

Quadratic Unitary Coupled-Cluster Singles and Doubles Scheme: Efficient Implementation, Benchmark Study, and Formulation of an Extended Version

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Abstract

An efficient implementation of the quadratic unitary coupled-cluster singles and doubles (qUCCSD) scheme for calculations of electronic ground and excited states using an unrestricted molecular spin-orbital formulation and an efficient tensor contraction library is reported. The accuracy of the qUCCSD scheme and the efficiency of the present implementation is demonstrated using extensive benchmark calculations of excitation energies and an application to $S_0 \rightarrow S_1$ vertical excitation energies for *cis*- and *trans*-4*a*,4*b*-dihydrotriphenylene. The qUCCSD scheme has been shown to provide improved excitation energies compared with the UCC3 scheme formulated based on perturbation theory. A UCC truncation scheme that can provide excitation energies

correct through fourth order is also presented to further improve the accuracy of the qUCCSD scheme.

1 Introduction

The coupled-cluster (CC)¹⁻⁹ and equation-of-motion CC (EOM-CC)¹⁰⁻²² methods are being widely used in calculations of electronic ground and excited states for atoms and molecules aiming at high accuracy. CC theory can provide size-extensive treatments of dynamical correlation effects that are rapidly convergent with respect to the rank of excitations in the cluster operator; CC singles and doubles (CCSD) and EOM-CCSD methods have been amply demonstrated to provide accurate results.^{8,9,22} The success of CC methods lies in the ability to accurately treat not only simple molecules around equilibrium structures, but also molecules exhibiting strong orbital relaxation effects²³ or in moderately stretched geometries. The applicability of CC and EOM-CC methods is being extended to large molecules using pair natural orbital and reduced scaling techniques,²⁴⁻⁵³ to solids using periodic boundary conditions,⁵⁴⁻⁶³ and to heavy-atom-containing molecules in combination with relativistic Hamiltonians.⁶⁴⁻⁸³

CC and EOM-CC feature a non-Hermitian similarity-transformed Hamiltonian that naturally terminates at the fourth power of cluster operators. These methods benefit tremendously from this compactness. On the other hand, the non-Hermiticity of CC theory introduces non-trivial fundamental problems. CCSD calculations in combination with complex-valued Hamiltonians, e.g., Hamiltonians in the presence of a finite external magnetic field⁸⁴⁻⁸⁷ or with spin-orbit coupling,^{71,74,76,83} produce complex ground-state energies in general.⁸⁸ While real parts of CCSD energies in these calculations may practically serve as good approximations to corresponding full configuration interaction energies, the emergence of complex energies is still a non-trivial formal problem of CC theory. Further, the non-Hermiticity of the CC transformed Hamiltonian gives rise to incorrect crossing conditions in EOM-CCSD cal-

culations of intersections between electronic states of the same symmetry (‘same-symmetry conical intersections’).⁸⁸⁻⁹¹ Calculations of same-symmetry conical intersections with CC accuracy is of significant interest to study of molecular spectroscopy and photochemistry. One promising route towards achieving this is to modify EOM-CCSD to rectify the crossing conditions. Köhn and Tajti⁹⁰ have developed a simple correction scheme to obtain meaningful potential energy surfaces in the vicinity of intersection points. More recently, Koch and collaborators have developed a similarity constrained CCSD method to maintain the orthogonality of computed excited states and hence correct crossing conditions.⁹¹⁻⁹³ An alternative route is to develop CC approaches that are explicitly Hermitian, e.g., the unitary version of CC (UCC) theory.

UCC is a natural solution to these fundamental problems of CC theory due to non-Hermiticity. UCC⁹⁴⁻¹⁰⁹ uses an anti-Hermitian form for the cluster operator and thus ensures the unitarity of the wave operator and the Hermiticity of the transformed Hamiltonian. A UCC method with a truncation of the cluster operator to a given excitation rank has the potential to provide the same accuracy as the corresponding CC method, e.g., UCCSD has been shown to recover a similar percentage of dynamic correlation energies as CCSD.¹⁰¹ While the present work is focused on UCC in classical computations, we should mention that recent years have seen a surge of interest in using UCC in the field of quantum computing.^{105,110-122} A major challenge in UCC theory for classical computations is the non-terminating expansion of the UCC transformed Hamiltonian. Most practical UCC truncation schemes are based on Møller-Plesset (MP) perturbation theory.^{96,97,104} These elegant approaches perform well for simple molecules around equilibrium structures, while the performance decays for complex molecules in the absence of smooth convergence of the low-order MP series. An alternative route is to use commutator-rank truncation schemes, i.e., to truncate the commutator expansion to given ranks of commutators.^{109,122-124} This forms a promising framework for developing non-perturbative UCC methods.

We have recently developed a third-order UCC (UCC3) scheme¹⁰⁴ and a quadratic

UCCSD (qUCCSD) scheme¹⁰⁹ aiming at balanced truncation schemes for UCC ground-state and excited-state equations. The strict version of UCC3 is found to be equivalent to the strict version of the third-order algebraic diagrammatic construction [ADC(3)]^{125–127} method, revealing the close relation between UCC and ADC methods.¹⁰⁴ The qUCCSD scheme based on commutator-rank truncation schemes has been shown to provide significantly improved performance for molecules exhibiting strong orbital relaxation and/or electron correlation compared with the UCC3 method.¹⁰⁹ Our previous implementations of UCC3¹⁰⁴ and qUCCSD¹⁰⁹ have used the infrastructure of the spin-orbit CC code of the CFOUR program package.^{81,128,129} It thus can in principle handle calculations including spin-orbit coupling but is not efficient for non-relativistic and scalar-relativistic calculations. Hodecker *et al.* have reported a non-relativistic/scalar-relativistic spin-orbital based implementation for the UCC3 scheme.^{130,131} While both UCC3 implementations have the correct N^6 scaling, a detailed analysis of the computational cost of UCC3 has not been reported. Here we report an efficient implementation of qUCCSD (and UCC3) using **the (spin-integrated) spin-orbital formalism** and a recently developed tensor contraction library TBLIS¹³² together with an analysis of the computational costs for these methods. The theory and details about the implementation are presented in Sect 2.1 and 2.2. To demonstrate the usefulness of the new implementation, we report benchmark calculations for excitation energies in the “QUEST #1” benchmark set developed by Loos *et al.*^{133,134} as well as calculations of $S_0 \rightarrow S_1$ vertical transition energies for *cis*- and *trans*-4*a*,4*b*-dihydrotriphenylene ($C_{18}H_{14}$) of interest to study of photocyclization of *ortho*-terphenyl.¹³⁵ The computational details are presented in Sect. 2.3 with the accuracy and limitation of the qUCCSD scheme discussed in Sect. 3.1 and 3.2. Finally, in Sect. 3.3 we discuss the formulation for an extended version of the qUCCSD (e-qUCCSD) scheme and a non-iterative triples correction aiming to develop a UCC scheme with excitation energies correct up to fourth order, before closing the paper with a summary and an outlook in Sect. 4.

2 Theory and computational details

2.1 Commutator truncation schemes for unitary coupled-cluster theory

The unitary coupled-cluster (UCC) wave function is obtained by applying a unitary wave operator e^σ parametrized as an exponential of an anti-Hermitian cluster operator σ on the ground-state Hartree-Fock wavefunction Φ_0

$$|\Psi_{\text{gr}}\rangle = e^\sigma |\Phi_0\rangle, \quad \sigma = T - T^\dagger, \quad (1)$$

with T being a linear combination of excitation operators. For example, in the UCC singles and doubles (UCCSD) method T can be written as

$$T = T_1 + T_2, \quad (2)$$

$$T_1 = \sum_{ai} \sigma_i^a \{a_a^\dagger a_i\}, \quad T_2 = \frac{1}{4} \sum_{abij} \sigma_{ij}^{ab} \{a_a^\dagger a_b^\dagger a_j a_i\}, \quad (3)$$

in which $\{i, j, \dots\}$ and $\{a, b, \dots\}$ denote occupied orbitals and virtual orbitals, respectively, and σ_i^a and σ_{ij}^{ab} represent cluster amplitudes. The UCCSD ground-state energy and amplitude equations are given by

$$\langle \Phi_0 | \bar{H} | \Phi_0 \rangle = E_{\text{gr}}, \quad \langle \Phi_l | \bar{H} | \Phi_0 \rangle = 0, \quad (4)$$

with Φ_l 's denoting singly and doubly excited determinants and \bar{H} the transformed Hamiltonian $e^{-\sigma} H e^\sigma$ that is now Hermitian. The excited-state wave functions are written as a linear combination of excited-state basis functions obtained by acting a manifold of transformed

excitation operators^{136,137} $\{e^\sigma \hat{\tau}_I^\dagger e^{-\sigma}\}$ on Φ_{gr}

$$|\Phi_r^{\text{ext}}\rangle = \sum_I C_{Ir} e^\sigma \hat{\tau}_I^\dagger |\Phi_0\rangle, \quad (5)$$

in which $\hat{\tau}_I^\dagger$ is an original excitation operator, i.e., $\{\hat{\tau}_I^\dagger\} = \{a_a^\dagger a_i\} \cup \{a_a^\dagger a_b^\dagger a_j a_i\}$ in UCCSD.

This leads to the eigenvalue equations

$$\sum_I \bar{H}_{JI} C_{Ir} = E_r C_{Jr}, \quad \bar{H}_{JI} = \langle \Phi_0 | \hat{\tau}_J \bar{H} \hat{\tau}_I^\dagger | \Phi_0 \rangle, \quad (6)$$

to determine excited-state energies E_r 's and excited-state wavefunction parameters C_{Ir} 's.

The structures of UCCSD ground-state and excited-state equations are the same as those of CCSD and EOM-CCSD, except that \bar{H} is Hermitian and involves a non-terminating commutator expansion. We adopt a Bernoulli-number expansion for \bar{H} ¹⁰⁴

$$\bar{H} = \bar{H}^0 + \bar{H}^1 + \bar{H}^2 + \dots, \quad (7)$$

$$\bar{H}^0 = F + V, \quad (8)$$

$$\bar{H}^1 = [F, \sigma] + \frac{1}{2}[V, \sigma] + \frac{1}{2}[V_R, \sigma], \quad (9)$$

$$\bar{H}^2 = \frac{1}{12}[[V_N, \sigma], \sigma] + \frac{1}{4}[[V, \sigma]_R, \sigma] + \frac{1}{4}[[V_R, \sigma]_R, \sigma], \quad (10)$$

in which F and V represent the Fock operator and the fluctuation potential, respectively. “ N ” represents excitation and de-excitation operators and “ R ” refers to the rest. This expansion scheme eliminates higher than linear commutators between F and σ and offers a compact framework for developing UCC methods. The central task is then to develop balanced truncation schemes for \bar{H} that is both accurate and computationally efficient.

We adopt simple truncation schemes based on the powers of the UCCSD cluster amplitudes, or equivalently, on the order of commutators in \bar{H} . The ground-state amplitude

equations can be equivalently written as

$$\bar{H}_{ai} = 0, \quad \bar{H}_{ab,ij} = 0. \quad (11)$$

The UCC ground-state energy corresponds to the constant part of \bar{H} and involves contractions between H and σ . Therefore, we retain the commutators in the energy expression one order higher than in the amplitude equations. The UCCSD excited-state secular equations can be rewritten in a block form as

$$\begin{bmatrix} \bar{H}_{SS} & \bar{H}_{SD} \\ \bar{H}_{DS} & \bar{H}_{DD} \end{bmatrix} \begin{bmatrix} C_S \\ C_D \end{bmatrix} = E \begin{bmatrix} C_S \\ C_D \end{bmatrix}. \quad (12)$$

Here \bar{H}_{SS} refers to the singles-singles block, \bar{H}_{SD} and \bar{H}_{DS} represent the singles-doubles block and doubles-singles block, and \bar{H}_{DD} is the doubles-doubles block. Applying partitioning technique^{138,139} to Eq. (12) to fold the contributions from double excitations into the space of singles, the eigenvalue equations can be rewritten as

$$[\bar{H}_{SS} + \bar{H}_{SD}(E - \bar{H}_{DD})^{-1}\bar{H}_{DS}]C_S = EC_S. \quad (13)$$

Since V and σ represent a similar measure for the magnitude of electron correlation, the sum of the powers of V and σ serves as a metric for determining the importance of a term. Since \bar{H}_{SD} and \bar{H}_{DS} are at least linear in the combined power of V and σ , a balanced scheme should truncate \bar{H}_{SS} to commutators of V and σ one order higher than $\bar{H}_{SD}/\bar{H}_{DS}$ and two orders higher than \bar{H}_{DD} .

Since linearized amplitude equations are in general inaccurate, the lowest truncation scheme we consider is a quadratic unitary coupled-cluster singles and double (qUCCSD) scheme,¹⁰⁹ in which both the ground-state amplitude equations and \bar{H}_{SS} in the excited-state equations are truncated to up to double commutators between V and σ . We mention that, for a perturbative formulation, a truncation scheme having \bar{H}_{SS} correct to third order in MP

Table 1: Commutator truncation schemes for UCC methods.

| | UCC3 | qUCCSD | e-qUCCSD | cUCCSD |
|--------------------------------|------|-----------------------------------|-----------------------------------|---|
| $\bar{H}_{ai}, \bar{H}_{abij}$ | 3rd | $[[V, \sigma], \sigma]$ | $[[V, \sigma], \sigma]$ | $[[[V, \sigma], \sigma], \sigma]$ |
| E_{gr} | 4th | $[[[V, \sigma], \sigma], \sigma]$ | $[[[V, \sigma], \sigma], \sigma]$ | $[[[[V, \sigma], \sigma], \sigma], \sigma]$ |
| \bar{H}_{SS} | 3rd | $[[V, \sigma], \sigma]$ | $[[[V, \sigma], \sigma], \sigma]$ | $[[[V, \sigma], \sigma], \sigma]$ |
| $\bar{H}_{SD/DS}$ | 2nd | $[V, \sigma]$ | $[[V, \sigma], \sigma]$ | $[[V, \sigma], \sigma]$ |
| \bar{H}_{DD} | 1st | V | $[V, \sigma]$ | $[V, \sigma]$ |

perturbation theory, \bar{H}_{SD} and \bar{H}_{DS} to second order, and \bar{H}_{DD} to first order ensures excitation energies to be correct through third order. This corresponds to a ‘‘UCC3’’ method.¹⁰⁴ The commutator truncation schemes for qUCCSD and UCC3 are summarized in Table 1. We also include in Table 1 schemes to improve over qUCCSD, including the extended qUCCSD (e-qUCCSD) scheme and the cubic UCCSD (cUCCSD) scheme, and will discuss them in Sect. 3.3 after discussing qUCCSD results in Sect. 3.1 and 3.2.

2.2 Efficient implementation of the qUCCSD scheme

In order to enable comprehensive assessment and extensive applications of the qUCCSD scheme, we have implemented the qUCCSD scheme in the NCC module of the CFOUR program package^{128,129} using the spin-orbital formulation and an efficient tensor contraction library. This library, TBLIS, implements dense tensor contraction using high-performance matrix multiplication primitives while avoiding explicit tensor transposition which can become a performance bottleneck, especially on parallel architectures.¹³² Additionally, TBLIS natively handles Abelian point group symmetry and incorporates the efficient Direct Product Decomposition¹⁴⁰ procedure within the tensor contraction operation.¹⁴¹

We refer the readers to Ref. 109 for a complete account of working equations for the qUCCSD scheme and focus the present discussion on terms in qUCCSD working equations that make significant contributions to the computational cost of qUCCSD calculations. Similar to CCSD, the floating-point operation (FLOP) count for the qUCCSD ground-state amplitude equations is dominated by terms with $N_v^4 N_o^2$ scaling or $N_v^3 N_o^3$ scaling, in which N_v

and N_o refer to the number of α virtual and occupied orbitals, respectively. To simplify the discussion, we assume that the numbers of β virtual and occupied orbitals are identical to the α ones, i.e., $N_v = N_{v,\alpha} \approx N_{v,\beta}$ and $N_o = N_{o,\alpha} \approx N_{o,\beta}$, which is an approximation with negligible errors in FLOP counts. Recall that each iteration in the iterative solution of CCSD amplitude equations evaluates one “particle-particle ladder” contribution to the residue of double excitations $(\Delta R)_{ij}^{ab}$ with a FLOP count of $5/4N_v^4N_o^2$

$$\frac{1}{2} \sum_{cd} \langle ab||cd \rangle \tau_{ij}^{cd} \rightarrow (\Delta R)_{ij}^{ab}, \quad (14)$$

in which τ is an intermediate quantity $\tau_{ij}^{ab} = \sigma_{ij}^{ab} + \sigma_i^a \sigma_j^b - \sigma_i^b \sigma_j^a$, and two “ring contractions” each with a FLOP count of $10N_v^3N_o^3$

$$\sum_{me} \sigma_{im}^{ae} W_{mbej} \rightarrow (\Delta R)_{ij}^{ab}, \quad (15)$$

$$- \sum_{nf} \left(\frac{1}{2} \sigma_{jn}^{fb} + \sigma_j^f \sigma_n^b \right) \langle mn||ef \rangle \rightarrow W_{mbej}. \quad (16)$$

The total FLOP count of these terms in CCSD thus amounts to $5/4N_v^4N_o^2 + 20N_v^3N_o^3$.¹⁴⁰

The qUCCSD amplitude equations have two contributions involving $\langle ab||cd \rangle$ -type molecular integrals

$$\sum_{cd} \frac{1}{2} \langle ab||cd \rangle \tau_{ij}^{cd} \rightarrow (\Delta R)_{ij}^{ab}, \quad (17)$$

$$\sum_{jbcd} \frac{1}{4} (\sigma_j^c)^* \langle ac||bd \rangle \sigma_{ij}^{bd} \rightarrow (\Delta R)_i^a. \quad (18)$$

In the calculations presented here, we have chosen to perform two particle-particle ladder contractions $\sum_{cd} \langle ab||cd \rangle \tau_{ij}^{cd}$ and $\sum_{cd} \langle ab||cd \rangle \sigma_{ij}^{cd}$ for evaluation of these two terms. This gives a FLOP count of $5/2N_v^4N_o^2$. An alternative approach that has a smaller FLOP is to first perform the contraction $\sum_c (\sigma_j^c)^* \langle ac||bd \rangle$ and then contract the resulting intermediate with σ_{ij}^{bd} in the evaluation of the second term. However, the contraction $\sum_c (\sigma_j^c)^* \langle ac||bd \rangle$ involves

the expansion of packed indices in the large $\langle ac||bd \rangle$ integral matrix. Consequently, this approach is more time-consuming for calculations of small- and medium-sized molecules than performing a particle-particle ladder contraction. The qUCCSD amplitude equations also consist of the following terms involving ring contractions

$$-\sum_{jklbc} (\sigma_{jk}^{bc})^* \langle bl||ji \rangle \sigma_{kl}^{ca} + \sum_{jkbcd} (\sigma_{jk}^{bc})^* \langle ab||dj \rangle \sigma_{ki}^{cd} \rightarrow (\Delta R)_i^a, \quad (19)$$

$$P(ij)P(ab) \sum_{kc} \langle ak||ic \rangle \sigma_{jk}^{bc} \rightarrow (\Delta R)_{ij}^{ab}, \quad (20)$$

$$P(ij)P(ab) \sum_{klcd} \frac{1}{3} \langle kl||cd \rangle \sigma_{ik}^{ac} \sigma_{jl}^{bd} + P(ij)P(ab) \sum_{klcd} \frac{1}{3} (\sigma_{kl}^{cd})^* \langle ad||il \rangle \sigma_{jk}^{bc} \rightarrow (\Delta R)_{ij}^{ab}, \quad (21)$$

$$-P(ij)P(ab) \sum_{lcd} (\sigma_l^c)^* \langle ac||dj \rangle \sigma_{il}^{bd} + P(ij)P(ab) \sum_{klc} (\sigma_l^c)^* \langle bk||li \rangle \sigma_{jk}^{ca} \rightarrow (\Delta R)_{ij}^{ab}, \quad (22)$$

$$-P(ij)P(ab) \sum_{klc} \langle kl||cj \rangle \sigma_l^b \sigma_{ik}^{ac} + P(ij)P(ab) \sum_{kcd} \langle kb||cd \rangle \sigma_j^d \sigma_{ik}^{ac} \rightarrow (\Delta R)_{ij}^{ab}. \quad (23)$$

Efficient calculations of these terms include the evaluation of intermediates

$$(I_1)_{ib}^{aj} = \sum_{kc} (\sigma_{jk}^{bc})^* \sigma_{ki}^{ca}, \quad (24)$$

$$(I_2)_{ic}^{ak} = \frac{1}{2} \langle ak||ic \rangle + \frac{1}{3} \sum_{ld} \sigma_{il}^{ad} \langle lk||dc \rangle + \sum_f \langle ak||fc \rangle \sigma_i^f - \sum_l \langle lk||ic \rangle \sigma_l^a, \quad (25)$$

and calculations of Eq. (19) as

$$-\sum_{lbj} (I_1)_{lb}^{aj} \langle bl||ji \rangle + \sum_{dbj} (I_1)_{ib}^{dj} \langle ab||dj \rangle \rightarrow (\Delta R)_i^a, \quad (26)$$

and Eqs. (20), (21), (22), and (23) as

$$P(ij)P(ab) \sum_{kc} [(I_2)_{ic}^{ak} + (I_2)_{ka}^{ci*}] \sigma_{jk}^{bc} \rightarrow (\Delta R)_{ij}^{ab}. \quad (27)$$

These computations involve three ring contractions and have a FLOP count of around

$30N_v^3N_o^3$. In addition, each of the following two contributions

$$-P(ab)\frac{1}{2}\sum_{kcd}\langle ka||cd\rangle\sigma_k^b\sigma_{ij}^{dc}\rightarrow(\Delta R)_{ij}^{ab}\quad(28)$$

$$-\sum_{lcd}(\sigma_l^c)^*\langle ab||dl\rangle\sigma_{ij}^{dc}\rightarrow(\Delta R)_{ij}^{ab}\quad(29)$$

involves a $N_v^3N_o^3$ step with a FLOP count of $5/2N_v^3N_o^3$. Altogether, the FLOP count for these significant terms in one iteration of solving qUCCSD amplitude equations amounts to $5/2N_v^4N_o^2+35N_v^3N_o^3$. The computational cost of a ground-state qUCCSD calculation thus is roughly twice that of CCSD. We mention that we have used a more complete factorization for the terms involving ring contractions than in Ref. 109 and hence the lower FLOP count for those terms presented here.

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. On the other hand, the construction of \bar{H}_{ab} and $\bar{H}_{ia,bj}$ involves several computationally demanding contributions

$$-\frac{1}{8}\sum_{ijcdf}(\sigma_{ij}^{fd})^*\langle df||cb\rangle\sigma_{ij}^{ac}=-\frac{1}{8}\sum_{ijc}\sigma_{ij}^{ac}\left[\sum_{df}(\sigma_{ij}^{fd})^*\langle df||cb\rangle\right]\rightarrow\bar{H}_{ab},\quad(30)$$

$$\frac{1}{4}\sum_{kcde}(\sigma_{ik}^{ce})^*\langle ce||bd\rangle\sigma_{jk}^{ad}=\frac{1}{4}\sum_{kd}\sigma_{jk}^{ad}\left[\sum_{ce}(\sigma_{ik}^{ce})^*\langle ce||bd\rangle\right]\rightarrow\bar{H}_{ia,bj},\quad(31)$$

$$\sum_{kcde}(\sigma_{ik}^{de})^*\langle ad||cb\rangle\sigma_{jk}^{ce}=\sum_{cd}\langle ad||cb\rangle\left[\sum_{ke}(\sigma_{ik}^{de})^*\sigma_{jk}^{ce}\right]\rightarrow\bar{H}_{ia,bj},\quad(32)$$

$$\sum_{klcd}(\sigma_{kl}^{cb})^*\langle ic||dj\rangle\sigma_{kl}^{ad}=\sum_{cd}\langle ic||dj\rangle\left[\sum_{kl}(\sigma_{kl}^{cb})^*\sigma_{kl}^{ad}\right]\rightarrow\bar{H}_{ia,bj}.\quad(33)$$

The calculations of Eqs. (30) and Eq. (31) share one particle-particle ladder contraction (the expressions in the brackets in Eqs. (30) and Eq. (31)). Eq. (31) also involves one ring contraction. The contributions in Eqs. (32) and (33) are the most expensive terms in the construction of the qUCCSD transformed Hamiltonian; Eq. (32) and Eq. (33) have a FLOP count of $10N_v^4N_o^2+10N_v^3N_o^3$ and $45/4N_v^4N_o^2$, respectively, the derivation of which is

documented in detail in the Appendix. Altogether these three terms have a FLOP count of $45/2N_v^4N_o^2 + 20N_v^3N_o^3$ and constitute the main overhead in the construction of the qUCCSD \bar{H} compared with that of EOM-CCSD. The construction of \bar{H} for qUCCSD thus is typically several times more expensive than that for EOM-CCSD. The effect of this non-iterative step on the total computing time varies with respect to the size of the molecule and the number of iterations required to converge the EOM-CCSD excited-state eigenvalue equations. The qUCCSD calculations presented here are in total, including the computational time for ground- and excited-state calculations, around a few times as expensive as the corresponding CCSD and EOM-CCSD calculations together.

The UCC3 scheme consists of a subset of terms in the qUCCSD scheme. We thus have also obtained an efficient implementation for UCC3. Following the same analysis as above and excluding terms originating from $[[V, \sigma_2], \sigma_1]$, we obtain the FLOP count for the significant terms in each iteration of UCC3 amplitude equations as $5/4N_v^4N_o^2 + 30N_v^3N_o^3$, to be compared with the qUCCSD value of $5/2N_v^4N_o^2 + 35N_v^3N_o^3$ and the CCSD value of $5/4N_v^4N_o^2 + 20N_v^3N_o^3$. The construction of UCC3 \bar{H} involves the expensive terms in Eqs. (31), (32), and (33) and is essentially as expensive as in the qUCCSD scheme.

2.3 Computational details

For benchmark calculations we have used 107 excitation energies in the “QUEST #1” benchmark set dominated by single excitations, for which the “theoretical best estimate” (TBE) values have been obtained from high-level coupled-cluster or full configuration interaction calculations^{133,134} and serve as excellent reference values for benchmarking the accuracy of the qUCCSD scheme. In other words, we have used all excitation energies in the “QUEST #1” set except the 3^1A_g state of ethylene, the 3^1A_1 state of formaldehyde, and the $3^1A'$ set of nitrosomethane, which are double excitations, as well as transitions to three 1A_1 states in formamide, for which the TBE values have not been determined to high accuracy. Our calculations have used the same structures and basis sets as in Ref. 134. We have reproduced

EOM-CCSD and ADC(3) results in Ref. 134 to ensure the correctness of the computational setup. UCC3 calculations have also been performed for these excitation energies for comparison. To facilitate the discussion, in Sect. 3.1 we will present statistical error analyses for these calculations including standard deviations, mean absolute deviations, mean deviations, and maximum absolute deviations with respect to the TBE values, while we have documented all computed excitation energies in the Supplementary Material.

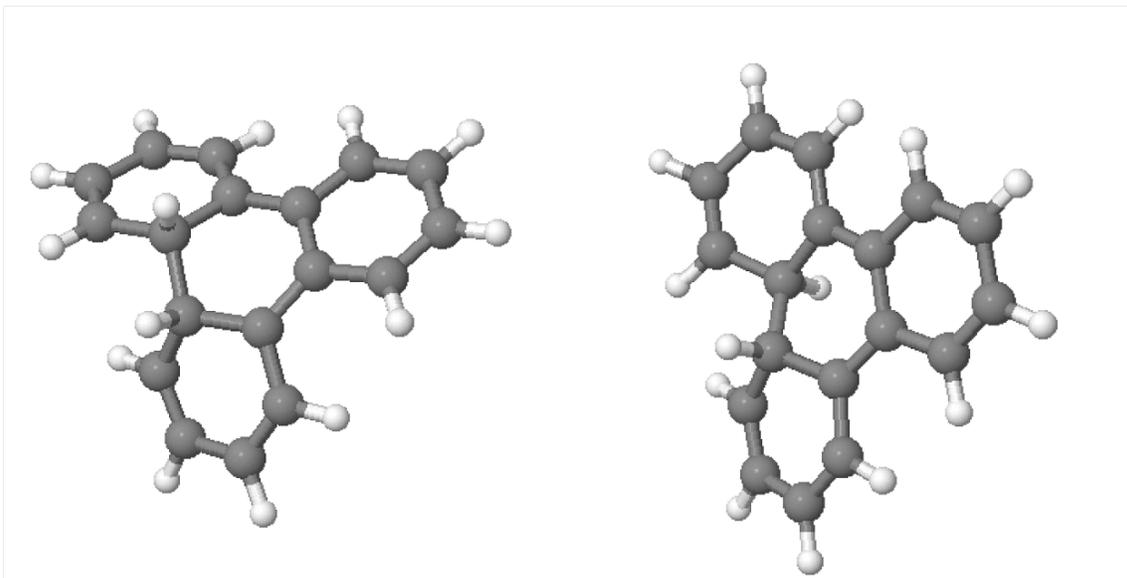


Figure 1: *cis*-4a,4b-dihydrotriphenylene (on the left) and *trans*-4a,4b-dihydrotriphenylene (on the right).

As an example for calculations of larger molecules, we have performed qUCCSD calculations for the $S_0 \rightarrow S_1$ vertical transition energies of the *cis*- and *trans*-4a,4b-dihydrotriphenylene ($C_{18}H_{14}$, see Fig. 1) using 6-31G* and 6-31+G* basis sets^{142–144} as well as the aug-cc-pVDZ basis set for C and the cc-pVDZ basis set for H,^{145,146} denoted as the “aVDZ” basis in the following discussions. These two excitation energies have been measured and used in recent experimental study that identifies these two molecules as products of 6π photocyclization of *ortho*-terphenyl through two distinct photochemical reaction pathways.¹³⁵ We have also carried out EOM-CCSD¹⁶ and EOM-CCSD(T)(a)*¹⁴⁷ calculations for comparison. The ground-state structures obtained from density-functional theory calculations in Ref. 135 have been used in these calculations.

3 Results and Discussions

3.1 Benchmark calculations of excitation energies in the “QUEST #1” set

Table 2: Statistical error analyses for EOM-CCSD, ADC(3), UCC3, and qUCCSD results of 107 excitation energies in the QUEST #1 set. “SD”, “MaxAD”, “MAD”, and “MD” refer to standard deviation, maximum absolute deviation, mean absolute deviation, and mean deviation (eV) with respect to the theoretical best estimate values in Ref. 134.

| | SD | MaxAD | MAD | MD |
|----------|------|-------|------|-------|
| EOM-CCSD | 0.11 | 0.40 | 0.08 | 0.05 |
| ADC(3) | 0.28 | 0.79 | 0.23 | -0.15 |
| UCC3 | 0.28 | 0.63 | 0.23 | -0.16 |
| qUCCSD | 0.24 | 0.63 | 0.20 | -0.16 |

The qUCCSD, UCC3, and ADC(3) methods are all Hermitian excited-state methods that provide excitation energies correct up to third order. As shown in Table 2, the standard deviation of qUCCSD excitation energies with respect to theoretical best estimate values amounts to 0.24 eV for 107 excitation energies in the “QUEST #1” set, a little lower than the UCC3 and ADC(3) values of 0.28 eV. This is in line with the expectation that the qUCCSD results should be qualitatively similar to those of UCC3 and ADC(3) for these simple molecules around equilibrium structures, but nevertheless should feature an improvement over these perturbation theory based methods.

The value of -0.16 eV for the mean deviation indicates that the qUCCSD scheme tends to underestimate excitation energies. A close inspection reveals that indeed most of the qUCCSD excitation energies are smaller than the corresponding theoretical best estimate values. This is in interesting contrast with EOM-CCSD, which has a mean deviation of 0.05 eV and tends to overestimate excitation energies. Note that the other Hermitian excited-state methods providing excitation energies correct up to third order, ADC(3) and UCC3, also tend

to underestimate excitation energies. It is logical to expect the fourth-order contributions in Hermitian excited-state methods to increase the values of computed excitation energies.

The qUCCSD excitation energies for the “QUEST #1” set are in general less accurate than the corresponding EOM-CCSD ones; EOM-CCSD results exhibit a smaller standard deviation of 0.11 eV from theoretical best estimate values. The maximum absolute deviation of qUCCSD excitation energies occurs as 0.63 eV for the emission energy of the $^1A''$ state of diazomethane. The other third-order Hermitian excited-state methods also exhibit difficulties in obtaining accurate emission energies, for example, the maximum absolute deviation of ADC(3) excitation energies occurs as 0.79 eV for the emission energy of the 1A_u state of acetylene. This might indicate that the excited-state structures of these methods would substantially deviate from the CC3¹⁷ structures used for these calculations. These observations show that, while qUCCSD is an improvement compared with UCC3 and ADC(3), it is necessary to include higher commutators in the UCC excited-state eigenvalue equations to further improve the accuracy of qUCCSD, in order to approach the accuracy and robustness of the EOM-CCSD method.

3.2 $S_0 \rightarrow S_1$ vertical excitation energies for *cis*- and *trans*-4*a*,4*b*-dihydrotriphenylene

Table 3: The $S_0 \rightarrow S_1$ vertical excitation energies (eV) for *cis*- and *trans*-4*a*,4*b*-dihydrotriphenylene (*cis*- and *trans*-DHT).

| Basis set | Method | <i>cis</i> -DHT | <i>trans</i> -DHT | Relative shift |
|---------------------------|-----------------|-----------------|-------------------|----------------|
| 6-31G* | EOM-CCSD | 2.60 | 2.71 | 0.11 |
| | EOM-CCSD(T)(a)* | 2.50 | 2.60 | 0.10 |
| | qUCCSD | 2.16 | 2.34 | 0.18 |
| 6-31+G* | EOM-CCSD | 2.42 | 2.61 | 0.19 |
| | EOM-CCSD(T)(a)* | 2.33 | 2.50 | 0.17 |
| | qUCCSD | 1.99 | 2.19 | 0.20 |
| aVDZ | EOM-CCSD | 2.33 | 2.51 | 0.18 |
| | qUCCSD | 1.88 | 2.08 | 0.20 |
| Experiment ¹³⁵ | | 1.99 | 2.18 | 0.19 |

Calculations of *cis*-4*a*,4*b*-dihydrotriphenylene (DHT) using the 6-31+G* basis sets involve the correlation of 43 occupied valence orbitals (86 valence electrons) and 291 virtual orbitals. Each iteration in the iterative solution of qUCCSD ground-state amplitude equations took around 790 seconds using 12 cores on an Intel® Xeon® Gold 6248R Processor, roughly twice the CCSD value of around 400 seconds per iteration. The computational time for one iteration of a qUCCSD/aVDZ calculation involving 423 virtual orbitals amounts to around 2600 seconds and is around twice the corresponding value of 1300 seconds in a CCSD calculation. These timings are consistent with the analysis in Sect. 2.2 that the floating-point operation count for a qUCCSD ground-state iteration is around twice that of CCSD. The construction of qUCCSD transformed Hamiltonian took 4900 seconds when using the 6-31+G* basis and 21700 seconds when using the aVDZ basis. These qUCCSD computing times are around 5 times those of EOM-CCSD, which amount to around 1100 seconds when using the 6-31+G* basis and 4500 seconds when using the aVDZ basis. Each iteration in the solution of excited-state eigenvalue equations took around 280 seconds when using the 6-31+G* basis and 830 seconds when using the aVDZ basis in both qUCCSD and

EOM-CCSD calculations. The total computational time for a qUCCSD calculation of *cis*- or *trans*-DHT is around twice that of a CCSD and EOM-CCSD calculation. This example demonstrates that the new implementation enables applications of the qUCCSD scheme to sizable molecules and forms the basis for further developments of more accurate truncation schemes.

The EOM-CCSD, EOM-CCSD(T)(a)*, and qUCCSD excitation energies have been summarized in Table 3 and compared with experimental peak positions. The qUCCSD/6-31+G* $S_0 \rightarrow S_1$ vertical transition energy for *cis*-DHT amounts to 1.99 eV and exhibits a red shift of 0.20 eV compared with the corresponding value of 2.19 eV for *trans*-DHT. This agrees fairly well with the experimentally measured shift of 0.19 eV between these two transitions. Comparison of qUCCSD and EOM-CCSD values with the EOM-CCSD(T)(a)* values shows that the qUCCSD scheme underestimates the absolute values of these excitation energies, while EOM-CCSD calculations exhibit an overestimation. This is consistent with the observation for the excitation energies in the “QUEST #1” set in the previous subsection. The excellent agreement between qUCCSD/6-31+G* vertical excitation energies and the experimental peak positions appears to be fortuitous. Enlargement of basis sets is expected to reduce computed excitation energies, e.g., the qUCCSD/aVDZ vertical excitation energies are lower than experimental peak positions by 0.1 eV. Furthermore, a Franck-Condon simulation is perhaps required to enable direct comparison between computations and experimental peak positions. A close inspection of excited-state wave functions shows that the qUCCSD scheme tends to overestimate contributions from double excitations in the case of *trans*-DHT. These observations together with the benchmark calculations presented in the previous subsection indicates that it is necessary to further improve the accuracy of the qUCCSD truncation scheme.

3.3 Formulating a UCC scheme with excitation energies correct to fourth order: an extended qUCCSD scheme and a non-iterative triples correction

While the qUCCSD ground-state energy includes all fourth-order contributions within UCCSD, the qUCCSD excitation energies are complete only to third order. It is a natural extension to further include all fourth-order contributions to excitation energies within the UCCSD excited-state equations. This leads to an extended qUCCSD (e-qUCCSD) scheme in Table 1. The e-qUCCSD scheme augments qUCCSD with triple commutators in \bar{H}_{SS} , double commutators in \bar{H}_{SD} and \bar{H}_{SD} , and single commutators in \bar{H}_{DD} . The e-qUCCSD scheme is expected to provide better performance than the qUCCSD scheme in calculations of excitation energies and to approach the accuracy of the EOM-CCSD method.

A further augmentation of the e-qUCCSD scheme with a non-iterative triples correction to excitation energies will provide excitation energies correct through fourth order, which is a very attractive feature. The Hermiticity of UCCSD allows a simple formulation of a non-iterative triples correction to excitation energies. Applying the partitioning technique to fold triples (T) space into the singles doubles (SD) space, the UCC excited-state eigenvalue equations can be written as

$$[\bar{H}_{PP} + \bar{H}_{PQ}(E - \bar{H}_{QQ})^{-1}\bar{H}_{QP}]C_P = EC_P. \quad (34)$$

Here Q and P represent the T space and the SD space, respectively. The triples correction to excitation energies can thus be written as $C_P^\dagger \bar{H}_{PQ}(E - \bar{H}_{QQ})^{-1} \bar{H}_{QP} C_P$. Importantly, since $\bar{H}_{ab,ij} = \bar{H}_{ij,ab} = 0$ because of the UCCSD amplitude equations, \bar{H}_{ST} has to involve three-body terms and is at least of second order. The leading contributions to \bar{H}_{DT} are of first order, those to C_S are of zeroth order, and those to C_D are of first order. Therefore, a simple

non-iterative triples obtained as

$$\begin{aligned}
 E_{(T)} = & (C_{S, \text{UCCSD}}^\dagger \bar{H}_{ST}^{[2]} + C_{D, \text{UCCSD}}^\dagger \bar{H}_{DT}^{[1]}) \{ (E - \bar{H}_{TT})^{-1} \}^{[0]} \\
 & (\bar{H}_{TS}^{[2]} C_{S, \text{UCCSD}} + \bar{H}_{TD}^{[1]} C_{D, \text{UCCSD}}),
 \end{aligned}
 \tag{35}$$

in which the superscripts $[n]$ refer to terms correct to the “n-th” order of the MP series, includes all fourth-order contributions to excitation energies in the triples contributions. Let us refer to augmenting e-qUCCSD with this triples correction as an “e-qUCCSD(T)” scheme. This scheme can provide excitation energies correct through fourth order while involving only iterative N^6 steps in the e-qUCCSD equations and a non-iterative N^7 step as given in Eq. (35). The e-qUCCSD(T) scheme thus has the potential to enable highly accurate calculations of excitation energies for small- and medium-sized molecules. Note that the implementation for the non-iterative triples correction in the e-qUCCSD(T) scheme can straightforwardly use the available implementation for non-iterative triples corrections for EOM-CCSD,¹⁴⁷⁻¹⁵¹ which include Eq. (35) as one of the contributions.

For systems with larger σ amplitudes in ground-state calculations, it is important to include cubic commutators in the ground-state amplitude equations and quartic commutators in the energy expression. For example, the qUCCSD results for ground-state properties of ozone were found to be less accurate than CCSD ones, although qUCCSD exhibits a dramatic improvement compared with perturbation theory based schemes for this molecule.¹⁰⁹ Therefore, it will be valuable to explore the cubic UCCSD (cUCCSD) scheme in Table 1 to further improve the accuracy for calculations of ground-state properties.

4 Summary and Outlook

We report an efficient implementation of the quadratic unitary coupled-cluster singles and doubles (qUCCSD) scheme using the spin-orbital formulation and a recently developed efficient tensor contraction library. An efficient factorization for computationally significant

terms is presented and the computational cost of qUCCSD is shown to be around twice that of CCSD. We also present benchmark calculations for excitation energies. The qUCCSD scheme is demonstrated to be an improvement compared with the UCC3 method. An extended qUCCSD scheme augmented with a non-iterative triples correction for further improvement of accuracy is also formulated, aiming at a Hermitian excited-state method correct through fourth order for excitation energies.

Future work will be focused on the derivation and implementation of the extended qUCCSD scheme and the non-iterative triples correction to excitation energies introduced here. Calculations of metal-containing molecules will also be of significant interest to understanding the performance of UCC-based methods for complex molecular systems.

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A Appendix: Floating-Point Operation Counts for Eqs. (32) and (33)

Eqs. (32) and (33) represent two terms in the construction of \bar{H} in the qUCCSD scheme that are the most time-consuming. We present detailed floating-point operation (FLOP) counts for these two terms. The calculation of Eq. (32) consists of the construction of an

intermediate

$$(I_3)_{dj}^{ic} = \sum_{ke} (\sigma_{ik}^{de})^* \sigma_{jk}^{ce} \quad (36)$$

that has the same FLOP count as a ring contraction, i.e., $N_{v,\alpha}^3 N_{o,\alpha}^3 + N_{v,\beta}^3 N_{o,\beta}^3 + 3N_{v,\alpha}^2 N_{o,\alpha}^2 N_{v,\beta} N_{o,\beta} + 3N_{v,\alpha} N_{o,\alpha} N_{v,\beta}^2 N_{o,\beta}^2 + N_{v,\alpha}^2 N_{o,\alpha} N_{v,\beta} N_{o,\beta}^2 + N_{v,\alpha} N_{o,\alpha}^2 N_{v,\beta}^2 N_{o,\beta} \approx 10N_v^3 N_o^3$, and a subsequent contraction

$$\sum_{cd} \langle ad || cb \rangle (I_3)_{dj}^{ic} \rightarrow \bar{H}_{ia,bj}. \quad (37)$$

Eq. (37) requires calculations of the contributions to six spin cases for $\bar{H}_{ia,bj}$

$$\sum_{cd} \langle ad || cb \rangle (I_3)_{dj}^{ic} + \sum_{\bar{c}\bar{d}} \langle a\bar{d} || \bar{c}\bar{b} \rangle (I_3)_{\bar{d}j}^{\bar{ic}} \rightarrow \bar{H}_{ia,bj}, \quad (38)$$

$$\sum_{\bar{c}\bar{d}} \langle \bar{a}\bar{d} || \bar{c}\bar{b} \rangle (I_3)_{\bar{d}j}^{\bar{ic}} + \sum_{cd} \langle \bar{a}d || c\bar{b} \rangle (I_3)_{dj}^{\bar{ic}} \rightarrow \bar{H}_{\bar{i}\bar{a},\bar{b}j}, \quad (39)$$

$$\sum_{cd} \langle \bar{a}d || c\bar{b} \rangle (I_3)_{dj}^{\bar{ic}} \rightarrow \bar{H}_{\bar{i}\bar{a},\bar{b}j}, \quad (40)$$

$$\sum_{cd} \langle \bar{a}d || c\bar{b} \rangle (I_3)_{dj}^{ic} + \sum_{\bar{c}\bar{d}} \langle \bar{a}\bar{d} || \bar{c}\bar{b} \rangle (I_3)_{\bar{d}j}^{\bar{ic}} \rightarrow \bar{H}_{\bar{i}\bar{a},\bar{b}j}, \quad (41)$$

$$\sum_{cd} \langle ad || cb \rangle (I_3)_{dj}^{\bar{ic}} + \sum_{\bar{c}\bar{d}} \langle a\bar{d} || \bar{c}\bar{b} \rangle (I_3)_{\bar{d}j}^{\bar{ic}} \rightarrow \bar{H}_{\bar{i}\bar{a},\bar{b}j}, \quad (42)$$

$$\sum_{\bar{c}\bar{d}} \langle a\bar{d} || \bar{c}\bar{b} \rangle (I_3)_{\bar{d}j}^{\bar{ic}} \rightarrow \bar{H}_{\bar{i}\bar{a},\bar{b}j}, \quad (43)$$

in which $\{p\}$ and $\{\bar{p}\}$ represent α and β orbitals, respectively, and involves 10 contractions with a total FLOP count of $N_{v,\alpha}^4 N_{o,\alpha}^2 + N_{v,\beta}^4 N_{o,\beta}^2 + N_{v,\alpha}^4 N_{o,\beta}^2 + N_{v,\beta}^4 N_{o,\alpha}^2 + 2N_{v,\alpha}^2 N_{o,\alpha}^2 N_{v,\beta}^2 + 2N_{v,\alpha}^2 N_{o,\beta}^2 N_{v,\beta}^2 + 2N_{v,\alpha}^2 N_{o,\alpha} N_{v,\beta}^2 N_{o,\beta} \approx 10N_v^4 N_o^2$. Altogether the FLOP count for calculation of Eq. (32) amounts to $10N_v^3 N_o^3 + 10N_v^4 N_o^2$.

The evaluation of Eq. (33) involves the construction of an intermediate

$$(I_4)_{cb}^{ad} = \sum_{kl} (\sigma_{kl}^{cb})^* \sigma_{kl}^{ad}, \quad (44)$$

which has the same FLOP count of $1/8N_{v,\alpha}^4N_{o,\alpha}^2+1/8N_{v,\beta}^4N_{o,\beta}^2+N_{v,\alpha}^2N_{o,\alpha}N_{v,\beta}^2N_{o,\beta} \approx 5/4N_v^4N_o^2$ as a particle-particle ladder contraction, and a subsequent contraction

$$\sum_{cd} \langle ic || dj \rangle (I_4)_{cb}^{ad} \rightarrow \bar{H}_{ia,bj}. \quad (45)$$

Eq. (45) has the same spin factorization as Eq. (37) and hence the same FLOP count of $10N_v^4N_o^2$. The total FLOP count for calculation of Eqs. (32) and (33) thus is $10N_v^3N_o^3 + 85/4N_v^4N_o^2$.

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Graphical TOC Entry

