A new “gold standard”: perturbative triples corrections in unitary coupled cluster theory and prospects for quantum computing

Zachary W. Windom,[1, 2] Daniel Claudino,[3] and Rodney J. Bartlett[1]
[1)] *Quantum Theory Project, University of Florida, Gainesville, FL, 32611, USA*
[2)] *Quantum Information Science Section, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA*
[3)] *Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA*

(*Electronic mail: claudinodc@ornl.gov)

(Dated: 15 May 2024)

A major difficulty in quantum simulation is the adequate treatment of a large collection of entangled particles, synonymous with electron correlation in electronic structure theory, with coupled cluster (CC) theory being the leading framework in dealing with this problem. Augmenting computationally affordable low-rank approximations in CC theory with a perturbative account of higher-rank excitations is a tractable and effective way of accounting for the missing electron correlation in those approximations. This is perhaps best exemplified by the “gold standard” CCSD(T) method, which bolsters the baseline CCSD with effects of triple excitations using considerations from many-body perturbation theory (MBPT). Despite this established success, such a synergy between MBPT and the unitary analog of CC theory (UCC) has not been explored. In this work, we propose a similar approach wherein converged UCCSD amplitudes are leveraged to evaluate energy corrections associated with triple excitations - leading to the UCCSD[T] method. In terms of quantum computing, this correction represents an entirely classical post-processing step that improves the energy estimate by accounting for triple excitation effects without necessitating new quantum algorithm developments or increasing demand for quantum resources. The rationale behind this choice is shown to be rigorous by studying the properties of finite-order UCC energy functionals, and our efforts do not support the addition of the fifth-order contributions as in the (T) correction. We assess the performance of these approaches on a collection of small molecules, and demonstrate the benefits of harnessing the inherent synergy between MBPT and UCC theories.

I. INTRODUCTION

The exact solution of the time-independent, non-relativistic Schrödinger equation is the “holy grail" of quantum chemistry, as *ab initio* prediction of several important molecular and materials properties becomes immediately accessible.[1] Unfortunately, full configuration interaction (FCI), i.e., the accounting of all possible electronic configurations in a one-particle basis, scales combinatorially with system size, meaning that the exact solution is beyond reach for the vast majority of chemical space. Nevertheless, methods based on low-rank coupled-cluster (CC) theory have the advantage of converging rapidly to the FCI limit in polynomial time,[2] and therefore are of immense value to the computational chemistry and materials science communities.[3] In fact, systematic convergence to FCI is assured by considering higher-rank cluster operators into the ansätze albeit at increasing computational cost.[4,5]

Contrary to approaches centered around expectation values, CC lends itself to a series of residual equations emerging from projections of the Schrödinger equation onto the space of excitations out of the reference function, typically Hartree-Fock (HF), but applicable to any single determinant that overlaps with the exact wavefunction. One way to circumnavigate the mounting intractability in including arbitrarily high-orders of the cluster operator is to introduce corrections *post hoc* based on some flavor of perturbation theory. The most prominent of these methods is the perturbative energy correction for triple excitations with infinite-order single (S) and double (D) excitations that results in the CCSD(T) method[6–8] - the so-called “gold standard" of quantum chemistry. And, on the same token, a similar philosophy can be used to bolster - for example, CCSDT - by incorporating a perturbative treatment of missed quadruple excitations.[9–11] This framework ultimately culminates in a hierarchy of methods whose focus is to provide a perturbative estimate of electron correlation associated with higher-rank cluster operators that are explicitly omitted once the cluster operator has been truncated.[12] Methods based on the factorization theorem of MBPT have also been proposed and investigated,[13] showing that further reduction in calculation cost can be achieved while simultaneously providing some estimate of higher-order correlation effects.[14–16]

A simplistic view of the CC ansatz would define it as an exponential map of excitation operators, which is used in its predominant projective variant. This “simplicity" arises by virtue of the natural truncation of the Baker-Campbell-Hausdorff expansion of the similarity-transformed Hamiltonian, and it comes at the expense of a loss of unitarity/variationality. However, other perspectives have investigated alternative CC ansätze[17] in the pursuit of satisfying exact conditions,[17,18] such as the generalized Hellman-Feynman (GHF) theorem.[19] The original expectation value formalism[20] - which, in the limit, converges toward variational CC[21,22] - and the unitary CC (UCC) ansätze[23] fall into this category. By design, these ansätze are arguably more suitable for the calculation of properties as compared to the standard CC formulation. Unfortunately, they inherently scale as FCI since the Hamiltonian-cluster commutator expansion does not truncate.[4] Again, perturbation theory can be used to “pick" a suitable truncation point for tractability,[24] although admittedly methods that are truncated at low-orders do not necessarily provide results that are comparable to similar, standard CC counterparts.[25,26] Alternatively, truncations based on commutator-rank have also been explored.[27,28]

This impasse between projective and alternative ansätze may potentially be solved with the emergence of quantum computing paradigms, which would enable UCC without resorting to arbitrary truncation. This is because the UCC ansätze can be effectively encoded as a series of gate-based operations acting on an *easy-to-prepare* state,[29,30] e.g. HF. In fact, there is supporting evidence that untruncated UCC theory provides more accurate results than the equivalent, standard CC method.[5,22,31] Nevertheless, fundamental issues inhibit routine UCC calculations on a quantum computer; notably, circuit width and depth – either of which ultimately restrict the maximal rank of the cluster operator.[32] This is unfortunate since CC/UCC typically converges toward the exact solution of the Schrödinger equation (in a basis set) by adding the abovementioned higher-rank cluster operators.[2] The convergence properties of a hierarchy of UCC methods that systematically include up to hextuple excitations is studied in more detail in Ref.[5], where it is shown that UCCSDTQPH is reliably close the FCI. A less *typical* approach is to relax the concept of excitation rank by considering generalized excitations, e.g., $i^\dagger j$ or $a^\dagger b$. Within this paradigm, one is afforded to converge to FCI without explicit inclusion of higher excitation manifold.[5,33] A further point of consideration lies in the distinction between the complete, non-terminating UCC ansatz and the Trotterized, or so-called *disentangled*, counterpart, with the latter rising from known product formulas and proven exact under certain conditions.[34]

To address the lack of a framework enabling perturbative corrections for the UCC ansatz, we explore potential synergies between MBPT and UCC theory which have not been scrutinized until now. By studying the properties of finite-order UCC equations, we propose a pathway towards perturbative corrections to the infinite-order UCCSD energy designed to recover the missed effects of higher-rank excitations. While other strategies are similar in spirit,[35–37] extending even to excited states,[28] we introduce the explicit unitary analogs of the pioneering perturbative accounting for triple excitations, leading to the UCCSD[T] method. We show that such an approach is a robust way of recovering electron correlation that is missed by restricting the unitary cluster operator. By employing what can be seen as a post-processing step born from rigorous theory, our results reinforce the perspective that resource-efficient interplay between quantum and classical computers should be harnessed to achieve more accurate results without imposing extra burden on current, fragile quantum computers.

II. THEORY

We motivate the problem using semi-canonicalized orbitals for a general reference function, e.g., non-HF. The normal-ordered Hamiltonian is then of the form

$$\begin{aligned} H_N = &\underbrace{\sum_p \varepsilon_{pp}\{p^\dagger p\}}_{f_N} \\ &\underbrace{+\sum_{ia} f_{ia}\{i^\dagger a\} + \sum_{ai} f_{ai}\{a^\dagger i\} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{p^\dagger q^\dagger sr\}}_{W_N}, \end{aligned} \tag{1}$$

where indices $a,b,c,d\cdots$, $i,j,k,l\cdots$, and $p,q,r,s\cdots$ specify virtual, occupied, and arbitrary spin-orbitals. Note that the perturbation W_N now contains the occupied/virtual blocks of the Fock operator.

Standard CC theory begins by defining the form of the cluster operator, T,

$$T = T_1 + T_2 + T_3 + \cdots, \tag{2}$$

where each T_n can be expressed in the language of second quantization as

$$T_n = \frac{1}{(n!)^2}\sum_{\substack{a,b,c,\cdots \\ i,j,k,\cdots}} t_{ijk\cdots}^{abc\cdots}\{a^\dagger i b^\dagger j c^\dagger k\cdots\}. \tag{3}$$

Once an appropriate level of cluster restriction has been chosen, the unitary cluster operator can be defined as

$$\tau = T - T^\dagger, \tag{4}$$

where our working assumption is that we are using real orbitals, hence $t_{ij\cdots}^{ab\cdots *} = t_{ij\cdots}^{ab\cdots}$. In this context, the Schrödinger equation becomes

$$H_N e^\tau|0\rangle = \left(H_N e^\tau\right)_C|0\rangle = \Delta E e^\tau|0\rangle, \tag{5}$$

with C indicating a restriction to connected diagrams and $\Delta E = E_{\mathrm{CC}} - E_{\mathrm{HF}}$ being the correlation energy. We point out that if we follow the traditional CC route of projecting Equation 5 onto elements of the excitation manifold, the resulting residual equations will not terminate. Therefore, we have to pick a point to truncate the resulting expressions based on some specified criteria. In order to generalize upon prior work on the topic,[23,38] we define orders in terms of W_N assuming a non-canonical HF reference, denoted by $|0\rangle$. In other words, f_N is zeroth-order and W_N arises in first-order of MBPT and therefore both τ_1 and τ_2 show up at first-order whereas the remaining higher-order operators, τ_n, arise in the $(n-1)$-order wavefunction of MBPT.

For the purposes of this work, our starting point is the complete, fourth-order UCC(4) energy functional

$$
\begin{aligned}
\Delta E(4) = &- \langle 0| \frac{1}{3!}\left((T_1^\dagger)^2 T_1 f_N T_1 (T_2^\dagger)^2 T_2 f_N T_2 \right) + \frac{1}{2}\left(T_3^\dagger T_1 f_N T_2 + T_3^\dagger T_2 f_N T_1 \right) - \frac{1}{3} T_1^\dagger T_2^\dagger T_1 f_N T_2 + T_2^\dagger T_1^\dagger T_2 f_N T_1 \\
&- \frac{1}{3!}\left((T_1^\dagger)^2 T_1 W_N \right) + \frac{1}{3!}\left((T_2^\dagger)^2 T_2 W_N \right) + \frac{1}{2}\left(T_3^\dagger T_1 W_N + T_3^\dagger T_2 W_N \right) - \frac{1}{3} T_1^\dagger T_2^\dagger T_1 W_N + T_2^\dagger T_1^\dagger T_2 W_N \\
&- \frac{1}{6} T_2^\dagger T_1 T_1^\dagger f_N T_2 + T_2^\dagger T_1 T_1^\dagger W_N + \frac{1}{4}(T_1^\dagger)^2 f_N T_1^2 + (T_2^\dagger)^2 f_N T_2^2 + T_3^\dagger f_N T_3 + T_3^\dagger f_N T_1 T_2 + T_1^\dagger T_2^\dagger f_N T_1 T_2 \\
&+ \frac{1}{2}(T_1^\dagger)^2 W_N T_1 + (T_2^\dagger)^2 W_N T_2 + T_3^\dagger W_N (T_1 + T_2) + T_2^\dagger T_1^\dagger W_N (T_1 + T_2) \\
&- \frac{1}{2} T_2^\dagger T_1 W_N (T_1 + T_2) + \frac{1}{2}(T_1^\dagger)^2 W_N T_2 + \text{h.c.}|0\rangle.
\end{aligned}
\tag{6}
$$

Although Equation 6 involves fully linked diagrams that are connected overall, there may be instances where a given diagram is internally disconnected and therefore requires cancellation. The Supplementary Material discusses how to resolve such examples, and also provides the complete derivations for UCC(2), UCC(3), and UCC(4) in the case of non-canonical HF orbitals.

With this in mind, several internal cancellations are found in Equation 6, leading to a simplified expression for the UCC(4) functional. From there, the residual equations can be formulated:

$$
\frac{\partial \Delta E(4)}{\partial T_1^\dagger} = 0 \Rightarrow D_1 T_1 = W_N + W_N T_2 + W_N T_1 + \frac{1}{4} W_N T_1^2 + \frac{1}{2} T_1^\dagger W_N T_1 + T_2^\dagger W_N T_2, \tag{7a}
$$

$$
\frac{\partial \Delta E(4)}{\partial T_2^\dagger} = 0 \Rightarrow D_2 T_2 = W_N + W_N T_2 + W_N T_1 + \frac{1}{4} W_N T_2^2 + \frac{1}{2} T_2^\dagger W_N T_2 + W_N T_3 + T_1^\dagger W_N T_2 + W_N T_1 T_2, \tag{7b}
$$

$$
\frac{\partial \Delta E(4)}{\partial T_3^\dagger} = 0 \Rightarrow D_3 T_3 = W_N T_2. \tag{7c}
$$

After inserting these stationary conditions into the simplified form of Equation 6, the final, reduced UCC(4) energy is shown to be

$$
\begin{aligned}
\Delta E(4) = &\langle 0|W_N T_2|0\rangle + \langle 0|W_N T_1|0\rangle \\
&- \frac{1}{4}\left(\langle 0|(T_1^\dagger)^2 W_N T_1|0\rangle + \langle 0|(T_2^\dagger)^2 W_N T_2|0\rangle \right).
\end{aligned}
\tag{8}
$$

The following developments focus on Equations 7 and 8 where we are only interested in fully iterating the singles/doubles equations. In order to derive perturbative corrections designed to account for missing T_3-like excitations in UCCSD and variants, we “trace" the residual equations - starting with the T_3 equation of Equation 7 - to determine this operator’s role in the UCC(4) energy. As the derived UCC(4) equations are subsumed within those of UCC($n \to \infty$), any set of T_3 corrections designed for UCCSD(4) are equally viable for infinite-order UCCSD.

This procedure starts by circumnavigating the explicit solution for the T_3 equations by adopting the approximation

$$
T_3^{[2]} = \frac{1}{D_3}(W_N T_2)_C \tag{9}
$$

using T_2 amplitudes from any converged, UCCSD-like calculation. The superscript denotes the order in MBPT through which this contribution is correct, meaning that in this case, $T_3^{[2]}$ is correct through second-order in MBPT. Although T_3 is not directly specified in Equation 8, it does couple to the T_2 equation. Inserting Equation 9 into 7b, we find that

$$
T_2^{[3]} \equiv \frac{1}{D_2}(W_N T_3^{[2]})_C. \tag{10}
$$

Note that these contributions are “new" in the sense that they originate from an approximate solution to T_3. By inserting this “new" $T_2^{[3]}$ into the first term of Equation 8, we can recover a correction to either UCCSD(4) and/or the infinite-order UCCSD energy which solely originates from $T_3^{[2]}$

$$
\begin{aligned}
\Delta E(T_3^{[2]}) &= \langle 0|W_N T_2^{[3]}|0\rangle \\
&\approx \langle 0|T_2^\dagger \left(W_N T_3^{[2]} \right)_C |0\rangle .
\end{aligned}
\tag{11}
$$

Note that the standard convention is to cap with an infinite-order $T_2^\dagger$, shown in the final line of Equation 11. These two terms ultimately lead to diagram C in Figure 1, which defines the [T] correction[6] to infinite-order UCCSD as well as UCCSD(4).

In light of the [T] diagram showing up in both standard and unitary coupled cluster theory, it is reasonable to see if there is

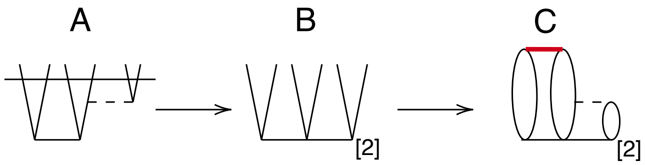

FIG. 1. Outline of the procedure to extract triples’ energy corrections by first A) approximating T_3 with $(W_N T_2)_C$, which B) is correct through second-order in MBPT. If the UCC(4) equations are traced, diagram C) is shown to originate at fourth-order in MBPT and completely defines the [T] correction.

any further overlap in perturbative correction definitions that can be found. A natural place to start in the context of T_3 is the remaining two diagrams that define the (T) correction in standard coupled cluster theory. The first term that shows up in standard CC (T) is of the form $\langle 0|T_2^\dagger f_{ia} T_3^{[2]}|0\rangle$. However, in the second line of Equation S17 (Supplementary Material) this term and its hermitian conjugate are internally cancelled in UCC(4), and as a consequence, this diagram will not appear in any perturbative triples correction to UCC. The remaining (T) diagram is of the form $\langle 0|T_1^\dagger W_N T_3^{[2]}|0\rangle$. Here again, we show in the first line of Equation S17 that this term is also internally canceled in the UCC(4) functional. Because these two diagrams are entirely neglected in UCC theory, it does not have a (T) equivalent.

However, a similar term of the form $Q_1\left(T_2^\dagger (W_N T_2)_C\right)$ does exist in the UCC(4) T_1 equation, where the subtle relationship with the T_3 equations is noted and Q_1 is the projector onto single excitations. Inserting this term directly into the UCC(4) energy expression gives rise to a diagram that is strikingly similar a constituent term in (T), but which is independent of the set of triples excitations that are directly tied to the T_3 operator; this can be seen by the absence of any factors of $\frac{1}{D_3}$. Despite yielding a net excitation effect that *appears* as triples, the overall diagram is managed solely by products of T_1, T_2, and W_N making its contribution redundant for our purposes.

III. COMPUTATIONAL DETAILS

The following UCC results are obtained using the XACC quantum computing framework,[39,40] and PySCF[41] to generate the Hamiltonians, to calculate FCI energies, and to select important τ’s suggested by CCSD amplitudes. Converged UCC amplitudes are then manipulated by the UT2 python module[42], a software dedicated to rapidly prototype alternative coupled cluster theories, to extract the triples corrections. Standard CC calculations were performed using CFOUR[43] and ACESII[44]. The STO-6G[45] basis set was used throughout this work, and core orbitals were dropped, with details regarding the electronic state and geometries being provided in Table S1 of the Supplementary Material. Errors with respect to FCI are defined as $E_{\text{method}} - E_{\text{FCI}}$, where E_{method} represents the energy of a particular UCC method. All FCI, UCCSD, and UCCSD[T] energies are provided in Table S2 of the Supplementary Material.

IV. RESULTS AND DISCUSSION

With quantum computing in the background, two forms of UCC ansatz are adopted here. The first follows closely the standard CC formalism where we simply replace the routine T cluster operator by its anti-Hermitian analog τ and construct the exponential wave operator:

$$|\Psi_{\text{UCCSD}}\rangle = e^{\sum_{ia}\theta_i^a (a^\dagger i - \text{h.c.}) + \sum_{ijab}\theta_{ij}^{ab}(a^\dagger b^\dagger ij - \text{h.c.})}|0\rangle. \qquad (12)$$

As previously noted, this ansatz does not naturally truncate the underlying Schrödinger equation as does the standard e^T. A similar operator more suitable for implementation on a quantum computer is the Trotterized or disentangled form of the ansatz, which we refer to as tUCCSD hereafter

$$|\Psi_{\text{tUCCSD}}\rangle = \prod_{IA} e^{\theta_I^A (A^\dagger I - \text{h.c.})} e^{\theta_{\bar{I}}^{\bar{A}} (\bar{A}^\dagger \bar{I} - \text{h.c.})} \times$$
$$\prod_{\substack{I<J \\ A<B}} e^{\theta_{IJ}^{AB}(A^\dagger B^\dagger IJ - \text{h.c.})} e^{\theta_{\bar{I}\bar{J}}^{\bar{A}\bar{B}}(\bar{A}^\dagger \bar{B}^\dagger \bar{I}\bar{J} - \text{h.c.})} \prod_{IJAB} e^{\theta_{I\bar{J}}^{A\bar{B}}(A^\dagger \bar{B}^\dagger I\bar{J} - \text{h.c.})}|0\rangle, \qquad (13)$$

with I,J,A,B indexing α orbitals and $\bar{I},\bar{J},\bar{A},\bar{B}$ indexing the corresponding β orbitals.

While the UCCSD ansatz in Equation 12 is unique, the composition of the excitation operators alone will not uniquely define its Trotterized analog, since such operators do not commute in general. The potential ambiguity is removed by fully specifying the indices over the products in Equation 13. Such ordering is in line with previous results. However, it is not adequate for geometries away from equilibrium, as will be discussed later.[46] As shown later on, the energy difference between UCCSD and tUCCSD - as well as the corresponding triples corrections - is nominal.

In this work we analyze the performance of three classes of CC/UCC methods:

1. “Standard" CC methods that incorporate triples corrections into CCSD, namely CCSD[T], CCSD(T), CCSDT-1, and ΛCCSD(T);
2. Finite UCC methods based on a truncated energy functional that is correct through fourth-order in MBPT;
3. Infinite-order UCCSD and tUCCSD and the corresponding [T] corrections.

The main goal of this paper is to evaluate the performance of methods under class 3, that is, UCCSD[T] and tUCCSD[T]. Those are built with the set of optimal τ_1 and τ_2 learned by subjecting the two choices of ansätze to the Variational Quantum Eigensolver algorithm (VQE)[47]

$$\tau_1^*, \tau_2^* = \underset{\tau_1,\tau_2}{\arg\min}\, \langle \Psi(\tau_1,\tau_2)|H|\Psi(\tau_1,\tau_2)\rangle\,, \qquad (14)$$

with τ_1^* and τ_2^* being employed in the diagrams of Figure 1 and Equation 11.

Table I records the error of each method against FCI, and the corresponding percentage of total correlation energy. “Standard" CC methods largely align with FCI, with CCSD missing up to 16 mH of correlation energy in the worst case. The inclusion of (T) that perturbatively accounts for triple excitations represents a significant improvement. As an aside, we note that $T_2^\dagger$ is the lowest-order approximation to the complete solution of the left-hand eigenvalue problem defining Λ_2 in standard coupled cluster theory.[48] If we cap the relevant (T) diagram using Λ_1 and Λ_2 instead of $T_1^\dagger$ and $T_2^\dagger$, respectively, the resulting method is known as ΛCCSD(T). To this end, we note that ΛCCSD(T) leads to results that are slightly worse than CCSD(T), except for CO. This is somewhat counter-intuitive, but is a trend that has been previously observed.[49] Overall, the infinite-order CCSDT-1 shows the best performance amongst the methods we consider, except for LiF. This method takes the T_2 portion of the diagram in Figure 1 and adds it to the CCSD T_2 residual equations, accounting for some coupling between T_2 and a diagram that originates from T_3 at lowest order. Thus, the energy “feels" effects from this diagram that originate from $T_3^{[2]}$, which is responsible for this improvement.

Moving to the truncated UCC methods, we see that UCC(2) - or equivalently MBPT(2) - captures 71-98% of the correlation energy across the set of molecules tested, and is consistently above FCI by 3-30 mH. UCC(3) - or equivalently LCCD - is generally a marked improvement, reporting errors no larger than 15 mH except in the case of LiF. The results from UCC(4) are less straightforward; except in the case of CO, UCC(3) results are in overall better agreement with FCI. We also note that - except in the case of the $^1\Delta$ state of O_2 - UCC(4) consistently underestimates FCI. A byproduct of prematurely terminating the commutator expansion is that we forgo any guarantee of achieving an upper bound to FCI, as might otherwise be realized by a fully variational method. Noting the exception of O_2 again, we find that omitting the triples portion of UCC(4) - which defines the UCCSD(4) method - has been shown to lead to improvements,[25] and is of comparable quality to UCC(3). In fact, the UCCSD(4) method is the only truncated UCC method reasonably close to FCI. By adding the [T] correction for the missed triple excitations on top of UCCSD(4), the resulting UCCSD(4)[T] method - with the exception being O_2 - seems to represent a middle ground between UCCSD(4) and UCC(4). This indicates that adding perturbative triples corrections is a step toward the complete UCC(4) method which iterates the triples residual equations.

Turning to the infinite-order UCC methods, both the UCCSD and tUCCSD methods are of comparable or superior quality to the standard CCSD method, and for either ansatz, adding [T] yields a clear and consistent improvement over the baseline ansätze. In fact, for H_2O and N_2 the [T] variants of UCCSD are within 1% of the FCI. For O_2 and C_2, adding [T] improves upon the UCCSD and tUCCSD energies by 2%. This is also true for CO when using UCCSD[T], but for this case the tUCCSD[T] result recovers 6% to the tUCCSD correlation energy. For LiF, the results are more dramatic: the [T] correction improves upon both UCCSD and tUCCSD by more than 20%.

A visual comparison of these infinite-order UCC methods and their “standard" CC counterparts is shown in Figure 2. Here, we see that the UCC-based [T] offers the best performance for both N_2 and O_2, whereas the standard CC methods that attempt to correct for triples excitations generally yield better results for CO and C_2. In the case of LiF, there is a clear benefit from adding some flavor of triples correction to the underlying singles/doubles-only method with the exception of CCSDT-1.

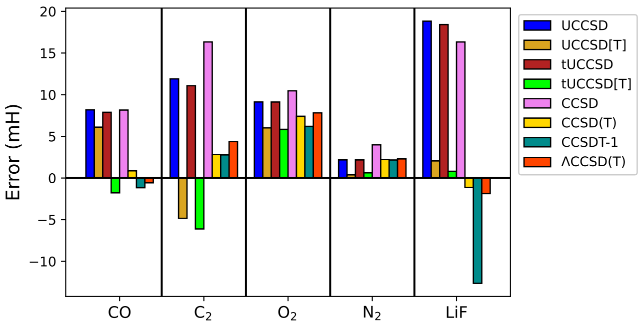

FIG. 2. Bar plot of the errors (with respect to FCI) reported in Table I.

Outside the equilibrium region, the [T] correction to UCCSD yields more dramatic improvements as compared to the standard CCSD and CCSD(T) methods. This is illustrated in Figure 3, which shows the potential energy surface (PES) of N_2. Around 1.75 Å, standard CCSD/CCSD(T) methods begin to diverge with respect to FCI. However, both UCCSD[T] and tUCCSD[T] lead to results that are better-behaved in this regime.

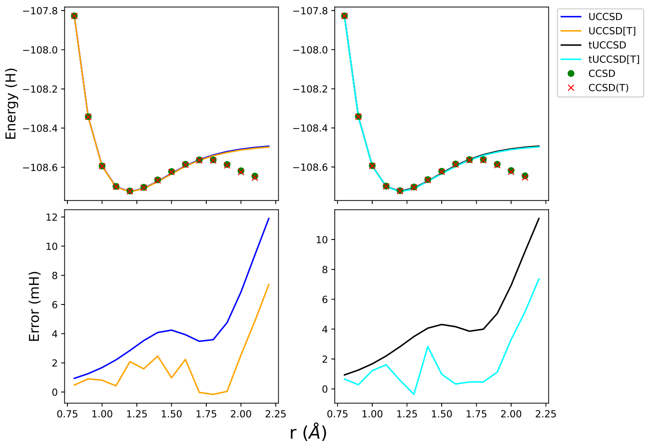

FIG. 3. Comparison of the UCCSD/[T] and tUCCSD/[T] results for the dissociation of N_2. Errors are reported with respect to FCI.

Beyond 2.2 Å, tUCCSD[T] exhibits perplexing behavior that is not seen in UCCSD[T], as shown in Figure S1 of the Supplementary Material. It is known that one byproduct of the tUCCSD ansatz is the inherent sensitivity to operator ordering.[46] While both UCCSD and tUCCSD ansätze remain

TABLE I. Error with respect to FCI, in mH, and the corresponding percentage of the total correlation energy (in parentheses). ‡ denotes an all-electron calculation, with errors corresponding to the all-electron FCI.

Method	H_2O	CO	C_2	O_2	N_2	LiF
UCCSD	0.100 (99.79)	8.183 (94.12)	11.90 (95.61)	9.132 (94.15)	2.176 (98.62)	18.84 (73.24)
UCCSD[T]	0.023 (99.95)	6.105 (95.61)	-4.841 (101.78)	6.018 (96.14)	0.383 (99.75)	2.053 (97.08)
tUCCSD	0.098 (99.80)	7.888 (94.33)	11.08 (95.91)	9.122 (94.16)	2.172 (98.62)	18.42 (73.82)
tUCCSD[T]	0.020 (99.95)	-1.776 (101.27)	-6.109 (102.25)	5.842 (96.25)	0.623 (99.60)	0.809 (98.85)
CCSD	0.118 (99.76)	8.157 (94.14)	16.33 (93.98)	10.47 (93.29)	3.983 (97.48)	16.33 (76.79)
CCSD(T)	0.050 (99.89)	0.865 (99.37)	2.817 (98.96)	7.411 (95.25)	2.231 (98.59)	-1.142 (101.62)
CCSDT-1	0.048 (99.9)	-1.163 (100.83)	2.774 (98.97)	6.201 (96.02)	2.164 (98.63)	-12.64 (117.97)
ΛCCSD(T)	0.085 (99.82)	-0.574 (100.41)	4.375 (98.38)	7.819 (94.99)	2.294 (98.55)	-1.870 (102.66)
UCC(2)	14.22 (71.56)	10.74 (92.28)	25.29 (90.68)	29.76 (80.94)	2.921 (98.15)	12.34 (82.46)
UCC(3)	-0.338 (100.67)	9.795 (92.96)	14.97 (94.48)	2.312 (98.51)	1.036 (99.34)	22.59 (67.90)
UCC(4)‡	-0.942 (101.88)	-9.555 (106.84)	-31.46 (111.56)	21.77 (88.81)	-1.707 (101.07)	-36.78 (152.27)
UCCSD(4)‡	-0.858 (101.71)	-2.326 (98.33)	-6.288 (102.31)	31.61 (83.75)	0.346 (99.78)	6.161 (91.24)
UCCSD(4)[T]‡	-0.936 (101.87)	-7.697 (105.51)	-19.81 (107.28)	29.77 (84.7)	-1.396 (100.87)	-24.11 (134.27)

variational upper bounds to FCI - as expected - it is intriguing that only the [T] corrections built upon tUCCSD behave poorly in this region. Further analysis of the role of the operator ordering is deferred to the Supplementary Material.

V. CONCLUSION AND OUTLOOK

In summary, we study finite-orders of UCC theory to design a perturbative treatment for triple excitations in infinite-order UCCSD, in line with what gave rise to the so-called "gold standard" of quantum chemistry. We show that such an approach reliably improves the energy of several small molecules at - or near - equilibrium geometries as compared to baseline UCCSD. This result is independent of whether the full or Trotterized UCCSD operator is used. An important finding is that the triples correction presented here is much more resilient to the divergent tendencies of analogous methods in standard coupled cluster theory that similarly use perturbation theory to build corrections that account for higher-rank excitations. This becomes particularly evident when stretching N_2 beyond the Coulson-Fischer point, where the [T] correction is surprisingly robust when using unitary cluster amplitudes. However, we note that tUCCSD[T] eventually displays erroneous behavior albeit at bond lengths well beyond the point in which standard perturbative corrections are known to break down; this can be attributed to the operator ordering in the tUCCSD ansätze.

In determining τ_1 and τ_2 according to the VQE algorithm, this step presently constitutes the main computational bottleneck, constraining the present approach to minimal/small basis sets. This likely prevents certain quantitative correlation effects to be observed that would otherwise appear if larger basis sets were used, such as in the case of O_2, which has only 2 virtual orbitals. With advances in quantum computing simulators and hardware, the true benefit of turning to our approach will become apparent, while also revealing the $\mathscr{O}(N^7)$ scaling that is a signature of non-iterative triples corrections. Another relevant limitation of this approach is that, while UCCSD is variational, hence conforming with the GHF theorem, the [T] correction implies the energy functional is no longer stationary with respect to T_1 and T_2, nor does it satisfy an eigenvalue problem. The immediate consequence of this is that properties no longer follow from derivatives of the energy functional. Nonetheless, it is not uncommon to evaluate properties in terms of a variational piece and perturbation contribution, which we anticipate being the most obvious approach for calculating properties within UCCSD[T].

The current work opens the door to several topics worth exploring. The most immediate is that it naturally lends itself to the development of additional perturbative corrections. For example, it is conceivable that energy corrections originating from T_1 could be constructed to account for missing single excitation effects in infinite-order UCCD and tUCCD by studying the UCC(4) equations for T_1 and tracing the logic followed in the development of UCCSD[T]. In addition to the inherit formal contribution of MBPT in conjunction with the UCC ansatz, the ideas presented here have potential applications in quantum computing. More specifically, energy corrections become accessible from hybrid algorithms – e.g. VQE – with a classical post-processing step free from requiring extra quantum resources. This is embodied by the evaluation of the diagrams in Figure 1 constructed using τ_1 and τ_2, which can be obtained on a quantum computer. Continued efforts focusing on the symbiotic relationship between MBPT and UCC that exploit hybrid classical/quantum computing algorithm paradigms will be the target of forthcoming work.

SUPPLEMENTARY MATERIAL

The supplementary material contains detailed derivations of the working equations, geometric and spectroscopic information, raw energy values, and a discussion on the effect of operator ordering.

ACKNOWLEDGMENTS

D.C. and Z.W.W. thank Karol Kowalski for various fruitful discussions. Z.W.W also thanks Dr. Taylor Barnes of MolSSI for his guidance in developing the UT2 software. This work was supported by the Air Force Office of Scientific Research under AFOSR Award No. FA9550-23-1-0118. Z.W.W. thanks the National Science Foundation and the Molecular Sciences Software Institute for financial support under Grant No. CHE-2136142. Z.W.W. also acknowledges support from the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists, Office of Science Graduate Student Research (SCGSR) program. The SCGSR program is administered by the Oak Ridge Institute for Science and Education (ORISE) for the DOE. ORISE is managed by ORAU under contract number DE-SC0014664. D.C. acknowledges support by the "Embedding Quantum Computing into Many-body Frameworks for Strongly Correlated Molecular and Materials Systems" project, which is funded by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, the Division of Chemical Sciences, Geosciences, and Biosciences.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the article and its supplementary material.

[1] R. J. Bartlett, "Coupled-cluster approach to molecular structure and spectra: a step toward predictive quantum chemistry," J. Phys. Chem. **93**, 1697–1708 (1989).

[2] R. J. Bartlett and M. Musiał, "Coupled-cluster theory in quantum chemistry," Rev. Mod. Phys. **79**, 291 (2007).

[3] I. Y. Zhang and A. Grüneis, "Coupled cluster theory in materials science," Front. Mater. **6**, 123 (2019).

[4] I. Shavitt and R. J. Bartlett, *Many-body methods in chemistry and physics: MBPT and coupled-cluster theory* (Cambridge university press, 2009).

[5] A. Köhn and J. Olsen, "Capabilities and limits of the unitary coupled-cluster approach with generalized two-body cluster operators," J. Chem. Phys. **157** (2022).

[6] M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, "Towards a full CCSDT model for electron correlation," J. Chem. Phys. **83**, 4041–4046 (1985).

[7] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, "A fifth-order perturbation comparison of electron correlation theories," Chem. Phys. Lett. **157**, 479–483 (1989).

[8] J. D. Watts, J. Gauss, and R. J. Bartlett, "Coupled-cluster methods with noniterative triple excitations for restricted open-shell Hartree–Fock and other general single determinant reference functions. Energies and analytical gradients," J. Chem. Phys. **98**, 8718–8733 (1993).

[9] S. A. Kucharski and R. J. Bartlett, "Coupled-cluster methods that include connected quadruple excitations, T4: CCSDTQ-1 and Q (CCSDT)," Chem. Phys. Lett. **158**, 550–555 (1989).

[10] Y. J. Bomble, J. F. Stanton, M. Kállay, and J. Gauss, "Coupled-cluster methods including noniterative corrections for quadruple excitations," J. Chem. Phys. **123**, 054101 (2005).

[11] M. Kállay and J. Gauss, "Approximate treatment of higher excitations in coupled-cluster theory," J. Chem. Phys. **123**, 144101 (2005).

[12] R. J. Bartlett, J. Watts, S. Kucharski, and J. Noga, "Non-iterative fifth-order triple and quadruple excitation energy corrections in correlated methods," Chem. Phys. Lett. **165**, 513–522 (1990).

[13] S. A. Kucharski and R. J. Bartlett, "Fifth-order many-body perturbation theory and its relationship to various coupled-cluster approaches," in *Adv. Quantum Chem.*, Vol. 18 (Elsevier, 1986) pp. 281–344.

[14] S. A. Kucharski and R. J. Bartlett, "An efficient way to include connected quadruple contributions into the coupled cluster method," J. Chem. Phys. **108**, 9221–9226 (1998).

[15] S. A. Kucharski and R. J. Bartlett, "Noniterative energy corrections through fifth-order to the coupled cluster singles and doubles method," J. Chem. Phys. **108**, 5243–5254 (1998).

[16] S. A. Kucharski and R. J. Bartlett, "Sixth-order energy corrections with converged coupled cluster singles and doubles amplitudes," J. Chem. Phys. **108**, 5255–5264 (1998).

[17] P. G. Szalay, M. Nooijen, and R. J. Bartlett, "Alternative ansätze in single reference coupled-cluster theory. III. A critical analysis of different methods," J. Chem. Phys. **103**, 281–298 (1995).

[18] R. J. Bartlett, S. A. Kucharski, J. Noga, J. D. Watts, and G. W. Trucks, "Some consideration of alternative ansätz in coupled-cluster theory," in *Many-Body Methods in Quantum Chemistry: Proceedings of the Symposium, Tel Aviv University 28–30 August 1988* (Springer, 1989) pp. 125–149.

[19] T. U. Helgaker and J. Almlöf, "A second-quantization approach to the analytical evaluation of response properties for perturbation-dependent basis sets," Int. J. Quantum Chem. **26**, 275–291 (1984).

[20] R. J. Bartlett and J. Noga, "The expectation value coupled-cluster method and analytical energy derivatives," Chem. Phys. Lett. **150**, 29–36 (1988).

[21] T. Van Voorhis and M. Head-Gordon, "Benchmark variational coupled cluster doubles results," J. Chem. Phys. **113**, 8873–8879 (2000).

[22] B. Cooper and P. J. Knowles, "Benchmark studies of variational, unitary and extended coupled cluster methods," J. Chem. Phys. **133**, 234102 (2010).

[23] R. J. Bartlett, S. A. Kucharski, and J. Noga, "Alternative coupled-cluster ansätze II. The unitary coupled-cluster method," Chem. Phys. Lett. **155**, 133–140 (1989).

[24] A. G. Taube and R. J. Bartlett, "New perspectives on unitary coupled-cluster theory," Int. J. Quantum Chem. **106**, 3393–3401 (2006).

[25] J. D. Watts, G. W. Trucks, and R. J. Bartlett, "The unitary coupled-cluster approach and molecular properties. Applications of the UCC(4) method," Chem. Phys. Lett. **157**, 359–366 (1989).

[26] J. N. Byrd, V. F. Lotrich, and R. J. Bartlett, "Correlation correction to configuration interaction singles from coupled cluster perturbation theory," J. Chem. Phys. **140**, 234108 (2014).

[27] J. Liu and L. Cheng, "Unitary coupled-cluster based self-consistent polarization propagator theory: A quadratic unitary coupled-cluster singles and doubles scheme," J. Chem. Phys. **155**, 174102 (2021).

[28] J. Liu, D. A. Matthews, and L. Cheng, "Quadratic unitary coupled-cluster singles and doubles scheme: Efficient implementation, benchmark study, and formulation of an extended version," J. Chem. Theory Comput. **18**, 2281–2291 (2022).

[29] A. Anand, P. Schleich, S. Alperin-Lea, P. W. Jensen, S. Sim, M. Díaz-Tinoco, J. S. Kottmann, M. Degroote, A. F. Izmaylov, and A. Aspuru-Guzik, "A quantum computing view on unitary coupled cluster theory," Chem. Soc. Rev. **51**, 1659–1684 (2022).

[30] J. Chen, H.-P. Cheng, and J. K. Freericks, "Quantum-inspired algorithm for the factorized form of unitary coupled cluster theory," J. Chem. Theory Comput. **17**, 841–847 (2021).

[31] F. A. Evangelista, "Alternative single-reference coupled cluster approaches for multireference problems: The simpler, the better," J. Chem. Phys. **134**, 224102 (2011).

[32] D. Claudino, "The basics of quantum computing for chemists," Int. J. Quantum Chem. **122**, e26990 (2022).

[33] J. Lee, W. J. Huggins, M. Head-Gordon, and K. B. Whaley, "Generalized unitary coupled cluster wave functions for quantum computation," J. Chem. Theory Comput. **15**, 311–324 (2018).

[34] F. A. Evangelista, G. K. Chan, and G. E. Scuseria, "Exact parameterization of fermionic wave functions via unitary coupled cluster theory," J. Chem. Phys. **151**, 244112 (2019).

[35] C. Li and F. A. Evangelista, "Connected three-body terms in single-reference unitary many-body theories: Iterative and perturbative approximations," J. Chem. Phys. **152**, 234116 (2020).

[36] B. Peng and K. Kowalski, "Mapping renormalized coupled cluster methods to quantum computers through a compact unitary representation of nonunitary operators," Phys. Rev. Res. **4**, 043172 (2022).

[37] I. Magoulas and F. A. Evangelista, "Unitary coupled cluster: Seizing the quantum moment," J. Phys. Chem. A **127**, 6567–6576 (2023).

[38] W. Kutzelnigg, "Error analysis and improvements of coupled-cluster theory," Theoret. Chim. Acta **80**, 349–386 (1991).

[39] A. J. McCaskey, D. I. Lyakh, E. F. Dumitrescu, S. S. Powers, and T. S. Humble, "XACC: a system-level software infrastructure for heterogeneous quantum–classical computing," Quantum Sci. Technol. **5**, 024002 (2020).

[40] D. Claudino, A. J. McCaskey, and D. I. Lyakh, "A Backend-agnostic, Quantum-classical Framework for Simulations of Chemistry in C++," ACM Trans. Quantum Comput. **4**, 1–20 (2022).

[41] Q. Sun, T. C. Berkelbach, N. S. Blunt, G. H. Booth, S. Guo, Z. Li, J. Liu, J. D. McClain, E. R. Sayfutyarova, S. Sharma, *et al.*, "PySCF: the python-based simulations of chemistry framework," Wiley Interdiscip. Rev. Comput. Mol. Sci **8**, e1340 (2018).

[42] "Ut2: A python-based suite of coupled-cluster methods designed to converge towards an "ultimate" t2 method," `https://github.com/zww-4855/ut2`.

[43] D. A. Matthews, L. Cheng, M. E. Harding, F. Lipparini, S. Stopkowicz, T.-C. Jagau, P. G. Szalay, J. Gauss, and J. F. Stanton, "Coupled-cluster techniques for computational chemistry: The CFOUR program package," J. Chem. Phys. **152**, 214108 (2020).

[44] A. Perera, R. J. Bartlett, B. A. Sanders, V. F. Lotrich, and J. N. Byrd, "Advanced concepts in electronic structure (ACES) software programs," J. Chem. Phys. **152**, 184105 (2020).

[45] W. J. Hehre, R. F. Stewart, and J. A. Pople, "Self-consistent molecular-orbital methods. i. use of gaussian expansions of slater-type atomic orbitals," J. Chem. Phys. **51**, 2657–2664 (1969).

[46] H. R. Grimsley, D. Claudino, S. E. Economou, E. Barnes, and N. J. Mayhall, "Is the trotterized UCCSD ansatz chemically well-defined?" J. Chem. Theory Comput. **16**, 1–6 (2019).

[47] A. Peruzzo, J. McClean, P. Shadbolt, M.-H. Yung, X.-Q. Zhou, P. J. Love, A. Aspuru-Guzik, and J. L. O'Brien, "A variational eigenvalue solver on a photonic quantum processor," Nat. Commun. **5** (2014), 10.1038/ncomms5213.

[48] A. G. Taube and R. J. Bartlett, "Rethinking linearized coupled-cluster theory," J. Chem. Phys. **130**, 144112 (2009).

[49] A. G. Taube and R. J. Bartlett, "Improving upon CCSD(T): λCCSD(T). I. Potential energy surfaces," J. Chem. Phys. **128**, 044110 (2008).