Cluster decomposition of full configuration interaction wave functions: a tool for chemical interpretation of systems with strong correlation

Susi Lehtola,1 Norm M. Tubman,2 K. Birgitta Whaley,2 and Martin Head-Gordon1,2
1) Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
2) University of California, Berkeley, California 94720, United States

Approximate full configuration interaction (FCI) calculations have recently become tractable for systems of unforeseen size thanks to stochastic and adaptive approximations to the exponentially scaling FCI problem. The result of an FCI calculation is a weighted set of electronic configurations, which can also be expressed in terms of excitations from a reference configuration. The excitation amplitudes contain information on the complexity of the electronic wave function, but this information is contaminated by contributions from disconnected excitations, i.e. those excitations that are just products of independent lower-level excitations. The unwanted contributions can be removed via a cluster decomposition procedure, making it possible to examine the importance of connected excitations in complicated multireference molecules which are outside the reach of conventional algorithms. We present an implementation of the cluster decomposition analysis and apply it to both true FCI wave functions, as well as wave functions generated from the adaptive sampling CI (ASCI) algorithm. The cluster decomposition is useful for interpreting calculations in chemical studies, as a diagnostic for the convergence of various excitation manifolds, as well as as a guidepost for polynomially scaling electronic structure models. Applications are presented for (i) the double dissociation of water, (ii) the carbon dimer, (iii) the π space of polyacenes, as well as (iv) the chromium dimer. While the cluster amplitudes exhibit rapid decay with increasing rank for the first three systems, even connected octuple excitations still appear important in Cr₂, suggesting that spin-restricted single-reference coupled-cluster approaches may not be tractable for some problems in transition metal chemistry.

I. INTRODUCTION

The main problem of quantum chemistry is to solve the Schrödinger equation

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$

(1)

for the many-electron wave function $|\Psi\rangle$. The wave function can be expanded in terms of a set of single-particle states $\{\psi_i\}$ (commonly referred to as orbitals) through the resolution of the identity $\sum_i |\psi_i\rangle \langle \psi_i| = 1$ as

$$|\Psi\rangle = c_{n_1,\ldots,n_i,\ldots,n_j} \cdots |\psi_{n_1}\rangle \cdots |\psi_{n_i}\rangle \cdots |\psi_{n_j}\rangle \cdots$$

(2)

Because the wave function must satisfy Fermi statistics

$$\Psi(x_1,\ldots,x_i,\ldots,x_j,\ldots) = -\Psi(x_1,\ldots,x_j,\ldots,x_i,\ldots),$$

it is seen that the tensor $c$ must be completely antisymmetric. However, its form is otherwise unknown a priori.

In order to motivate the topic of the present manuscript – the cluster decomposition – we begin by describing two well-known parametrizations for the many-electron wave function $|\Psi\rangle$: configuration interaction (CI) theory and coupled-cluster (CC) theory. CI and CC are equivalent at the limit of exactness: when all possible electronic excitations are included in the models, yielding the full CI (FCI) and full CC (FCC) methods, the models only differ in the way the wave function is parametrized. The cluster decomposition is a way of converting FCI wave functions to FCC wave functions (and vice versa), thus allowing for each method to be used where it is technically most favorable, all the while enabling one to elucidate the structure of the resulting many-electron wave function.

A. Configuration interaction

In configuration interaction theory, equation (2) is recast into an equivalent form based on Slater determinants $|\Phi_k\rangle$:

$$|\Psi\rangle = \sum_{k=0}^{N_{dets}-1} C_k |\Phi_k\rangle$$

(3)

which builds in the necessary spin statistics and is accessible to numerical implementation. A Slater determinant is defined by the orbitals that the electrons occupy in it, which is why it is often referred to as an electron configuration. The expansion coefficients $C_k$ (as well as the orbitals $\psi_n$ in case only a subset of configurations are included – such as $N_{dets} = 1$ in the Hartree–Fock model) can be solved by minimizing the expectation value $\langle \Psi | \hat{H} | \Psi \rangle$. This results in a linear eigenvalue equation for the expansion coefficients $C_k$.

Thanks to its simplicity and its fulfillment of a variational theorem, CI theory is the traditional approach for solving the Schrödinger equation in a given one-electron basis set. The exact solution to the Schrödinger equation can be obtained by including all the electronic configurations in the problem, via the use of the FCI method. However, the dimension of the FCI wave function – the
number of possible Slater determinants for \( n \) electrons on \( N \) orbitals, denoted as \((n_e,n_o)\), scales as (ignoring any symmetries)

\[
\dim \mathcal{H} \approx (N)!/[(N-n/2)!(n/2)!]^2, \tag{4}
\]

highlighting the difficulty of the exact solution to the Schrödinger equation. As can be seen from equation (4), the dimension of the wave function increases exponentially with increasing system size, and this exponential wall\(^1\) is not affected by the massive increase of computational power given by Moore’s law\(^2\). Millions of determinants – e.g. the \((13e,13o)\) problem – could be handled in the early 1980s,\(^3\) while billion-determinant FCI calculations – corresponding to \((18e,18o)\) – have been around since the late 1980s,\(^4\)–\(^6\) The best calculations to date have only included tens of billions of determinants,\(^7\)–\(^10\) i.e. \((20e,20o)\), with problem sizes close to a trillion determinants i.e. \((24e,24o)\) becoming feasible in the near future on massively parallel architectures.\(^11\) Due to the steep scaling of FCI, many different models have been proposed over the years to selectively capture correlation effects in the wave function, which will be discussed next.

If good orbitals are used for the problem, the expansion of equation (3) for a ground state is often dominated by the Aufbau configuration \(\Phi_0\). In this case, it is appealing to rewrite the wave function in terms of excitations from the reference configuration as

\[
\Psi = \mathcal{N} \left( 1 + \hat{C}_1 + \hat{C}_2 + \ldots \right) \Phi_0, \tag{5}
\]

where \(\mathcal{N}\) is a normalization constant, and \(\hat{C}_n\) is an \(n\)-fold excitation operator. Typically, one sets \(\mathcal{N} = 1\) to simplify manipulations – this is known as intermediate normalization – requiring that the normalization be restored at the end in any calculations. A natural suggestion to circumvent the exponential scaling of FCI with system size would be to impose restrictions on the allowed configuration space, such as only considering single and double excitations from the reference by setting \(\hat{C}_n = 0\) for \(n > 2\) in equation (5). This yields the CISD method. Unfortunately, while it is still variational, truncated CI is not size consistent. CISD is exact for a single helium atom, but when applied to \(\text{He}_2\) its performance is degraded, as the triple and quadruple excitations necessary for exactness for the four-electron system are excluded – even if the two atoms are infinitely far apart.

Alternatively, the cost may be brought down by reducing the number of electrons and orbitals considered in the FCI problem. This is the approach pursued in multi-configurational (MC) self-consistent field (SCF) theory in general, and in its most popular variant, the complete active space (CAS) SCF method.\(^12\),\(^13\) where the FCI problem is only solved within an orbital active space. Developments on the CASSCF method, such as the generalized active space (GAS) SCF method,\(^14\)–\(^16\) further tailor the number of configurations considered in the wave function by the introduction of occupancy restrictions on the active orbitals.\(^15\)–\(^22\) It is also possible to reduce the number of configurations in the diagonalization procedure by expressing a part of them only perturbatively.\(^23\)–\(^25\)

Still, a FCI or CASSCF wave function typically contains many insignificant configurations: chemical accuracy \((10^{-3}E_h)\) is achievable by retaining only a small fraction of the configurations.\(^26\)–\(^29\) With a smart way of choosing the configurations \(\{\Phi_k\}\) that are included in the expansion (equation (3)), accurate solutions may still be achieved for systems that would be too difficult to solve exactly. Some of us have recently developed a fast and efficient CI approach called adaptive sampling CI (ASCI),\(^30\) in which only the important configurations are considered. There has been much recent interest in the ASCI approach due to its demonstrated ability to treat strongly correlated systems. The inspiration for the ASCI technique is in selected CI methods\(^31\)–\(^42\) and FCI quantum Monte Carlo methods.\(^43\)–\(^55\) Based on these ideas, a variety of improvements and other deterministic-adaptive approaches have also been recently suggested.\(^56\)–\(^58\) In addition, several incremental schemes that do not yield a wave function have also been recently proposed for the estimation of FCI energies.\(^59\),\(^60\)

In contrast to both the CAS approach, where the smallness of the feasible active space poses significant limitations, and to the RAS and GAS approaches, which allow for slightly larger active spaces at the cost of having to specify the structure of the wave function – that is often far from trivial – the adaptive approaches can handle large active spaces with minimal user intervention. For instance, the ASCI method which is used in the present work consists of an iterative process in which a new and improved set of determinants is found during each step. At each step, a new basis set of configurations is picked by choosing the most significant configurations in the current estimate for the wave function, and adding in any other configurations that are strongly coupled through the Hamiltonian to these significant configurations. An improved estimate for the wave function is then obtained by diagonalizing the Hamiltonian in the basis of this newly picked configuration basis, and the procedure is repeated until convergence. Only the expansion length is specified by the user, the optimal structure of the wave function arising automatically during the solution: significant determinants are generated, while insignificant ones are ignored. ASCI is generally variational, reproducing the best wave function with a given number of determinants.\(^30\)

Once the strong correlation in the CI wave function has been sufficiently captured, dynamic correlation can be efficiently treated with a perturbative approach,\(^30\),\(^52\) similarly to what is done e.g. in the traditional CASPT2 \{CAS with second order perturbation theory\} approach.\(^51\)–\(^63\)
B. Coupled-cluster

The idea in coupled-cluster (CC) theory is to replace the linear ansatz of equation (5) with an exponential one

$$|\Psi\rangle = e^{T_1 + T_2 + \ldots} |\Phi_0\rangle,$$

(6)

where $T_n$ are again $n$-fold excitation operators and intermediate normalization is used. The difference between equations (5) and (6) is that the CC expansion retains size consistency even when truncated to e.g. single and double excitations from the reference. This is easy to understand by Taylor expanding the exponential in equation (6), which yields products of the $T_n$ excitation operators, coupling up to arbitrarily high rank. Thanks to this, while CC with single and double excitations (CCSD) is exact for a single helium atom alike CISD, CCSD is also exact for an arbitrary number of non-interacting helium atoms, in contrast to CISD. In addition to the connected double excitation in $T_2$, CCSD also includes a disconnected double excitation arising from $\frac{1}{2}T_1^2$. The disconnected excitations appear at all ranks, and increase in complexity with increasing rank.

Thus, CC is a more compact way of parametrizing the wave function than CI, as disconnected excitations appear from the Taylor expansion of equation (6). The more sophisticated ansatz allows CC to converge faster in the excitation amplitudes than CI does. Unfortunately, the size consistency and faster convergence come at the cost of a loss of variationality. Namely, as even truncated versions of variational CC scale exponentially, the usual approach is to solve the CC energy and amplitudes by projection

$$E = \langle \Phi_0 | He^T | \Phi_0 \rangle,$$

(7)

$$0 = \langle \Phi^a_1 | e^{-T} He^T | \Phi_0 \rangle,$$

(8)

$$0 = \langle \Phi^{ab}_{ij} | e^{-T} He^T | \Phi_0 \rangle,$$

(9)

where equations (8) and (9) determine the single and double excitation amplitudes, respectively, and $\Phi^a_1$ (and $\Phi^{ab}_{ij}$) are singly (and doubly) excited determinants, with electrons $i$ (and $j$) being promoted to unoccupied orbitals $a$ (and $b$). The projective CC approaches are not guaranteed to yield an upper bound for the energy, and indeed, projective CC truncated at low orders often underestimates the energy in systems with significant strong correlation.

Variational behavior can still be recovered by increasing the maximum excitation level, but this also leads to a significant increase in the computational cost. But, despite the fast convergence of CC in excitation rank, high-rank excitations may still be necessary even in CC to properly describe systems with significant strong correlation effects. Thus, while CC is very well adapted to compactly describing dynamic (weak) correlations due to its cluster type product structure, CC is not as well adapted to describing strong correlation, which has motivated recently motivated alternative approaches such as CC valence bond theory and projected Hartree–Fock theory. This problem is further complicated by the fact that unfortunately, one cannot go very far in the CC expansion in practice: to our knowledge, the highest-order available efficient dense-tensor CC implementation is CC with single through quadruple excitations (CCSDTQ) in the NWChem and Aces II programs. A sparse-tensor implementation of CC with single through hex-tuple excitations (CCSDTQ56) has also been reported.

C. Motivation for cluster decomposition

The feasibility of CC calculations is limited to somewhat low rank due to the complexity of the solution of the CC amplitude equations. Implementations of high-order CC theory are typically based on conventional FCI programs, which operate on determinant strings, making the CC calculation as costly as a FCI calculation. In contrast to recently developed adaptive FCI methods, the feasibility of an adaptive FCC approach is at present unclear. A stochastic CC approach has been suggested in the literature but it is still reliant on string-based methods.

In CI, the amplitudes are easy to solve, involving simply the solution of an eigenvalue equation. As discussed above, multiple adaptive FCI approaches have been recently suggested, and shown to be quite powerful for the description of challenging multiconfigurational systems. However, due to the contamination in the CI amplitudes by disconnected diagrams, it would be interesting to see if one could rewrite the selected CI wave functions in CC form and thereby extract better information on the underlying correlations in the system.

As an example, orbital optimization in SCF theory corresponds to $e^{T_1}$ according to Thouless’ theorem. Thus, while non-optimal reference orbitals only appear in $T_1$, in the CI expansion they will show up not only in $C_1$, but in all ranks of excitations $C_n$, which complicates the analysis of the excitation amplitudes. Thus, a poor choice of orbitals may result in all $C_n$ being significant for a system of $N$ non-interacting helium atoms, while only $T_1$ and $T_2$ are necessary for obtaining the exact solution of this system.

Being able to break down the FCI wave function into a cluster decomposition that unambiguously shows the importance of irreducible higher order excitations would clearly be useful first to understand the physics and chemistry of systems with complicated electronic structure, and second to point the way to building better scaling electronic structure models than the (quasi)exponentially scaling FCI. Cluster amplitudes extracted from FCI might be used for treating dynamical correlation within a CC-type approach or help in developing novel types of truncations of CC theory for the
treatment of strong correlations.\textsuperscript{81-86}

While a special case of the cluster decomposition has been published,\textsuperscript{87} we are not aware of any general implementation thereof. In the present manuscript we present a general implementation of the cluster decomposition, applicable to any FCI-type wave function in a Slater determinant basis – including CAS, GAS as well as selected CI approaches – and apply it to both FCI wave and ASCI wave functions.

The organization of the manuscript is the following. Next, in the Theory section, we briefly review the mathematics of the cluster decomposition. Then, in the Implementation section, the approach used to implement the procedure is described. Details of the calculations are described in the Computational Details section. Various applications of the procedure are shown in the Results section. The article terminates with a short Summary and Discussion section.

II. \textbf{THEORY}

As the exact wave function is the same regardless of the parametrization used, from equations (5) and (6) we get the connection between the CI and CC amplitudes as

\[
\exp \hat{T} = 1 + \hat{C}.
\]

Taylor expanding the exponential operator in equation (10)

\[
\hat{T} + \frac{1}{2} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \cdots = \hat{C}
\]

the excitation can be matched rank by rank to yield

\[
\hat{T}_1 = \hat{C}_1, \quad \frac{1}{2} \hat{T}_1^2 + \hat{T}_2 = \hat{C}_2, \quad \frac{1}{3!} \hat{T}_1^3 + \frac{1}{2} \left( \hat{T}_1 \hat{T}_2 + \hat{T}_2 \hat{T}_1 \right) + \hat{T}_3 = \hat{C}_3, \quad \vdots
\]

as has been discussed by Monkhorst.\textsuperscript{88} Next, the individual excitation operators can be written out explicitly in second quantized form as

\[
\hat{O}_n = \frac{1}{(n!)^2} \sum_{i_1 a_1 \ldots i_n a_n} a^\dagger_{i_1} \ldots a^\dagger_{i_n} a_{a_1} \ldots a_{a_n},
\]

and the equations for the individual amplitudes be determined from the expressions by projection onto the relevant determinant, e.g.

\[
e_{ij}^b = \langle \Phi^b_{ij} | \hat{C}_2 | \Phi_0 \rangle = \langle \Phi^b_{ij} | \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 | \Phi_0 \rangle = \langle \Phi^b_{ij} | a_{ij}^\dagger a_{ij} \Phi_0 \left( \frac{1}{4} t^c_{ikl} a^\dagger_{i} a^\dagger_{j} a_{ikl} + \frac{1}{2} (t^k_{ia} a^\dagger_{ia} a^\dagger_{ij}) \right) | \Phi_0 \rangle = t^a_{ij} + t^a_{ij}^b - t^a_{ij} t^a_{ij},
\]

where the operator strings in the equations can easily be evaluated with e.g. Wick contractions.\textsuperscript{67,89} The resulting equations are easily solved to obtain recursive equations for the \( l \) amplitudes: \( T_n \) is obtained from \( C_n \) by removing products of \( T_l \) with \( l = 1, \ldots, n - 1 \).

Interestingly, the factors \( 1/n! \) in the Taylor expansion are cancelled out by the number of tensor permutations within a given term. For example, in the equation for \( t^a_{ijk} \), the Wick contractions of \( \hat{T}_1 \hat{T}_2 \) yield both \( t^a_{ijk} \) and \( t^a_{ijk} \), exactly canceling out the prefactor \( 1/2 \) of the term. Thus, the only thing that is left over are terms in which indices are swapped between different amplitude tensors,

\[
t^a_i = e^a_i \quad \tag{17}
\]

\[
t^a_{ij} = \epsilon_{ij}^a - t^a_i t^a_j + \epsilon^a_{ij} \quad \tag{18}
\]

\[
t^a_{ijk} = e_{ijk}^a - t^a_{ij} t^a_{jk} + t^a_{ij} t^a_{ik} - t^a_{ik} t^a_{jk} - t^a_{ij} t^a_{jk} + t^a_{ik} t^a_{jk} - \epsilon^a_{ijk} \quad \tag{19}
\]

for the singles, doubles, and triples. For the quadruples we get
III. IMPLEMENTATION

We have written a C++ program which generates the recursion routines by Wick contractions of antisymmetrized products. As is already obvious from equations (17) to (20), the total number of contractions increases rapidly with tensor rank, as is further illustrated in table I. Due to the rapidly increasing computational requirements, we have only generated the recursion relations up to octuple excitations, for which the instructions in text format take roughly 500 megabytes. The number of terms in the recursion relations can be analysed by studying the ratio of consecutive ranks

\[ f(n) = N(n)/N(n-1). \]  

For an exponentially scaling \( N(n) \propto a^n \) the ratio is constant, \( f(n) = a \). However, examination of the actual scaling of the number of terms with increasing rank (table I) reveals that the decomposition scales superexponentially with respect to its rank. The reason for this, of course, is the exponential scaling wall of the CI problem. However, the decomposition scales only linearly with respect to the length of the CI expansion, even though the time to decompose a given determinant (i.e. the prefactor for the linear scaling) depends on its rank.

While low-rank implementations of the cluster decomposition could be generated on-the-fly and/or implemented in computer source code, already for hextuples the latter becomes infeasible due to the large size of the generated source. For higher ranks, also the former approach – the generation of the recursion relations – becomes costly. Because of this, we have chosen to generate and store the recursion relations on disk in text format. The relations can then be read in by a separate program that runs the decomposition in a spin-orbital basis. The ClusterDec suite,\(^9\) composed of the generator and the runtime programs, is freely available on the internet.

A mathematically correct implementation of the cluster decomposition of a given CI wave function would require the full evaluation of the elements of \( T_{\text{CI}} \). However, this would require the calculation and storage of \( o^{n \cdot n} \) elements for a rank-\( n \) expansion, quickly exhausting any computational resources available to the user. But, the very same scaling problem exists also for the original FCI problem, where it has been solved in the adaptive and stochastic approaches by using a sparse representation for \( C_n \) instead of storing all its \( o^{n \cdot n} \) elements. As our main goal is to use the decomposition with sparse FCI vectors, the implementation in ClusterDec uses the same sparse representation for \( T_{\text{CI}} \) as is used in the input wave function \( C_n \). In other words, we assume that \( T_{\text{CI}} \) is fully spanned by the same subspace as \( C_n \) that is found variationally by the adaptive FCI routines.

This procedure is mathematically non-rigorous, as \( c_{ijkl} = \rho_{ijkl} + \text{products of lower-order } t \)'s = connected + disconnected diagrams. Thus, a negligible

| \( n \) | \( N(n) \) | \( f(n) \) |
|---|---|---|
| 2 | 2 | 2 |
| 3 | 15 | 7.50 |
| 4 | 130 | 8.67 |
| 5 | 1495 | 11.5 |
| 6 | 22481 | 15.0 |
| 7 | 426832 | 19.0 |
| 8 | 9934562 | 23.3 |

Table I: Number of disconnected terms \( N \) contained in \( C_n \) and the resulting ratio \( f(n) \).
\( \varepsilon_{ijk...} \) (that is omitted from the truncated CI expansion) does not necessarily imply that the matching \( \varepsilon_{ijkl...} \) is also negligible, as it is possible that the CI expansion coefficient vanishes due to destructive interference of the connected and disconnected diagrams.

However, this approximation is not only necessary for a practical implementation, but also makes physical sense. Consider, for example, the system of \( n \) non-interacting helium atoms discussed in the Introduction. Again, the FCC wave function will be fully spanned by helium atoms discussed in the Introduction. Again, the connected and disconnected diagrams.

To express the much slower convergence rate of the CI expansion, the CI and CC expansions are numerically similar, and the truncated CI expansion is again an excellent basis for truncating the CC expansion.

Real calculations are somewhere in-between the two extremes. Disconnected diagrams become dominant in extended systems, as electron correlation is well known to be a local phenomenon. While we have imposed a mathematically non-rigorous truncation of the CC expansion, the exact decomposition can in principle always be recovered in the limit of no truncation of the original CI wave function, as this will also mean that the full determinant basis is used for the cluster decomposition. In any case, even if the full (i.e. non-sparse) cluster decomposition of a truncated CI wave function were performed, it would still be necessary to check the convergence of the decomposition with respect to the truncation of the original CI wave function.

Thus, the rationale for the chosen tensor basis can be summarized in two cases. If on the one hand a true FCI wave function is used, there is no truncation in the cluster decomposition, because all elements of the excitation tensors are spanned. On the other hand, if a truncated CI wave function is used, then it might be the case that the CI wave function itself is not sufficiently converged, and the convergence with respect to the expansion length must be checked. As the CI wave function is pushed towards convergence, the basis for the cluster decomposition is also being improved towards convergence. For the physical reasons detailed in the preceding paragraphs, the CI wave function is less sparse than the CC wave function, and thus the error from the incomplete decomposition basis for the CC coefficients derived from an incomplete CI expansion is much smaller than the error in the original CI wave function itself. A convergence check for the CI expansion will be always necessary, as convergence of the energy does not imply sufficient convergence of the wave function.

The importance of connected and disconnected contributions in the CI amplitudes can be examined by studying the ratio \( r_1 = ||T|| / ||C|| \), where the usual \( L_2 \) norm is used

\[
||O_n|| = \sqrt{\sum_{i_1...i_n} (c_{i_1...i_n}^a)^2}.
\]

In the case where the disconnected excitations are dominant, this ratio is smaller than one: \( r_1 \ll 1 \). This is easily the case when the connected diagrams are small in amplitude; that is, when the correlations are weak, or, of a dynamical nature. Because the CC hierarchy recovers correlation effects much faster than the CI expansion – especially in extended systems – the ratio should thus decrease rapidly with increasing \( l \). Cases where the connected excitations are dominant, the ratio is close to one \( r_1 \approx 1 \). Finally, cases in which there is destructive interference in the CI coefficients are revealed by \( r_1 > 1 \).

The excitation amplitudes are stored in \textsc{ClusterDec} in bit string form as

\[
\hat{O}_n = \sum_{i_1<...<i_n \atop a_1<...<a_n} a_{i_1}^{a_1}...a_n^{a_n} a_{i_1}^\dagger ...a_n^\dagger,
\]

similarly to what is done in FCI approaches. To extract elements of the CI amplitude tensor, such as \( c_{ij}^l \), we note that it is necessary to project the CI wave function \( |\Phi\rangle \) onto the wanted determinant \( |\Phi_n^o\rangle \), as the Wick contraction of the bit strings may contribute a change of sign. For instance, for a (2e, 2o) problem with orbitals 1 and 2 occupied and 3 and 4 unoccupied in the reference determinant, we have

\[
\langle \Phi_2^l | a_1^\dagger a_2^\dagger 0 \rangle = \langle a_1^\dagger a_2^\dagger \Phi_0 | a_1^\dagger a_2^\dagger 0 \rangle
\]

\[
= \langle a_1^\dagger a_2^\dagger a_3^\dagger a_4^\dagger | a_1^\dagger a_2^\dagger 0 \rangle
\]

\[
= 0
\]

\[
| a_2 a_1 a_3 a_4^\dagger 0 \rangle = 1
\]

while

\[
\langle \Phi_1^l | a_2^\dagger a_4^\dagger 0 \rangle = \langle a_2^\dagger a_4^\dagger \Phi_0 | a_2^\dagger a_4^\dagger 0 \rangle
\]

\[
= \langle a_1^\dagger a_2^\dagger a_3 a_4^\dagger | a_2^\dagger a_4^\dagger 0 \rangle
\]

\[
= 0
\]

\[
| a_2 a_1 a_4 a_2^\dagger 0 \rangle = -1.
\]

The necessary sign for any determinant string is easily found using automatic Wick contraction routines.

IV. COMPUTATIONAL DETAILS

Two types of FCI wave functions are considered. True FCI wave functions, obtained via the diagonalization of
the molecular Hamiltonian operator in the full determinant space, are calculated using Psi4.\textsuperscript{91,92}

In cases where the FCI function would be too large, selected CI wave functions are computed using the ASCI approach,\textsuperscript{30} which tries to find the best possible compact approximation to the true FCI wave function by treating only its most important configurations. The ASCI method is an iterative process, which can be summarized as follows:

0. Set the starting wave function which is defined with a set of coefficients \( \{ C_k \} \) and corresponding determinants \( \{ \Phi_k \} \).

1. Estimate expansion coefficients for additional configurations as\textsuperscript{30}

\[
A_i = \frac{\sum_{j \neq i} H_{ij} C_j}{H_{ii} - E},
\]

over all single and double substitutions \( D^{SD} \) from the configurations \( \{ \Phi_k \} \) in the current wave function, where \( H_{ij} = \langle \Phi_i | H | \Phi_j \rangle \).

2. Use the largest values of \( \{ A_i \} \) from the singles and doubles space and \( \{ C_i \} \) from the core space to rank and select a new set of determinants, denoted as \( \{ \Phi^1 \} \).

3. Form the new matrix elements for the Hamiltonian in the basis of the determinants \( \{ \Phi^1 \} \), diagonalize, and use the resulting wave function as input for the next iteration.

At each iteration, an improved set of configurations is picked by choosing the most significant configurations in the current estimate for the wave function according to step 2, and adding in any other configurations that are strongly coupled through the Hamiltonian to these significant configurations. A new wave function is then obtained by diagonalizing the Hamiltonian in the basis of these newly picked configurations, and the procedure is repeated until convergence.

In an ASCI calculation performed using \( N \) determinants in the diagonalization, all but the last coefficients of the expansion are typically found to be converged with respect to the true FCI wave function.\textsuperscript{30} Details on the algorithms and implementation of ASCI are available elsewhere.\textsuperscript{30,56}

For the simulations performed in this work, we generated very large ASCI wave functions to help ensure that we were generating the top determinants for use in the cluster decomposition. In most of the simulations over \( 10^7 \) determinants were generated. For purposes of the cluster decomposition, we converged the parameter for our search space, (referred to as \( cdets \) in ref.\textsuperscript{30}), such that the configurations that appear in the resulting wave function did not change anymore upon a further increase of \( cdets \). Convergence was generally found to be achieved with a \( cdets \) value in the range of 50,000 to 100,000.

\section{RESULTS}

To study the suitability of the cluster decomposition to truncated wave functions with the further approximation of the sparse tensor basis described in section §III, the FCI and ASCI wave functions are analyzed by running the decomposition on a further truncation of the wave function. This is done by only including the first \( n \) determinants from the fixed input wave function, sorted in descending absolute value. To simplify the analysis, the truncated wave functions were not renormalized. The bulk of the norm is typically contained within the first few dozen determinants, which are always included in the analysis, thus renormalization should have little to no effect on the results of the analysis.

\subsection{Double dissociation of water}

\subsubsection{FCI/6-31G}

The double dissociation of water has been studied by Olsen et al with FCI and CC methods in the cc-pVDZ basis set.\textsuperscript{65,93} Here, we repeat the calculation in the 6-31G basis set\textsuperscript{94} where the FCI wave function contains 165,636 determinants. A restricted HF reference configuration is used. Following Olsen et al, five different OH bond lengths are used, with the equilibrium geometry taken as \( \langle \text{HOH} \rangle = 110.6^\circ \) and \( r_{\text{OH}} = 1.84345 \text{ bohr.} \textsuperscript{65} \)

Although the FCI problem is solved here in the full determinant space, we study the suitability of wave function truncation in figure 1. The weights of the HF reference and FCI energies are given in table II. The best way to start analyzing the results of figure 1 is through its rightmost column, which corresponds to the use of the full FCI wave function, and thus contains no approximations at all. \( \text{H}_2\text{O} \) at equilibrium is dominated by dynamic correlation effects, which is clearly visible in the rapidly decaying cluster expansion of figure 1d. For instance, inclusion of all \( T_n \) for \( ||T_n|| \lesssim 10^{-4} \) would require CCSDT. Stretching the OH bond length towards double dissociation monotonically significantly increases the importance of the excitation operators, which is not explained simply by the change of the amplitude of the HF configuration (see table II). For the most stretched geometry, the same criterion of \( ||T_n|| \lesssim 10^{-4} \) would require CCSDTQ5. For reference, results from calculations up to CCSDTQ5, performed with Q-Chem,\textsuperscript{72,95} are shown in table III.

The minimal framework for describing the two single bonds in \( \text{H}_2\text{O} \) is the \( (4e,4o) \) problem. This is seen at stretched geometries, as the cluster decomposition shows a multi-peak structure with the largest changes with respect to the decomposition at equilibrium being seen for \( T_4 \). At \( 3r_{\text{OH}}^0 \) (a 200\% stretched geometry), quadruple excitations are the second most important amplitude, after \( T_2 \). Note that both CCSD and CCSDT with restricted orbitals are well known to undergo variational collapse for
Table II: Weights of the HF reference $C_0$ as well as HF and FCI energies for the double dissociation of water in the 6-31G basis.

| $r_{OH}/r_{OH}$ | $\Delta E_{\text{CCSDT}}$ | $\Delta E_{\text{CCSDT}}$ | $\Delta E_{\text{CCSDTQ}}$ | $\Delta E_{\text{CCSDTQ}}$ |
|------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 1.0              | $1.6 \times 10^{-3}$     | $-6.2 \times 10^{-4}$    | $-3.9 \times 10^{-4}$    | $-2.9 \times 10^{-4}$    |
| 1.5              | $1.6 \times 10^{-3}$     | $-7.3 \times 10^{-4}$    | $-4.9 \times 10^{-4}$    | $-3.9 \times 10^{-4}$    |
| 2.0              | $1.5 \times 10^{-3}$     | $-7.0 \times 10^{-4}$    | $-5.0 \times 10^{-4}$    | $-4.0 \times 10^{-4}$    |
| 2.5              | $1.4 \times 10^{-3}$     | $-7.0 \times 10^{-4}$    | $-5.0 \times 10^{-4}$    | $-4.0 \times 10^{-4}$    |
| 3.0              | $1.3 \times 10^{-3}$     | $-7.0 \times 10^{-4}$    | $-5.0 \times 10^{-4}$    | $-4.0 \times 10^{-4}$    |

Table III: Discrepancy between FCI and CC energies for the double dissociation of water in the 6-31G basis. NC: no convergence achieved within the run time.

2. ASCI/cc-pVTZ

Repeating the calculation in the cc-pVTZ basis\cite{30} yields (10e,58o) i.e. a Hilbert space of $2.1 \times 10^{13}$ determinants, which is intractable with the conventional FCI algorithm; however, the calculation is a simple one when adaptive methods are employed. The results for a 1M determinant ASCI wave function in a natural orbital basis are shown in figure 2. As before, the decompositions have converged with 100k determinants, and the plots look much like the 6-31G ones. The largest differences between the exact 6-31G FCI wave function and the cc-pVTZ ASCI wave function are seen at the equilibrium geometry, where the ASCI wave function appears to lack highly excited determinants. However, these have very small norm even in 6-31G and are likely due to dynamic correlation, which the ASCI method can capture with a perturbation theory correction\cite{30} that has not been used here.

B. Carbon dimer

The carbon dimer is a well-known multiconfigurational system which has been studied by multiple authors.\cite{30,45,96,97} In figure 3, we show the decompositions for the carbon dimer at a stretched geometry, $r_{CC} = 2.2$ Å, for three kinds of orbitals: double-$\zeta$ HF, triple-$\zeta$ HF, and triple-$\zeta$ natural orbitals (NOs), with a varying number of determinants in the wave function. The double-$\zeta$ calculations use the cc-pVDZ basis, yielding (12e,28o) for which $\Delta E \approx 1.4 \times 10^{-11}$, whereas for the triple-$\zeta$ use cc-pVTZ yielding (12e,60o) and $\Delta E \approx 2.5 \times 10^{-15}$. The ASCI wave functions contain 25M determinants for the double-$\zeta$ calculation, 7.1M determinants for the triple-$\zeta$ calculation with HF orbitals, and 10.2M determinants for the triple-$\zeta$ calculation with NOs.

The resulting decompositions are shown in figure 3. Based on the decomposition, $C_2$ at $r_{CC} = 2.2$ Å does not appear to be very strongly correlated, as the $T$-amplitudes bear the hallmark of dynamic correlation, i.e. a rapid convergence to zero with increasing rank. Judging from the decomposition, the role of connected octupole excitations in the 12-electron system is negligible.

As in the previous case of water, the cluster decomposition is seen to converge rapidly with the increasing size of the CI wave function. The triple-$\zeta$ calculations are an interesting comparison, as according to Thouless’ theorem a rotation of the orbitals is tantamount to $T_1$.\cite{79} Indeed, $T_1$ is much smaller for the NOs than for the HF orbitals, as is evident from figure 3. While in theory $T_n$ for $n > 1$ should match between the HF and NO calculations, this is no longer true when the wave functions are truncated, but the differences still remain small.

C. Polyacenes

Polyacenes are thought to exhibit strong correlation in the $\pi$ space, based on DMRG calculations in the STO-3G basis set.\cite{98} for more discussion, see reference 86 and references therein. Some of us have recently argued that quintuplet and hexuplet excitations have only a small role in the strong correlation effects, even for the largest acenes.\cite{86} We demonstrate this in the STO-3G basis with the (10e,10o), (14e,14o), (18e,18o) and (26e,26o) ASCI wave functions of 2acene, 3acene, 4acene and 6acene, re-
spectively, shown in figure 4, using geometries from reference 98. For 2acene, a 12k determinant ASCE wave function was used, which is almost FCI for this system. A 1M determinant ASCE wave function was used for 3acene, whereas the 4acene and 6acene wave functions contained over 6M determinants.

Comparing the cluster decompositions for 2acene, 3acene and 4acene shows that they are strikingly similar. Connected doubles are by far the most important amplitudes, followed by connected triples. Singles and quadruples are equally important, with quintuples and higher excitations being an order of magnitude less important, displaying the signature of dynamic correlation as was seen above in the case of water.

Due to its considerably larger Hilbert space, the 6acene decomposition appears still far from convergence at 4M determinants. But, in all the wave functions the convergence behavior of the cluster decomposition is apparent: the excitations converge roughly order of increasing rank. Comparison to the non-converged truncations of the smaller acenes again reveals striking similarities between the wave functions.

These findings thus appear to fully confirm the speculation in reference 86: quadruple excitations should suffice for the treatment of static correlation in the acenes.

**D. Chromium dimer**

The chromium dimer is a challenging system which is not well described by even CCSDTQ, as a 14 mEh difference has been found in the total energy in a (24e,30o) active space at an interatomic distance of $R = 1.7$ Å. Here, we study Cr$_2$ in a Karlsruhe split-valence (SV) basis set, with (48e,42o), giving a size of the Hilbert space of $1.3 \times 10^{23}$.

The decompositions at $R = 1.6$ Å to $R = 2.0$ Å based on a natural orbital reference are shown in figure 5. It is apparent that the strong correlation effects increase significantly in magnitude when the atoms are pulled apart. Furthermore, compared to all the other systems in the present study, the speed of convergence of the cluster expansion is alarmingly slow even around $R = 1.6$ Å. The weights of the connected excitations decay only gradually. The inclusion of all $||T_n|| \lesssim 10^{-4}$ would require the description of hextuples at $R = 1.6$ Å, while already at $R = 1.8$ Å octuples become significant. For distances $R > 1.6$ Å the decomposition does not appear converged, suggesting that approaches based on spin-restricted single-reference CC may be intractable for many multireference problems in transition metal chemistry.
VI. SUMMARY AND DISCUSSION

We have presented an implementation of the cluster decomposition technique, which can be used to translate full configuration interaction (FCI) wave functions into full coupled-cluster (CC) expansions. The decomposition is also applicable to FCI within an active space, i.e. for interpreting CASSCF calculations, as well as to selected CI wave functions such as the ones produced by the ASCI method. The decomposition is based on an iterative algorithm which subtracts the contributions from disconnected excitations (independent products of lower-rank excitations) from a given CI expansion coefficient, forming the CC expansion one rank at a time. The complexity of the recursion relations grows rapidly with increasing rank, due to which our implementation only supports the conversion up to octuple excitations. Due to their sheer number, the rate-determining steps in both the generation and application of the cluster expansion have to do with terms involving products of single excitations. The decomposition could be pushed much further by performing the CI calculations with Brueckner orbitals, which make $T_1$ vanish.

The interest in the decomposition stems from the recent emergence of stochastic and adaptive FCI wave functions, which have made calculations possible on systems of unforeseen sizes. The technique which yields information on the connected excitations in a system is useful in multiple aspects. First, it can be used to analyze which level of CC theory is necessary to qualitatively describe the system. Second, it can serve as a measure of the convergence of the adaptive FCI wave function in cases where it is known that no connected excitations should emerge beyond a certain rank (for example, $C_{n>2} \neq 0$ but $T_{n>2} = 0$ for a system of non-interacting helium atoms).

We have studied the convergence of the cluster decomposition based on FCI as well as ASCI wave functions. For each system, the convergence with respect to the wave function length was performed by performing calculations with various truncations of the fixed input wave function. Although we have introduced a sparse approximation for carrying out the procedure, the decompositions have been found to converge rapidly with increasing wave function length, highlighting the usefulness of our approach.

While the results of the present work are for spin-restricted orbitals, we believe that the results for calculations with spin-unrestricted would be similar. Namely, spin unrestricted would only decrease $T_1$ – which is relatively small in all the calculations of the present
As is well known, calculations based on the coupled-cluster method converge rapidly with respect to excitation rank used in the calculation, which has also been used recently to construct blazing fast approximate CASSCF approaches.\textsuperscript{81–86} However, the speed of convergence of coupled-cluster theory may still be too low to be able to cost-efficiently treat challenging strong correlation problems. Our results on Cr\textsubscript{2} lead us to believe that single-reference CC approaches cannot be faithfully applied on challenging problems in transition metal chemistry, leaving room for alternative approaches.

This work was supported through the Scientific Discovery through Advanced Computing (SciDAC) program funded by the U.S. Department of Energy, Office of Science, Advanced Scientific Computing Research and Basic Energy Sciences, and by the Director, Office of Basic Energy Sciences, Chemical Sciences, Geoscience and Biosciences Division of the US Department of Energy under Contract No. DE-AC02-05CH11231. Computational resources provided by the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by the National Science Foundation Grant No. OCI-1053575, are gratefully acknowledged.

Figure 3: CI (green) and CC (orange) coefficients for double-ζ (DZ) and triple-ζ (TZ) ASCI wave functions of the carbon dimer at $R = 2.2$ Å with Hartree–Fock (HF) or natural orbitals (NOs), plots with 1k, 10k, and 1M determinants, increasing from the left. Note logarithmic scale.
Figure 4: CI (turquoise) and CC (pink) coefficients for STO-3G $\pi$-space ASCI wave functions in polyacenes.

APPENDIX

The format used by the ClusterDec program\textsuperscript{90} is the following:

\[
N_{\text{dets}} \ N_{\text{orb}} \ N_{\alpha} \ N_{\beta} \\
\text{coeff}_1 \ \text{bitstring}_1 \\
\vdots \\
\text{coeff}_{N_{\text{dets}}} \ \text{bitstring}_{N_{\text{dets}}}
\]

where $N_{\text{dets}}$, $N_{\text{orb}}$, $N_{\alpha}$, and $N_{\beta}$ denote the number of determinants, spatial molecular orbitals, and alpha and beta electrons, respectively. The rest of the file contains the $N_{\text{dets}}$ CI coefficient and determinant string entries.

To run an analysis, the user first calculates a wave function using e.g. FCI or ASCI, and feeds it to the program. The syntax of the program is

```
clusterdec wf rank ndets
```

The wave function contained in file `wf` is sorted in decreasing absolute amplitude, is truncated to `ndets` determinants if necessary, after which the decomposition is calculated up to `rank`.

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Figure 5: CI (blue) and CC (red) coefficients for chromium dimer with first 10k, 100k, 1M and 4M determinants out of a $\geq$4.8M determinant ASCI wave function. Note logarithmic scale.

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