal{G}}\} = \langle r_{12}^{-1} \hat{Q}_1 \hat{\mathcal{S}}_{13} \hat{\mathcal{R}}_{13}\rangle_{pqr}^{stu} \hat{E}_{stu}^{pqr} \tag{17}$$

$$\hat{\mathcal{H}}_{3\mathrm{q}} = \mathcal{B}\{\frac{1}{2}\hat{H}_2\hat{\mathcal{G}}\hat{\mathcal{G}}\} = \langle r_{12}^{-1} \hat{Q}_1 \hat{Q}_2 \hat{\mathcal{U}}_{123}\rangle_{pqr}^{stu} \hat{E}_{stu}^{pqr} \tag{18}$$

$$\hat{\mathcal{H}}_4 = \mathcal{B}\{\frac{1}{2}\hat{H}_2\hat{\mathcal{G}}\hat{\mathcal{G}}\} = \langle r_{12}^{-1} \hat{Q}_1 \hat{Q}_2 \hat{\mathcal{W}}_{1234}\rangle_{pqrs}^{tuvw} \hat{E}_{tuvw}^{pqrs}, \tag{19}$$

the lines connecting operators denote Wick contractions of ordinary products, the short-hand notation like $\langle\ldots\rangle_{pq}^{rs} = \langle pq|\ldots|rs\rangle$ is used, and $\hat{\mathcal{U}}_{123}$ and $\hat{\mathcal{W}}_{1234}$ are defined as

$$\hat{\mathcal{U}}_{123} = \frac{1}{2}\hat{\mathcal{S}}_{23}\hat{\mathcal{R}}_{23}(\hat{P}_2\hat{\mathcal{S}}_{12}\hat{\mathcal{R}}_{12} + \hat{P}_3\hat{\mathcal{S}}_{13}\hat{\mathcal{R}}_{13}) \tag{20}$$

$$\hat{\mathcal{W}}_{1234} = \frac{1}{2}\hat{\mathcal{S}}_{13}\hat{\mathcal{R}}_{13}\hat{\mathcal{S}}_{24}\hat{\mathcal{R}}_{24}. \tag{21}$$

It is straightforward to obtain the matrix elements using the generalized Wick theorem.[53] $\hat{h}_1$ contains the frozen-core contribution and the core indices are excluded from $\hat{\mathcal{H}}_{\mathrm{pTC}}$ for the frozen-core approximation. Among the operators, $\hat{\mathcal{H}}_{2\mathrm{h}}$ and $\hat{\mathcal{H}}_{2\mathrm{w}}$, play an essential role for the fast convergence. With respect to the leading terms of singlet and triplet pairs, r_{12}^0 and r_{12}^1, respectively, the Coulomb singularity $r_{12}^{-1}|rs\rangle$ of $\hat{\mathcal{H}}$ is regularized by the kinetic energy operator in $\hat{\mathcal{H}}_{2\mathrm{h}}$ as

$$(\hat{t}_1 + \hat{t}_2)\hat{\mathcal{R}}_{12}|rs\rangle = \{-r_{12}^{-1} + O(r_{12}^0)\}|rs\rangle, \tag{22}$$

both for $r+s$ (singlet) and $r-s$ (triplet).[5] Instead, $\hat{\mathcal{H}}_{2\mathrm{w}}$ represents the residual correlation in the complementary space. The integrals in the above expressions can be computed either by using (complementary) auxiliary basis set [(C)ABS],[54,55] or numerical integrations[43,56] after the decompositions of $\hat{Q}_n = 1 - \hat{P}_n$, $\hat{\mathcal{Q}}_{12}$, and $\hat{\mathcal{S}}_{12}$, with two-electron objects for $1/r_{12}$, $f(r_{12})$, and $f(r_{12})/r_{12}$. The two-body operators quadratic to the correlation factor, $f^2(r_{12})$ and $\nabla f(r_{12}) \cdot \nabla f(r_{12})$, in the usual F12 methods do not appear in pTC.

B. Connection to the F12 wavefunction

$\hat{\mathcal{H}}_{\mathrm{pTC}}$ gives the same energy spectrum of the original Hamiltonian $\hat{H}$ in CBS. We look into $\hat{\mathcal{H}}_{\mathrm{pTC}}$ pertubatively using the Hartree-Fock (HF) reference with the modified Møller-Plesset (MP) partitioning,

$$\hat{\mathcal{H}}_{\mathrm{pTC}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{V}}_{\mathrm{pTC}} \tag{23}$$

$$\hat{\mathcal{V}}_{\mathrm{pTC}} = \hat{\mathcal{V}} + \hat{\mathcal{H}}_{2\mathrm{h}} + \hat{\mathcal{H}}_{2\mathrm{w}} + \hat{\mathcal{H}}_3 + \hat{\mathcal{H}}_4, \tag{24}$$

with $\hat{\mathcal{H}}_0 = \mathcal{B}\{\hat{H}_0\}$ and $\hat{\mathcal{V}} = \mathcal{B}\{\hat{V}\}$. The second order energy of MP2-F12 with the same generator $\hat{\mathcal{G}}$ is derived from the Hylleraas energy functional,

$$E^{(2)} = \langle\Psi^{(1)}|\hat{H}_{0\mathrm{N}}|\Psi^{(1)}\rangle + 2\langle\Psi^{(1)}|\hat{V}|\Phi\rangle \geq E_\infty^{(2)}, \tag{25}$$

where $\hat{H}_{0\mathrm{N}} = \hat{H}_0 - E^{(0)}$, $E_\infty^{(2)}$ is the exact second order energy, and $\Psi^{(1)}$ is a sum of the contribution from GBS and explicitly correlated part,

$$|\Psi^{(1)}\rangle = |\Psi_{\mathrm{O}}^{(1)}\rangle + \hat{\mathcal{G}}|\Phi\rangle. \tag{26}$$

Minimizing $E^{(2)}$ with respect to $\Psi_{\mathrm{O}}^{(1)}$ yields

$$E^{(2)} = E_{\mathrm{MP2}} + B + 2V, \tag{27}$$

with the conventional correlation energy, E_{MP2}, and F12 terms,

$$B = \langle\hat{\mathcal{G}}^\dagger\hat{H}_{0\mathrm{N}}\hat{\mathcal{G}} - \hat{\mathcal{G}}^\dagger\hat{H}_{0\mathrm{N}}\hat{\mathcal{H}}_{0\mathrm{N}}^{-1}\hat{H}_{0\mathrm{N}}\hat{\mathcal{G}}\rangle \tag{28}$$

$$V = \langle\hat{V}\hat{\mathcal{G}} - \hat{V}\hat{\mathcal{H}}_{0\mathrm{N}}^{-1}\hat{H}_{0\mathrm{N}}\hat{\mathcal{G}}\rangle, \tag{29}$$

where $\langle\hat{A}\rangle = \langle\Phi|\hat{A}|\Phi\rangle$, and $\hat{\mathcal{H}}_{0\mathrm{N}}^{-1}$ means the MP preconditioner within the excitation manifold of GBS. We do not repeat the derivation of detailed expressions for MP2-F12, which are available in the literature.[47,54,56]

For later discussions, $\hat{\mathcal{H}}_{3\mathrm{l}}$ is divided into the contribution of the HF mean field, and its residual,

$$\hat{\mathcal{H}}_{3\mathrm{l}} = \hat{\mathcal{H}}_{2\mathrm{v}} + [\hat{\mathcal{H}}_{3\mathrm{l}}]_{\mathrm{r}} \tag{30}$$

$$\hat{\mathcal{H}}_{2\mathrm{v}} = \langle pq|\hat{v}_1^{(\mathrm{HF})}\hat{Q}_1\hat{\mathcal{S}}_{12}\hat{\mathcal{R}}_{12}|rs\rangle\hat{E}_{rs}^{pq}, \tag{31}$$

and the contraction with the Fock operator, $\hat{f}_1 = \hat{h}_1 + \hat{v}_1^{(\mathrm{HF})}$, is defined as

$$\hat{\mathcal{H}}_{2\mathrm{f}} = \hat{\mathcal{H}}_{2\mathrm{h}} + \hat{\mathcal{H}}_{2\mathrm{v}}. \tag{32}$$

This division is unique in the SR case, but not in general. Table II summarizes the orders of the operators. At first glance of the expectation value $\langle\hat{\mathcal{V}}_{\mathrm{pTC}}\rangle$, any components in B, which are quadratic to $\hat{\mathcal{G}}$, are absent. $\langle\hat{\mathcal{H}}_{3\mathrm{q}}\rangle$ and $\langle\hat{\mathcal{H}}_4\rangle$ are third-order contributions from $\frac{1}{2}\hat{\mathcal{G}}^2$ with different operator alignments. Actually, besides the higher-order corrections from $\hat{\mathcal{H}}_{3\mathrm{q}}$ and $\hat{\mathcal{H}}_4$, $\langle\hat{\mathcal{V}}_{\mathrm{pTC}}\rangle$ is identified with V under the assumption of the extended Brillouin condition (EBC),[54] $[\hat{P}_1, \hat{f}_1] = 0$, plus the first-order contribution of $\langle\hat{\mathcal{H}}_{2\mathrm{f}}\rangle$ not

23 April 2024 04:34:50

Published under an exclusive license by AIP Publishing

TABLE II. Operators in each order of perturbation.

Order	Operators		
1	$\hat{\mathcal{V}}$	$\hat{\mathcal{H}}_{2h}$	$\hat{\mathcal{H}}_{2v}$
2	$\hat{\mathcal{H}}_{2w}$	$[\hat{\mathcal{H}}_{3l}]_r$	
3	$\hat{\mathcal{H}}_{3q}$	$\hat{\mathcal{H}}_4$	

present in the standard MP2-F12 due to $\hat{\mathcal{G}}^{(SO)}$ and the assumption of the generalized Brillouin condition (GBC),[51] $[\hat{O}_1, \hat{f}_1] = 0$. The correction term to EBC arises from the second order energy, $\langle -\hat{\mathcal{V}}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{H}}_{2f}\rangle$ [cf. Eq. (28) in Ref. 56] by the relation,

$$\langle ab|\hat{F}_{12}\,\hat{\mathcal{Q}}_{12}\,\hat{\mathcal{R}}_{12}|ij\rangle = \langle ab|(\hat{F}_{12} - \epsilon_i - \epsilon_j)\,\hat{\mathcal{R}}_{12}|ij\rangle - \langle ab|\hat{\mathcal{R}}_{12}|ij\rangle\Delta_{ab,ij}, \tag{33}$$

where we use the notations,

$$\hat{F}_{12} = \hat{f}_1 + \hat{f}_2 \tag{34}$$

$$\Delta_{ab,ij} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j. \tag{35}$$

$\langle -\hat{\mathcal{H}}_{2f}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{V}}\rangle$ is also absent in the standard MP2-F12 due to the GBC. In this way, $\langle\hat{\mathcal{H}}_{pTC}\rangle$ contains no contributions in the B-term of MP2-F12. However, provided a near-optimum generator $\hat{\mathcal{G}}$ minimizing $E^{(2)}$ is available, the approximation, $V \approx -B$, holds and thus

$$E^{(2)} \overset{\text{opt}}{\approx} E_{MP2} + V. \tag{36}$$

This approximation was employed in solid state calculations by Grüneis.[57] Nevertheless, a variational optimization of $\hat{\mathcal{G}}$ again requires the integrals over $f^2(r_{12})$ and $\nabla f(r_{12}) \cdot \nabla f(r_{12})$ within the F12 framework, which has limited the flexibility in the choice of $f(r_{12})$ or $f(\mathbf{r}_1, \mathbf{r}_2)$.

Higher-order F12 contributions can be automatically included by plugging $\hat{\mathcal{H}}_{pTC}$ into correlated calculations. $\langle -\hat{\mathcal{V}}\hat{\mathcal{H}}_{0N}^{-1}(\hat{\mathcal{H}}_{2w} + \hat{\mathcal{H}}_{3l})\rangle$ corresponds to the MP3(F12) correction[58,59] as the leading term of approximate CCSD-F12 models.[60–65] The extended SP ansatz of Köhn[66] for explicitly correlated connected triples is included as the contraction between $\hat{\mathcal{H}}_{pTC}$ and $\hat{T}_2$ in CCSD with $\hat{\mathcal{H}}_{pTC}$. Other contributions from the three- and four-electron operators, $\hat{\mathcal{H}}_{3q}$ and $\hat{\mathcal{H}}_4$, containing two $\hat{\mathcal{R}}_{12}$ connected with $1/r_{12}$ through $\hat{\mathcal{Q}}_n$ is considered to be very small and usually neglected in F12 theory.

C. Hybrid ansatz for core-valence correlation

The SP ansatz is the generalization of the linear r_{12} treatment of He-like ions by Kutzelnigg with fixed geminal coefficients,[1] and the association with the Slater-type factor usually gives very accurate results. It is intended to employ core functions for core-valence correlation effects, since basis functions in lower angular momentum are presumed to be saturated for fast CI convergence of partial wave expansions with the r12 behavior.[1] cc-pCVnZ-F12 basis sets[67,68] have been developed with this objective, with fewer augmented functions compared to the standard cc-pCVXZ basis sets.[69–71] However, the SP ansatz does not show a sufficient ability for core-valence energies with an ill-matched basis set. Optimizing geminal amplitudes can improve this problem, but introduces other difficulties. The orbital-invariant (OI) ansatz[72] for four-index amplitudes is known to suffer from linear-dependency problem in the B-intermediate. The diagonal (D) ansatz is free from linear-dependency, violating the orbital invariance. The pair-specific geminal approach[73] and relaxing constrained amplitudes method[74] have been proposed to improve upon this situation.

In this work, we introduce the hybrid (HYB) ansatz, which adopts different ansätze for different orbital pairs, i.e. SP, D, and OI for valence-valence (VV), core-valence (CV), and core-core (CC) pairs, respectively,

$$\hat{\mathcal{G}}^{(HYB)} = \hat{\mathcal{G}}_{VV} + \hat{\mathcal{G}}_{CV} + \hat{\mathcal{G}}_{CC} \tag{37}$$

$$\hat{\mathcal{G}}_{VV} = \frac{1}{2}\langle\kappa\lambda|\,\hat{\mathcal{Q}}_{12}\,\hat{\mathcal{R}}_{12}|v'w'\rangle\hat{E}^{\kappa\lambda}_{v'w'} \tag{38}$$

$$\hat{\mathcal{G}}_{CV} = \langle\kappa\lambda|\,\hat{\mathcal{Q}}_{12}\,f(r_{12})(|i'v'\rangle t^{i'v'}_{i'v} + |v'i'\rangle t^{i'v'}_{v'i'})\hat{E}^{\kappa\lambda}_{i'v'} \tag{39}$$

$$\hat{\mathcal{G}}_{CC} = \frac{1}{2}\langle\kappa\lambda|\,\hat{\mathcal{Q}}_{12}\,f(r_{12})|k'l'\rangle t^{k'l'}_{i'j'}\,\hat{E}^{\kappa\lambda}_{i'j'}, \tag{40}$$

where $t^{i'v'}_{i'v'}$ and $t^{i'v'}_{v'i'}$ are geminal amplitudes for the CV block, and $t^{k'l'}_{i'j'}$ are those for CC. The HYB ansatz is orbital invariant with respect to the transformations within the core and valence spaces separately, and the drawbacks of OI in the scaling and linear dependency are substantially reduced owing to the application within CC. OI requires cumbersome B-term intermediates with different orbital energies in numerators and denominators. We avoid this problem using the geminal amplitudes of MP2-F12 under the EBC, and the correction to the EBC approximation is added in the V-term similarly to Eq. (33). We examine the performance of the HYB adaptation of pTC in Sec. III.

III. RESULTS AND DISCUSSION

We investigate pTC numerically by comparing the second order contribution of $\hat{\mathcal{H}}_{pTC}$ [pTC(2)] with variational MP2-F12 for the selection of small closed-shell molecules, $CH_2(^1A_1)$, H_2O, NH_2, HF, N_2, CO, Ne, and F_2, employed in the previous assessments,[43,54,56] with aug-cc-p(C)VXZ basis sets.[69–71] The augmentation with diffuse functions is not essential for discussions but improves the long-range correlation that is not universal.[43] The present pTC(2) implementation resembles that for MP2-F12.[43,56] All necessary integrals are calculated using numerical integrations along with extra operations over two- and three-index objects (QD2 scheme in MP2-F12)[43] containing extra operations for $\hat{t}_1\phi_p(\mathbf{r}_1)$ and $\hat{v}_1\phi_p(\mathbf{r}_1)$ with the ultra-fine grid of our new Lebedev implementation in the GELLAN program package[75] resulting in 9340 integration points for hydrogen and 23 842 points for the other atoms before imposing the point group symmetry. The three-index integrals for $f(r_{12})$, and $f(r_{12})/r_{12}$ are computed from the generalized Boys function, $G_m(T, U)$.[44,56] The latest version of subroutines for $G_m(T, U)$ contain a minor revision for $T > 20$ and $U > 200$

23 April 2024 04:34:50

Published under an exclusive license by AIP Publishing

TABLE III. Energy components of pTC(2) in mE_h for the valence-correlation energy of H_2O in the aug-cc-pVXZ basis sets. The MP2 limit is about −300.5 mE_h.

	X				
	D	T	Q	5	6
1 $\langle\hat{\mathcal{H}}_{2h}\rangle$	19.13	1.00	0.21	0.01	0.01
2 $\langle\hat{\mathcal{H}}_{2v}\rangle$	−16.97	−0.39	−0.11	0.00	0.00
3 $\langle\hat{\mathcal{H}}_{2w}\rangle$	−79.11	−31.88	−14.27	−7.46	−4.46
4 $\langle[\hat{\mathcal{H}}_{3l}]_r\rangle$	12.98	2.13	0.22	0.04	0.01
5 $\langle-\hat{\mathcal{V}}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{H}}_{2h}\rangle$	−3.27	−0.56	−0.20	−0.02	−0.02
6 $\langle-\hat{\mathcal{V}}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{H}}_{2v}\rangle$	4.60	0.86	0.28	0.07	0.02
7 $\langle-\hat{\mathcal{H}}_{2h}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{V}}\rangle$	−1.66	−0.02	−0.01	0.00	0.00
8 $\langle-\hat{\mathcal{H}}_{2v}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{V}}\rangle$	1.61	0.02	0.01	0.00	0.00
9 $\langle-\hat{\mathcal{H}}_{2f}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{H}}_{2f}\rangle$	0.00	0.00	0.00	0.00	0.00
SUM	−62.67	−28.83	−13.88	−7.37	−4.45
MP2	−219.35	−268.36	−285.93	−292.92	−295.97
pTC(2)	−282.02	−297.19	−299.80	−300.29	−300.42
Δ	18.48	3.31	0.70	0.21	0.08

TABLE IV. Energy components of pTC(2) in mE_h for all-electron calculations of H_2O in the aug-cc-pCVXZ basis sets. The MP2 limit is about −362.1 mE_h.

	X				
	D	T	Q	5	6
1 $\langle\hat{\mathcal{H}}_{2h}\rangle$	110.47	3.06	0.38	0.04	0.01
2 $\langle\hat{\mathcal{H}}_{2v}\rangle$	−106.74	−2.20	−0.16	−0.01	−0.01
3 $\langle\hat{\mathcal{H}}_{2w}\rangle$	−129.38	−36.77	−15.61	−8.07	−4.79
4 $\langle[\hat{\mathcal{H}}_{3l}]_r\rangle$	39.02	2.08	0.10	0.01	0.00
5 $\langle-\hat{\mathcal{V}}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{H}}_{2h}\rangle$	−10.94	−2.43	−0.72	−0.28	−0.14
6 $\langle-\hat{\mathcal{V}}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{H}}_{2v}\rangle$	7.59	0.97	0.26	0.07	0.02
7 $\langle-\hat{\mathcal{H}}_{2h}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{V}}\rangle$	−3.92	−0.09	−0.01	0.00	0.00
8 $\langle-\hat{\mathcal{H}}_{2v}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{V}}\rangle$	3.89	0.10	0.00	0.00	0.00
9 $\langle-\hat{\mathcal{H}}_{2f}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{H}}_{2f}\rangle$	−0.02	0.00	0.00	0.00	0.00
SUM	−90.02	−35.29	−15.76	−8.26	−4.91
MP2	−259.25	−324.15	−345.65	−353.65	−357.12
pTC(2)	−349.27	−359.44	−361.41	−361.91	−362.03
Δ	12.83	2.66	0.69	0.19	0.07

with the downward recurrence relation starting with marginal m to improve the accuracy. Other implementations for Slater integrals with Chebyshev interpolation can be found elsewhere.[76,77] The Slater exponent $\gamma = 1.5$ is used throughout this work. Since pTC(2) does not require integrals for the B-term intermediates, the computational cost is almost half that of MP2-F12.

We first investigate the energy components of pTC(2). Tables III and IV list the basis set dependency of these components along with the deviation from the exact second order energy,

$$\Delta = E^{(2)} - E_{\infty}^{(2)}, \tag{41}$$

for valence- and all-electron correlation energies of H_2O in aug-cc-pVXZ and aug-cc-pCVXZ basis set, respectively. The sum of the terms 3 and 4 corresponds to the V-term of MP2-F12 under EBC, and that of 5 and 6 is equivalent to the correction to EBC. The other terms absent in the standard MP2-F12 arise from the use of $\hat{Q}_{12}^{(U)}$, $\langle-\hat{\mathcal{H}}_{2f}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{H}}_{2f}\rangle$ is negligibly small overall. The others possess large contributions in aug-cc-p(C)VDZ and decay very quickly as the cardinal number X increases except for $\langle\hat{\mathcal{H}}_{2w}\rangle$ complementing the slow convergence of MP2. $\langle\hat{\mathcal{H}}_{2h}\rangle$ and $\langle\hat{\mathcal{H}}_{2v}\rangle$ include the contractions containing $\hat{h}_1$ and $\hat{v}_1^{(HF)}$ that cancel each other under the GBC, $\hat{Q}_1(\hat{h}_1 + \hat{v}_1^{(HF)})|i\rangle = 0$, usually employed in F12 methods. Similar cancelation from GBC takes place between $\langle-\hat{\mathcal{H}}_{2h}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{V}}\rangle$ and $\langle-\hat{\mathcal{H}}_{2v}\hat{\mathcal{H}}_{0N}^{-1}\hat{\mathcal{V}}\rangle$, albeit each contribution is much smaller. For the general use of pTC, it is essential to argue each convergence of the terms since such cancellation is unavailable. The rapid convergence of $\langle\hat{\mathcal{H}}_{2v}\rangle$ indicates the contributions of the third order operators, $\hat{\mathcal{H}}_{3q}$ and $\hat{\mathcal{H}}_4$, quadratic to $\hat{Q}_n$ attenuate even faster in correlation energies from the third order, and can be omitted especially for $X \geq$ T.

We compare pTC(2) with MP2-F12 for the test set molecules. To assess the role of cusp conditions, we use the SS ansatz imposing the s-wave cusp condition both for singlet and triplet pairs,

$$\hat{\mathcal{R}}_{12}^{(SS)} = \frac{1}{2}f(r_{12}). \tag{42}$$

As an example, the errors of all-electron energies in aug-cc-pCVTZ are shown in Fig. 1. The pTC(2) energies resemble those of MP2-F12 quite well, while the differences become significantly large with the SS ansatz detariorating the triplet cusp condition. The pTC(2)(SS) energies are always lower than pTC(2) with the SP ansatz in contradiction to the variational behavior of MP2-F12 $E_{MP2-F12(SS)} > E_{MP2-F12}$.

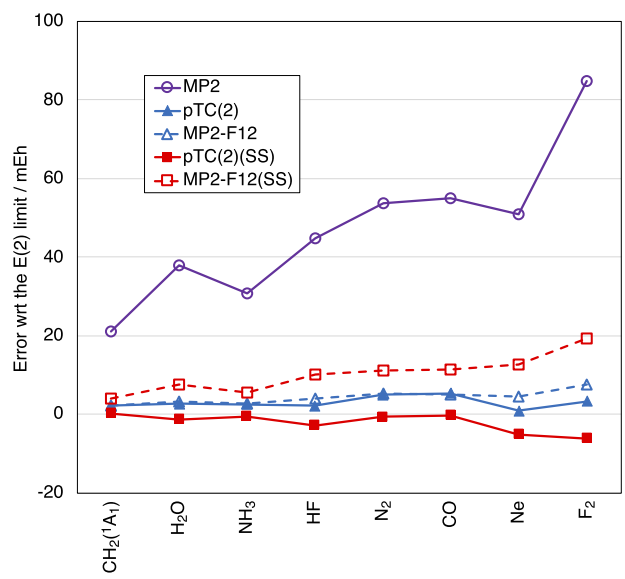


FIG. 1. Errors of all-electron correlation energies in the aug-cc-pCVTZ basis set. The pTC(2) and MP2-F12 results are indicated by solid and dashed lines, respectively, and those with the SP and SS ansätze are displayed in blue and red.

23 April 2024 04:34:50

Published under an exclusive license by AIP Publishing

TABLE V. Statistical measures of valence-electron correlation energies (mE_h) in aug-cc-pVXZ basis sets.

		X				
		D	T	Q	5	6
$\bar{\Delta}$	MP2	98.70	39.88	18.56	9.79	5.86
	pTC(2)	21.77	3.48	0.78	0.23	0.09
	pTC(2) (SS)	8.30	−1.13	−0.91	−0.44	−0.21
	MP2-F12	12.71	3.89	1.46	0.58	0.23
	MP2-F12(SS)	18.61	9.06	3.80	1.62	0.71
$\bar{\Delta}_{abs}$	pTC(2)	21.77	3.48	0.80	0.26	0.12
	pTC(2) (SS)	11.00	2.96	1.03	0.47	0.22
$\bar{\Delta}_{cusp}$	pTC(2)	−13.47	−4.60	−1.69	−0.66	−0.30
	MP2-F12	5.90	5.17	2.34	1.04	0.47
$\bar{\Delta}_{opt}$	SP ansatz	9.78	2.49	0.84	0.39	0.16
	SS ansatz	14.96	10.20	4.71	2.05	0.92

TABLE VI. Statistical measures of all-electron correlation energies (mE_h) in aug-cc-pCVXZ basis sets.

		X				
		D	T	Q	5	6
$\bar{\Delta}$	MP2	127.64	47.37	20.79	10.85	6.43
	pTC(2)	15.25	3.00	0.88	0.24	0.11
	pTC(2) (SS)	−6.41	−2.05	−0.55	−0.32	−0.14
	MP2-F12	22.19	4.31	0.96	0.25	0.08
	MP2-F12(SS)	47.74	10.22	2.66	0.85	0.33
$\bar{\Delta}_{abs}$	pTC(2)	15.40	3.00	0.88	0.24	0.11
	pTC(2) (SS)	14.35	2.10	0.58	0.34	0.15
$\bar{\Delta}_{cusp}$	pTC(2)	−21.66	−5.06	−1.43	−0.56	−0.25
	MP2-F12	25.56	5.91	1.70	0.60	0.25
$\bar{\Delta}_{opt}$	SP ansatz	10.01	1.35	0.16	0.09	0.04
	SS ansatz	54.16	9.90	3.21	1.18	0.47

We detail the discussion employing the statistical measures, the mean error $\bar{\Delta}$, the mean absolute error $\bar{\Delta}_{abs}$ for the non-variational pTC, the mean deviation of the SS energy from SP to indicate the error due to the p-wave cusp condition,

$$\bar{\Delta}_{cusp} = \overline{E_{SS} - E_{SP}}, \tag{43}$$

and the mean absolute deviation of pTC(2) from MP2-F12 for the optimality of the geminal ansatz,

$$\bar{\Delta}_{opt} = \overline{|E_{pTC}(2) - E_{MP2-F12}|}. \tag{44}$$

The measures for the valence- and all-electron correlation energies are given in Tables V and VI. In contrast to the others, $\bar{\Delta}$ of pTC(2) (SS) converges from below except for the valence correlation in aug-cc-pVDZ, where the first-order $\langle \hat{\mathcal{H}}_{2h} + \mathcal{H}_{2v} \rangle$ makes large positive contributions for several systems. $\bar{\Delta}_{cusp}$ is always negative for pTC(2) contrary to MP2-F12. Accordingly, pTC(2) (SS) contains error cancelation between the deficiency of the triplet cusp condition and basis set incompleteness with negative and positive contributions, respectively. The optimality index $\bar{\Delta}_{opt}$ of the SP ansatz is several times as small as the SS one, indicating the importance of the cusp conditions for proper transcorrelation.

We finally discuss the treatment of core-valence correlation energies. Figure 2 exhibits the errors of all-electron correlation energies of H_2O in aug-cc-pVTZ. Comparred to the result with aug-cc-pCVTZ in Fig. 1, the errors increase significantly in the absence of the core functions both for pTC and MP2-F12. This deterioration gives negative and positive impacts for pTC(2) and MP2-F12, respectively. MP2-F12(HYB) markedly improves the error in the CC and CV correlation energies. pTC(2) (HYB) employs the CC and CV geminal amplitudes of MP2-F12 to show a similar performance.

The statistical measures of the corresponding calculations for the test set molecules are listed in Table VII. The mean errors of MP2-F12(HYB) and pTC(2) (HYB) across 10 mE_H from X = T to Q. The optimality index $\bar{\Delta}_{opt}$ of the HYB ansatz is from 20 to 100 times as small as the SP one for $X \geq$ T, suggesting the possibility of diverting geminal amplitudes from low-order F12 theory to higher-order pTC calculations. Nevertheless, the very sharp convergence as in Table VI is not attained solely by the optimization of amplitudes, and augmentations with core functions appear to be the best method for highly accurate core-valence correlation energies.

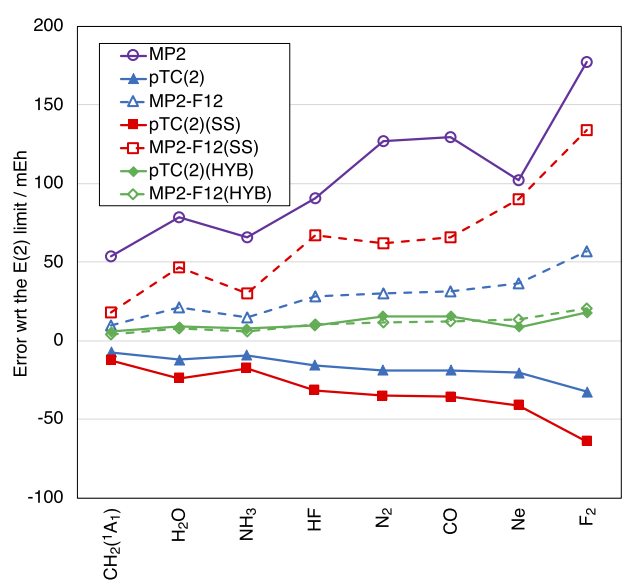


FIG. 2. Errors of all-electron correlation energies in the aug-cc-pVTZ basis set. The expressions are same as those in Fig. 1 except for the HYB result indicated in green.

23 April 2024 04:34:50

Published under an exclusive license by AIP Publishing

TABLE VII. Statistical measures of all-electron correlation energies (mE_h) in aug-cc-pV*X*Z basis sets.

		X				
		D	T	Q	5	6
$\bar{\Delta}$	MP2	178.88	103.12	60.76	43.23	31.56
	pTC(2)	2.05	−16.82	−14.92	−11.59	−8.12
	pTC(2) (SS)	−26.89	−32.67	−22.33	−15.34	−9.97
	pTC(2) (HYB)	34.74	11.20	5.24	3.74	2.87
	MP2-F12	44.54	28.66	17.85	12.50	8.28
	MP2-F12(SS)	91.74	64.30	36.86	23.65	14.36
	MP2-F12(HYB)	23.45	10.81	5.81	4.07	3.02
$\bar{\Delta}_{abs}$	pTC(2)	9.24	16.82	14.92	11.59	8.12
	pTC(2) (SS)	27.01	32.67	22.33	15.34	9.97
	pTC(2) (HYB)	34.74	11.20	5.24	3.74	2.87
$\bar{\Delta}_{opt}$	SP ansatz	42.47	45.48	32.77	24.09	16.40
	SS ansatz	118.63	96.98	59.19	38.99	24.33
	HYB ansatz	11.97	2.63	0.80	0.37	0.17

IV. CONCLUSIONS

We have introduced a projective transcorrelation inspired by the F12 ansatz. The effective Hamiltonian $\hat{\mathcal{H}}_{pTC}$ is universal, spin-free, satisfying the s- and p-wave cusp conditions simultaneously, and terminates at the four-body interaction. In the SR case, the second order contribution of $\hat{\mathcal{H}}_{pTC}$ is equivalent to the V-term of MP2-F12 plus additional terms not present in MP2-F12 with GBC and $\hat{Q}_{12}^{(SO)}$. Higher-order contribution can be automatically incorporated by involving $\hat{\mathcal{H}}_{pTC}$ in correlated calculations. Numerical results of pTC(2) indicate that single contractions through the complementary projector $\hat{Q}_n = 1 - \hat{P}_n$ decay very rapidly with the basis set size. This suggests that $\hat{\mathcal{H}}_{pTC}$ can be practically approximated by omitting the three- and four-body operators, $\hat{\mathcal{H}}_{3q}$ and $\hat{\mathcal{H}}_4$ quadratic to $\hat{Q}_n$ as

$$\hat{\mathcal{H}}_{pTC} \approx \hat{\mathcal{H}} + \hat{\mathcal{H}}_{2h} + \hat{\mathcal{H}}_{2w} + \hat{\mathcal{H}}_{3l}, \tag{45}$$

in accord with common approximations of four-electron integrals in F12 theory, which makes the implementation extremely easy. These features are significant advantages over the previous TC of Boys and Handy.

Due to the non-hermitian nature of the effective Hamiltonian, we need to pay special attention to the accuracy of transcorrelation. The deficiency of cusp conditions and basis set incompleteness can contribute with opposite signs, leading to error cancelation. The cusp conditions play an important role in transcorrelation, and the validity of the ansatz must be confirmed through comparisons with variational calculations. The pTC is universal and will provide useful applications when combined with FCI solvers. We plan to report on the integration of pTC with promising solvers for strongly correlated electrons, including selected coupled-cluster[78,79] and model space QMC.[80,81]

ACKNOWLEDGMENTS

This work is partially supported by the Grant-in-Aids for Scientific Research (A) (Grant No. 22H00316) from the Japan Society for the Promotion of Science (JSPS) and MEXT as "Program for Promoting Researches on the Supercomputer Fugaku" (Realization of innovative light energy conversion materials, Grant No. JPMXP1020210317).

AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

Seiichiro L. Ten-no: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Software (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] W. Kutzelnigg, "r_{12}-Dependent terms in the wave function as closed sums of partial wave amplitudes for large *l*," Theor. Chim. Acta **68**, 445–469 (1985).
[2] W. Klopper, F. R. Manby, S. Ten-no, and E. F. Valeev, "R12 methods in explicitly correlated molecular electronic structure theory," Int. Rev. Phys. Chem. **25**, 427–468 (2006).
[3] T. Halgaker, W. Klopper, and D. P. Tew, "Quantitative quantum chemistry," Mol. Phys. **106**, 2107–2143 (2008).
[4] S. Ten-no and J. Noga, "Explicitly correlated electronic structure theory from R12/F12 ansätze," Wiley Interdiscip. Rev.: Comput. Mol. Sci. **2**, 114–125 (2012).
[5] S. Ten-no, "Explicitly correlated wave functions: Summary and perspective," Theor. Chem. Acc. **131**, 1070 (2012).
[6] C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, "Explicitly correlated electrons in molecules," Chem. Rev. **112**, 4–74 (2012).
[7] L. Kong, F. A. Bischoff, and E. F. Valeev, "Explicitly correlated R12/F12 methods for electronic structure," Chem. Rev. **112**, 75–107 (2012).
[8] T. Shiozaki and H.-J. Werner, "Multireference explicitly correlated F12 theories," Mol. Phys. **111**, 607–630 (2013).
[9] A. Grüneis, S. Hirata, Y.-y. Ohnishi, and S. Ten-no, "Perspective: Explicitly correlated electronic structure theory for complex systems," J. Chem. Phys. **146**, 080901 (2017).
[10] Q. Ma and H.-J. Werner, "Explicitly correlated local coupled-cluster methods using pair natural orbitals," Wiley Interdiscip. Rev.: Comput. Mol. Sci. **8**, e1371 (2018).
[11] J. O. Hirschfelder, "Removal of electron-electron poles from many-electron Hamiltonians," J. Chem. Phys. **39**, 3145 (1963).

23 April 2024 04:34:50

Published under an exclusive license by AIP Publishing

[12]T. Kato, "On the eigenfunctions of many-particle systems in quantum mechanics," Commun. Pure Appl. Math. **10**, 151–177 (1957).
[13]S. F. Boys and N. C. Handy, "A condition to remove the indeterminacy in interelectronic correlation functions," Proc. R. Soc. London, Ser. A **309**, 209 (1969).
[14]S. F. Boys and N. C. Handy, "The determination of energies and wavefunctions with full electronic correlation," Proc. R. Soc. A **310**, 43 (1969).
[15]N. C. Handy, "On the minimization of the variance of the transcorrelated Hamiltonian," Mol. Phys. **21**, 817–828 (1971).
[16]S. Ten-no, "A feasible transcorrelated method for treating electronic cusps using a frozen Gaussian geminal," Chem. Phys. Lett. **330**, 169 (2000).
[17]S. Ten-no, "Three-electron integral evaluation in the transcorrelated method using a frozen Gaussian geminal," Chem. Phys. Lett. **330**, 175 (2000).
[18]O. Hino, Y. Tanimura, and S. Ten-no, "Biorthogonal approach for explicitly correlated calculations using the transcorrelated Hamiltonian," J. Chem. Phys. **115**, 7865 (2001).
[19]O. Hino, Y. Tanimura, and S. Ten-no, "Application of the transcorrelated Hamiltonian to the linearized coupled cluster singles and doubles model," Chem. Phys. Lett. **353**, 317 (2002).
[20]E. A. G. Armour, "The calculation of the ground-state energy of the free-electron gas by the transcorrelated method," J. Phys. C: Solid State Phys. **13**, 343 (1980).
[21]N. Umezawa and S. Tsuneyuki, "Ground-state correlation energy for the homogeneous electron gas calculated by the transcorrelated method," Phys. Rev. B **69**, 165102 (2004).
[22]H. Luo, "Transcorrelated calculations of homogeneous electron gases," J. Chem. Phys. **136**, 224111 (2012).
[23]R. Sakuma and S. Tsuneyuki, "Electronic structure calculations of solids with a similarity-transformed Hamiltonian," J. Phys. Soc. Jpn. **75**, 103705 (2006).
[24]M. Ochi, K. Sodeyama, R. Sakuma, and S. Tsuneyuki, "Efficient algorithm of the transcorrelated method for periodic systems," J. Chem. Phys. **136**, 094108 (2012).
[25]M. Ochi and S. Tsuneyuki, "Optical absorption spectra calculated from a first-principles wave function theory for solids: Transcorrelated method combined with configuration interaction singles," J. Chem. Theory Comput. **10**, 4098 (2014).
[26]M. Ochi, K. Sodeyama, and S. Tsuneyuki, "Optimization of the Jastrow factor using the random-phase approximation and a similarity-transformed Hamiltonian: Application to band-structure calculation for some semiconductors and insulators," J. Chem. Phys. **140**, 074112 (2014).
[27]A. J. Cohen, H. Luo, K. Guther, W. Dobrautz, D. P. Tew, and A. Alavi, "Similarity transformation of the electronic Schrödinger equation via Jastrow factorization," J. Chem. Phys. **151**, 061101 (2019).
[28]W. Dobrautz, A. J. Cohen, A. Alavi, and E. Giner, "Performance of a one-parameter correlation factor for transcorrelation: Study on a series of second row atomic and molecular systems," J. Chem. Phys. **156**, 234108 (2022).
[29]J. P. Haupt, S. M. Hosseini, P. López Ríos, W. Dobrautz, A. Cohen, and A. Alavi, "Optimizing Jastrow factors for the transcorrelated method," J. Chem. Phys. **158**, 224105 (2023).
[30]A. Baiardi and M. Reiher, "Transcorrelated density matrix renormalization group," J. Chem. Phys. **153**, 164115 (2020).
[31]A. Baiardi, M. Lesiuk, and M. Reiher, "Explicitly correlated electronic structure calculations with transcorrelated matrix product operators," J. Chem. Theory Comput. **18**, 4203–4217 (2022).
[32]K. Liao, H. Zhai, E. M. Christlmaier, T. Schraivogel, P. L. Ríos, D. Kats, and A. Alavi, "Density matrix renormalization group for transcorrelated Hamiltonians: Ground and excited states in molecules," J. Chem. Theory Comput. **19**, 1734–1743 (2023).
[33]A. Ammar, E. Giner, and A. Scemama, "Optimization of large determinant expansions in quantum Monte Carlo," J. Chem. Theory Comput. **18**, 5325–5336 (2022).
[34]A. Ammar, A. Scemama, and E. Giner, "Extension of selected configuration interaction for transcorrelated methods," J. Chem. Phys. **157**, 134107 (2022).
[35]S. McArdle and D. P. Tew, "Improving the accuracy of quantum computational chemistry using the transcorrelated method," arXiv:2006.11181 (2020).
[36]I. O. Sokolov, W. Dobrautz, H. Luo, A. Alavi, and I. Tavernelli, "Orders of magnitude increased accuracy for quantum many-body problems on quantum computers via an exact transcorrelated method," Phys. Rev. Res. **5**, 023174 (2023).
[37]T. Yanai and T. Shiozaki, "Canonical transcorrelated theory with projected Slater-type geminals," J. Chem. Phys. **136**, 084107 (2012).
[38]M. Motta, T. P. Gujarati, J. E. Rice, A. Kumar, C. Masteran, J. A. Latone, E. Lee, E. F. Valeev, and T. Y. Takeshita, "Quantum simulation of electronic structure with a transcorrelated Hamiltonian: Improved accuracy with a smaller footprint on the quantum computer," Phys. Chem. Chem. Phys. **22**, 24270–24281 (2020).
[39]P. Schleich, J. S. Kottmann, and A. Aspuru-Guzik, "Improving the accuracy of the variational quantum eigensolver for molecular systems by the explicitly-correlated perturbative $[2]_{R12}$-correction," Phys. Chem. Chem. Phys. **24**, 13550–13564 (2022).
[40]A. Kumar, A. Asthana, C. Masteran, E. F. Valeev, Y. Zhang, L. Cincio, S. Tretiak, and P. A. Dub, "Quantum simulation of molecular electronic states with a transcorrelated Hamiltonian: Higher accuracy with fewer qubits," J. Chem. Theory Comput. **18**, 5312–5324 (2022).
[41]R. T. Pack and W. Byers-Brown, "Cusp conditions for molecular wavefunctions," J. Chem. Phys. **45**, 556 (1966).
[42]W. Kutzelnigg and J. D. Morgan III, J. Chem. Phys. **96**, 4484 (1992).
[43]S. Ten-no, "Explicitly correlated second order perturbation theory: Introduction of a rational generator and numerical quadratures," J. Chem. Phys. **121**, 117–129 (2004).
[44]S. Ten-no, "Initiation of explicitly correlated Slater-type geminal theory," Chem. Phys. Lett. **398**, 56–61 (2004).
[45]D. P. Tew and W. Klopper, "A comparison of linear and nonlinear correlation factors for basis set limit Møller-Plesset second order binding energies and structures of He2, Be2, and Ne2," J. Chem. Phys. **125**, 094302 (2006).
[46]W. Klopper and W. Kutzelnigg, "MP2-R12 calculations on the relative stability of carbocations," J. Phys. Chem. **94**, 5625–5630 (1990).
[47]H.-J. Werner, T. B. Adler, and F. R. Manby, "General orbital invariant MP2-F12 theory," J. Chem. Phys. **126**, 164102 (2007).
[48]A. Köhn, "A modified ansatz for explicitly correlated coupled-cluster wave functions that is suitable for response theory," J. Chem. Phys. **130**, 104104 (2009).
[49]S. Ten-no, "A simple F12 geminal correction in multi-reference perturbation theory," Chem. Phys. Lett. **447**, 175 (2007).
[50]T. Shiozaki and H.-J. Werner, "Communication: Second-order multireference perturbation theory with explicit correlation: CASPT2-F12," J. Chem. Phys. **133**, 141103 (2010).
[51]W. Kutzelnigg and W. Klopper, "Wave functions with terms linear in the interelectronic coordinates to take care of the correlation cusp. i. general theory," J. Chem. Phys. **94**, 1985 (1991).
[52]M. Torheyden and E. F. Valeev, "Universal perturbative explicitly correlated basis set incompleteness correction," J. Chem. Phys. **131**, 171103 (2009).
[53]W. Kutzelnigg, "Quantum chemistry in Fock space," in *Aspects of Many-Body Effects in Molecules and Extended Systems, February 1–10, 1988*, edited by D. Mukherjee (Springer Science & Business Media, 2012), Vol. 50.
[54]W. Klopper and C. C. M. Samson, "Explicitly correlated second-order Møller-Plesset methods with auxiliary basis sets," J. Chem. Phys. **116**, 6397–6410 (2002).
[55]E. F. Valeev, "Improving on the resolution of the identity in linear R12 *ab initio* theories," Chem. Phys. Lett. **395**, 190–195 (2004).
[56]S. Ten-no, "New implementation of second-order Møller-Plesset perturbation theory with an analytic Slater-type geminal," J. Chem. Phys. **126**, 014108 (2007).
[57]A. Grüneis, "Efficient explicitly correlated many-electron perturbation theory for solids: Application to the Schottky defect in mgo," Phys. Rev. Lett. **115**, 066402 (2015).
[58]C. Hättig, D. P. Tew, and B. Helmich, "Local explicitly correlated second- and third-order Møller-Plesset perturbation theory with pair natural orbitals," J. Chem. Phys. **136**, 204105 (2012).
[59]Y.-y. Ohnishi and S. Ten-no, "Alternative formulation of explicitly correlated third-order Møller–Plesset perturbation theory," Mol. Phys. **111**, 2516–2522 (2013).
[60]H. Fliegl, W. Klopper, and C. Hättig, "Coupled-cluster theory with simplified linear-r_{12} corrections: The CCSD(R12) model," J. Chem. Phys. **122**, 084107 (2005).

23 April 2024 04:34:50

Published under an exclusive license by AIP Publishing

[61] D. P. Tew, W. Klopper, C. Neiss, and C. Hättig, "Quintuple-ζ quality coupled-cluster correlation energies with triple-ζ basis sets," Phys. Chem. Chem. Phys. **9**, 1921–1930 (2007).
[62] T. B. Adler, G. Knizia, and H.-J. Werner, "A simple and efficient CCSD(T)-F12 approximation," J. Chem. Phys. **127**, 221106 (2007).
[63] M. Torheyden and E. F. Valeev, "Variational formulation of perturbative explicitly-correlated coupled-cluster methods," Phys. Chem. Chem. Phys. **10**, 3410–3420 (2008).
[64] G. Knizia, T. B. Adler, and H.-J. Werner, "Simplified CCSD (T)-F12 methods: Theory and benchmarks," J. Chem. Phys. **130**, 054104 (2009).
[65] D. Bokhan, S. Bernadotte, and S. Ten-no, "Implementation of the CCSD(T)(F12) method using numerical quadratures," Chem. Phys. Lett. **469**, 214–218 (2009).
[66] A. Köhn, "Explicitly correlated connected triple excitations in coupled-cluster theory," J. Chem. Phys. **130**, 131101 (2009).
[67] J. G. Hill, S. Mazumder, and K. A. Peterson, "Correlation consistent basis sets for molecular core-valence effects with explicitly correlated wave functions: The atoms B–Ne and Al–Ar," J. Chem. Phys. **132**, 054108 (2010).
[68] J. G. Hill and K. A. Peterson, "Correlation consistent basis sets for explicitly correlated wavefunctions: Valence and core–valence basis sets for Li, Be, Na, and Mg," Phys. Chem. Chem. Phys. **12**, 10460–10468 (2010).
[69] T. H. Dunning, "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen," J. Chem. Phys. **90**, 1007 (1989).
[70] R. A. Kendall, T. H. Dunning, Jr, and R. J. Harrison, "Electron affinities of the first-row atoms revisited. systematic basis sets and wave functions," J. Chem. Phys. **96**, 6796–6806 (1992).
[71] D. E. Woon and T. H. Dunning, "Gaussian basis sets for use in correlated molecular calculations. V. Core-valence basis sets for boron through neon," J. Chem. Phys. **103**, 4572 (1995).
[72] W. Klopper, "Orbital-invariant formulation of the MP2-R12 method," Chem. Phys. Lett. **186**, 583–585 (1991).
[73] H.-J. Werner, G. Knizia, and F. R. Manby, "Explicitly correlated coupled cluster methods with pair-specific geminals," Mol. Phys. **109**, 407–417 (2011).
[74] D. P. Tew and D. Kats, "Relaxing constrained amplitudes: Improved f12 treatments of orbital optimization and core–valence correlation energies," J. Chem. Theory Comput. **14**, 5435–5440 (2018).
[75] S. Ten-no *et al.*, "GELLAN: A hierarchical quantum chemistry program," (Kobe University, 2023).
[76] T. Shiozaki, "Evaluation of Slater-type geminal integrals using tailored Gaussian quadrature," Chem. Phys. Lett. **479**, 160 (2009).
[77] E. Valeev *et al.* (2022). "Libint: A library for the evaluation of molecular integrals of many-body operators over Gaussian functions," Github. http://libint.valeyev.net/
[78] E. Xu, M. Uejima, and S. L. Ten-no, "Full coupled-cluster reduction for accurate description of strong electron correlation," Phys. Rev. Lett. **121**, 113001 (2018).
[79] E. Xu, M. Uejima, and S. L. Ten-no, "Towards near-exact solutions of molecular electronic structure: Full coupled-cluster reduction with a second-order perturbative correction," J. Phys. Chem. Lett. **11**, 9775–9780 (2020).
[80] S. Ten-no, "Stochastic determination of effective Hamiltonian for the full configuration interaction solution of quasi-degenerate electronic states," J. Chem. Phys. **138**, 164126 (2013).
[81] S. L. Ten-no, "Multi-state effective Hamiltonian and size-consistency corrections in stochastic configuration interactions," J. Chem. Phys. **147**, 244107 (2017).

23 April 2024 04:34:50

Published under an exclusive license by AIP Publishing