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Revisitation of Nonorthogonal Spin Adaptation in Coupled Cluster Theory

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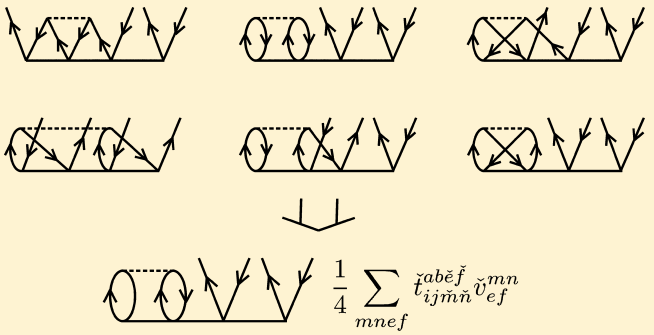
ABSTRACT: The benefits of what is alternatively called a nonorthogonally spin-adapted, spin-free, or orbital representation of the coupled cluster equations is discussed relative to orthogonally spin-adapted, spin−orbital, and spin-integrated theories. In particular, specific linear combinations of the orbital cluster amplitudes, denoted spin-summed amplitudes, are shown to reduce the number of contractions that must be explicitly performed and to simplify the expressions and their derivation. The computational efficiency of the spin-summed approach is discussed and compared to orthogonally spin-adapted and spin-integrated approaches. The spin-summed approach is shown to have significant computational advantages relative to the other methods for CCSDT and CCSDTQ.



1. INTRODUCTION

The coupled cluster method[1] is perhaps the most successful electronic structure theory ever developed.[2−6] However, to credit the success of the past several decades to a single, unified theory is misleading, as the coupled cluster label is in fact descriptive of a varied family of methods. While all of these methods are eventually unified in the use of an exponential ansatz, differences in implementation and function arise rapidly. For example, the cluster amplitudes can either be solved for variationally or by projection, leading to a rift between VCC[7] and other methods. Within projection-based methods, the transformation of the Hamiltonian can also be either unitary[8] or a similarity transform. Of course, there also are methods that sit between these extremes such as XCC.[9] The cluster expansion itself is also open to much flexibility, both in precisely which cluster operators or operator products to include, leading to methods such as LCCSD (CEPA-0),[10] CCD (CPMET),[1] QCISD,[11] CC*n*,[12] and CCSDT-*n*,[13] and for methods with a nonterminating expansion, at which point to terminate the expansion. Approximations in this vein abound, as do a multitude of noniterative corrections such as CCSD(T),[14] CCSD+T(CCSD),[15] and CCSD-T.[16]

One finer point of coupled cluster theory, and the point that is the focus of this work, is the choice of the zero-order basis, and similarly the precise operator form of the cluster operators. It was long ago recognized that for open-shell cases, even if the reference determinants are chosen to be eigenfunctions of the total angular momentum operator $\hat{S}^2$ (i.e., states of definite spin), the final coupled cluster wave function is in general *not* so.[17] It was also recognized that for closed-shell molecules, even though the coupled cluster wave function is a spin eigenfunction, the representation of the configuration space in terms of simple spin-free Slater determinants is nonorthogonal and linearly dependent for triple excitations and beyond.[18] Similarly, the cluster amplitudes in the spin-free representation are linearly dependent for CCSDT, CCSDTQ, etc. This led to the development of explicit orthogonally spin-adapted coupled cluster theories that both guarantee spin character of the wave function and deal only in linearly independent and orthogonal configuration spaces.

Much work has been done with these theories, including application to open-shell systems[19] and extensions to triple excitations and higher[18,20] and to multireference coupled cluster methods.[19,21] However, the formal benefits of orthogonal spin adaptation come with a price, both in difficulty deriving the equations and—at least to date—efficient implementation of the result. It is the goal of this work to show that although the traditional spin-free approach is not as satisfying mathematically, it leads to an efficient and easily implemented coupled cluster method.

2. THEORY

The coupled cluster family of methods define the correlated wave function using an exponential ansatz, where the exact wave function is written as an exponential excitation operator applied to some reference wave function (a single Slater determinant),

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Phi_0\rangle \tag{1}$$

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$\hat{T}$ is an excitation operator defined in terms of single-particle annihilation and creation operators (a_p and $a_p^\dagger$, respectively),

$$\hat{T} = \sum_n^N \hat{T}_n$$

$$\hat{T}_n = \left(\frac{1}{n!}\right)^2 \sum_{\substack{a_1 \ldots a_n \\ i_1 \ldots i_n}} t_{i_1 \ldots i_n}^{a_1 \ldots a_n} a_{a_1}^\dagger \ldots a_{a_n}^\dagger a_{i_n} \ldots a_{i_1} \tag{2}$$

The standard notation is used here, where the letters i, j, k, l ... refer to occupied orbitals in the reference wave function, a, b, c, d ... refer to unoccupied (virtual) orbitals, and p, q, r, s ... refer to any orbitals. In addition, no explicit mention is made here of spin functions; rather, each orbital index is assumed to run over all spin−orbitals. The most commonly used method to determine the cluster amplitudes $t_{i_1 \ldots i_n}^{a_1 \ldots a_n}$ and the energy is to require that the projection of the Schrödinger equation onto the set of excited reference determinants vanishes,

$$E_{CC} = \langle \Phi_0 | (\hat{H}\ e^{\hat{T}})_c | \Phi_0 \rangle \tag{3}$$

$$0 = \langle \Phi_{i_1 \ldots i_n}^{a_1 \ldots a_n} | (\hat{H}\ e^{\hat{T}})_c | \Phi_0 \rangle \tag{4}$$

where $|\Phi_{i_1 \ldots i_n}^{a_1 \ldots a_n}\rangle$ is an excited determinant and $()_c$ refers to only the connected components of the operator product (i.e, components where at least one annihilation/creation operator of $\hat{H}$ is contracted with each $\hat{T}_n$ operator in the expansion of $e^{\hat{T}}$).[1,22]

At this point, spin−orbital, spin-integrated, spin-free, and orthogonally spin-adapted methods all agree on paper, with the differences lying in the definition of the action of the a_p and $a_p^\dagger$ operators. Spin−orbital approaches leave these as spin−orbital operators, with p running over both α and β orbitals. Spin-integrated approaches simply break the operators into α ($a_p \equiv a_{\alpha,p}$) and β ($\overline{a}_p \equiv a_{\beta,p}$) parts and discard terms where the spin part integrates to zero. These methods are entirely equivalent and applicable to reference functions of any spin, although they do not guarantee the spin of the coupled cluster wave function (except in the closed-shell case).

Instead of explicitly classifying each label of $|\Phi_{i_1 \ldots i_n}^{a_1 \ldots a_n}\rangle$ and $t_{i_1 \ldots i_n}^{a_1 \ldots a_n}$ as a definite spin, the orthogonally spin-adapted approach labels the states and amplitudes using orbital labels only and instead adds explicit spin quantum numbers for the intermediate and final coupled spins. These spin-adapted quantities are linear combinations of the spin-integrated ones, corresponding to electronic Gel'fand states.[23−25] The spin-adapted states and amplitudes also display symmetry relations on permutation of either virtual or occupied indices. This allows the indices to be placed in canonical order and lowers the number of $\hat{T}_k$ amplitudes to $\sim N_S(k)((n_v^k n_o^k)/(k!)^2)$ where $N_S(k)$ gives the number of intermediate spin combinations for k-fold excitations (1, 2, 5, 14 for single, double, triple, and quadruple excitations etc.).[18,26]

In contrast, the nonorthogonally spin-adapted method takes the spin-integrated quantities as linear combinations of orbital, or as denoted here, skeleton quantities for a restricted closed-shell reference. The spin-integrated quantities are formed from these by antisymmetrization of same-spin groups of indices, for example,

$$t_{ij\overline{k}}^{ab\overline{c}} = t_{i\overline{j}k}^{a\overline{b}c} = P_-(a/b)\check{t}_{ijk}^{abc} \tag{5}$$

where $\check{t}$ denotes a skeleton amplitude; for the spin-integrated amplitude, no bar (bar) denotes α (β) spin. P_- is the antisymmetrization operator. Unless otherwise noted, in this and all following equations the same relations hold true for amplitudes of all levels of excitation and triple excitations are used only representatively. The skeleton amplitudes have the symmetry property that they are invariant under permutation of columns of occupied/virtual indices,

$$\check{t}_{ijk}^{abc} = \check{t}_{ikj}^{acb} = \check{t}_{jik}^{bac} = \check{t}_{jki}^{bca} = \check{t}_{kij}^{cab} = \check{t}_{kji}^{cba} \tag{6}$$

The number of skeleton amplitudes for $\hat{T}_k$ is then $\sim((n_v^k n_o^k)/k!)$. Since $k! = 1, 2, 6, 24, \ldots \geq N_S(k)$, the amplitude equations become increasingly overdetermined, although the factor is still less than two for CCSDTQ. The following two sections detail how the skeleton amplitudes can be used to efficiently implement the closed-shell coupled cluster equations, despite their greater number compared to orthogonal spin adaptation.

3. SPIN SUMMATION

For a closed-shell system, the coupled cluster equations can be formulated and solved entirely in terms of the skeleton $\hat{T}$ amplitudes and using spin-free Slater determinants.[27] The Goldstone diagrams give a powerful method to derive these equations without resorting to spin−orbital or spin-integrated intermediate expressions. However, the Goldstone diagrams are particularly numerous, exceeding the number of spin−orbital diagrams by up to 8-fold for CCSDTQ[26] (if permutation factors are handled properly). Instead, the spin-free skeleton-based equations can be factored using specific linear combinations, denoted spin-summed amplitudes. The initial impetus for the use of the spin-summed amplitudes came in attempting to find the most efficient form for the closed-shell CCSD equations, particularly, the particle-hole (ring) part of $D_2T_2 \leftarrow W_NT_2^2$.[28] The optimal implementation for this contraction involves a first term involving linear combinations of different orbital label orderings for both T_2 amplitudes and for the integrals, and a second term involving a simple permutation and no linear combination, which partially cancels with the first term.[28] Further work extended this seemingly esoteric form of the ring-type terms to higher orders of coupled cluster. Other terms such as $D_1T_1 \leftarrow W_NT_3$ and $D_2T_2 \leftarrow W_NT_3$ were also found to have a related structure involving linear combinations of amplitudes and/or integrals. In addition, the implementations of closed-shell CCSD(T) and CCSDT energies, gradients, and second derivatives in the CFOUR program suite[29] have used the skeleton and spin-summed amplitudes to simplify the equations and the representation of the amplitudes since 1996. Although the details of this implementation were never published, the ideas and techniques therefrom served as a foundation for extension to arbitrary orders of coupled cluster. The results here also resemble somewhat the compact expressions for closed-shell CCSD and CCSDT equations derived for example by Lee and Rice and Scuseria et al.[28,30,31] and Scuseria and Schaefer.[32] However, the goal of this work is to formulate a method for expressing compact forms of the coupled cluster equations in the general case.

The result of this extension is a hierarchy of amplitudes formed by successive spin summation over pairs of virtual/occupied indices,

$$\check{t}_{ijk}^{abc} \xrightarrow{2-P_b^a-P_c^a} \check{t}_{\check{i}jk}^{\check{a}bc} \xrightarrow{2-P_c^b} \check{t}_{\check{i}\check{j}k}^{\check{a}\check{b}c} \xrightarrow{2} \check{t}_{\check{i}\check{j}\check{k}}^{\check{a}\check{b}\check{c}} \tag{7}$$

where P_b^a interchanges the labels a and b. The hacek (upside-down caret) on the labels denotes spin summation (the order of summation for multiple pairs of indices is arbitrary). The spin summation procedure can also be undone by applying a pseudoinverse of the summation operation.[33] The "spin summation" designation of these quantities refers to the fact that for the totally spin-summed amplitudes,

$$\check{t}_{\check{i}\check{j}\check{k}}^{\check{a}\check{b}\check{c}} = \sum_{\gamma\delta\eta=\alpha,\beta} t_{i_\gamma j_\delta k_\eta}^{a_\gamma b_\delta c_\eta} \tag{8}$$

Using the spin-summed amplitudes where possible, *the number of unique contractions necessary to evaluate all Goldstone diagrams deriving from a given spin−orbital (Brandow) diagram is reduced to one in most cases and at most two.*[34] In addition, permutations arising from external lines on distinct fragments and from accounting for equivalent internal and external lines are combined into a single overall factor for diagrams reducing to one contraction, and the same factor plus a simple permutation for the second contraction if present. This overall factor is a simple permutation of pairs of external lines only and is the same for every diagram contributing to a given ket state,

$$\begin{aligned}
\langle\Phi_i^a| &\rightarrow\ 1,\\
\langle\Phi_{ij}^{ab}| &\rightarrow\ (1 + P_{bj}^{ai}),\\
\langle\Phi_{ijk}^{abc}| &\rightarrow\ (1 + P_{bj}^{ai})(1 + P_{ck}^{ai} + P_{ck}^{bj}),\\
\langle\Phi_{ijkl}^{abcd}| &\rightarrow\ (1 + P_{bj}^{ai})(1 + P_{ck}^{ai} + P_{ck}^{bj})(1 + P_{dl}^{ai} + P_{dl}^{bj} + P_{dl}^{ck}), \ldots
\end{aligned} \tag{9}$$

where P_{bj}^{ai} interchanges pairs of indices. An example of the utility of spin summation is given by the diagrams in Figure 1. Using Goldstone diagrams only, eight terms are obtained,

$$\begin{aligned}
\check{z}_{ijk}^{abc} = (1 + P_{ck}^{ai} + P_{ck}^{bj})[&4\check{t}_{ijm}^{abe}\check{t}_{nk}^{fc}\check{v}_{ef}^{mn} - 2(1 + P_{bj}^{ai})\check{t}_{ijm}^{aeb}\check{t}_{nk}^{fc}\check{v}_{ef}^{mn}\\
&- 2\check{t}_{ijm}^{abe}\check{t}_{nk}^{cf}\check{v}_{ef}^{mn} - 2\check{t}_{ijm}^{abe}\check{t}_{nk}^{fc}\check{v}_{fe}^{mn} + (1 + P_{bj}^{ai})\check{t}_{ijm}^{aeb}\check{t}_{nk}^{cf}\check{v}_{ef}^{mn}\\
&+ (1 + P_{bj}^{ai})\check{t}_{ijm}^{aeb}\check{t}_{nk}^{fc}\check{v}_{fe}^{mn} + \check{t}_{ijm}^{abe}\check{t}_{nk}^{cf}\check{v}_{fe}^{mn} + (1 + P_{bj}^{ai})\\
&\times \check{t}_{ijm}^{aec}\check{t}_{nk}^{bf}\check{v}_{fe}^{mn}]
\end{aligned} \tag{10}$$

Since the objective of the current work is to reduce the number of contractions by using linear combinations, it should be pointed out that the above eight contractions can be reduced to four by simple inspection (for example, combining terms 1, 3, 4, and 7, and terms 2 and 5 or terms 2 and 6), but further reduction requires less obvious manipulation. The spin-summed amplitudes give a much more compact expression involving only two unique contractions,

$$\begin{aligned}
\check{z}_{ijk}^{abc} = (1 + P_{bj}^{ai})(1 + P_{ck}^{ai} + P_{ck}^{bj})\Bigg[&\frac{1}{4}\check{t}_{ijm}^{abe}\check{t}_{nk}^{f\,c}\check{v}_{ef}^{mn}\\
&+ \left(\frac{1}{2} + P_c^b\right)\check{t}_{ijm}^{aeb}\check{t}_{nk}^{cf}\check{v}_{fe}^{mn}\Bigg]
\end{aligned} \tag{11}$$

The transition from the Goldstone equations to this form is not an obvious or straightforward one, even if it assumed (correctly) that the final answer can be written in terms of the spin-summed amplitudes. Instead, it is possible to write the final spin-summed expression from a single representative Goldstone diagram[35] in an unambiguous way.

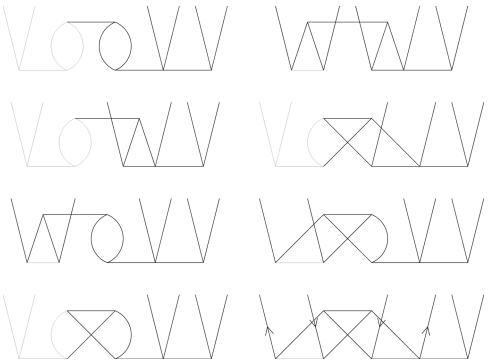

Figure 1. Goldstone diagrams for the particle-hole part of $D_3T_3 \leftarrow W_NT_2T_3$.

A practical example of the utility of the spin-summed amplitudes can be seen when they are used to express the full, closed-shell CCSDT equations. For brevity, the CCSD contributions are not reproduced here (compact CCSD equations for closed-shell systems are given by Scuseria et al.[28]). Definitions for the majority of the intermediates used here are given by Scheiner et al.[36] and are related to the present notation as $W_{ij}^{mn} = -a_{mn}^{ij}$, $W_{ef}^{ab} = -b_{ab}^{ef}$, $W_{ie}^{mn} = 2/3j_{mn}^{ie} + 1/3j_{nm}^{ie}$, $W_{ef}^{am} = -2/3H_{am}^{ef} - 1/3H_{am}^{fe}$, $W_{\check{e}\check{i}}^{\check{m}\check{a}} = 2q_{ma}^{ei} - r_{ma}^{ei}$, $W_{ie}^{ma} = r_{ma}^{ei}$, $F_{\check{i}}^{\check{m}} = k_m^i$, $F_e^a = -g_a^e$, and $F_e^m = I_m^e$. The two remaining intermediates $\tilde{W}_{ej}^{ab}$ and W_{ij}^{mb} include an additional term from $\check{t}_{ijk}^{abc}$ and, in the case of $\tilde{W}_{ej}^{ab}$, removal of a term to prevent overcounting,

$$\tilde{W}_{ej}^{ab} = -F_{ab}^{ej} + \sum_m F_e^m\check{t}_{mj}^{ab} - \sum_{mnf} v_{ef}^{mn}\check{t}_{mj\check{n}}^{ab\check{f}} \tag{12}$$

$$W_{ij}^{mb} = E_{mb}^{ij} + \sum_{nef} v_{ef}^{mn}\check{t}_{ij\check{n}}^{eb\check{f}} \tag{13}$$

With these intermediates, the CCSDT equations can be written rather simply,

$$\check{z}_i^a = \check{z}_i^a(\mathrm{CCSD}) + \frac{1}{2}\sum_{mnef} v_{ef}^{mn}\check{t}_{i\check{m}\check{n}}^{a\check{e}\check{f}} \tag{14}$$

$$\begin{aligned}
\check{z}_{ij}^{ab} = \check{z}_{ij}^{ab}(\mathrm{CCSD}) + (1 + P_{bj}^{ai})\Bigg\{&\sum_{mef} W_{ef}^{am}\check{t}_{ij\check{m}}^{eb\check{f}}\\
&- \sum_{mne} W_{ie}^{mn}\check{t}_{mj\check{n}}^{ab\check{e}} + \frac{1}{2}\sum_{me} F_e^m\check{t}_{ij\check{m}}^{ab\check{e}}\Bigg\}
\end{aligned} \tag{15}$$

$$\begin{aligned}
\check{z}_{ijk}^{abc} = (1 + P_{bj}^{ai})(1 + P_{ck}^{ai} + P_{ck}^{bj})\Bigg\{&\sum_e \tilde{W}_{ej}^{ab}\check{t}_{ik}^{ec}\\
&- \sum_m W_{ij}^{mb}\check{t}_{mk}^{ac} + \frac{1}{2}\sum_e F_e^a\check{t}_{ijk}^{ebc} - \frac{1}{2}\sum_m F_i^m\check{t}_{mjk}^{abc}\\
&+ \frac{1}{2}\sum_{ef} W_{ef}^{ab}\check{t}_{ijk}^{efc} + \frac{1}{2}\sum_{mn} W_{ij}^{mn}\check{t}_{mnk}^{abc} + \frac{1}{4}\sum_{me} W_{\check{e}\check{i}}^{\check{m}\check{a}}\check{t}_{\check{m}jk}^{\check{e}bc}\\
&- \left(\frac{1}{2} + P_b^a\right)\sum_{me} W_{ie}^{ma}\check{t}_{mjk}^{bec}\Bigg\}
\end{aligned} \tag{16}$$

where $\check{z}_{ij\ldots}^{ab\ldots} = \check{t}_{ij\ldots}^{ab\ldots}D_{ij\ldots}^{ab\ldots}$ and $D_{ij\ldots}^{ab\ldots} = f_i^i + f_j^j + \ldots - f_a^a - f_b^b\ldots$ are the usual energy denominators.

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4. EFFICIENT REPRESENTATION

While the use of spin-summed amplitudes produces a very simple and compact set of equations, even for complicated ring-type diagrams, the efficiency of an actual implementation relies in no small part on the physical layout of the amplitudes and how they must be manipulated to perform the necessary contractions. For the skeleton amplitudes, the column symmetry given by eq 6 implies that only $\sim^1/_6$ of the amplitudes must be actually stored for $\check{t}_{ijk}^{abc}$. One could, for example, store elements of $\check{t}_{ijk}^{abc}$ for which $(ai) \leq (bj) \leq (ck)$. In practice, however, and as was pointed out by Kucharski and Bartlett,[26] it is much more advantageous to store either the virtual or occupied indices without restrictions and then store only amplitudes with $i \leq j \leq k$ or $a \leq b \leq c$ respectively. Additionally, amplitudes with $i = j = k$ (or any three indices equal for higher CC orders) can be omitted as they cannot contribute to any "real" spin cases. In terms of computer implementation, this allows for the use of fast, vectorized matrix multiply routines, for example from the BLAS libraries,[37] to perform the parts of each contraction involving the unrestricted indices. This is especially beneficial for the expensive particle−particle ladder term if the virtual indices are unrestricted. If point group symmetry is considered as well, storing half of the indices unrestricted also allows for efficient symmetry packing, for example using the DPD scheme[38] to reduce both storage and computational cost. Of course, this layout is not optimal in terms of sparsity, as redundant amplitudes are stored for $i = j$ or $j = k$. However, the amount of overhead incurred scales as only $O(n^5)$ for triples compared to $O(n^6)$ for the total amplitudes and so on for higher orders.

The relative cost of moving and rearranging data from disk, between computers, or even just in memory, compared to the cost of performing floating point operations has increased dramatically over the past two decades and will likely increase further in the years to come. Therefore, it is important to consider memory-only operations in addition to floating point efficiency. In particular, permutation operations can take a considerable amount of time in coupled cluster calculations. The partially unrestricted packing scheme allows for an efficient handling of these operations induced by the explicit permutation factors present in every spin-summed expression. If the restricted indices (in this case ijk) are handled explicitly, then a permutation of the type P_{bj}^{ai} can be handled by physically permuting the unrestricted indices $abc \rightarrow bac$ and then logically interchanging the i and j labels. Six permutations of each dense abc block and six partial contractions (partial because only final ijk indices obeying $i \leq j \leq k$ are considered, regardless of whether this is true for the inputs) are then needed to compute all contributions to a given full contraction. Of course, these same six permutations are needed for every contraction contributing to the triples, and so, all of the permutations can be performed only once per iteration.

Further permutations are needed on the inputs as well when packing is used. For example, the contractions from $D_2T_2 \leftarrow W_NT_3$ require elements of $\check{t}_{ijk}^{abc}$ for which, as written, $i \leq j \leq k$ is not satisfied. A permutation of the triples is then needed to order ijk to the "canonical" ordering. Again, there are six permutations required to compute all possible contributions for these contractions, and the permutations can be performed once for all contractions involving a triples input. One might surmise, then, that the $D_3T_3 \leftarrow W_NT_3$ contractions would require 36 permutations (six for the output for each of six for the input) to compute all contributions. However, closer inspection reveals that all contributions can in fact be covered by a special sequence of permutations, where both T_k and D_kT_k are taken only once through each of the $k!$ orderings, although not in the same order. The specific details of such permutation cycles are deferred to a later publication. It should be noted that, while reducing the cost of memory movement, this rearrangement of the permutations does not decrease the number of floating point operations. However, this property does allow, in general, for all contributions involving T_k to be computed with at most $k!$ permutations, with those permutations only being performed once per iteration although not applied to both T_k and D_kT_k in the same order. Contractions that connect T_k and $D_{k'}T_{k'}$ with $k \neq k'$ (for example, $D_kT_k \leftarrow (F_N+W_N)T_{k\pm1}$ and $D_kT_k \leftarrow W_NT_{k+2}$) cannot in general be performed with only one set of $k!$ or $k'!$ permutations, since the permutations of T_k and $D_{k'}T_{k'}$ do not correspond, and one of the quantities must be permuted a full $k!k'!$ times. In this case, though, the quantity of lower order can be chosen to undergo the additional permutations with minimal cost.

5. DISCUSSION

The advantages of the spin-summed form of the coupled cluster equations are evident from the comparisons to both the orthogonally spin-adapted theory and to a spin−orbital or equivalently a spin-integrated (UHF) theory.

In comparison to orthogonal spin adaptation, spin summation has advantages in both the derivability and the implementability of the working expressions. For example, the spin-summed expression from eq 7 can also be compared to the orthogonally spin-adapted expressions for the same orbital diagram,[18]

$$
\begin{aligned}
z_{a_1a_2a_3}^{a^1a^2a^3}(\tilde{\mathcal{S}}) = -\sum_{\kappa,\lambda=1}^{3}\sum_{\mathcal{S}} & [\delta_{\tilde{S}_I S_I} D_\lambda(\tilde{S}_I;\, \tilde{S}_{12},\, S_{12}) \\
& \times D_\kappa(\tilde{S}_I;\, \tilde{S}^{12},\, S^{12}) \sum_{b^1b_1} v_{b^1a_{\lambda+1}}^{a^{\kappa+1}b_1} t_{b_1a_{\lambda+2}a_\lambda}^{b^1a^{\kappa+2}a^\kappa}(\mathcal{S}) \\
& + [\tilde{S}_I,\, S_I]^{1/2}[S_{12}]^{-1}\delta_{S^{12}S_{12}} D_\lambda(\tilde{S}_I;\, \tilde{S}^{12},\, S_{12}) \\
& \times D_\kappa(\tilde{S}_I;\, \tilde{S}_{12},\, S_{12}) \sum_{b^1b_1} v_{b^1a_\lambda}^{a^\kappa b_1} t_{a_{\lambda+1}a_{\lambda+2}b_1}^{a^{\kappa+1}a^{\kappa+2}b^1}(\mathcal{S})]
\end{aligned}
$$

where $a^4 \equiv a^1$ and $a^5 \equiv a^2$. The symbols $\tilde{S}$ and $\mathcal{S}$ label intermediate spin quantum numbers $\mathcal{S} = \{S^{12}, S_{12}, S_I\}$, while D_λ and $[S] = 2S + 1$ are numerical prefactors from spin coupling and normalization. Besides the added complexity of these numerical prefactors and the additional logic implied by the delta factors, a naïve sum over permutations κ,λ and spin $\mathcal{S}$ give a grand total of 228 contractions to be performed. Additionally, the indices of the T_3 amplitudes must be returned to canonical ordering, invoking additional factors and possibly summations. Of course, the equation given here is not unique, as a variety of orthogonal spin adaptation techniques exist[39,40] that give varying degrees of sparsity of the T amplitudes. However, all of these methods share the fact that they result in expressions that appear to be suboptimal from an implementation perspective, requiring nonuniform memory access patterns, data reorganization, and index accounting, all of which provide a possible performance penalty. It is not at all clear from the expression as written how to simplify this into an efficient implementation, especially one that could take advantage of

optimized linear algebra libraries such as BLAS since the sparsity of the amplitudes is destroyed when arranging the amplitudes as a dense matrix or tensor. In contrast, the spin-summed expression can almost be implemented as written, except for the handling of the overall permutation factors. For the singlet case, the main advantage usually attributed to the orthogonally spin-adapted approach is a reduction in the number of cluster amplitudes. However, for the T_3 amplitudes, there is only a $\sim^5/_6$ reduction,[18] while for quadruple excitations, the reduction in amplitudes is $\sim^7/_{12}$,[26] both of which would require increases in computational efficiency for the non-orthogonally spin-adapted approach within the reach of improvement due to efficient matrix multiplication and simplification of data layout to overcome the greater number of amplitudes. Beyond CCSDTQ, the situation may be very different, as the reduction in the number of amplitudes becomes significant; however, it is clear that CCSDT and CCSDTQ are cases where the simpler, albeit less sparse, nonorthogonal approach may be competitive.

The spin−orbital and spin-integrated theories (hereafter, only the spin-integrated approach is discussed, since an efficient spin−orbital implementation is spin-integrated in practice) do not suffer from difficulty in deriving or necessarily in implementing the working equations. The permutational antisymmetry of the same-spin indices of course necessitates a packed representation for efficiency; however, algorithms exist for performing contractions on such tensors at arbitrary order.[41] The main disadvantage of the spin-integrated approach for singlet systems (where the reference is spin-restricted) is the increase in the number of spin cases and especially in the number of distinct contractions that must be performed. As the α and β spatial orbitals are the same, the problem of the number of spin cases (and consequently of the number of amplitudes relative to the spin-free case) can be ameliorated by using spin-reversal symmetry. Additionally, "high-spin" amplitudes (that is, amplitudes with excitations of mostly one spin or the other) can be decomposed into amplitudes of "lower" spin. For example, T_3 can be represented entirely by the $t_{ijk}^{ab\bar{c}}$ amplitudes while T_4 can be represented by $t_{ijkl}^{abc\bar{d}}$ and $t_{ijkl}^{ab\bar{c}\bar{d}}$. However, the number of contractions to be performed is not significantly reduced and is considerable for many diagrams in CCSDT and especially CCSDTQ. For example, the particle-hole part of $D_4T_4 \leftarrow W_NT_2T_4$ requires 38 contractions compared to 2 in the spin-summed approach. Of course, a significant advantage of the spin-integrated approach is that it is easily applied to open-shell systems and can be applied to unrestricted references. The spin-summed form as presented *is applicable only to restricted, singlet systems*, but as Lee et al. demonstrated for several restricted open-shell perturbation theories,[42] the "closed-shell" parts of the coupled cluster equations with an ROHF determinant could be written using the spin-summed amplitudes while the remaining terms involving half-filled orbitals could be written using the spin-integrated formalism. As the number of half-filled orbitals is often much smaller than the number of doubly filled or empty orbitals, the "closed-shell" terms will dominate and give a total cost close to that of the singlet spin-summed approach. A drawback to this approach would be the steep increase in difficulty of implementation due the many additional "non-closed-shell" terms in CCSDT or CCSDTQ, as well as the fact that, as in the spin-integrated approach, the wave function is still susceptible to spin contamination.

One problem with the spin-free approach, as pointed out by various authors[18,26] is the fact that the skeleton amplitudes for CCSDT and higher are overdetermined and linearly dependent. In particular, the coupled cluster solution (energy and any other one- or two-particle property) is invariant with respect to a constant shift of each set of skeleton amplitudes related by permutations of indices. Although the spin-integrated amplitudes are similarly overdetermined, they do not show this same indeterminacy to shifts, since above CCSD each spin-integrated amplitude is formed from the skeleton amplitudes by at least one antisymmetrization, which removes any shift. If this shift becomes excessive, then, the equations may suffer from numerical accuracy issues and fail to converge. However, it is possible to remove such a shift at each iteration to maintain numerical stability. For example, one could simply renormalize each set of $\check{t}_{ijk}^{abc}$ and its permutations so that the average is zero (or any other constant). In particular, the spin summation process provides a means to renormalize the skeleton amplitudes. As can be seen from eq 7, all fully spin-summed amplitudes for CCSDT and above must include some summation step such as $2 - P_e^f - P_g^e$ for some e,f,g. This step, similar to the antisymmetrization in the spin-integrated amplitudes will remove any constant shift. As discussed previously, the spin-summed amplitudes can then be inverted to give a "canonical" form of the skeleton amplitudes (which will depend on the choice of pseudoinverse since it is not unique). This is the approach taken in the CFOUR implementation of CCSDT, and in combination with the DIIS procedure[43] for more difficult cases such as moderately multireference closed-shell systems, the convergence of spin-free coupled cluster is similar to the spin-integrated case.

6. CONCLUSIONS AND FUTURE WORK

A spin-free, or orbital representation of the cluster amplitudes, in combination with the technique of spin summation has been shown to produce a very simple set of working equations that can be efficiently implemented in a computer program. Even though the number of amplitudes is greater than in the orthogonally spin-adapted approach, the simplicity of the equations should allow for a highly efficient implementation. A CCSDTQ program using this approach is currently being developed as part of the CFOUR program suite.[29]

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Notes

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