Unitary coupled-cluster based self-consistent polarization propagator theory: a quadratic unitary coupled-cluster singles and doubles scheme

Junzi Liu and Lan Cheng

Department of Chemistry, The Johns Hopkins University, Baltimore, MD, 21218, USA

The development of a quadratic unitary coupled-cluster singles and doubles (qUCCSD) based self-consistent polarization propagator method is reported. We present a simple strategy for truncating the commutator expansion of the UCC transformed Hamiltonian $\bar{H}$. The qUCCSD method for the electronic ground-state includes up to double commutators for the amplitude equations and up to cubic commutators for the energy expression. The qUCCSD excited-state eigenvalue equations include up to double commutators for the singles-singles block of $\bar{H}$, single commutators for the singles-doubles and doubles-singles blocks, and the bare Hamiltonian for the doubles-doubles block. Benchmark qUCCSD calculations of the ground-state properties and excitation energies for representative molecules demonstrate significant improvement of the accuracy and robustness over the previous UCC3 scheme derived using Møller-Plesset perturbation theory.

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a)Electronic mail: latrix1247@gmail.com
b)Electronic mail: lcheng24@jhu.edu
I. INTRODUCTION

The equation-of-motion coupled-cluster (EOM-CC) methods\textsuperscript{1–9} and the closely-related CC linear response (CC-LR) theory\textsuperscript{8,10–17} have been established as useful tools for treating electronically excited states of small and medium-sized molecules. Recent efforts have also been devoted to extending the applicability of EOM-CC and similarity-transformed EOM-CC methods\textsuperscript{18,19} to large molecules\textsuperscript{20–24} and solids.\textsuperscript{25–29} In spite of the tremendous success, the non-hermitian nature of the CC theory poses difficult unsolved problems. CC calculations in combination with complex Hamiltonians, e.g., the Hamiltonian in magnetic fields and/or including spin-orbit coupling have been shown to produce complex ground-state energies.\textsuperscript{30} This is a non-trivial formal problem of the standard CC theory, although the real part of the complex CC energy is expected to serve as an accurate approximation to the full configuration interaction energy. Further, EOM-CC calculations have been demonstrated to have incorrect crossing conditions for intersections between electronic states of the same symmetry (known as “same-symmetry conical intersection”).\textsuperscript{30–33} To enable CC calculations of same-symmetry conical intersections, K"ohn and Tajti\textsuperscript{32} have proposed a simple correction to obtain physically meaningful potential energy surfaces around conical intersections. Koch and collaborators have recently developed a similarity constrained coupled-cluster singles and doubles (SCCSD) method that introduces an additional parameter associated with a triple excitation and determines this parameter by requiring the eigenvectors of two target states to be orthogonal to each other.\textsuperscript{34,35} These correction schemes have to introduce a substantial modification to the wavefunctions in order to enforce orthogonalization in two otherwise parallel eigenvectors. For example, the resulting SCC wavefunction often involves a significant contribution from a triply excited determinant.\textsuperscript{34,35} On the other hand, SCCSD produces excitation energies similar to that of CCSD.

Same-symmetry conical intersections play essential roles in photochemistry.\textsuperscript{36–38} Available calculations of same symmetry conical intersections have used hermitian excited-state formulations such as the algebraic diagrammatic construction (ADC) methods\textsuperscript{31,39} time-dependent density functional theory (TDDFT)-based techniques,\textsuperscript{40,41} constrained density functional theory-configuration interaction (CDFT-CI) method,\textsuperscript{42} and multireference techniques including complete active space self-consistent-field (CASSCF) method,\textsuperscript{43} CAS second-order perturbation theory (CASPT2),\textsuperscript{44} multi-reference perturbation theory
(MRPT) and multi-reference configuration interaction (MRCI) methods. The MRCI method as a non-perturbative wavefunction based approach has exhibited robust performance. However, the lack of size-extensivity in MRCI often poses difficulties in obtaining accurate electronic energies. For example, while MRCI calculations provided high-quality potential energy surfaces to gain insights into nonadiabatic tunneling dynamics of phenol dissociation, an energetic shift had to be applied to the computed potential energy surfaces to obtain a good agreement with the experimental energetics. The size-inextensivity problem of MRCI is expected to be more serious for calculations of larger molecules. Therefore, the development of new non-perturbative size-extensive/size-intensive hermitian excited-state theories to enhance the capability to treat same-symmetry conical intersections is of significant interest to photochemistry applications.

The unitary version of coupled-cluster (UCC) theory appears to be a natural approach to solve the formal problems of the CC theory arising from nonhermiticity and to enable CC studies of same-symmetry conical intersections. Analyses of the formal properties for the UCC theory and the relation with the standard CC methods have been reported. Numerical studies of the UCC methods have been carried out. The UCC methods truncated up to a given rank of excitation operators have been shown to recover a similar amount of dynamic correlation energies compared with the standard CC methods involving the same ranks of excitation operators. However, a formidable challenge in the UCC theory is to develop a practically tractable truncation scheme for the non-terminating expansion of the transformed Hamiltonian while maintaining the computational accuracy. Several truncation schemes for the ground-state UCC theory have been reported. The UCC(4) and UCC(5) methods have been developed using a perturbative analysis of the UCC energy expression. Taube and Bartlett have reported a truncation scheme exact for two-electron systems. The commutator truncation schemes have been explored for the multireference version of UCC theory and the canonical transformation methods. A stochastic approach to select excitation operators in UCC calculations has recently been developed. The recent development of density-cumulant functional theory has also provided information about the accuracy of the truncation schemes for hermitian formulations. We mention the rapidly growing interest in using UCC in quantum computations and refer the readers to recent publications and the references therein for this exploding field.
Concerning UCC-based excited-state theories, the second-order version UCC linear response theory has been shown to be identical to the second-order version of ADC [ADC(2)]\cite{82}. We have recently developed a third-order formulation for calculations of both ground-state energies and excitation energies within the UCC-based polarization propagator (PP) framework (the UCC3 scheme)\cite{83}. Interestingly, the strict version of UCC3 (UCC3-s) has been shown to be equivalent to the strict version of the third order ADC [ADC(3)]\cite{84-86} establishing the relation between the UCC-based polarization propagator theory and ADC\cite{83}. Hodecker et al. have reported an implementation of UCC3\cite{87} and a combination with a second-order density matrix for calculations of properties\cite{88}. Although the schemes based on perturbation theory performs well for simple molecules around the equilibrium structures, the performance decays quickly for more complex molecules in the absence of smooth convergence of the Møller-Plesset (MP) perturbation series. Therefore, we base our present work on an alternative strategy of truncating the expansion of the UCC transformed Hamiltonian to up to a certain power of cluster amplitudes. In Section II, We report the formulation and implementation of a quadratic UCCSD scheme (qUCCSD) for calculations of ground-state energies and excitation energies. The details about the benchmark calculations are discussed in Section III. The benchmark results for ground-state properties and excitation energies are presented and discussed in section IV. Finally, a summary and a perspective about future work are presented in Section V.

II. THEORY

A. Unitary coupled-cluster based polarization propagator theory

In this subsection, we present a succinct summary of unitary coupled-cluster based polarization propagator (UCC-PP) theory in the language of wavefunction theory. We refer the readers to Refs. \cite{83} and \cite{89} for a detailed account of the UCC-PP theory and to the literature\cite{90-99} for Green’s function methods based on the biorthogonal CC representation. The self-consistent polarization propagator methods represent the polarization propagator in an approximate many-electron basis by applying the inner-projection technique\cite{100} with a self-consistent operator manifold to decouple the forward and backward polariza-
tion propagator. In the UCC-based self-consistent polarization propagator method, the ground-state wavefunction adopts the UCC parameterization

$$|\Psi_{gr}\rangle = e^{\sigma}|\Phi_{0}\rangle,$$

in which the cluster operator $\sigma$ comprises both excitation and de-excitation operators, e.g., in the UCC singles and doubles (UCCSD) method $\sigma$ can be written as

$$\sigma = \sigma_1 + \sigma_2,$$

$$\sigma_1 = \sum_{ai} \sigma_{ia}^2 \{a^\dagger_a a_i\} - \sum_{ai} (\sigma_{ia}^a)^* \{a^\dagger_i a_a\},$$

$$\sigma_2 = \frac{1}{4} \left[ \sum_{abij} \sigma_{ij}^{ab} \{a^\dagger_a a^\dagger_b a_j a_i\} - \sum_{abij} (\sigma_{ij}^{ab})^* \{a_a a_b a^\dagger_j a^\dagger_i\} \right].$$

$i, j, \ldots$ and $a, b, \ldots$ denote occupied orbitals and virtual orbitals, respectively. $\sigma_{ia}^a$ and $\sigma_{ij}^{ab}$ represent the cluster amplitudes. This anti-hermitian form of the cluster operator $\sigma$ ensures the wave operator $e^{\sigma}$ to be unitary. The UCCSD ground-state energy and amplitude equations are given by

$$\langle \Phi_{0}|\bar{H}|\Phi_{0}\rangle = E_{gr},$$

$$\langle \Phi_{l}|\bar{H}|\Phi_{0}\rangle = 0.$$

Here the transformed Hamiltonian $\bar{H} = e^{-\sigma}He^{\sigma}$ is hermitian. $\Phi_{0}$ represents the ground-state Hartree-Fock wavefunction, while $\Phi_{l}$'s denote singly and doubly excited determinants. The UCC-based polarization propagator theory employs a self-consistent operator manifold consisting of the transformed excitation and de-excitation operators, $\{e^{\sigma}b^\dagger_I e^{-\sigma}\} \cup \{e^{\sigma}b_I e^{-\sigma}\}$, in which $b^\dagger_I$ is the original excitation operators, i.e., $\{b^\dagger_I\} = \{a^\dagger_a a_i\} \cup \{a^\dagger_a a^\dagger_b a_j a_i\}$ in the UCCSD method. This leads to the following eigenvalue equations

$$\sum_{l} \bar{H}_{IJ} C_{IL} = E_{L} C_{JL}, \quad \bar{H}_{JJ} = \langle \Phi_{0}|b_J \bar{H} b^\dagger_J|\Phi_{0}\rangle,$$

to determine excitation energies $E_{L}$ and the excited-state wavefunctions

$$|\Phi_{L}^{ext}\rangle = \sum_{l} C_{IL} e^{\sigma} b^\dagger_I |\Phi_{0}\rangle.$$

In other words, the UCCSD excited-state equations solve for eigenvalues and eigenstate of $\bar{H}$ within the space of singly and doubly excited determinants. The excited-state secular
equations can be rewritten in a block form as
\[
\begin{bmatrix}
\bar{H}_{SS} & \bar{H}_{SD} \\
\bar{H}_{DS} & \bar{H}_{DD}
\end{bmatrix}
\begin{bmatrix}
C_S \\
C_D
\end{bmatrix} = E
\begin{bmatrix}
C_S \\
C_D
\end{bmatrix}.
\]

(9)

Here \( \bar{H}_{SS} \) refers to the singles-singles block involving \( \bar{H}_{ij}, \bar{H}_{ab} \), and \( \bar{H}_{ia,bj} \), \( \bar{H}_{SD} \) and \( \bar{H}_{DS} \) represent the singles-doubles block and doubles-singles block involving the contributions from \( \bar{H}_{ci,ab}, \bar{H}_{jk,ia}, \bar{H}_{ajk,ibc} \) and \( \bar{H}_{ab,ci}, \bar{H}_{ia,jk}, \bar{H}_{ibc,a(jk),} \) and \( \bar{H}_{DD} \) is the doubles-doubles block involving \( \bar{H}_{ij}, \bar{H}_{ab}, \bar{H}_{ia,bj}, \bar{H}_{ij,kl}, \bar{H}_{ab,cd}, \bar{H}_{ia,cd}, \bar{H}_{ia,k,lb} \). The \( \bar{H} \) components pertinent to the UCCSD ground-state energy and amplitude equations as well as the excited-state secular equations thus can be summarized as

\[
\bar{H} = E_{gr} + \left( H_{ai}\{a_i^\dagger a_i\} + \frac{1}{4} H_{ab,ij}\{a_i^\dagger a_b^\dagger a_j a_i\} \right) + h.c.
\]

\[
+ \left( H_{ij}\{a_i^\dagger a_j\} + H_{ab}\{a_i^\dagger a_b\} + \frac{1}{4} H_{ij,kl}\{a_i^\dagger a_j^\dagger a_l a_k\} + \frac{1}{4} H_{ab,cd}\{a_i^\dagger a_b^\dagger a_d a_c\} + H_{ia,bj}\{a_i^\dagger a_a^\dagger a_j a_b\} \right)
\]

\[
+ \left( \frac{1}{2} H_{ij,ka}\{a_i^\dagger a_j^\dagger a_k a_a\} + \frac{1}{2} H_{ab,ci}\{a_i^\dagger a_b^\dagger a_c a_i\} \right) + h.c.
\]

\[
+ \left( \frac{1}{4} H_{ibc,a(jk)}\{a_i^\dagger a_j^\dagger a_k a_a\} \right) + h.c.
\]

\[
+ \left( \frac{1}{4} H_{ia,bj}\{a_i^\dagger a_j^\dagger a_a a_j\} + \frac{1}{4} H_{ija,k}a_{\{a_i^\dagger a_j^\dagger a_a a_k\} + h.c.} \right),
\]

(10)
in which \( E_{gr} \) is the UCCSD ground-state energy.

In contrast to that \( \bar{H} \) in the CC theory terminates at the quadruple commutators, the commutator expansion of \( \bar{H} \) in the UCC theory is non-terminating. We adopt an expansion using Bernoulli numbers for \( \bar{H}^{\infty} \).

\[
\bar{H} = \bar{H}^0 + \bar{H}^1 + \bar{H}^2 + \bar{H}^3 + \bar{H}^4 + \cdots
\]

(11)

\[
\bar{H}^0 = F + V,
\]

(12)

\[
\bar{H}^1 = [F, \sigma] + \frac{1}{2}[V, \sigma] + \frac{1}{2}[V_R, \sigma],
\]

(13)

\[
\bar{H}^2 = \frac{1}{12}[[V, \sigma], \sigma] + \frac{1}{4}[[V, \sigma], V_R, \sigma] + \frac{1}{4}[[V_R, \sigma], \sigma] + \frac{1}{4}[[V_R, \sigma], V_R, \sigma],
\]

(14)

\[
\bar{H}^3 = \frac{1}{24}[[[V, \sigma], \sigma], \sigma] + \frac{1}{8}[[[V, \sigma], V_R, \sigma], \sigma] + \frac{1}{8}[[[V, \sigma], \sigma], V_R, \sigma] + \frac{1}{8}[[[V, \sigma], \sigma], \sigma],
\]

(15)

\[
\bar{H}^4 = \frac{1}{16}[[[[V, \sigma], \sigma], \sigma], \sigma] + \frac{1}{16}[[[[V, \sigma], \sigma], \sigma], \sigma] + \frac{1}{16}[[[[V, \sigma], \sigma], \sigma], \sigma]
\]

\[
- \frac{1}{48}[[[V, \sigma], \sigma], \sigma] - \frac{1}{48}[[[V, \sigma], \sigma], \sigma] - \frac{1}{144}[[[V, \sigma], \sigma], \sigma]
\]

6
\[-\frac{1}{48}[[[V, \sigma], [\sigma], [\sigma], [\sigma]], [\sigma]] - \frac{1}{48}[[[V \sigma], [\sigma], [\sigma], [\sigma]], [\sigma]] - \frac{1}{720}[[[V \sigma], [\sigma], [\sigma]], [\sigma]]. \tag{16}\]

Here “N” refers to the joint set of excitation and de-excitation portions of the target operator, while “R” refers to the rest of the operator excluding the “N” part. This expansion using Bernoulli numbers eliminates higher than linear commutators with respect to the Fock operator and offers a compact framework for formulating practical UCCSD methods.

\[\bar{H} = H_{SS} + H_{SD}(E - H_{DD})^{-1}H_{DS}\]

\[\tag{17}\]

B. A general strategy for truncating the commutator expansion and the qUCCSD scheme

The magnitude of the cluster amplitudes serves as a faithful measure for the strength of dynamic correlation. We thus explore UCC truncation schemes based on the powers of the cluster amplitudes, or equivalently, on the order of commutators in the commutator expansion of \(\bar{H}\) using Bernoulli numbers. Note that, although \(\sigma_1\) emerges at the second order in Møller-Plesset perturbation theory, single-reference systems with strong orbital-relaxation effects exhibit large ground-state CC amplitudes for single excitations. The standard CC methods can provide accurate treatments of orbital relaxation through the exponential of single excitations. However, methods based on MP perturbation theory or truncation of single excitations to the linear terms could not treat these systems accurately, e.g., see Refs. Therefore, we truncate single and double excitations up to the same power in the present work. We use a general notation UCCSD\([k|l,m,n]\) to denote a scheme that include up to the \(k\)'th order commutators for the ground-state amplitude equations [(\(k+1\)'th order commutators for the ground-state energy expression)], \(l\)'th order commutators for the singles-singles block of the excited-state secular equations, \(m\)'th order for the singles-doubles and doubles-singles blocks, and \(n\)'th order commutators for the doubles-doubles block.

Applying the partitioning technique to Eq. (9) to fold the contributions from double excitations into singly excited states, the eigenvalue equations can be rewritten as

\[(\bar{H}_{SS} + \bar{H}_{SD}(E - \bar{H}_{DD})^{-1}\bar{H}_{DS})C_S = EC_S.\tag{17}\]

A balanced truncation scheme for the excited-state eigenvalue equations thus would involve expansions of \(\bar{H}_{SS}\) and \(\bar{H}_{SD}(E - \bar{H}_{DD})^{-1}\bar{H}_{DS}\) to the same accuracy. Since \(V\) serves as a similar measure of electron correlation as \(\sigma\), we count the power of \(V\) and \(\sigma\) together. \(\bar{H}_{SS}\) and \(\bar{H}_{DD}\) involve \(F\), \(V\), and commutators of \(V\) and \(\sigma\). The expansions of \(\bar{H}_{SS}\) and
\((E - H_{DD})^{-1}\) thus start with a contribution of \(F\), which is of the zeroth power of \(V\) and \(\sigma\). In contrast, \(H_{SD}\) and \(H_{DS}\) involve \(V\) and commutators of \(V\) and \(\sigma\), and thus are of at least linear power. Therefore, the truncation of \(\bar{H}_{SS}\) to the \(l\)'th order commutators of \(V\) and \(\sigma\), \(\bar{H}_{SD}\) and \(\bar{H}_{DS}\) to the \((l-1)'\)th order commutators, and \(\bar{H}_{DD}\) to the \((l-2)'\)th order commutators ensures \(\bar{H}_{SS}\) and \(\bar{H}_{SD}(E - H_{DD})^{-1}\bar{H}_{DS}\) to be correct up to the \(l + 1\)'th power of \(V\) and \(\sigma\) and provides a balanced description for the singly excited states. Further, we choose to include in \(\bar{H}_{SS}\) the same ranks of commutators as in the ground-state amplitude equations. The \(\text{UCCSD}[l,l-1,l-2]\) schemes thus emerge as promising options for treating ground state and singly excited states. Since the linearized methods usually are numerically not accurate, in the present work we explore the quadratic version, \(\text{UCCSD}[2,2,1,0]\), which we will refer to as the qUCCSD scheme.

We should mention that the present general strategy is also applicable to the Baker-Campbell-Hausdorff (BCH) expansion. Since \([F,\sigma]\) is of similar magnitude as \(V\), the commutators between \(F\) and \(\sigma\) in the BCH expansion should be truncated to one rank higher than the commutators between \(V\) and \(\sigma\). For example, the qUCCSD scheme within the BCH expansion consists of up to quadruple commutators for \(F\) and \(\sigma\) for the energy expression, triple commutators of \(F\) and \(\sigma\) for the ground-state amplitude equations, triple commutators of \(F\) and \(\sigma\) for \(\bar{H}_{SS}\), double commutators of \(F\) and \(\sigma\) for \(\bar{H}_{SD}\) and \(\bar{H}_{DS}\), and single commutators of \(F\) and \(\sigma\) for \(\bar{H}_{DD}\). The expansion using Bernoulli numbers is more compact than the BCH expansion. On the other hand, the BCH expansion is applicable to non-Hartree-Fock reference functions. The present work is focused on the qUCCSD scheme with the expansion using Bernoulli numbers.

C. The working equations for the qUCCSD scheme

The qUCCSD working equations have been derived using the recipe for \(\bar{H}\) discussed in the previous subsection and the standard diagrammatic techniques as in the CC methods.\(^{104,105}\) The expression for the qUCCSD ground-state energy \(E_{\text{gr}}^{\text{qUCCSD}}\) consists of up to the third commutators of the fully contracted part of \(\bar{H}\) and can be written as

\[
E_{\text{gr}}^{\text{qUCCSD}} = E_{HF} + \langle \Phi_0 | \bar{H}^1 | \Phi_0 \rangle + \langle \Phi_0 | \bar{H}^2 | \Phi_0 \rangle + \langle \Phi_0 | \bar{H}^3 | \Phi_0 \rangle,
\]

\[
\langle \Phi_0 | \bar{H}^1 | \Phi_0 \rangle = \sum_{ijab} \frac{1}{8} \langle ij || ab \rangle \sigma_{ij}^{ab} + h.c.,
\]
\[ \langle \Phi_0 | \hat{H}^2 | \Phi_0 \rangle = \sum_{ijab} \frac{1}{12} \langle ij || ab \rangle \sigma_i^a \sigma_j^b + h.c., \] (20)

\[ \langle \Phi_0 | \hat{H}^3 | \Phi_0 \rangle = \left( - \sum_{ijklabcd} \frac{1}{12} \langle \sigma_{cd}^{kl} || \langle ij || ab \rangle \sigma_{ik}^{bc} \sigma_{jl}^{bd} + \frac{1}{24} \langle \sigma_{cd}^{kl} || \langle ij || ab \rangle \sigma_{ij}^{bc} \sigma_{kl}^{bd} \right) \]

\[ + \sum_{ijklabcd} \frac{1}{24} \langle \sigma_{cd}^{kl} || \langle ij || ab \rangle \sigma_{ik}^{bc} \sigma_{jl}^{bd} - \frac{1}{96} \langle \sigma_{cd}^{kl} || \langle ij || ab \rangle \sigma_{ij}^{bc} \sigma_{kl}^{bd} + h.c. \right) \]

\[ \left( \sum_{ijklabc} \frac{1}{4} \langle \sigma_{jl}^{bc} || \langle ij || ab \rangle \sigma_i^a \sigma_j^b \sigma_k^c - \sum_{ijklabcd} \frac{1}{4} \langle \sigma_{cd}^{kl} || \langle ic || ab \rangle \sigma_i^c \sigma_j^d \right) \]

\[ + \sum_{ijklabc} \frac{1}{2} \langle \sigma_{jl}^{bc} || \langle kj || ai \rangle \sigma_j^b \sigma_{kl}^c - \sum_{ijklabcd} \frac{1}{2} \langle \sigma_{cd}^{kl} || \langle ic || ab \rangle \sigma_j^b \sigma_k^d \right) \]

\[ + \sum_{ijklabc} \frac{1}{12} \langle \sigma_{jl}^{bc} || \langle kj || ia \rangle \sigma_j^a \sigma_k^b - \sum_{ijklabcd} \frac{1}{12} \langle \sigma_{cd}^{kl} || \langle ic || ab \rangle \sigma_j^a \sigma_k^b \right) \]

\[ - \sum_{ijklabc} \frac{1}{8} \langle \sigma_{jl}^{bc} || \langle kj || ia \rangle \sigma_j^a \sigma_k^b + \sum_{ijklabcd} \frac{1}{8} \langle \sigma_{cd}^{kl} || \langle ci || ab \rangle \sigma_j^d \sigma_k^b + h.c. \right) \]

\[ \left( - \sum_{ijklabc} \frac{1}{12} \langle \sigma_{jl}^{bc} || \langle ij || ab \rangle \sigma_i^a \sigma_j^b + \sum_{ijklabc} \frac{1}{12} \langle \sigma_{jl}^{bc} || \langle ij || ab \rangle \sigma_i^a \sigma_j^b \right) \]

\[ + \sum_{ijklabc} \frac{1}{12} \langle \sigma_{jl}^{bc} || \langle ij || ab \rangle \sigma_i^a \sigma_j^b + \sum_{ijklabc} \frac{1}{12} \langle \sigma_{jl}^{bc} || \langle ij || ab \rangle \sigma_i^a \sigma_j^b \right) \]

\[ - \sum_{ijklabc} \frac{1}{12} \langle \sigma_{jl}^{bc} || \langle kl || ij \rangle \sigma_i^a \sigma_j^b - \sum_{ijklabcd} \frac{1}{12} \langle \sigma_{jl}^{bc} || \langle kl || ij \rangle \sigma_i^a \sigma_j^b \right) \]

\[ + \left( \sum_{ijklabc} \frac{1}{3} \langle \sigma_{jl}^{bc} || \langle ij || ai \rangle \sigma_j^a \sigma_k^b + \sum_{ijklabc} \frac{1}{3} \langle \sigma_{jl}^{bc} || \langle ij || ab \rangle \sigma_j^a \sigma_k^b + h.c. \right) \] (21)

The qUCCSD amplitude equations comprise up to double commutators for \( \hat{H}_{ai} \)

\[ \hat{H}_{ai}^{\text{qUCCSD}} = \hat{H}_{ai}^1 + \hat{H}_{ai}^2 = 0, \] (22)

\[ \hat{H}_{ai}^1 = \sum_b t_{b} b_{ti} - \sum_j t_{j} f_{ji} + \frac{1}{2} \sum_{jbc} \langle aj || cb \rangle \sigma_{ij}^{cb} - \frac{1}{2} \sum_{jkb} \langle kj || ib \rangle \sigma_{jk}^{ba} + \frac{1}{2} \sum_{jbc} \langle aj || ib \rangle \sigma_{ij}^{ba} \] (23)

\[ \hat{H}_{ai}^2 = - \sum_{jkbcd} \frac{1}{2} \langle \sigma_{jk}^{bc} || (al || ik) \sigma_{ij}^{bc} + \frac{1}{2} \langle \sigma_{jk}^{bc} || (ad || ic) \sigma_{ik}^{ba} - \sum_{jkbcd} \langle \sigma_{jk}^{bc} || (bl || ji) \sigma_{ij}^{ca} + \frac{1}{2} \sum_{jkbcd} \langle \sigma_{jk}^{bc} || (ab || dj) \sigma_{ij}^{cd} \]

\[ - \sum_{jkbcd} \frac{1}{4} \langle \sigma_{jk}^{bc} || (bl || jk) \sigma_{ij}^{ac} + \frac{1}{4} \langle \sigma_{jk}^{bc} || (bd || jk) \sigma_{ij}^{ac} - \sum_{jkbcd} \frac{1}{4} \langle \sigma_{jk}^{bc} || (bd || jk) \sigma_{ij}^{ac} - \sum_{jkbcd} \frac{1}{2} \langle \sigma_{jk}^{bc} || (al || jk) \sigma_{ij}^{cd} \]

\[ + \sum_{jkbcd} \frac{5}{12} \langle jk || bc \rangle \sigma_{ij}^{ac}\sigma_{ij}^{cd} - \sum_{jkbcd} \frac{1}{3} \langle jk || bc \rangle \sigma_{ij}^{ac}\sigma_{ij}^{cd} - \sum_{jkbcd} \frac{1}{3} \langle jk || bc \rangle \sigma_{ij}^{ac}\sigma_{ij}^{cd} - \sum_{jkbcd} \frac{1}{2} \langle \sigma_{jk}^{bc} || (cj || ib) \sigma_{jk}^{ba} \]
\[
- \sum_{jkb} \frac{1}{2} (\sigma^c_k) (\langle aj||kb \rangle \sigma^c_{ij} - \sum_{jkb} \frac{1}{3} (\sigma^b_{jk}) (\langle ab||ij \rangle \sigma^c_k - \sum_{jkb} \frac{1}{6} (\sigma^b_{jk}) (\langle bc||ji \rangle \sigma^c_k - \sum_{jkb} \frac{1}{6} (\sigma^b_{jk}) (\langle ab||kj \rangle \sigma^c_i \\
+ \sum_{jkb} \frac{1}{4} (\sigma^c_j) (\langle ac||bd \rangle \sigma^b_{ij} + \sum_{jkb} \frac{1}{4} (\sigma^b_k) (\langle jl||ik \rangle \sigma^b_{jl} \\
+ \sum_{jkb} \frac{1}{4} (\sigma^c_j) (\langle ac||bd \rangle \sigma^b_{ij} - \sum_{jkb} \frac{1}{2} (\sigma^c_j) (\langle ab||ij \rangle \sigma^b_k - \sum_{jkb} \frac{1}{2} (\sigma^c_j) (\langle kb||ij \rangle \sigma^c_k \\
+ \sum_{jkb} \frac{1}{2} (\sigma^c_j) (\langle ac||ib \rangle \sigma^b_j - \sum_{jkb} \frac{1}{2} (\sigma^c_j) (\langle ak||ij \rangle \sigma^b_k, \tag{24}

\]

and for \( \tilde{H}_{ab,ij} \)

\[
\tilde{H}^0_{ab,ij} = \tilde{H}^1_{ab,ij} + \tilde{H}^2_{ab,ij} = 0, \tag{25}
\]

\[
\tilde{H}^0_{ab,ij} = \langle ab||ij \rangle, \tag{26}
\]

\[
\tilde{H}^1_{ab,ij} = \sum_{c} f_{ac} \sigma^c_{ij} - \sum_{k} f_{ki} \sigma^b_{kj} + \frac{1}{2} \sum_{kl} (\langle kl||ij \rangle \sigma^c_{ij} + \frac{1}{2} \sum_{cd} (\langle ab||cd \rangle \sigma^d_{ij} + P(ij) P(ab) \sum_{kc} (\langle ak||ic \rangle \sigma^c_{jk} \\
- P(ab) \sum_{k} (\langle ka||ji \rangle \sigma^b_k + P(ij) \sum_{c} (\langle ab||ic \rangle \sigma^c_{ij}, \tag{27}
\]

\[
\tilde{H}^2_{ab,ij} = P(ij) P(ab) \sum_{kled} \frac{1}{3} (\langle kl||cd \rangle \sigma^c_{ij} \sigma^b_{kl} + \frac{1}{6} (\langle k||cd \rangle \sigma^d_{ij} \sigma^b_{kl} - P(ab) \sum_{kled} \frac{1}{3} (\langle kl||cd \rangle \sigma^d_{ij} \sigma^c_{kl} \\
- P(ij) \sum_{kled} \frac{1}{3} (\langle kl||cd \rangle \sigma^c_{ij} \sigma^b_{kl} + P(ij) P(ab) \sum_{kled} \frac{1}{3} (\langle cd||ij \rangle \sigma^c_{ij} \sigma^b_{kl} + \frac{1}{12} \sum_{kled} (\sigma^c_{kl}) (\langle ad||il \rangle \sigma^b_{ij} + \frac{1}{12} \sum_{kled} (\sigma^b_{kl}) (\langle cd||ij \rangle \sigma^d_{ij} \\
+ \sum_{kled} \frac{1}{12} (\sigma^c_{kl}) (\langle ab||kl \rangle \sigma^c_{ij} - P(ab) \sum_{kled} \frac{1}{6} (\sigma^c_{kl}) (\langle ad||ij \rangle \sigma^d_{ij} - P(ij) \sum_{kled} \frac{1}{6} (\sigma^c_{kl}) (\langle ab||il \rangle \sigma^d_{ij} \\
- P(ab) \sum_{kled} \frac{1}{6} (\sigma^c_{kl}) (\langle cb||kl \rangle \sigma^d_{ij} - P(ij) \sum_{kled} \frac{1}{6} (\sigma^d_{kl}) (\langle cd||kj \rangle \sigma^c_{ij} \\
- P(ij) \sum_{kled} (\sigma^c_{kl}) (\langle ck||lj \rangle \sigma^b_{ik} + P(ab) \sum_{kled} (\sigma^c_{kl}) (\langle bc||dl \rangle \sigma^b_{ik} + P(ij) \sum_{kled} \frac{1}{2} (\sigma^c_{kl}) (\langle ab||id \rangle \sigma^d_{ij} \\
- P(ab) \sum_{kled} \frac{1}{2} (\sigma^c_{kl}) (\langle ak||ij \rangle \sigma^b_{kl} + \sum_{kled} (\sigma^c_{kl}) (\langle ck||lj \rangle \sigma^b_{ik} + P(ij) \sum_{kled} (\sigma^c_{kl}) (\langle bk||li \rangle \sigma^c_{ik} \\
- P(ij) P(ab) \sum_{kled} (\sigma^c_{kl}) (\langle ac||dj \rangle \sigma^b_{il} - \sum_{kled} (\sigma^c_{kl}) (\langle ab||dl \rangle \sigma^b_{ij} - P(ij) \sum_{kled} (\langle kl||cj \rangle \sigma^c_{ij} \\
+ P(ab) \sum_{kled} (\langle kl||cd \rangle \sigma^b_{ij} - P(ij) P(ab) \sum_{kled} (\langle kl||cj \rangle \sigma^b_{il} + P(ij) P(ab) \sum_{kled} (\langle kb||cd \rangle \sigma^d_{ij} \sigma^c_{ik} \\
+ P(ij) \frac{1}{2} \sum_{kled} (\langle kl||ci \rangle \sigma^b_{kl} - P(ab) \frac{1}{2} \sum_{kled} (\langle ka||cd \rangle \sigma^d_{ik} \\
+ P(ab) \frac{1}{2} (\langle kl||ij \rangle \sigma^a_{ki} - P(ij) P(ab) \sum_{kled} (\langle ak||cj \rangle \sigma^b_{ik} + P(ij) \sum_{cd} \frac{1}{2} (\langle ab||cd \rangle \sigma^b_{ij} \\
- P(ab) \sum_{kled} \frac{1}{3} (\sigma^c_k) (\langle ac||ij \rangle \sigma^b_k - P(ij) \sum_{kled} \frac{1}{3} (\sigma^c_k) (\langle ab||ik \rangle \sigma^b_j. \tag{28}
\]

10
The qUCCSD scheme truncates $H_{ij}$, $H_{ab}$, and $H_{ia,bj}$ in the singles-singles block of the excited-state eigenvalue equations to up to the double commutators. The expressions for $\tilde{H}^0_{ij}^{\text{qUCCSD}}$ thus is given by

$$
\tilde{H}^0_{ij}^{\text{qUCCSD}} = H_{ij}^0 + H_{ij}^1 + H_{ij}^2,
$$

$$
\tilde{H}_{ij}^0 = f_{ij},
$$

$$
H_{ij}^1 = \frac{1}{4} \sum_{kab} (ik||ab)\sigma_{jk}^{ab} + \sum_{ka} (ik||ja)\sigma_{ja}^a + h.c.,
$$

$$
H_{ij}^2 = \left( \sum_{klabc} \frac{1}{2} (\sigma_{kl}^{bc})^* (ic||al)\sigma_{jk}^{ab} + \sum_{klmab} \frac{1}{8} (\sigma_{kl}^{ab})^* (im||kl)\sigma_{jm}^{ab} + h.c. \right) - \sum_{kklmab} \frac{1}{2} (\sigma_{kl}^{ab})^* (im||jl)\sigma_{km}^{ab}
$$

$$
+ \sum_{klabc} \frac{1}{2} (\sigma_{kl}^{ac})^* (ic||jb)\sigma_{ja}^b
$$

$$
+ \left( \sum_{kabc} \frac{1}{4} (\sigma_{k}^{b})^* (ib||ac)\sigma_{jk}^{ac} - \sum_{klab} \frac{1}{2} (\sigma_{k}^{b})^* (il||ak)\sigma_{jl}^{ab} + \sum_{klab} \frac{1}{2} (\sigma_{i}^{c})^* (ik||ja)\sigma_{kl}^{ab} + h.c. \right)
$$

$$
+ \left( \sum_{kab} \frac{5}{12} (ik||ab)\sigma_{jk}^{ab} + \sum_{kab} \frac{1}{2} (\sigma_{k}^{c})^* (ib||ak)\sigma_{j}^{a} + h.c. \right) - \sum_{kla} (\sigma_{i}^{c})^* (ik||jl)\sigma_{k}^{a}
$$

$$
+ \sum_{kab} (\sigma_{k}^{c})^* (ia||jb)\sigma_{ja}^{b}.
$$

Similarly, $\tilde{H}_{ab}^{\text{qUCCSD}}$ and $\tilde{H}_{ia,bj}^{\text{qUCCSD}}$ can be written as

$$
\tilde{H}_{ab}^{\text{qUCCSD}} = H_{ab}^0 + H_{ab}^1 + H_{ab}^2,
$$

$$
\tilde{H}_{ab}^0 = f_{ab},
$$

$$
H_{ab}^1 = \left( - \sum_{i} \frac{1}{4} (ij||bc)\sigma_{ij}^{ac} + \sum_{ic} (ai||bc)\sigma_{i}^{c} + h.c. \right),
$$

$$
H_{ab}^2 = \left( - \sum_{ijklcd} \frac{1}{2} (\sigma_{ijkl}^{cd})^* (kd||bj)\sigma_{ik}^{ca} - \sum_{ijcd} \frac{1}{8} (\sigma_{ij}^{cd})^* (df||cb)\sigma_{ij}^{ac} + h.c. \right) + \sum_{ijcd} \frac{1}{2} (\sigma_{ij}^{cd})^* (ad||bc)\sigma_{ij}^{fc}
$$

$$
- \frac{1}{2} \sum_{ijkcd} (\sigma_{ijkl}^{cd})^* (ka||jb)\sigma_{ik}^{cd}
$$

$$
+ \left( \sum_{ijkc} \frac{1}{4} (\sigma_{ij}^{c})^* (ik||bj)\sigma_{ik}^{ac} - \sum_{ijcd} \frac{1}{2} (\sigma_{ij}^{c})^* (ic||bd)\sigma_{ij}^{ad} + \sum_{ijcd} \frac{1}{2} (\sigma_{ij}^{c})^* (ia||cb)\sigma_{ij}^{ad} + h.c. \right)
$$

$$
+ \left( - \frac{5}{12} \sum_{ijc} (ij||bc)\sigma_{ij}^{ac} - \sum_{ijc} \frac{1}{2} (\sigma_{ij}^{c})^* (ic||bj)\sigma_{ij}^{a} + h.c. \right) - \sum_{ijc} (\sigma_{ij}^{c})^* (ja||ib)\sigma_{ij}^{c}
$$

$$
+ \sum_{icd} (\sigma_{ij}^{c})^* (ad||bc)\sigma_{ij}^{c},
$$

11
and

$$H_{ia,bj}^{\text{qUCCSD}} = H_{ia,bj}^0 + H_{ia,bj}^1 + H_{ia,bj}^2,$$  \hspace{1cm} (37)

$$H_{ia,bj}^0 = \langle ia||bj \rangle,$$  \hspace{1cm} (38)

$$H_{ia,bj}^1 = \frac{1}{2} \sum_{kc} (\sigma_{ik}^{bc}) \langle ac||jk \rangle + \sum_c \langle ai||cb \rangle \sigma_j^c - \sum_k \langle ki||jb \rangle \sigma_k^a + \text{h.c.},$$  \hspace{1cm} (39)

$$H_{ia,bj}^2 = \left( \frac{1}{4} \sum_{klmc} (\sigma_{kl}^{bd}) \langle im||kl \rangle \sigma_{jm}^{ac} + \frac{1}{4} \sum_{kced} (\sigma_{ik}^{ce}) \langle ce||bd \rangle \sigma_{jk}^{ad} - \frac{1}{2} \sum_{kled} (\sigma_{ik}^{cd}) \langle lc||kb \rangle \sigma_{jl}^{ad} 
- \frac{1}{2} \sum_{kled} (\sigma_{il}^{cd}) \langle ka||bl \rangle \sigma_{lj}^{cd} 
- \sum_{kled} (\sigma_{il}^{bd}) \langle ia||kc \rangle \sigma_{jl}^{cd} + \text{h.c.} \right) 
+ \sum_{klmc} (\sigma_{ik}^{bc}) \langle ik||lj \rangle \sigma_{km}^{ac} + \sum_{kced} (\sigma_{ik}^{de}) \langle ad||cb \rangle \sigma_{jk}^{ce} + \frac{1}{2} \sum_{kled} (\sigma_{ik}^{cd}) \langle ka||bl \rangle \sigma_{lk}^{cd} 
+ \frac{1}{2} \sum_{kled} (\sigma_{il}^{cd}) \langle ic||dj \rangle \sigma_{lk}^{ad} 
+ \left( -\frac{1}{2} \sum_{kld} (\sigma_{il}^{d}) \langle ik||bj \rangle \sigma_{kl}^{ac} + \frac{1}{2} \sum_{kld} (\sigma_{ik}^{d}) \langle ia||bc \rangle \sigma_{jk}^{ad} - \frac{1}{2} \sum_{kld} (\sigma_{ik}^{d}) \langle il||bk \rangle \sigma_{jl}^{ac} 
+ \frac{1}{2} \sum_{kld} (\sigma_{il}^{d}) \langle id||bc \rangle \sigma_{jk}^{ac} + \frac{1}{2} \sum_{kld} (\sigma_{ik}^{d}) \langle kd||cb \rangle \sigma_{jk}^{ac} - \frac{1}{2} \sum_{kld} (\sigma_{il}^{d}) \langle kl||kc \rangle \sigma_{jk}^{ac} 
- \frac{1}{4} \sum_{kld} (\sigma_{il}^{d}) \langle kl||bj \rangle \sigma_{lk}^{ac} + \frac{1}{2} \sum_{kld} (\sigma_{ik}^{d}) \langle ik||cj \rangle \sigma_{lk}^{ac} - \frac{1}{4} \sum_{kld} (\sigma_{ik}^{d}) \langle ia||cd \rangle \sigma_{lj}^{ac} 
- \frac{1}{2} \sum_{kld} (\sigma_{il}^{d}) \langle ka||bc \rangle \sigma_{lk}^{ad} + \text{h.c.} \right) 
+ \left( -\frac{2}{3} \sum_{kc} (\sigma_{ik}^{b}) \langle ic||bj \rangle \sigma_{kc}^a - \frac{1}{2} \sum_{kc} (\sigma_{ik}^{c}) \langle ic||bj \rangle \sigma_{kc}^a - \frac{1}{2} \sum_{kc} (\sigma_{ik}^{c}) \langle ia||bk \rangle \sigma_{kc}^c 
- \sum_{kc} (\sigma_{ik}^{b}) \langle ia||kc \rangle \sigma_{kc}^c + \text{h.c.} \right) + \sum_{kl} (\sigma_{ik}^{d}) \langle ik||lj \rangle \sigma_{lk}^a + \sum_{cd} (\sigma_{ik}^{d}) \langle ad||cb \rangle \sigma_{lk}^c, $$  \hspace{1cm} (40)

respectively. $H_{ab,ci}, H_{ia,kj}, H_{ibs,aik}$ are involved in the singles-doubles and doubles-singles block. They are truncated up to single commutators, i.e., $H_{ab,ci}^{\text{qUCCSD}}$ is given by

$$H_{ab,ci}^{\text{qUCCSD}} = H_{ab,ci}^0 + H_{ab,ci}^1,$$  \hspace{1cm} (41)

$$H_{ab,ci}^0 = \langle ab||ci \rangle,$$  \hspace{1cm} (42)

$$H_{ab,ci}^1 = P(ab) \sum_{jd} \langle aj||cd \rangle \sigma_{ij}^{bd} + \frac{1}{2} \sum_{kj} \langle jk||ci \rangle \sigma_{jk}^{ab} - \frac{1}{2} \sum_{j} (\sigma_{ij}^{*}) \langle ab||ji \rangle$$
\[
\hat{H}^{\text{qUCCSD}}_{ia,jk} = \hat{H}^{0}_{ia,jk} + \hat{H}^{1}_{ia,jk},
\]
\[
\hat{H}^{0}_{ia,jk} = \langle ia||jk \rangle, \tag{44}
\]
\[
\hat{H}^{1}_{ia,jk} = P(jk) \sum_{lb} \langle il||jb \rangle \sigma_{kl}^{ab} + \frac{1}{2} \sum_{bc} \langle ia||bc \rangle \sigma_{jk}^{bc} + \frac{1}{2} \sum_b (\sigma_i^b)^* \langle ba||jk \rangle 
- \sum_l \langle il||jk \rangle \sigma_l^a + P(jk) \sum_b \langle ai||bj \rangle \sigma_b^k, \tag{46}
\]
and the three-body term takes the form
\[
\hat{H}^{\text{qUCCSD}}_{ibc,ajk} = -P(jk) \sum_{il} \langle il||aj \rangle \sigma_{ij}^{ab} + P(bc) \sum_d \langle ib||ad \rangle \sigma_{jk}^{dc}. \tag{47}
\]

The contributions from this three-body term to the excited-state eigenvalue equation is evaluated using the efficient algorithms similar to those within the EOM-CCSD method, i.e., for the evaluation of the contribution \(\sum_{jkbc} \hat{H}^{\text{qUCCSD}}_{ibc,ajk} C_{ibc,ajk}\) to the singles residue one first contracts \(C_{ibc,ajk}\) with \(\sigma_{bc}^{kl}\) or \(\sigma_{dc}^{jk}\) to form one-body intermediates, while for the evaluation of the contribution \(\sum_{jkbc} \hat{H}^{\text{qUCCSD}}_{ibc,ajk} C_i^{ab}\) to the doubles residue one first contracts \(C_i^{ab}\) with \(\langle il||aj \rangle\) or \(\langle ib||ad \rangle\) to form one-body intermediates.

\(\hat{H}_{ij,kl}\) and \(\hat{H}_{ab,cd}\) contribute to the doubles-doubles block and in the qUCCSD scheme comprise only the bare Hamiltonian integral
\[
\hat{H}^{\text{qUCCSD}}_{ij,kl} = \langle ij||kl \rangle, \quad \hat{H}^{\text{qUCCSD}}_{ab,cd} = \langle ab||cd \rangle. \tag{48}
\]

Note that the qUCCSD scheme also uses the bare Hamiltonian integrals for \(\hat{H}_{ij}\), \(\hat{H}_{ab}\), and \(\hat{H}_{ia,bj}\) in the calculations of the contributions from \(\hat{H}_{DD}\) to the excited-state equations. \(\hat{H}_{ia,jcd}\) and \(\hat{H}_{ija,klb}\) do not contribute to the qUCCSD working equations.

The qUCCSD ground-state amplitude equations are solved using the same iterative procedure as CCSD, while the excited-state eigenvalue equations are solved using the Davidson algorithms. qUCCSD and CCSD or EOM-CCSD share “particle-particle ladder contractions” of the type \(\sum_{cd} \langle ab||cd \rangle \sigma_{ij}^{cd}\) with a \(N_o^2 N_v^4\) scaling and “ring contraction” of the type \(\sum_{kc} \langle ak||ic \rangle \sigma_{jk}^{bc}\) or \(\sum_{kc} \langle ik||ac \rangle \sigma_{jk}^{bc}\) with a \(N_o^3 N_v^3\) scaling, in which \(N_o\) and \(N_v\) represent the number of occupied and virtual orbitals, as the most time-consuming steps. The qUCCSD ground-state amplitude equations involve one particle-particle ladder contraction and four
ring contractions per iteration, to be compared with one particle-particle ladder contraction and two ring contractions in CCSD. Overall, the computing time of a qUCCSD ground-state calculation is expected to be around twice that of a CCSD calculations. The qUCCSD excited-state eigenvalue equations share the same particle-particle ladder and ring contractions as EOM-CCSD and thus have essentially identical computational cost per iteration as EOM-CCSD.

III. COMPUTATIONAL DETAILS

The qUCCSD method for the calculations of ground-state energies and excitation energies as detailed in Section II.C have been implemented in the X2CSOCC module of the CFOUR program on top of the previous implementation of the UCC3 method. In order to demonstrate the accuracy of the qUCCSD method for challenging ground-state problems, qUCCSD calculations for the equilibrium structures and harmonic frequencies of CuH, CuF, and O atoms using cc-pVTZ basis sets have been carried out and compared with the corresponding results obtained from CCSD, UCC(4), and UCC3 calculations. The copper-containing molecules have been chosen as examples with strong orbital-relaxation effects that have been shown to be difficult to treat using approximate variants of CC methods. The calculations of structural parameters for the ozone molecule, especially the vibrational frequency for the asymmetric stretching mode and the ordering of the asymmetric and symmetric stretching frequencies, played an important role in establishing the CCSD and CCSD(T) methods. In spite of a certain degree of diradical character in ozone, CCSD and CCSD(T) can provide qualitatively correct results. It is important for a UCC method with a truncation of the commutator expansion to have this robustness.

The classic benchmark set compiled by Trofimov et al. consisting of excitation energies in H₂O, HF, N₂, Ne, CH₂, BH, and C₂ have been used to demonstrate the accuracy of qUCCSD excitation energies. We have used the same structures and basis sets as in the previous calculations summarized in the footnotes and of Ref. The full configuration interaction (FCI) excitation energies have been given as reference values. The results obtained using EOM-CCSD, ADC(3), and UCC3 methods with the same computational scaling as qUCCSD have also been presented for comparison. We mention that the CC3 method includes an iterative treatment of triple excitations and thus is in general
more accurate but at the same time more time consuming than the qUCCSD method. Here H$_2$O, HF, N$_2$, and Ne serve as example molecules for which the perturbation series converge smoothly, and CH$_2$, BH, and C$_2$ as examples in the absence of a smooth convergence of the ADC series. We focus our discussion on the improvement of the performance of qUCCSD over the previous UCC3 method.

Although general characterization of same-symmetry conical intersections using qUCCSD will have to wait for the implementation of analytic gradients and derivative coupling, it is worthwhile mentioning that the hermitian nature of qUCCSD enables the description of degeneracies between electronic states. As an example, we have enclosed in the Supporting Information a qUCCSD calculation of potential energy surfaces in the immediate vicinity of one of the conical intersection point between the $2^1A_1$ and $3^1A_1$ states of the HOF molecule. The qUCCSD calculations show the correct degeneracy at the intersecting point and the correct linear behavior of the electronic energies with respect to the displacements. In contrast, EOM-CCSD calculations produce complex eigenvalues when the energies of these two state are within 0.03 eV of each other.

IV. RESULTS AND DISCUSSIONS

A. Equilibrium structures and harmonic frequencies for CuH, CuF, and O$_3$

Copper-containing molecules serve as excellent avenues to test the robustness for approximate many-body methods. They exhibit significant orbital-relaxation effects, e.g., the largest CCSD singles amplitudes in CuH and CuF amount to around 0.06. On the other hand, the wavefunctions are dominated by a single determinant and the CCSD and CCSD(T) methods can provide accurate results for properties of CuH and CuF, e.g., as shown in Refs. 102,103,124. Here we focus our discussion on the assessment of the qUCCSD, UCC3, and UCC(4) results using the CCSD results as the reference values. As shown in Table II, the UCC3 and UCC(4) results exhibit large discrepancies compared with the CCSD ones, e.g., the UCC3 harmonic frequency of 739 cm$^{-1}$ for CuF is more than 100 cm$^{-1}$ greater than the CCSD value of 609 cm$^{-1}$. In contrast, the qUCCSD results agree closely with the CCSD values, with the deviations in frequencies amounting to 8 cm$^{-1}$ for CuH and 2 cm$^{-1}$ for CuF. Interestingly, the UCC3 and UCC(4) calculations of CuH and CuF produced sin-
gles amplitudes larger than 0.2. This might be attributed to that UCC3 and UCC(4) have only linear terms involving single excitations in the amplitude equations, which results in larger $t_1$ amplitudes when attempting to account for the large orbital-relaxation effects. It thus is essential to include the quadratic terms involving single excitations in the amplitude equations to obtain robust performance.

Ozone is a classic molecule for testing the accuracy of electronic-structure methods. In particular, the asymmetric stretching frequencies, $\omega_3$, of $O_3$ is very sensitive to the treatment of electron correlation. For example, calculations of $\omega_3$ demonstrated the importance of the fifth-order contribution in the noniterative triples correction of the CCSD(T) method. Although the ground state of ozone possesses certain degree of biradical character, i.e., the largest $t_2$ amplitude amount to around 0.2, the CCSD and CCSD(T) methods can provide quite accurate equilibrium structures and vibrational frequencies. As shown in Table the UCC3 and UCC(4) calculations provide inaccurate results for the structures and harmonic frequencies of ozone. UCC3 grossly overestimated $\omega_3$ and UCC(4) produced an imaginary harmonic frequency for this mode. The qUCCSD method obtained structures and vibrational frequencies in close agreement with the CCSD results, demonstrating the robustness of the commutator truncation scheme. As expected, the qUCCSD results is slightly worse than the CCSD ones, with the latter obtaining the correct ordering of $\omega_2$ and $\omega_3$. The inclusion of higher commutators is expected to further improve the performance over qUCCSD.

B. Excitation energies of $H_2O$, HF, $N_2$, and Ne

We use $H_2O$, HF, $N_2$, and Ne as examples for which the Möller-Plesset perturbation series converge smoothly. The excitation energies for these molecules computed using the qUCCSD method are summarized in Tables together with the corresponding FCI, ADC(3), UCC3, and EOM-CCSD values. Here we use the FCI values as the reference and give the other results as the deviation from the FCI values. The balanced inclusion of high-order terms in the qUCCSD scheme provides uniformly better excitation energies than UCC3. The mean absolute deviations of the qUCCSD results amount to 0.12 eV for $H_2O$, 0.13 eV for HF, 0.19 eV for $N_2$, and 0.18 eV for Ne, which exhibit consistent improvement compared with the UCC3 values of 0.16 eV for $H_2O$, 0.19 eV for HF, 0.21 eV for $N_2$, and 0.22 eV for Ne. The
performance of qUCCSD for these molecules is similar to that of EOM-CCSD. The absolute mean deviations of the qUCCSD results with respect to FCI values are slightly larger than those of EOM-CCSD for H\textsubscript{2}O (by 0.04 eV) and N\textsubscript{2} (by 0.06 eV) and slightly smaller for HF (by 0.03 eV) and Ne (by 0.03 eV).

### C. Excitation energies of CH\textsubscript{2}, BH, and C\textsubscript{2}

The computed vertical excitation energies for CH\textsubscript{2} and BH are summarized in Table VI-VII as examples of simple molecules for which the ADC series do not converge smoothly\textsuperscript{84}. Here the mean and maximum absolute deviations of the ADC(3) method with respect to the FCI values are much larger than for the molecules in the previous subsection. UCC3 provides better results perhaps because of the iterative solutions of the ground-state amplitude equations\textsuperscript{83}. The performance of qUCCSD is similar to that of UCC3 for BH and CH\textsubscript{2}. The mean absolute deviation of the qUCCSD excitation energies with respect to the FCI results amount to 0.07 eV for CH\textsubscript{2} and 0.11 eV for BH, to be compared with 0.07 eV and 0.12 eV in the case of UCC3. The mean absolute deviations of qUCCSD are still greater than those of EOM-CCSD, by 0.05 eV for CH\textsubscript{2} and by 0.06 eV for BH.

The ground state of the C\textsubscript{2} molecule has a certain degree of biradical character with the largest \(t_2\) amplitude amounting to more than 0.2. The calculations of excitation energies for C\textsubscript{2} thus serves as a challenging test for the present truncated UCC-based polarization propagator methods. As shown in Table VIII, the absolute deviation of the qUCCSD vertical excitation energies with respect to the FCI values amount to 0.38 eV for the \(^1\Pi_u\) state, 0.53 eV for the \(^1\Sigma_u^+\) state, 0.54 eV for the \(^3\Pi_u\) state and 0.65 eV for the \(^3\Sigma_u^+\) state. These are significantly more accurate than the UCC3 values with errors as large as 0.64 eV, 1.02 eV, 0.74 eV, and 0.88 eV for \(^1\Pi_u\), \(^1\Sigma_u^+\), \(^3\Pi_u\), and \(^3\Sigma_u^+\), respectively. As expected, the qUCCSD method is still not as accurate as the EOM-CCSD method for the excitation energies for C\textsubscript{2}. On the other hand, the significant improvement of qUCCSD over UCC3 indicates that the commutator truncation scheme offers a promising pathway to obtain robust practical UCC-based methods; the inclusion of triple and higher commutators is expected to further improve the accuracy of the method.
V. SUMMARY AND OUTLOOK

We develop a self-consistent polarization propagator method using a quadratic unitary coupled-cluster singles and doubles (qUCCSD) parameterization for the ground state wave-function and the excitation manifold. Benchmark calculations of ground-state properties and excitation energies for representative small molecules show that the qUCCSD scheme using a commutator truncation scheme exhibits a uniform improvement of the accuracy and robustness over the previous UCC3 method derived using Møller-Plesset perturbation theory. The future work will be focused on an implementation of the qUCCSD scheme and its analytic gradients and derivative coupling within tensor contraction engines well developed for the non-relativistic CC machinery to enable extensive molecular applications and the development of a cubic UCCSD (cUCCSD) scheme, i.e., the UCCSD[3|3,2,1] scheme, to further improve the accuracy and robustness.

VI. ACKNOWLEDGEMENT

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VII. DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the article.
TABLE I. Computed equilibrium bond lengths (in Å), bond angle (in degree), and harmonic frequencies (in cm$^{-1}$) of CuH, CuF, and O$_3$. The cc-pVTZ basis sets were used for all the calculations presented here. The 1$s$ electrons of O and 1$s$, 2$s$, 2$p$, 3$s$, 3$p$ electrons of Cu have been kept frozen in the electron-correlation calculations.

| method   | CuH | CuF | O$_3$ |
|----------|-----|-----|------|
|          | $R_{\text{Cu-H}}$ | $\omega_e$ | $R_{\text{Cu-F}}$ | $\omega_e$ | $R_{\text{O-O}}$ | $\theta$ | $\omega_{1,e}(a_1)$ | $\omega_{2,e}(a_1)$ | $\omega_{3,e}(b_2)$ |
| UCC(4)   | 1.4616 | 2052 | 1.6998 | 646 | 1.3142 | 117.1 | 560 | 876 | 1922i |
| UCC3     | 1.4877 | 1948 | 1.7367 | 739 | 1.2659 | 117.9 | 674 | 1033 | 4698 |
| qUCCSD   | 1.4891 | 1829 | 1.7686 | 607 | 1.2488 | 117.5 | 767 | 1279 | 1314 |
| CCSD     | 1.4888 | 1837 | 1.7669 | 609 | 1.2499 | 117.6 | 763 | 1278 | 1266 |
TABLE II. Computed vertical excitation energies (in eV) of the H$_2$O molecule. The UCC3, qUCCSD, ADC(3), and CCSD values are presented as the differences relative to the corresponding FCI values. $\bar{\Delta}_{\text{abs}}$ and $\Delta_{\text{max}}$ denote the mean absolute error and maximum absolute error relative to the FCI results, respectively. The 1s electrons of O have been kept frozen in the electron-correlation calculations.

| State | FCI$^a$ | ADC(3)$^b$ | UCC3 | qUCCSD | CCSD$^a$ |
|-------|--------|------------|------|--------|----------|
| $2^1A_1$ | 9.87   | 0.14       | 0.20 | 0.13   | -0.07    |
| $1^1B_1$ | 7.45   | 0.13       | 0.18 | 0.14   | -0.07    |
| $1^1B_2$ | 11.61  | 0.18       | 0.23 | 0.15   | -0.09    |
| $1^1A_2$ | 9.21   | 0.17       | 0.20 | 0.15   | -0.09    |
| $1^3B_1$ | 7.06   | 0.09       | 0.14 | 0.11   | -0.08    |
| $1^3A_2$ | 9.04   | 0.14       | 0.19 | 0.14   | -0.08    |
| $1^3A_1$ | 9.44   | 0.10       | 0.15 | 0.10   | -0.08    |
| $2^3A_1$ | 10.83  | 0.01       | 0.04 | 0.06   | -0.11    |
| $2^3B_1$ | 11.05  | 0.11       | 0.14 | 0.11   | -0.09    |
| $1^3B_2$ | 11.32  | 0.13       | 0.17 | 0.11   | -0.08    |
| $\bar{\Delta}_{\text{abs}}$ | -      | 0.12       | 0.16 | 0.12   | 0.08     |
| $\Delta_{\text{max}}$ | -      | 0.18       | 0.23 | 0.15   | 0.11     |

$^a$ Results for the singlet states are from Ref. 121 and those for the triplet states are from Ref. 122.

$^b$ Ref. 84
TABLE III. Computed vertical excitation energies (in eV) of the HF molecule. The difference of ADC(3), UCC(3), qUCCSD, and CCSD results relative to the corresponding FCI values are presented. $\bar{\Delta}_{\text{abs}}$ and $\Delta_{\text{max}}$ denote the mean absolute error and maximum absolute error relative to the FCI results, respectively. The 1s electrons of F have been kept frozen in the electron-correlation calculations.

| State | FCI<sup>a</sup> | ADC(3)<sup>b</sup> | UCC3 | qUCCSD | CCSD<sup>a</sup> |
|-------|-----------------|------------------|------|--------|-----------------|
| 1 $^1\Pi$ | 10.44 | 0.18 | 0.23 | 0.15 | -0.14 |
| 2 $^1\Pi$ | 14.21 | 0.19 | 0.23 | 0.16 | -0.15 |
| 2 $^1\Sigma^+$ | 14.58 | 0.10 | 0.17 | 0.07 | -0.11 |
| 1 $^1\Delta$ | 15.20 | 0.12 | 0.16 | 0.12 | -0.17 |
| 1 $^1\Sigma^-$ | 15.28 | 0.12 | 0.15 | 0.12 | -0.18 |
| 3 $^1\Pi$ | 15.77 | 0.23 | 0.25 | 0.17 | -0.18 |
| 3 $^1\Sigma^+$ | 16.43 | 0.37 | 0.36 | 0.24 | -0.14 |
| 1 $^3\Pi$ | 10.04 | 0.14 | 0.20 | 0.13 | -0.15 |
| 1 $^3\Sigma^+$ | 13.54 | 0.05 | 0.09 | 0.02 | -0.13 |
| 2 $^3\Pi$ | 14.01 | 0.19 | 0.23 | 0.16 | -0.16 |
| 2 $^3\Sigma^+$ | 14.46 | 0.07 | 0.11 | 0.09 | -0.21 |
| 1 $^3\Delta$ | 14.93 | 0.10 | 0.13 | 0.11 | -0.19 |
| 1 $^3\Sigma^-$ | 15.25 | 0.12 | 0.16 | 0.12 | -0.18 |
| 3 $^3\Pi$ | 15.57 | 0.22 | 0.25 | 0.17 | -0.19 |
| $\bar{\Delta}_{\text{abs}}$ | – | 0.16 | 0.19 | 0.13 | 0.16 |
| $\Delta_{\text{max}}$ | – | 0.37 | 0.36 | 0.24 | 0.21 |

<sup>a</sup> Ref. 122
<sup>b</sup> Ref. 84
TABLE IV. Computed vertical excitation energies (in eV) of the N$_2$ molecule. The ADC(3), UCC3, qUCCSD, and CCSD values are presented as the differences relative to the corresponding FCI values. $\bar{\Delta}_{\text{abs}}$ and $\Delta_{\text{max}}$ denote the mean absolute error and maximum absolute error relative to the FCI results, respectively. The 1s electrons of N have been kept frozen in the electron-correlation calculations.

| State | FCI$^a$ | ADC(3)$^b$ | UCC3 | qUCCSD | CCSD$^a$ |
|-------|--------|------------|------|--------|---------|
| 1 $^1\Pi_g$ | 9.58 | -0.17 | -0.08 | -0.06 | 0.08 |
| 1 $^1\Sigma_u^-$ | 10.33 | -0.33 | -0.27 | -0.23 | 0.14 |
| 1 $^1\Delta_u$ | 10.72 | -0.37 | -0.25 | -0.21 | 0.18 |
| 1 $^1\Pi_u$ | 13.61 | -0.23 | -0.25 | -0.29 | 0.40 |
| 1 $^3\Sigma_u^+$ | 7.90 | -0.19 | -0.26 | -0.24 | -0.02 |
| 1 $^3\Pi_g$ | 8.16 | -0.29 | -0.13 | -0.11 | 0.06 |
| 1 $^3\Delta_u$ | 9.19 | -0.27 | -0.27 | -0.24 | 0.07 |
| 1 $^3\Sigma_u^-$ | 10.00 | -0.29 | -0.25 | -0.22 | 0.19 |
| 1 $^3\Pi_u$ | 11.44 | -0.19 | -0.11 | -0.12 | 0.10 |
| $\bar{\Delta}_{\text{abs}}$ | – | 0.26 | 0.21 | 0.19 | 0.13 |
| $\Delta_{\text{max}}$ | – | 0.37 | 0.27 | 0.29 | 0.40 |

$^a$ Results for the singlet states are from Ref. [121] and those for the triplet states are from Ref. [122].

$^b$ Ref. [84]
TABLE V. Computed vertical excitation energies (in eV) of the Ne atom. The ADC(3), UCC3, qUCCSD, and CCSD values are presented as the differences relative to the corresponding FCI values. $\bar{\Delta}_{\text{abs}}$ and $\Delta_{\text{max}}$ denote the mean absolute error and maximum absolute error relative to the FCI results, respectively. The 1s electrons of Ne have been kept frozen in the electron-correlation calculations.

| State | FCI$^a$ | ADC(3)$^b$ | UCC3 | qUCCSD | CCSD$^a$ |
|-------|---------|------------|------|--------|----------|
| $1 \, ^1P$ | 16.40 | 0.17 | 0.16 | 0.14 | -0.24 |
| $1 \, ^1D$ | 18.21 | 0.18 | 0.18 | 0.15 | -0.25 |
| $2 \, ^1P$ | 18.26 | 0.18 | 0.17 | 0.15 | -0.25 |
| $2 \, ^1S$ | 18.48 | 0.27 | 0.27 | 0.20 | -0.24 |
| $3 \, ^1S$ | 44.05 | 0.35 | 0.35 | 0.32 | -0.17 |
| $1 \, ^3P$ | 18.70 | 0.13 | 0.16 | 0.11 | -0.24 |
| $1 \, ^3S$ | 19.96 | 0.10 | 0.13 | 0.10 | -0.26 |
| $1 \, ^3D$ | 20.62 | 0.13 | 0.17 | 0.12 | -0.23 |
| $2 \, ^3P$ | 20.97 | 0.13 | 0.17 | 0.12 | -0.24 |
| $2 \, ^3S$ | 45.43 | 0.40 | 0.44 | 0.36 | -0.10 |
| $\bar{\Delta}_{\text{abs}}$ | – | 0.20 | 0.22 | 0.18 | 0.22 |
| $\Delta_{\text{max}}$ | – | 0.40 | 0.44 | 0.36 | 0.25 |

$^a$ Results for the singlet states are from Ref. 120 and those for the triplet states are from Ref. 122.

$^b$ Ref. 84
TABLE VI. Computed vertical excitation energies (in eV) of the CH$_2$ molecule. The ADC(3), UCC3, qUCCSD, and CCSD values are presented as the differences relative to the corresponding FCI values. $\bar{\Delta}_{\text{abs}}$ and $\Delta_{\text{max}}$ denote the mean absolute error and maximum absolute error relative to the FCI results, respectively.

| State   | FCI$^a$ | ADC(3)$^b$ | UCC3  | qUCCSD | CCSD$^a$ |
|---------|---------|------------|-------|--------|----------|
| 3 $^1$A$_1$ | 6.51   | -0.31      | -0.05 | -0.06  | -0.01    |
| 4 $^1$A$_1$ | 8.48   | -0.29      | -0.04 | -0.04  | -0.02    |
| 1 $^1$B$_2$ | 7.70   | -0.24      | 0.01  | 0.01   | 0.01     |
| 1 $^1$B$_1$ | 1.79   | -0.55      | -0.10 | -0.11  | -0.01    |
| 1 $^1$A$_2$ | 5.85   | -0.42      | -0.09 | -0.08  | 0.01     |
| 1 $^3$A$_1$ | 6.39   | -0.31      | -0.06 | -0.06  | -0.01    |
| 2 $^3$A$_1$ | 8.23   | -0.38      | -0.09 | -0.08  | -0.03    |
| 3 $^3$A$_1$ | 9.84   | -0.31      | -0.07 | -0.08  | 0.01     |
| 2 $^3$B$_2$ | 7.70   | -0.31      | -0.06 | -0.06  | -0.06    |
| 1 $^3$B$_1$ | -0.01  | -0.61      | -0.14 | -0.13  | -0.03    |
| 2 $^3$B$_1$ | 8.38   | -0.41      | -0.02 | -0.02  | 0.01     |
| 1 $^3$A$_2$ | 4.79   | -0.44      | -0.10 | -0.10  | 0.00     |
| $\bar{\Delta}_{\text{abs}}$ | –      | 0.38       | 0.07  | 0.07   | 0.02     |
| $\Delta_{\text{max}}$ | –      | 0.61       | 0.14  | 0.13   | 0.06     |

$^a$ Results for the singlet states are from Ref. 120 and those for the triplet states are from Ref. 123.

$^b$ Ref. 84.
TABLE VII. Computed vertical excitation energies (in eV) of the BH molecule. The ADC(3), UCC3, qUCCSD, and CCSD values are presented as the differences relative to the corresponding FCI values. $\bar{\Delta}_{\text{abs}}$ and $\Delta_{\text{max}}$ denote the mean absolute error and maximum absolute error relative to the FCI results, respectively.

| State   | FCI$^a$ | ADC(3)$^b$ | UCC3  | qUCCSD | CCSD$^a$ |
|---------|---------|------------|-------|--------|----------|
| 1 $^1\Pi$ | 2.94    | -0.61      | -0.10 | -0.10  | 0.02     |
| 2 $^1\Sigma^+$ | 6.38   | -0.43      | -0.07 | -0.07  | 0.04     |
| 2 $^1\Pi$   | 7.47    | -0.51      | -0.14 | -0.11  | 0.04     |
| 4 $^1\Sigma^+$ | 7.56   | -0.54      | -0.16 | -0.13  | 0.19     |
| 3 $^1\Pi$   | 8.24    | -0.50      | -0.15 | -0.12  | 0.04     |
| 1 $^3\Pi$   | 1.31    | -0.62      | -0.11 | -0.10  | -0.01    |
| 1 $^3\Sigma^+$ | 6.26   | -0.47      | -0.10 | -0.10  | 0.03     |
| 2 $^3\Sigma^+$ | 7.20   | -0.49      | -0.10 | -0.09  | 0.02     |
| 2 $^3\Pi$   | 7.43    | -0.51      | -0.14 | -0.13  | 0.00     |
| 3 $^3\Sigma^+$ | 7.62   | -0.52      | -0.14 | -0.13  | 0.05     |
| 3 $^3\Pi$   | 7.92    | -0.45      | -0.12 | -0.15  | 0.08     |
| $\bar{\Delta}_{\text{abs}}$ | –       | 0.51       | 0.12  | 0.11   | 0.05     |
| $\Delta_{\text{max}}$   | –       | 0.62       | 0.16  | 0.15   | 0.19     |

$^a$ Results for the singlet states are from Ref. 120 and those for the triplet states are from Ref. 122.

$^b$ Ref. 84
TABLE VIII. Computed vertical excitation energies (in eV) of the C$_2$ molecule. The UCC3, qUCCSD, and CCSD results are given as the difference relative to the corresponding FCI values. The 1s electrons of C have been kept frozen in the electron-correlation calculation.

| State   | FCI$^a$ | UCC3 | qUCCSD | CCSD$^a$ |
|---------|---------|------|--------|----------|
| $^1\Pi_u$ | 1.39    | -0.64 | -0.38  | 0.09     |
| $^1\Sigma^+_u$ | 5.60    | -1.02 | -0.53  | 0.20     |
| a$^3\Pi_u$ | 0.31    | -0.74 | -0.54  | -0.03    |
| c$^3\Sigma^+_u$ | 1.21    | -0.88 | -0.65  | -0.44    |

$^a$ Results for the singlet states are from Ref. 121 and those for the triplet states are from Ref. 122.
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