

New Perspectives on Unitary Coupled-Cluster Theory

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ABSTRACT: The advantages and possibilities of a unitary coupled-cluster (CC) theory are examined. It is shown that using a unitary parameterization of the wave function guarantees agreement between a sum-over-states polarization propagator and response theory calculation of properties of arbitrary order, as opposed to the case in conventional CC theory. Then, using the Zassenhaus expansion for noncommuting exponential operators, explicit diagrams for an extensive and variational method based on unitary CC theory are derived. Possible extensions to the approximations developed are discussed as well. © 2006 Wiley Periodicals, Inc. *Int J Quantum Chem* 106: 3393–3401, 2006

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Introduction

The conventional coupled-cluster (CC) ansatz [1] expresses the exact wave function as an exponential wave operator acting on a single-determinant reference function

$$|\Psi\rangle = e^T |0\rangle \quad (1)$$

under the assumption that $\langle 0|\Psi\rangle \neq 0$. The cluster operator T is defined to be a particle-hole excitation operator and can be divided according to particle-hole rank

$$T = T_1 + T_2 + T_3 + \cdots + T_N \quad (2)$$

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for an N electron system, where the subscript indicates how many particle-hole pairs are created by the action of T . Explicitly,

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

where the i, j, k, \dots are orbitals occupied in the reference function $|0\rangle$, and a, b, c, \dots are unoccupied orbitals. The CC ansatz has several advantages over other approaches to electronic correlation, such as configuration interaction (CI) [1]. Primary among those properties is extensivity, proper scaling of the energy with particle number [1].

Unfortunately, the price paid for extensivity is that the CC energy is not a variational bound to the exact energy. In conventional CC, the energy can be

written as a generalized expectation value

$$E = \langle 0 | (1 + \Lambda) e^{-T} H e^T | 0 \rangle, \quad (4)$$

where $e^{-T} H e^T$ defines the non-Hermitian CC effective Hamiltonian [1]. Because the energy is not given by a symmetric expectation value, it is not guaranteed to obey the variational theorem. Near equilibrium, the loss of a variational bound does not adversely affect results. However, in situations where the single reference determinant is a poor approximation of the exact wave function, the lack of a variational bound allows the CC energy to diverge toward negative infinity. For example, this type of behavior can be observed along the N₂ bond-breaking curve [2].

Another consequence of the non-Hermiticity of the effective Hamiltonian is that, as shown in Ref. [3], for second-order and higher properties, the sum-over-states polarization propagator formulae and the response theory formulae for approximate CC theory do not agree. The physical impact of this disagreement is that, for the sum-over-states equations [within CC theory, this is the equation-of-motion (EOM) method], the properties are not guaranteed to be linked. For the response theory approach, there is no well-defined excited state wave function to sum over, although the properties are linked.

To address these problems, one may consider using a Hermitian (yet still connected) effective Hamiltonian. These twin requirements are reflected most succinctly in the unitary coupled-cluster (UCC) ansatz.

It was shown long ago ([4–10]) that the exact wave function can be written in the form

$$|\Psi\rangle = \mathbf{U} |0\rangle, \quad \text{for } \langle \Psi | 0 \rangle \neq 0, \quad (5)$$

where \mathbf{U} is a unitary transformation in the whole Hilbert space (not solely in the one-particle subspace that comprises basis set transformations). A unitary transformation can always be parameterized as the exponential of an anti-Hermitian operator. One choice of parameterization is closely related to the CC ansatz. Define

$$\mathbf{U} = e^\tau = e^{T-T^\dagger}, \quad (6)$$

where T is the conventional CC excitation operator and, therefore, T^\dagger is a pure deexcitation operator. Clearly,

$$(e^\tau)^\dagger = e^{\tau^\dagger} = e^{T^\dagger - T} = e^{-\tau} = (e^\tau)^{-1}, \quad (7)$$

which verifies that this parameterization is, in fact, unitary. If the T and T^\dagger operators include up to N excitations, then for N electrons this wave function is exact. Inserting this parameterization for \mathbf{U} into the expectation value for the total energy, and using the norm-conserving properties of unitary transformations:

$$\begin{aligned} E &= \frac{\langle 0 | e^{T^\dagger - T} H e^{T - T^\dagger} | 0 \rangle}{\langle 0 | e^{T^\dagger - T} e^{T - T^\dagger} | 0 \rangle} \\ &= \langle 0 | e^{T^\dagger - T} H e^{T - T^\dagger} | 0 \rangle = \langle 0 | (H e^{T - T^\dagger})_C | 0 \rangle. \end{aligned} \quad (8)$$

Because this equation is an expectation value, it is, by the variational principle, an upper bound for the energy. The energy is also given by the expectation value of a connected operator $(H e^{T - T^\dagger})_C$; therefore, it is extensive [11].

The T amplitudes can be determined from this energy expression by enforcing the condition that

$$\frac{\partial E}{\partial t_k^\dagger} = 0 \quad (9)$$

for a given excited determinant $|K\rangle \in \{|_i^a\rangle, |_{ij}^{ab}\rangle, \dots\}$. Solving the coupled set of equations generated for a subset of $|K\rangle$ and enforcing the condition $T^\dagger = (T)^\dagger$ specifies all the amplitudes up to a given excitation.

The UCC ansatz is attractive for the calculation of quantum chemical systems because it is both extensive and variational. Unfortunately, formulating computationally feasible expressions from the UCC perspective is difficult. To see the source of this difficulty, define the (Hermitian) effective Hamiltonian \bar{H}

$$\bar{H} = e^{-\tau} H e^\tau. \quad (10)$$

Using the Baker–Campbell–Hausdorff expansion to expand this expression in commutators:

$$\begin{aligned} \bar{H} &= H + [H, T] + [T^\dagger, H] + \frac{1}{2} \{ [[H, T], T] \\ &\quad + [T^\dagger, [T^\dagger, H]] + [H, [T, T^\dagger]] \} + \dots \end{aligned} \quad (11)$$

As in conventional CC, terms that contain only excitation operators (e.g., $[[H, T], T]$), or that contain only deexcitation operators (e.g., $[T^\dagger, [T^\dagger, H]]$), will be nonzero only up to four commutators for a two-particle Hamiltonian [11]. Therefore, there is a finite (if large) number of terms in the conventional

CC equations. In the UCC case, however, there is another category of terms, such as $[H, [T, T^\dagger]]$. These terms depend on commutators between T and T^\dagger for which there is no natural termination point [12]. Therefore, the BCH series does not truncate, and the UCC energy and amplitude equations are infinite. However, in the case of two electrons in the UCCD approximation, the series can be resummed to all orders yielding a finite expression [12].

It is not computationally possible to solve equations with an infinite number of (unresummable) terms, so various approximations have been proposed in the literature. There are two primary approaches: the perturbative UCC(n) methods of Bartlett and coworkers [13–16] and the truncated VUCC(n) approach of Kutzelnigg [12]. In both methods, a finite number of terms are kept from the energy and amplitude equations based on some criterion of what the important terms are. For the UCC(n) methods, all terms from the UCC expression are kept that appear in the energy through n th-order in many-body perturbation theory from a Hartree–Fock reference. Assuming that these contributions are the most important ones requires that the reference determinant be a good approximation to the exact wave function. Unfortunately, the cases where the reference determinant is not a good approximation are exactly those cases for which one would expect UCC to be a significant improvement over conventional CC. In the VUCC(n) approach of Kutzelnigg, the equations are truncated at some power of T and T^\dagger . Although not explicitly perturbative, this approach can also be viewed as being based on a perturbative assumption; the infinite series of T amplitudes in the full UCC is only quickly convergent in the case where T is small. Therefore, restricting the highest power of T will be a good approximation, if, and only if, T is small. However, T will be larger the worse the reference determinant is as an approximation to the exact wave function.

These finite approximations to UCC introduce a fundamental assumption that the reference determinant is a good approximation to the exact wave function. This additional requirement limits the validity of both UCC(n) and VUCC(n) and makes them much less attractive alternatives to conventional CC. The truncated UCC approaches have two additional disadvantages. First, although both are rigorously extensive, neither maintains the variational bound of UCC, which is one of the primary reasons for choosing UCC over conventional CC. Second, in both truncations, one loses the exponential structure

of UCC, which is a hallmark of and source of many of the advantages of CC methods.

Theory

UNITARY LINEAR RESPONSE AND POLARIZATION PROPAGATOR

There are two perspectives for calculating the properties of a wave function: the propagator view-point [17–19] and the response function view-point [20]. For an exact wave function, these approaches must yield identical results but, for many approximate wave functions, that identity need not hold. For the sum-over-states propagator approach to agree with the response function approach through all orders of perturbation theory, the wave function must satisfy higher-order generalized Hellman–Feynman theorems: the n th-order perturbed energy $E^{(n)}$ must be independent of the n th-order perturbed wave function $|\psi^{(n)}\rangle$ [3].

Both sum-over-states and response theory have advantages. The primary advantage of the response theory approach is that because it is defined by the derivatives of a linked quantity, all the properties calculated through response theory are linked as well. Therefore, the properties will be extensive [18, 19, 21]. Unfortunately, for second- and higher-order properties, response theory does not yield a sum-over-states expression, nor does it give well-defined excited state wave functions [18, 19].

Within CC theory, the sum-over-states is developed through the EOM approach [17, 18, 22]. The EOM–CC approach has well-defined excited state wave functions, and all properties are given by generalized expectation values over them. However, because the EOM equations are defined by a CI-like set of equations, the higher-order EOM properties are not extensive [18, 19].

The explicit terms that lead to the difference between the CC response theory and EOM–CC methods were derived in Ref. [3]. This derivation was based on the non-Hermitian effective Hamiltonian of conventional CC theory. The unitary CC view-point is based on a Hermitian effective Hamiltonian and may therefore resolve the difference between the two methods to calculate properties.

Following the development of Ref. [3], define the UCC energy functional for the unperturbed problem:

$$E^{(0)} = \langle 0 | e^{-\tau} H^{(0)} e^{\tau} | 0 \rangle. \quad (12)$$

The amplitude equations that define T and T^\dagger are

$$Qe^{-\tau}H^{(0)}e^\tau|0\rangle = 0 \quad \langle 0|e^{-\tau}H^{(0)}e^\tau Q = 0, \quad (13)$$

where $Q = \mathbf{I} - |0\rangle\langle 0|$. The energy equation can also be written in projected form:

$$e^{-\tau}H^{(0)}e^\tau|0\rangle = E^{(0)}|0\rangle \quad \langle 0|e^{-\tau}H^{(0)}e^\tau = \langle 0|E^{(0)}. \quad (14)$$

Define the perturbed (bare) Hamiltonian, where λ is a formal perturbation parameter:

$$H = H^{(0)} + \lambda H^{(1)}. \quad (15)$$

Unitary-transforming the perturbed Hamiltonian,

$$\bar{H} = \bar{H}^{(0)} + \lambda \bar{H}^{(1)} \quad (16a)$$

$$\bar{H}^{(0)} = e^{-\tau}H^{(0)}e^\tau \quad (16b)$$

$$\bar{H}^{(1)} = e^{-\tau}H^{(1)}e^\tau. \quad (16c)$$

Then, the perturbed Hamiltonian obeys the equation,

$$\bar{H}|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle. \quad (17)$$

From the Rayleigh–Schrödinger perturbation series, one can write

$$|\psi(\lambda)\rangle = |\psi^{(0)}\rangle + \lambda|\psi^{(1)}\rangle + \lambda^2|\psi^{(2)}\rangle + \dots \quad (18)$$

$$= |0\rangle + \lambda|\psi^{(1)}\rangle + \lambda^2|\psi^{(2)}\rangle + \dots \quad (19)$$

$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

Equating equal powers of λ , then through first order:

$$[E^{(0)} - \bar{H}^{(0)}]|\psi^{(1)}\rangle = [\bar{H}^{(1)} - E^{(1)}]|0\rangle. \quad (20)$$

Projecting on the left by $\langle 0|$ and taking advantage of $\langle 0|\psi^{(1)}\rangle = 0$,

$$E^{(1)} = \langle 0|\bar{H}^{(1)}|0\rangle. \quad (21)$$

Let $P = |0\rangle\langle 0|$ and $Q = 1 - P = |\mathbf{f}\rangle\langle \mathbf{f}|$ be projectors onto the model space and its orthogonal complement space, respectively. The resolvent can then be written

$$\begin{aligned} \mathcal{R}_0^{\text{UCC}} &= [E^{(0)} - \bar{H}^{(0)}]^{-1}Q \\ &= |\mathbf{f}\rangle\langle \mathbf{f}| E^{(0)} - \bar{H}^{(0)} |\mathbf{f}\rangle^{-1} \langle \mathbf{f}|, \end{aligned} \quad (22)$$

where superscript UCC indicates that the resolvent is defined with respect to the ground-state UCC problem. One can then write the formal solution for the first-order perturbed wave function

$$|\psi^{(1)}\rangle = \mathcal{R}_0^{\text{UCC}}[\bar{H}^{(1)} - E^{(1)}]|0\rangle. \quad (23)$$

Going to higher orders in the perturbation:

$$E^{(2)} = \langle 0|[\bar{H}^{(1)} - E^{(1)}]\mathcal{R}_0^{\text{UCC}}[\bar{H}^{(1)} - E^{(1)}]|0\rangle$$

$$|\psi^{(2)}\rangle = \mathcal{R}_0^{\text{UCC}}[\bar{H}^{(1)} - E^{(1)}]\mathcal{R}_0^{\text{UCC}}[\bar{H}^{(1)} - E^{(1)}]|0\rangle \quad (24)$$

$$E^{(3)} = \langle 0|[\bar{H}^{(1)}\mathcal{R}_0^{\text{UCC}}]^2\bar{H}^{(1)}|0\rangle$$

$$|\psi^{(2)}\rangle = \mathcal{R}_0^{\text{UCC}}\bar{H}^{(1)}\mathcal{R}_0^{\text{UCC}}\bar{H}^{(1)}|0\rangle. \quad (25)$$

From a propagator viewpoint, the resolvent should be given by the complete set of excited states, not simply those states orthogonal to the reference state $|0\rangle$. In CC theory, the excited states correspond to using solutions of the EOM–CC theory equations. In EOM–UCC [23–26], the excited states $|\psi_K\rangle$ are parameterized as unitary transformations of excitations from the ground UCC state

$$\begin{aligned} |\psi_K\rangle &= \tilde{a}_0^K|\psi_0\rangle \\ &= e^\tau a_0^K e^{-\tau} e^\tau |0\rangle \\ &= e^\tau a_0^K |0\rangle = e^\tau |K\rangle, \end{aligned} \quad (26)$$

where a_0^K is a physical excitation from the ground state to some excited state $|K\rangle$. These can be determined by solving the Hermitian eigenvalue problem

$$\bar{H}^{(0)}|K\rangle = \omega_K|K\rangle \quad (27)$$

over the set of states $\{|0\rangle, |i^a\rangle, |ij^{ab}\rangle, \dots\}$ up to some maximum excitation level. After the excitations $|K\rangle$ have been determined, the resolution of the identity in the full excitation manifold is

$$\mathbf{I} = \sum_K |K\rangle\langle K|. \quad (28)$$

Therefore, the resolvent from the EOM–UCC polarization propagator perspective is written

$$\mathcal{R}_0^{\text{EOM-UCC}} = \sum_K |K\rangle\langle K| E^{(0)} - \bar{H}^{(0)} |K\rangle^{-1} \langle K|. \quad (29)$$

Since the state $|K\rangle$ was formed by diagonalization over the single, double, etc., excitations, the set of all $|K\rangle$ must span the same space as the original excitations did. Therefore, the states $|K\rangle$ are a unitary transformation of the original excitation space, and since the resolvent is invariant to unitary transformations

$$\mathcal{R}_0^{\text{EOM-UCC}} = \mathcal{R}_0^{\text{UCC}}, \quad (30)$$

and the polarization propagator formulation agrees with the RSPT expression for the UCC case in all orders, as would be expected.

The second approach to calculating properties is to focus on the response of the CC amplitudes to a perturbation. One can write

$$|\psi^{(0)}\rangle = e^\tau |\phi^{(0)}\rangle = e^\tau |0\rangle \quad (31a)$$

$$|\psi^{(1)}\rangle = e^\tau |\phi^{(1)}\rangle = e^\tau \tau^{(1)} |0\rangle \quad (31b)$$

$$|\psi^{(2)}\rangle = e^\tau |\phi^{(2)}\rangle = e^\tau \left[\frac{1}{2} \tau^{(1)} \tau^{(1)} + \tau^{(2)} \right] |0\rangle. \quad (31c)$$

Inserting these expressions into the RSPT series,

$$\begin{aligned} E^{(1)} &= \langle 0 | \bar{H}^{(1)} | 0 \rangle \quad (32) \\ E^{(2)} &= \langle 0 | [\bar{H}^{(1)} - E^{(1)}] \tau^{(1)} | 0 \rangle \\ &\quad - \frac{1}{2} \langle 0 | [E^{(0)} - \bar{H}^{(0)}] [\tau^{(1)}]^2 | 0 \rangle \\ &= \langle 0 | [\bar{H}^{(1)} - E^{(1)}] \mathcal{R}_0^{\text{UCC}} [\bar{H}^{(1)} - E^{(1)}] | 0 \rangle \\ &\quad - \frac{1}{2} \langle 0 | [E^{(0)} - \bar{H}^{(0)}] \tau^{(1)} \mathcal{R}_0^{\text{UCC}} [\bar{H}^{(1)} - E^{(1)}] | 0 \rangle. \end{aligned} \quad (33)$$

While the expression for $E^{(1)}$ agrees with that derived from the EOM-UCC viewpoint (21), the expression for $E^{(2)}$ appears not to agree with (24). In particular, the presence of the second term in (33) is what causes second-order properties from the EOM-CC and CC-LR viewpoints to differ. However, in UCC the effective Hamiltonian is, Hermitian, as described by (13) and (14). Therefore,

$$\langle 0 | [E^{(0)} - \bar{H}^{(0)}] \equiv 0. \quad (34)$$

Thus, it is clear that

$$E^{(2)} = \langle 0 | [\bar{H}^{(1)} - E^{(1)}] \mathcal{R}_0^{\text{UCC}} [\bar{H}^{(1)} - E^{(1)}] | 0 \rangle, \quad (35)$$

which agrees with the EOM-UCC expression (24). In Ref. [3], the expressions determined for the

third- and higher-order CC-LR equations are shown to differ from the EOM-CC viewpoint by

$$E_{\text{LR}}^{(n)} = E_{\text{EOM}}^{(n)} + \langle l_0 | [E^{(0)} - \bar{H}^{(0)}] F^{(n)} | r_0 \rangle, \quad (36)$$

where $F^{(n)}$ is some function of perturbed T amplitudes. The same idea holds true for UCC theory, where

$$E_{\text{UCC-LR}}^{(n)} = E_{\text{EOM-UCC}}^{(n)} + \langle 0 | [E^{(0)} - \bar{H}^{(0)}] \tilde{F}^{(n)} | 0 \rangle. \quad (37)$$

But in the UCC case, as a result of (34), the second term in this expression is zero (for all $\tilde{F}^{(n)}$), yielding

$$E_{\text{UCC-LR}}^{(n)} = E_{\text{EOM-UCC}}^{(n)}. \quad (38)$$

The linear response equations are automatically linked, because they are defined as derivatives of a linked quantity. Therefore, the EOM-UCC equations, which yield excited-state wave functions, are linked and extensive.

TRACTABLE APPROACH TO UCC

To maintain both extensivity and variational character in an approximate UCC expression, a perturbative truncation is not suitable. One way to better understand the structure of the UCC expression, while maintaining an infinite-order exponential structure to the equations is by using the Zassenhaus expansion [27, 28] for noncommuting exponentials:

$$e^{T-T^\dagger} = e^T e^{-T^\dagger} e^{\frac{1}{2}[T, T^\dagger]} e^{\text{DC}} e^{\text{TC}} \dots, \quad (39)$$

where

$$\text{DC} = \frac{1}{3}[T^\dagger, [T, T^\dagger]] + \frac{1}{6}[[T, T^\dagger], T] \quad (40)$$

$$\begin{aligned} \text{TC} &= \frac{1}{8}[T^\dagger, [T^\dagger, [T, T^\dagger]]] + \frac{1}{8}[T^\dagger, [[T, T^\dagger], T]] \\ &\quad + \frac{1}{24}[[[T, T^\dagger], T], T], \end{aligned} \quad (41)$$

and there are an infinite number of higher-order commutators of T and T^\dagger that follow in the product expansion.

Therefore, one can define the right eigenstate of the (bare) Hamiltonian as

$$|\Psi\rangle = e^T e^{-T^\dagger} e^{\frac{1}{2}[T, T^\dagger]} e^{\text{DC}} e^{\text{TC}} \dots |0\rangle. \quad (42)$$

Then, there are two choices for the left eigenstate in the energy functional: (i) the inverse of the expansion

of the right eigenstate; and (ii) the Hermitian conjugate of the expansion of the right eigenstate. Both choices of expansion are exact in the untruncated case (they are identically equal to the full unitary operator), but for any truncation they can be different. This difference becomes apparent when both choices of expansion are truncated by the number of exponentials:

$$E_{\text{inv}}^{[1]} = \langle 0 | e^{-T} H e^T | 0 \rangle = \langle 0 | (H e^T)_c | 0 \rangle$$

$$E_{hc}^{[1]} = \langle 0 | e^{T^\dagger} H e^T | 0 \rangle \quad (43)$$

$$E_{\text{inv}}^{[2]} = \langle 0 | e^{T^\dagger} e^{-T} H e^T e^{-T^\dagger} | 0 \rangle = \langle 0 | [e^{T^\dagger} (H e^T)_c]_c | 0 \rangle$$

$$E_{hc}^{[2]} = \langle 0 | e^{T^\dagger} H e^T | 0 \rangle \quad (44)$$

Examining the two forms, one can identify the inverse expansion as a “connected expansion” for all truncations. Therefore, the inverse expansion yields a fully linked effective Hamiltonian, with conventional CC as the first approximation, non-symmetric expectation value CC [29] as the second approximation, and higher-order variants that are progressively “more unitary.” Unfortunately these truncations, while clearly extensive, break the variational condition. One could look at this expansion as the generator of many different CC ansätze, however, for the case of $E_{\text{inv}}^{[2]}$ and higher-order variants, the computational cost becomes untenable. In the case of nonsymmetric expectation value CC, the cost scales as $O(N^{10})$ [29], and the higher-order expressions will be even more expensive.

The other choice of expansion, based on Hermitian conjugates, is related to the expectation value CC (XCC) methods [29, 30]. Unfortunately, because UCC is always properly normalized, these XCC variants do not have denominators. Therefore, one cannot write these energy expressions in connected form [29]. Because of the importance of extensivity (and, therefore, of connected operators), these variants will not be considered further in the present study.

LEFT AND RIGHT EIGENVECTORS

Although the above energy expressions are relatively simple, the correct CC Lagrangian expression, where the generalized Hellman–Feynman theorem is enforced, is more complicated. First, examine the

case $E_{\text{inv}}^{[1]}$, above. The ket wave function is parameterized in that case

$$|\Psi\rangle = e^T |0\rangle. \quad (45)$$

Comparing it with the Zassenhaus expansion,

$$|\Psi\rangle = e^T e^{-T^\dagger} e^{\frac{1}{2}[T, T^\dagger]} e^{\text{DC}} e^{\text{TC}} \dots |0\rangle, \quad (46)$$

one can define the operator \mathcal{R} as the terms that have been removed from the Zassenhaus expansion

$$\mathcal{R} = e^{-T^\dagger} e^{\frac{1}{2}[T, T^\dagger]} e^{\text{DC}} e^{\text{TC}} \dots \quad (47)$$

Examining the bra wave function,

$$\langle\Psi| = \langle 0 | e^{-T} \quad (48)$$

and comparing it with the full Zassenhaus expansion, it is clear that one can define an operator \mathcal{L} such that

$$\mathcal{L} = \dots e^{\text{TC}^\dagger} e^{\text{DC}^\dagger} e^{\frac{1}{2}[T^\dagger, T]} e^{T^\dagger}. \quad (49)$$

Then the exact (untruncated) energy expression is

$$E = \langle 0 | \mathcal{L} e^{-T} H e^T \mathcal{R} | 0 \rangle. \quad (50)$$

The presence of additional operators \mathcal{R}, \mathcal{L} on both sides of the effective Hamiltonian is surprising: in conventional CC, one has only an added operator on the left side of the effective Hamiltonian, i.e., the Λ operator of CC gradient theory.

From more general (higher-order) inverse expansions, the exact energy functional is

$$E = \langle 0 | \mathcal{L} \bar{H} \mathcal{R} | 0 \rangle, \quad (51)$$

where \bar{H} is an effective Hamiltonian generated by truncating the Zassenhaus expansion, and \mathcal{L} and \mathcal{R} are all the terms of the Zassenhaus expansion not included in the effective Hamiltonian. Therefore, one has the relation

$$\mathcal{L} = \mathcal{R}^{-1}. \quad (52)$$

This relationship guarantees that the full effective Hamiltonian remains connected; for any arbitrary truncation of the operators within T or \mathcal{L} , as long as (52) holds, $\mathcal{L} \bar{H} \mathcal{R}$ will be connected. Normally, however, one is less concerned with the entire effective Hamiltonian, than with the linkedness of the ground-state energy. Enforcing the requirement that the ground-state energy be linked is a weaker

requirement than (52); in fact, the ground-state energy will be linked as long as (52) holds within the ground-state sector of the effective Hamiltonian. Therefore, by choosing the parameterization

$$\mathcal{R} = \mathbf{I}, \quad (53)$$

all that is necessary to maintain the connectedness of the energy is for

$$\mathcal{L} = \mathbf{I} + \mathcal{L}' \quad \text{such that } \langle 0 | \mathcal{L}' = 0. \quad (54)$$

Similar to the way Λ can be defined exactly in terms of T and T^\dagger , but generally allowed to vary independently of T , one can relax the constraint on \mathcal{L} and \mathcal{R} derived from the Zassenhaus expansion. Then the energy can take on a more general form than (51). It is easy to impose condition (52) if one chooses an exponential parameterization for the left- and right-hand operators. For example, one could choose to define

$$\mathcal{L} = e^{s^\dagger}, \quad (55)$$

then, by (52),

$$\mathcal{R} = e^{-s^\dagger} \Rightarrow \mathcal{R} |0\rangle = |0\rangle. \quad (56)$$

Therefore, this parameterization of \mathcal{L} yields the extended CC theory energy functional [31]:

$$E = \langle 0 | e^{s^\dagger} \bar{H} | 0 \rangle. \quad (57)$$

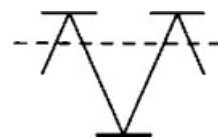
Similarly, by parameterizing $\mathcal{R} = e^s$, one arrives at the Hermitian conjugate of (57). Another simple choice would be to choose another unitary parameterization of both \mathcal{L} and \mathcal{R} . Of course, this choice leads back to a reformulation of the original UCC ansatz.

TRUNCATING THE ZASSENHAUS EXPANSION

By using the Zassenhaus expansion, one is able to disentangle the excitation and deexcitation operators from UCC so that there is (in principle) a well-defined set of similarity transforms that yield the exact UCC result. Unfortunately, the expressions do not look computationally tractable, because the product is infinite.

However, for any given number of electrons, N , the number of terms in the Zassenhaus product truncates in an N -dependent way. For example, for one electron, all that is necessary for an exact wavefunction is T_1 , and terms such as $[T_1^\dagger, [T_1, T_1^\dagger]] =$

$[T_1^\dagger [T_1 T_1^\dagger]_c]_c$, can be represented diagrammatically [32] as


(58)

Interpreting this diagram, above the dashed line (which is *not* a perturbation theory denominator) is a double deexcitation. Since there is only a single electron in this case, the double deexcitation is a priori zero, and, therefore, the whole diagram must be zero as well. Similar analysis shows that the effective Hamiltonian form of the Zassenhaus expansion of UCC is a finite and exact product of exponentials for any (finite) number of electrons.

In the case of one- and two-electron systems, one has

$$1e^- : \text{UCCS1} \quad |\Psi_{\text{exact}}\rangle = e^{T_1} e^{-T_1^\dagger} e^{\frac{1}{2}[T_1, T_1^\dagger]} |0\rangle \quad (59)$$

$$2e^- : \begin{cases} \text{UCCD2} & |\Psi_{\text{UCCD}}\rangle = e^{T_2} e^{-T_2^\dagger} e^{\frac{1}{2}[T_2, T_2^\dagger]} |0\rangle \\ \text{UCCSD2} & |\Psi_{\text{exact}}\rangle = e^T e^{-T^\dagger} e^{\frac{1}{2}[T, T^\dagger]} \\ & \times e^{\frac{1}{3}[T_1^\dagger, [T, T_1^\dagger]] + \frac{1}{6}[[T_1, T^\dagger], T_1]} \\ & \times e^{\frac{1}{8}[T_1^\dagger, [[T_1, T_1^\dagger], T_1]]} |0\rangle \end{cases} \quad (60)$$

For larger numbers of electrons, more complicated expressions can be derived, with the general rule that for N electrons, the highest commutator term is one that contains N T_1 terms and N T_1^\dagger terms. With these parameterizations of the wave function, equations for the energy and for the T amplitudes can be derived through straightforward (although tedious) manipulation of the diagrammatic equivalents of these wavefunctions.

Because of the additive separability of the UCC energy and multiplicative separability of the UCC wave function, the UCC- N expressions are equally exact for the case of M noninteracting sets of N electrons. Therefore, one can define an approximate ansatz for an N electron system by treating it as $N/2$ two-electron systems, and using the UCCD2 or UCCSD2 ansatz.

Within the UCCD2 approximation (for an arbitrary number of electrons), the energy can be written diagrammatically

$$E = \left(\text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \text{diagram 4} \right) \quad (61)$$

$$= \text{Re} \left[2 \left(\text{diagram 1} + \text{diagram 2} + \text{diagram 3} \right) \right] \quad (62)$$

Requiring the energy to be stationary with respect to variations in T_2^\dagger yields the T_2 equations:

$$\text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} - x = 0 \quad (63)$$

Note that because the goal is a theory that maintains Hermiticity, the condition that $(T)^\dagger = T^\dagger$ is enforced, i.e., (63) determines both T_2 and T_2^\dagger .

A more complete description is given by the UCCSD2 approximation:

$$E = Re \left\{ 2 \left(\text{Diagram 1} \right) + \text{Diagram 2} - x + 2 \left(\text{Diagram 3} \right) + \text{Diagram 4} + \text{Diagram 5} - x + 2 \left(\text{Diagram 6} \right) + \text{Diagram 7} \right. \\ + 2 \left(\text{Diagram 8} \right) + 2 \left(\text{Diagram 9} \right) + 2 \left(\text{Diagram 10} \right) + \text{Diagram 11} + \text{Diagram 12} - x + \frac{4}{3} \left(\text{Diagram 13} \right) - x \\ \left. + \text{Diagram 14} - x + \text{Diagram 15} + \frac{1}{3} \left(\text{Diagram 16} \right) - x + \frac{4}{3} \left(\text{Diagram 17} \right) \right\} \quad (64)$$

The coefficients of some of these diagrams are quite different from what one would expect within conventional CC theory. However, they are required to take into account the coefficients of the commutators in the Zassenhaus expansion. For both the UCCD2 and UCCSD2 methods, the computational cost should be at most $O(N^6)$, comparable to CCSD. Because the methods presented here are both extensive and variational, it seems likely that there must be a downside as well. Unlike the full versions of UCC, the UCCD2 and UCCSD2 methods are not exact for more than two electrons. However, one can converge to the exact answer by allowing progressively higher numbers of electrons (e.g., UCCSD3, UCCSD4), but that will increase the computational cost substantially, thus defeating the advantage of these methods.

These approximations have been made under the assumption that every diagram that requires more than N (in the cases discussed above, two) particles is zero. However, in an interacting system of more than N electrons (rather than a group of noninteracting systems), this is obviously an approximation. Until the method has been implemented and tested, one cannot know how well this truncation will perform. One possible extension, which would increase computational cost but still yield a finite set of energy diagrams and reasonable computational cost, would be to forbid only contractions between T and T^\dagger operators above a certain electron number. That would mean that Hamiltonian diagrams of all possible electron numbers would be included. This approximation is not explicitly presented in the

present study, but if in the course of further investigations we find that it is necessary to achieve sufficient accuracy to go beyond the formulation here, that would likely be the first generalization to attempt.

Conclusion

The unitary CC ansatz, in its exact form, satisfies many of the desiderata for an accurate correlated electronic structure method [29]: (i) it is extensive; (ii) it is variational; (iii) it satisfies a Hellman–Feynman theorem, (iv) it is exact in the full T limit, and (v) it is symmetric with respect to the left and right eigenstates. Further, it is shown that UCC unifies the EOM and LR formulations of higher-order properties. Therefore, the excited-state wave function from an EOM–UCC calculation is extensive and also corresponds to a sum-over-states polarization propagator expression.

However, the UCC energy functional is an infinite commutator series, which makes it computationally intractable. Prior approaches to truncate this series are based on a perturbative expansion around a given reference state, limiting the range of applicability of the approximate UCC methods. Also, these approximations do not maintain the variational bound. On more aesthetic grounds, the approximations lose the desirable exponential structure of CC theory (although they are extensive).

The approach advocated is to truncate UCC based on an explicitly exponential formulation

of UCC through the Zassenhaus expansion of noncommuting exponentials. Therefore, by truncating at a given number of exponentials, one is left with a connected effective Hamiltonian and a finite number of terms. Unfortunately, even with this approximation, the computational cost of the approximate UCC would be too high to allow general applications. Therefore, a further approximation based on keeping only those terms that are nonzero for up to two electrons is defined within the UCCD2 and UCCSD2 variants. The UCCSD2 approximation is exact for two electrons, and the energy is given by a Hermitian expectation value, and is therefore an upper bound to the exact energy. Also, because UCCSD2 is formulated through a connected effective Hamiltonian, it is rigorously linked for all numbers of electrons. The effectiveness of these approximations has not yet been tested, but they offer a new route to using the UCC ansatz for practical calculations.

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