Ansätze for Density Cumulant Theory

by

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(Under the Direction of Henry F. Schaefer III)

Abstract

Density cumulant theory is an electronic structure method to solve the full configuration interaction problem. The central task of approximations to the method is to efficiently parameterize the cumulant of the rank-two reduced density matrix. After reviewing the full configuration interaction problem and reduced density matrix methods, we study the definition of the cumulant in detail and find that it can be defined in a way extremely similar to coupled cluster theory. We then study ansätze for the parameterization. Approximations of the previously proposed ansatz, which we call OUDCT, are found to lead to a poor description of H_2 dissociation. It is shown that the exact method encounters numerically unstable near-zero denominators. We then introduce a new ansatz, in which the parameters of the theory shift from unitary coupled cluster amplitudes to "off-diagonal" elements of the cumulant of arbitrary rank. It is shown that this ansatz is rigorously free of the near-zero denominators. Benchmark results indicate that this ansatz is able to describe H_2 dissociation well. However, this ansatz also requires the inclusion of triples to improve equilibrium properties compared to previously known methods.

Index words: Electronic structure theory, cumulants, density matrices, unitary coupled cluster, power series inversion, orbital optimization

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And of first principles, some are beheld by way of examples, others by sense perception, others by becoming experienced in some habit, and others in other ways. So one must try to go after each of them by the means that belong to its nature, and be serious about distinguishing them rightly, since this has great weight in what follows. For the beginning seems to be more than half of the whole, and many of the things that are inquired after become illuminated along with it. (Aristotle, Book I of *The Nicomachean Ethics*)

Contents

List of Figures

List of Tables

Chapter 1

Introduction and Literature Review

The density cumulant theory discussed in this dissertation tries to solve the full configuration interaction problem within a given one-electron basis set, drawing on ideas from both wavefunction approaches and reduced density matrix approaches. This introduction first states the full configuration problem. We then remark on the structure of wavefunctions before cataloguing and briefly describing the families of reduced density matrix approaches. Unlike wavefunction approaches, these are not discussed in common textbooks. With this background, we then discuss the current state of density cumulant theory and give the structure of this dissertation.

1.1 The Electronic Structure Problem

In quantum mechanics, definite energies can be assigned only to wavefunctions that are eigenfunctions of the Hamiltonian operator:

$$\hat{H}\Psi = E\Psi \tag{1.1}$$

where the variables of the wavefunction Ψ are irrelevant at this level of abstraction. $\hat{H}$ denotes the Hamiltonian, consisting of a kinetic energy operator plus a potential energy operator. The eigenvalue E is the energy.

In atomic units, the Hamiltonian for a system consisting of a single molecule is given by

$$\hat{H}(r,R) = -\sum_a \frac{\nabla_a^2}{2} - \sum_A \frac{\nabla_A^2}{2M_A} + \sum_{i>j} \frac{1}{|r_i - r_j|} - \sum_{i,A} \frac{Z_A}{|r_A - r_i|} + \sum_{A>B} \frac{Z_A Z_B}{|r_A - r_B|} \quad . \tag{1.2}$$

The Born–Oppenheimer approximation is to instead consider the operator

$$\hat{H}_{\text{el}}(r;R) = -\sum_a \frac{\nabla_a^2}{2} + \sum_{i>j} \frac{1}{|r_i - r_j|} - \sum_{i,A} \frac{Z_A}{|r_A - r_i|} + \sum_{A>B} \frac{Z_A Z_B}{|r_A - r_B|} \tag{1.3}$$

where uppercase letters index nuclei, lowercase letters index electrons, r indexes spatial coordinates, and M indexes nuclear masses. This operator is the Hamiltonian if nuclei were not allowed to move. The computational advantage of this operator is that it can act on functions of r alone, provided that a 'parameter' set of R is given to the operator, reducing the number of variables to be considered. The conceptual advantage of this operator is that it allows a picture of reality where wavefunctions exist at individual nuclear geometries. For example, the energy of a reaction becomes the energy at the product geometry minus the energy at the reactant geometry, rather than the energy difference between two different states involving electrons and nuclei.

The task of ground state electronic structure theory is to efficiently approximate the lowest eigenvalue of the operator (1.3). If (1.3) commutes with all the operators of some symmetry group, the task may further be extended to efficiently approximate the lowest eigenvalue of each irreducible representation of (1.3). This dissertation will not consider this extended task further.

1.2 Basis Set Approximation

The time-independent Schrödinger equation, (1.1), is a partial differential equation. The coordinates of each electron are given by three continuous spatial coordinates and one discrete spin coordinate, so for an n-electorn system, (1.1) is a partial differential equation in $3n$ variables. Analytic solutions are not practical, but neither is a pure numerical solution. Instead, the space of possible solutions is typically approximated by the introduction of a 'single-particle basis' that plays the role of the orbitals introduced to the beginning chemist.

Suppose a system of n electrons. A set of at least n linearly independent wavefunctions of three spatial coordinates and one spin coordinate is first introduced. This set is called the "basis set." From every subset of n functions, a new n-electron wavefunction is constructed. The n functions are put in some arbitrary order. Then for each permutation ρ of n objects, assign function i the coordinates of electron $\rho(i)$, multiply the functions together, multiply by the parity of ρ, sum over all permutations, and then normalize. This construction is usually called a Slater determinant, as it is identical to the following

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots \chi_N(x_2) \\ \vdots & \vdots & \ddots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots \chi_N(x_N) \end{vmatrix} \tag{1.4}$$

assuming that all the linearly independent wavefunctions were orthonormal. A Slater Determinant is used to enforce the fact that wavefunctions must be antisymmetric with respect to permuting the coordinates

of any two fermions. The resulting Slater determinants are all orthogonal and are an instance of what is known to mathematicians as an exterior product.

Once these determinants are constructed, the Hamiltonian can be projected into the vector space spanned by these determinants. The lowest eigenvalue of this resulting energy is called the full configuration interaction (FCI) energy for the basis set. Although the matrix is finite-dimensional, its dimension is exponential in the number of functions in the basis set. Hence, these methods can only be applied with small basis sets, and even then, methods are needed to approximate the FCI energy within the given basis set. This defines the FCI problem, and solving this is the aim of most approximate electronic structure methods.

We note that the accuracy of even the exact FCI energy depends on how accurately the space of Slater determinants derived from the basis set approximates the exact eigenfunction of the true $\hat{H}_{\text{el}}$. To approximate the energy of the full Hamiltonian requires a basis set that yields a space of Slater determinants that well approximates the exact eigenfunction. Fortunately, for most applications, the exact energy is not needed. Instead, only energy differences at various geometries are needed. This is not as sensitive to the basis set used, as there is a cancellation of basis set error between the two geometries.

1.3 Wavefunction Structure

Most methods to solve the FCI problem require a function from some space to the energy, and a set of acceptable input parameters to search over. In the most direct approach to the FCI problem, this requires both the set of acceptable wavefunctions to search and a way to determine the energy of a wavefunction. Fortunately, these are both simply obtained. Within a given basis set approximation, the set of possible wavefunctions is quite straightforward. Any wavefunction is possible that is in the span of the Slater determinants constructed in the previous section, and there is one Slater determinant for every set of n orbitals. Furthermore, the energy of a normalized wavefunction is given by

$$\frac{\langle \Psi | \, H \, | \Psi \rangle}{\langle \Psi | \, | \Psi \rangle} \quad . \tag{1.5}$$

Upon resolving the wavefunction into its basis elements, all that is needed is to compute Hamiltonian matrix elements using determinants. This is easily done via the famed Slater–Condon rules. So we have both an easily characterized space of wavefunctions to search over for our minimum, and an easily computed energy.

Unfortunately, the space of wavefunctions is still very large. Typical approximations in wavefunction methods search only over a subset of the available wavefunctions. They do, however, benefit from an easily known space of wavefunctions and energy function. This space of wavefunctions is usually determined by the use of some kind of second quantized operator which is truncated after the components of rank k, where $k < n$. For example, k may be a number of excitations. Such an approach will lead to a "many-body" structure in the equations, expressed in terms of tensor contractions. These contractions typically involve

integrals of the Hamiltonian and wavefunction parameters associated with a particular determinant. For example, the configuration interaction doubles approximation parameterizes the wavefunction as

$$|\Psi\rangle = (1 + \frac{1}{4} c_{ab}^{ij} a_{ij}^{ab}) |\Phi\rangle \quad . \tag{1.6}$$

The amplitudes c represent the importance of determinants that are "excited" with respect to some reference determinant. The operator a_{ij}^{ab} is said to be a second quantized fermionic operator and acts on determinants by eliminating and then adding orbitals to a given determinant. The energy for the converged c amplitudes is

$$h_i^i + \frac{1}{2} g_{ij}^{ij} + \frac{1}{4} \bar{g}_{ij}^{ab} c_{ab}^{ij} \tag{1.7}$$

and the converged c amplitudes satisfy

$$\begin{aligned} \frac{1}{4} \bar{g}_{kl}^{cd} c_{cd}^{kl} c_{ab}^{ij} = \bar{g}_{ab}^{ij} + f_a^c c_{cb}^{ij} - f_b^c c_{ca}^{ij} - f_k^i c_{ab}^{kj} + f_k^j c_{ab}^{ki} + \frac{1}{2} \bar{g}_{ab}^{cd} c_{cd}^{ij} + \frac{1}{2} \bar{g}_{kl}^{ij} c_{ab}^{kl} \\ + \bar{g}_{ak}^{ic} c_{bc}^{jk} - \bar{g}_{ak}^{jc} c_{bc}^{ik} + \bar{g}_{bk}^{ic} c_{ac}^{jk} - \bar{g}_{bk}^{jc} c_{ac}^{ik} \end{aligned} \tag{1.8}$$

Using this energy functional requires solving a nonlinear system of equations. As this example suggests, more accurate wavefunction parameterizations involving determinants that are more excited with respect to the reference wavefunction require larger and larger tensors. Using more accurate parameterizations quickly requires bigger tensors, more tensor contractions, and more expensive tensor contractions.

1.4 Reduced Density Matrix Theories

There is another class of electronic structure methods called reduced density matrix methods. These are often motivated as a way to bypass the large number of tensor contractions common in wavefunction-based theories. It can be shown[1] that the electronic Hamiltonian (1.3) can be written in terms of second quantized operators as

$$H_{\text{el}} = h_q^p a_p^q + \frac{1}{4} \bar{g}_{rs}^{pq} a_{pq}^{rs} \quad . \tag{1.9}$$

The numerical values of the tensors h and g are unimportant. What is important is that the expectation value of this with the definitions of the reduced density matrices

$$\gamma_p^q = \langle \Psi | \, a_p^q \, | \Psi \rangle \tag{1.10}$$

and

$$\gamma_{pq}^{rs} = \langle \Psi | \, a_{pq}^{rs} \, | \Psi \rangle \tag{1.11}$$

the energy expectation value becomes

$$E = h_q^p \gamma_p^q + \frac{1}{4} \bar{g}_{rs}^{pq} \gamma_{pq}^{rs} \quad . \tag{1.12}$$

In this equation, the variables are the elements of the reduced density matrices, (1.10) and (1.11). To see if this has reduced the size of our variational space, let us estimate the number of variables in (1.12) compared to the number of wavefunction parameters. We do this by accounting for antisymmetry but neglecting all other devices which may allow us to *a priori* relate other variables to each other. If there are n basis functions, then there are $n^2 + \frac{n^4}{4}$ variables in (1.12). But to enumerate all possible determinants of m electrons would require $\frac{n!}{m!(n-m!)}$. This grows asymptotically as n^m, which is much worse for most systems of interest. So a reduced density matrix theory has, in principle, much fewer variables and theoretically allows for superior scaling.

However, the energy function (1.12) cannot simply be varied with respect to these reduced density matrices. They must be constrained so as to match the values possible from (1.10) and (1.11). This is called requiring our reduced density matrices to be pure n-representable.

There is no known, efficient way to constrain our reduced density matrices to be pure n-representable. Accordingly, a variety of methods have been developed that approximate this constraint in different ways. These are described in the remainder of this section, for comparison with density cumulant theory.

Much recent development[2–5] is concerned with electronic excited states, but we do not discuss them here.

1.4.1 Variational Reduced Density Matrix Theory

In variational reduced density matrix theory, the energy function (1.12) is minimized, subject to *necessary but insufficient* constraints on the n-representability of the 2RDM. (The 1RDM can be constructed from the 2RDM by a partial trace.) An especially important set of these constraints are positive semidefiniteness constraints.

Consider the set of wavefunctions given by $\{a_i a_j \, | \Psi \rangle\}$, and construct its overlap matrix. The result, being an overlap matrix, must have eigenvalues of zero or higher, i.e., is positive semidefinite. However, the matrix elements of this result are $S_{kl,ij} = \gamma_{ij}^{kl}$. The requirement that this matrix be positive semidefinite thus constrains the elements of the 2RDM. This particular requirement is known as the D-condition. The analagous result for $\{a_i^\dagger a_j^\dagger \, | \Psi \rangle\}$ is called the Q condition, and the result for $\{a_i^\dagger a_j \, | \Psi \rangle\}$ is called the G condition.[6] It is also possible in principle to use such non-negativity conditions involving three or more second quantized operators. Satisfying these implies the positive semidefiniteness of the overlap matrices involving only two second quantized operators. However, this involves working with the 3RDM or higher, so these are rarely used in full,[7] even among practitioners of the theory. However, linear

combinations of these can be constructed where the 3RDM dependence is eliminated, producing the less expensive[8] T_1 and T_2 conditions that are sometimes enforced. Enforcing these constraints usually requires methods of semidefinite programming.

Other constraints commonly applied to the 2RDMs in these methods include antisymmetry, hermiticity, that the wavefunction has a well-defined spin and spin-projection, that partial traces of spin blocks of the 2RDM give the exact value, and that the reduced density matrix is consistent with a wavefunction having a given point group symmetry.[9] This can even be extended to continuous point group symmetries, when applicable.[10]

While variational reduced density matrix theory has been used to simulate CASSCF,[9] where the alternative is exponential scaling, there has also been research into using variational reduced density matrix methods further constrained to mimic doubly occupied configuration interaction wavefunctions.[11–14] Although the computational cost of these methods is fairly low, the energy accuracy of the doubly occupied ansatz is unfavorable.[15–17]

1.4.2 Parametric Reduced Density Matrix Theory

In parametric reduced density matrix theories, the n-representable reduced density matrices are approximated as the image of some explicit function. The ground-state reduced density matrices can be determined by minimizing the energy computed with the reduced density matrices of these functions. The task of these methods is then to obtain an accurate parameterization. Methods of this kind can be classified into two groups. The first group parameterizes them as functions of the 1RDM's natural orbitals and their occupation numbers. Such methods are discussed in Section 1.4.3. The remaining methods have tensors of parameters and use tensor contractions to construct the final reduced density matrices. This is a formal similarity with wavefunction theories, even though they explicitly use reduced density matrices. Known methods of this family can be further divided into two groups.

Density Cumulant Theory (DCT) methods[18] are the subject of this dissertation. In these methods, the primary task is to parameterize the cumulant of the 2RDM in terms of occupied and virtual orbitals. Once the 2RDM is obtained, the number of 1RDMs that might come from the same wavefunction is strongly constrained, and a 1RDM can be chosen with the aid of the occupied and virtual orbitals. (This is described in detail in Chapter 3 of this dissertation.) Previous work has given two strategies for how the cumulant might be parameterized.

1. Derive relationships between cumulant elements to various orders in "perturbation theory" and choose cumulant parameterizations that give perturbative expansions of the cumulants consistent with the derived relationships.[18] We caution that the "perturbation theory" originally used[19] in this approach came from a paper that used two different Hamiltonian partitionings: one using second quantized operators normal ordered[20] with respect to $\Psi(0)$, and one using second quantized operators normal ordered with respect to $\Psi(\lambda)$. These partitionings are not identical, so their perturbation expansions are not, either.

2. Given a wavefunction parameterization, map from the parameters to the cumulant element given by the wavefunction with those parameters. This has been specifically suggested with unitary coupled cluster, but the principle is more general.[21] (This will also be described in detail in Chapter 3 of this dissertation.)

Other tensor methods do not determine the 1RDM from the 2RDM cumulant, but parameterize both independently. The first such method was originally proposed by Kollmar,[22] but more extensive work has been done by Mazziotti and co-workers.[23–25] Their work can be motivated by observing that the energy of a configuration interaction doubles wavefunction can be written in such a way that all of the size-extensivity failure is due to the coefficient c_0, which is determined from the other coefficients by normalization. By ignoring normalization and replacing c_0 with $c^{ij}_{ab,0}$ in the condition that the amplitude is stationarity with respect to c^{ij}_{ab}, new methods may be created. $c^{ij}_{ab,0}$ is defined to include a "topological factor", different choices of which can interpolate between the original configuration interaction doubles wavefunction and the coupled electron pair approximation zero. The methods of this familly consists of different choices of the topological factor, chosen to maintain size-extensivity of the final energy while either maintaining positive semidefiniteness of matrices needed for n-representability conditions or mirroring coupled electron pair approximation energy functions. We also mention that while the use of cumulants can rationalize the coupled electron pair approximation zero form of such methods, the literature has always motivated the "topological factor" of the method from configuration interaction doubles.

1.4.3 1RDM Functional Theory

In these methods, the energy (1.12) is expressed as a function of the 1RDM alone. This is achieved through the functional

$$E_2(\gamma_1) = \frac{1}{4} \min_{\gamma_2 \to \gamma_1} \bar{g}^{pq}_{rs} \gamma^{rs}_{pq} \quad . \tag{1.13}$$

We emphasize that not all of these methods parameterize γ^{rs}_{pq}. Those that do can be regarded as parametric reduced density matrix methods. In any case, the energy can be found as the minimum of

$$E(\gamma_1) = h^p_q \gamma^q_p + E_2(\gamma_1) \quad . \tag{1.14}$$

Compared to approaches with an explicit 2RDM, it is no longer explicitly necessary to consider which 2RDMs are n-representable, but the function E_2 is needed in a computationally useful form. Only approximations for this exist. These approximations avoid tensor contractions and use as their parameters only the 1RDM, often through its natural orbitals and their occupation numbers.

This is probably the most actively researched category of density matrix methods and has recently been reviewed by Pernal in 2015.[26] In that review, density matrix methods were divided into four categories. The first category of methods attempt to generalize the E_2 functional for two-electron systems,[27] which is known up to sign factors. The second category of methods parameterizes the 2RDM in terms of its

cumulant expansion and has been exclusively studied by Piris and coworkers.[28] The parameters are chosen by considerations ranging from considerations of 2-electron systems[29] to positive semidefiniteness as in V2RDM,[30] to reproducing a known ansatz.[28, 31] In the third class, the energy functional is not written as an explicit function of the natural orbitals and their occupation numbers, but an implicit one. This typically involves other parameters, the values of which are constrained based on the 1RDM.[32, 33] The final class has empirically chosen parameters.

The vast majority of these methods use an approximation for E_2 of JK-only type, consisting only of the g^{pq}_{pq} and g^{pq}_{qp} integrals. (g^{pq}_{rs} denotes $\langle \phi^*_p(1)\phi^*_q(2)r_{12}^{-1}\phi^*_r(1)\phi^*_s(2)\rangle$, a classical electron repulsion integral.) Others are of JKL-type and also include g^{pp}_{qq} integrals. The use of such parameterizations has come into question. The JKL-only ansatz comes from a wavefunction parameterization that is not accurate enough for chemical purposes,[15, 16] and such parameterizations cannot possibly account for the same-spin component of the second order energy correction, in perturbation theory.[34] While the OP-NOFT ansatz[35] is not JKL only, only the OP-NOFT-0 approximation has been implemented, and that approximation is JK-only. Motivated by these concerns, one non-JKL function has recently appeared.[15] Fleeing the standard approaches that lead to JK-only methods, one paper has even reported a functional based on many-body perturbation theory.[36]

Additionally, most density matrix functionals vary over the space of density matrices obtained by taking linear combinations of 1RDMs,[37] not the space of 1RDMs that can be derived from a single wavefunction.[38] These are known as ensemble n-representability and pure n-representability, respectively. The mathematical importance of this distinction is disputed.[39] At least one functional motivated by this distinction has been reported.[40]

1.4.4 Contracted Schrodinger Equation

Suppose that Ψ is an eigenfunction of $\hat{H}$ with eigenfunction E. It follows that for any operator Z

$$\langle \Psi | \, Z(\hat{H} - E) \, | \Psi \rangle = 0 \tag{1.15}$$

and

$$\langle \Psi | \, [\hat{H}, Z] \, | \Psi \rangle = 0 \quad . \tag{1.16}$$

(1.15) is alternately known as the Contracted Schrödinger Equation and the Hermitian Contracted Schrödinger Equation. (1.16) is known as the Generalized Brillouin Condition, the Antihermitian Contracted Schrödinger Equation, and the Hypervirial Relation. Both of these equations may be written in terms of the reduced density matrices. We note that neither of these are size-extensive as written for a rank-k second quantized operator, but size-extensive forms of the equations can be written.[19, 41–44]

Hermitian

The Hermitian Contracted Schrödinger Equation did not see much use when it was first proposed. When (1.15) is expressed in terms of reduced density matrices for Z a second quantized operator of rank k, the resulting expression contains density matrices of rank k, $k+1$, and $k+2$. Satisfying the equation for all operators of rank $k=2$ for n-representable density matrices guarantees that the wavefunction that generated them is a Hamiltonian eigenstate.[45] Unfortunately, this means dealing with rank 4 reduced density matrices, so the Hermitian Contracted Schrödinger Equation did not see much use for some time.

This changed when Valdemoro and coworkers began approximating the higher rank density matrices in terms of the lower rank density matrices.[46, 47] After some years, these approximation strategies were unified in terms of cumulant expansions. In this strategy, the target reduced density matrices were written in terms of their cumulants. Low-rank cumulants were used exactly, but high rank cumulants had to be approximated.[48]

With these reduced density matrix approximations, steps need to be used to proceed from an input density matrix to density matrices that solve the Hermitian Contracted Schrödinger Equation. However, these density matrices further need to be n-representable. To maintain the n-representability of the density matrices along the iterations, it was found further necessary to adjust the density matrices after an iteration. This procedure became known as purification.[49] The problem of purifying density matrices proved quite difficult for strongly correlated systems, but the computational scaling was too steep to be competitive for weakly correlated systems.[50–52] This caused most interest in the Hermitian Contracted Schrödinger Equation to flow to the generalized Brillouin condition.

Generalized Brillouin Condition

The generalized Brillouin condition dates back to 1960,[53] although using it as the basis of a quantum chemical method was not proposed until 1979.[54–56] Restricting Z to second quantized operators of rank k gives the k-body equation.

To motivate the strategy used to approximate the solution to this equation, note that (1.16) restricted to antihermitian Z is the stationarity condition for wavefunction variations of the form $\Psi \rightarrow \exp(Z)\Psi$. We may take a sequence of these exponential transformations to evolve Ψ until it satisfies (1.16), using the left-hand side of (1.16) as a gradient. In practice, this is only enforced for $k=1,2$,[57] but the rank k condition requires the k-RDM and the $k+1$-RDM. This is approximated from the k-RDM, often by taking the cumulant expansion of the $k+1$-RDM, approximating the $k+1$ cumulant, and evaluating all other terms in the expansion exactly.[52, 57, 58] Unlike the Hermitian Contracted Schrödinger Equation, these unitary evolutions are inherently n-representable.

The original algorithm to solve these equations use differential equations that are numerically integrated.[57] A crucial step in the derivation is to create a variable called ε and then to evaluate $\frac{d}{d\lambda}$ as $\frac{d}{d\varepsilon}|_{\varepsilon=0}$. These two operations are not the same. A newer algorithm[59] to solve these equations instead takes a sequence of finite steps explicitly, after computing a target step length. A convenient feature in either

case is the possibility of treating multireference molecules by using a multiconfigurational initial guess RDM.[60]

Related techniques apply to the G-particle-hole hypervirial equation, where the role of Z in (1.16) is instead played by $a^p_q(I - |\Psi\rangle\langle\Psi|)a^r_s$.[61–63]

1.5 Prospectus

In density cumulant theory, the use of exact wavefunction ansätze provide a way for further development towards an exact theory, bypassing the problem of ensuring the reduced density matrices are pure n-representable. The price to be paid is that the resulting methods acquire a tensor contraction structure which is likely to yield additional computational expense. However, this may still be worthwhile if the methods are sufficiently accurate for their computational expense.

Whether they are sufficiently accurate is not yet known. The prime method of density cumulant theory is ODC-12, which is known to have very good accuracy for its cost. However, there has only been one study of density cumulant theory methods intended to surpass this in accuracy. This method constructs an exact ansatz and proposes to implement its approximations.[21] The method had worse performance than ODC-12 for the simple problem of H_2 dissociation. It was proposed, but not tested numerically, that a different way of approximating the ansatz would lead to an accuracy improvement over ODC-12.

This dissertations revisits the foundations of density cumulant theory. Chapter 2 reviews the foundations of cumulants and provides a new definition for them, much simpler than previous works. It is shown that the relation between reduced density matrices and their cumulants is exactly analoagous to the well-known relationship between configuration interaction amplitudes and the coupled cluster amplitudes. Chapter 3 specifically revisits density cumulant theory. It studies the foundations of the method as well as the particular ansatz previously proposed.[21] The approximations studied are found to not perform as well as hoped. They demonstrate worse performance than ODC-12 for H_2 dissociation, culminating in convergence failure. For equilibrium properties, they have similar performance than ODC-12, but slightly worse, indicating that cluster operators beyond doubles must be included. It also shows the troubling result that the cumulant update equations become singular as triples are included to at least degree four, but excluding these degree four terms causes degree two terms of the 1RDM reconstruction to be incorrect. Chapter 4 investigates a new ansatz for density cumulant theory. In the ansatz it proposes, the fundamental variables are switched from unitary coupled cluster amplitudes to off-diagonal cumulant elements, of the form λ^i_a, λ^{ij}_{ab}, and so forth. It is shown that with this change of variables, the theory becomes rigorously free of the singularities, as the space of occupied orbitals of the theory becomes identical to the space of occupied natural spin-orbitals of the theory. Further, the degree four approximation with only λ^{ij}_{ab} does improve on the performance of ODC-12 for the dissociation of H_2. It is, however, found that higher rank cumulants are needed to improve the accuracy of the method.

Chapter 2

Reduced Density Matrix Cumulants: The Combinatorics of Size-Consistency and Generalized Normal Ordering[1]

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2.1 Abstract

Reduced density matrix cumulants play key roles in the theory of both reduced density matrices and multiconfigurational normal ordering. We present a new, simpler generating function for reduced density matrix cumulants that is formally identical to equating the coupled cluster and configuration interaction ansätze. This is shown to be a general mechanism to convert between a multiplicatively separable quantity and an additively separable quantity, as defined by a set of axioms. It is shown that both the cumulants of probability theory and reduced density matrices are entirely combinatorial constructions, where the differences can be associated to changes in the notion of "multiplicative separability" for expectation values of random variables compared to reduced density matrices. We compare our generating function to that of previous works and criticize previous claims of probabilistic significance of the reduced density matrix cumulants. Finally, we present a simple proof of the Generalized Normal Ordering formalism to explore the role of reduced density matrix cumulants therein. While the formalism can be used without cumulants, the combinatorial structure of expressing RDMs in terms of cumulants is the same combinatorial structure on cumulants that allows for a simple extended generalized Wick's Theorem.

2.2 Introduction

Reduced density matrix cumulants are fundamental in both reduced density matrix (RDM) theories and multireference theories that use the generalized normal ordering formalism (GNO) of Kutzelnigg and Mukherjee.[20,65–68] To RDM theories, RDM cumulants are the additively separable, size-extensive parts of the RDMs. This is one of the primary reasons why cumulants are either parameterized or varied directly in many RDM-based theories.[28,45,69–72] Additive separability of cumulants is a crucial consideration in the derivations of References [41], [44], and Section IIC of [21]. In GNO, second quantized operators are decomposed into linear combinations of operators "normal ordered" with respect to an arbitrary reference, Ψ, via the Generalized Wick's Theorem. This theorem gives the expansion coefficients of the linear combination in terms of contractions. This is analogous to the normal ordering procedure and contractions familiar from correlated single-reference wavefunction theory.[1,73] However, in the single-reference theory, the contractions are Kronecker deltas. In GNO, the contractions are no longer just Kronecker deltas but now include the RDM cumulants of Ψ. The GNO formalism has also been used in many studies.[74–77]

Broadly speaking, there have been four approaches to defining reduced density matrix cumulants in the literature. One definition is an explicit formula for them in terms of reduced density matrices.[50,51,78] Apart from one presentation of the two-body cumulant,[44] this presentation is *ad hoc*, and the connection to additive separability is not established. Alternatively, Mukherjee defined the cumulants as an intermediate in a proof of the Generalized Wick's Theorem, which involved several unitary coupled cluster similarity transformations.[65] While this definition is natural within that proof, it is not known in other contexts. Another definition begins by identifying the connected components of the perturbation expansion of the n-particle propagators.[79] The terms can then be related to terms of a perturbation expansion of the

reduced density matrices,[80] and the connected terms isolated. These latter two definitions were nearly immediately replaced with the remaining definition. This definition is based on Kubo's presentation of cumulants in probability theory[81] and is now the exclusive formalism used to discuss additive separability of the RDM cumulants.[44,82–86]

Given random variables $X_1, ..., X_n$, Kubo began by defining the moment generating function

$$M(t_1, ..., t_n) = \langle \exp(\sum_{i=0}^{N} t_i X_i) \rangle \tag{2.1}$$

and the cumulant generating function

$$K(t_1, ..., t_n) = \log M(t_1, ..., t_n) \quad . \tag{2.2}$$

Any moment, or expectation value, of a product of the variables can be written in the form $\langle \prod_{n=0}^{N} X_n^{i_n} \rangle$. That moment is the coefficient of $\prod_{n=0}^{N} (i_n!)^{-1} t_n^{i_n}$ in (2.1). Kubo defined the cumulant of random variables, which we call the probabilistic cumulant, as the coefficient of $\prod_{n=0}^{N} (i_n!)^{-1} t_n^{i_n}$ in (2.2). Kubo showed that the probabilistic cumulants so defined are "additively separable" with respect to variables that are "multiplicatively separable." Specifically, Kubo defined sets of random variables as being statistically independent if any moment of variables factors into a product of moments, one for each set. For example, if the sets $\{X\}$ and $\{Y, Z\}$ are statistically independent, then $\langle X^2 Y Z \rangle = \langle X^2 \rangle \langle Y Z \rangle$. Then the value of any cumulant of variables from multiple independent sets is its original value if the variables are from the same subset, and zero otherwise. This is the probabilistic analogue of the additive separability of coupled cluster amplitudes for non-interacting subsystems producing a "high-spin", i.e., antisymmetrized product, combined wavefunction.

To adapt Kubo's definition of probabilistic cumulants to define RDM cumulants, we must change expectation values of random variables to expectation values of second quantized operators. However, Kubo's proof of additive separability assumed that the random variables commute, but our second quantized operators do not. To define cumulants of non-commuting objects while keeping additive separability, Kubo proposed that the multiplication appearing in the power series of $\exp$ and $\log$ from (2.1) and (2.2) be replaced with a "multiplication" which does make the objects commute. This idea has been key in the fourth approach to defining RDM cumulants, via a generalization of Kubo's generating functions.

We are convinced that the current definitions of RDM cumulants from generating functions, while perfectly legitimate, have left important points open to clarification, and that these points have hindered broader use of cumulants among electronic structure theorists:

1. It is not clear why a problem in quantum chemistry should need to borrow a tool from probability theory. This has led to speculation that RDM cumulants of arbitrary rank have some further probabilistic interpretation. Kutzelnigg and Mukherjee tried to offer such an interpretation[83] but later

said it did not apply to the "exclusion-principle violating" cumulants.[19] Kong and Valeev interpreted some RDM cumulant elements as probabilistic correlations of electron occupation, within some restrictive assumptions.[78] Hanauer and Köhn gave the same interpretation with looser assumptions, but could still not provide a definitive probabilistic interpretation for all RDM cumulant elements.[82] The latter paper was explicitly motivated by trying to understand the analogy between probabilistic cumulants and RDM cumulants. The formal results of those papers do not depend on the probabilistic interpretation. What is at stake instead is a compelling physical picture of cumulants, to make them more digestible to new users of cumulant formalisms.

2. Adapting cumulants from probability theory to RDMs requires modifying the definition of multiplication in the $\exp$ and $\log$ series, but it is not *a priori* obvious what the "correct" definition is. This has led to two distinct schemes to adapt Kubo's cumulants to RDM cumulants.

   (a) The approach dominant in generalized normal ordering literature was pioneered by Kutzelnigg and Mukherjee,[83] and a variant was later made by Hanauer and Köhn.[82] Accordingly, we call it the KMHK approach. In this formalism, the analogue of random variables are the particle-conserving operators a^p_q, and $\exp$ and $\log$ must be redefined. The two variants redefine them differently. In the original version of Kutzelnigg and Mukherjee, the $\exp$ in the analogue of (2.1) is modified to use a normal ordered product, while the $\log$ in the analogue of (2.2) uses an unrelated antisymmetrized product operation. The two functions are no longer inverses, as in the probabilistic case. In the variant of Hanauer and Köhn, the relevant $\exp$ and $\log$ series are inverses but use a modified normal ordered product, the significance of which is unclear. Further, the presentation of Hanauer and Köhn uses six different product operations: the Grassmann product ($\wedge$), the alternative Grassmann product ($\otimes$), the normal order product ($\{\}$), the scalar product of tensors ($\cdot$), the antisymmetrized tensor product ($\times_A$), and the modified normal order product ($\{\}'$).

   (b) The approach dominant in reduced density matrix literature was pioneered by Mazziotti.[84] In this formalism, the analogue of random variables are the creation and annihilation operators $a^\dagger_p$ and a_q, and the exponential is modified by applying an "ordering" operator. The analogue of the "formal variables", $t_1, \ldots, t_n$, are neither real nor complex numbers, but anticommuting numbers. Throughout the literature, it has been typical[44,48,84,85,87–89] to obtain RDM cumulants by using the exponentiated analogue of (2.2), rather than using the $\log$ series, and to differentiate with respect to the formal variables rather than match coefficients of products of formal variables. (The two actions are equivalent.) The required differentiation operators also anticommute. Obtaining an n-electron RDM cumulant element requires $2n$ differentiations or $2n$ variables. This is surprising, as both the probabilistic cumulants and the KMHK approach for the n-electron RDM cumulant require n differentiations or n variables.

3. Some sources have cautioned that cumulants are not size-extensive in general, but will be if the wavefunction is full configuration interaction (FCI) in some active space.[65,78,90] Mukherjee's proof of additive separability further depends on the multiplicative separability of the wavefunction.[65] From

this, the fact that cumulants from non-multiplicatively separable wavefunctions, e.g., spin-coupled energy eigenstates, are not additively separable[82,91,92] is expected. However, ensemble averages of such states can still be additively separable.[93] (Such qualifiers are frequently neglected without comment in the literature.) But it is not obvious from the generating function definition why a multiplicatively separable FCI wavefunction is of such importance to additive separability. This is so for two reasons. First, the proof that the RDM cumulants are additively separable using the KMHK definition is more complicated than in Kubo's case, because not all "random variables" can be assigned to one subsystem or the other.[82,94] (Mazziotti's approach does not have this drawback.) Second, when the formula for a cumulant is simplified to a polynomial, it is not clear why one polynomial is additively separable while another is not. For example, why is $\gamma^{pq}_{rs} - \gamma^p_r\gamma^q_s + \gamma^p_s\gamma^q_r$ additively separable but not $\gamma^{pq}_{rs} + \gamma^p_r\gamma^q_s - \gamma^p_s\gamma^q_r$? Neither generalization of Kubo's approach immediately offers insight.

4. We are aware of no attempt to explain the fact that the contractions of the GNO formalism are the cumulants defined via this generating function.

In this research, we address all these points. We begin by considering the question of additive separability. We propose a new definition of the RDM cumulants that starts not from the cumulant generating function of Kubo but by a generalization of the relationship between coupled cluster and configuration interaction amplitudes. This provides a familiar and convenient "generating function" for RDM cumulants that makes the combinatorial mechanism of their additive separability apparent. That analysis further motivates a more abstract definition of RDM cumulants using three axioms, inspired by Percus,[95] that characterize a solution to the general problem of breaking a multiplicatively separable second quantized quantity into additively separable parts. Our "generating function" for the RDM cumulants can thus be trivially adapted to construct an additively separable quantity from any multiplicatively separable one. All this will be covered in Section 2.3. We refer readers interested in a detailed look at the connection between our generating function and the combinatorial problem of the three axioms to Appendix 2.7.

In Section 2.4, we compare our generating function with that of the KMHK approach and the Mazziotti approach to analyze how they generalize the idea of Kubo, and how all three generating functions can lead to the same answer. Section 2.4.1 shall review generating functions in detail. Section 2.4.2 will analyze the use of generating functions in the definition of the probabilistic cumulant. We intend to establish that the probabilistic cumulant and RDM cumulant are similar because they both solve the problem of constructing an additively separable quantity from a multiplicatively separable one, and differences between the two can be understood in terms of differences in the notion of multiplicative separability. In Section 2.4.3, we discuss how the previous RDM cumulant generating functions of the KMHK and Mazziotti approaches simplify to ours and lead to the same answer. By this point in our argument, it will be clear that the analogy between the probabilistic and RDM cumulants is entirely a matter of combinatorics and the three axioms, and probability theory plays no role in the analogy. In Section 2.4.4, we shall criticize claims of a probabilistic interpretation of RDM cumulants.

Lastly, we return to RDM cumulants from the perspective of generalized normal ordering in Section 2.5. We consider why cumulants appear in the formalism of generalized normal ordering in Section 2.5

and give a relatively simple proof of the Generalized Wick Theorems. While cumulants are not strictly necessary (the theory can instead be formulated in terms of RDMs), choosing to use cumulants offers advantages such as the additive separability of contractions. Importantly, invoking cumulant decomposition also allows for a simple formula for normal order products in terms of the generalized normal order product, which in turns allows for a simple Extended Generalized Wick Theorem. This is best understood in terms of the formula to write an RDM in terms of cumulants.

2.3 Additive Separability from Multiplicative Separability

2.3.1 Cumulant Definition

Let us try to construct additively separable cumulants from the reduced density matrices. The well-known relation between additively separable coupled cluster (CC) amplitudes and the configuration interaction (CI) amplitudes is given by

$$1 + C = \exp(T) \tag{2.3}$$

where

$$C = \sum_{i,a} \frac{1}{(1!)^2} c_a^i a_i^a + \sum_{i,j,a,b} \frac{1}{(2!)^2} c_{ab}^{ij} a_{ij}^{ab} + ... \tag{2.4}$$

and

$$T = \sum_{i,a} \frac{1}{(1!)^2} t_a^i a_i^a + \sum_{i,j,a,b} \frac{1}{(2!)^2} t_{ab}^{ij} a_{ij}^{ab} + ... \tag{2.5}$$

and the operators a_i^a, a_{ij}^{ab}, etc. are the usual second quantized excitation operators of many-fermion theory.[1,73,96]

The excitation operators in (2.4) and (2.5) perform two roles. First, they make the left and right hand sides of (2.3) operators that transform the reference Φ into the target state Ψ.[97] The need for an operator to act on a wavefunction is the usual rationale for the appearance of second quantized operators in (2.3).[1,73,96,97] For our purposes, this role is irrelevant. Second, equating the coefficients of the operators a_i^a, a_{ij}^{ab}, etc. on each side of (2.3) gives a c amplitude as a polynomial in the t amplitudes.[97,98] After taking log of (2.3), matching coefficients on both sides then solves for a CC amplitude as a polynomial in CI amplitudes. This role is what we will generalize to define RDM cumulants.

Let us define RDM elements with

$$\gamma_{rs\cdots}^{pq\cdots} = \langle \Psi | \, a_{rs\cdots}^{pq\cdots} \, | \Psi \rangle \quad . \tag{2.6}$$

Other normalization conventions are known in the RDM literature. This is known as the McWeeny normalization[99] and is especially convenient for our purposes.

Since we want cumulant elements to be additively separable and expressed in terms of RDM elements, replace (2.4) and (2.5) with

$$\mathcal{C} = \sum_{p,q} \gamma_p^q a_q^p + \sum_{p,q,r,s} \frac{1}{(2!)^2} \gamma_{pq}^{rs} a_{rs}^{pq} + \ldots \tag{2.7}$$

and

$$\mathcal{T} = \sum_{p,q} \lambda_p^q a_q^p + \sum_{p,q,r,s} \frac{1}{(2!)^2} \lambda_{pq}^{rs} a_{rs}^{pq} + \ldots \quad . \tag{2.8}$$

We may attempt to use $1+\mathcal{C} = \exp(\mathcal{T})$, but our second quantized operators need not commute, so we lose the property that $\exp(A+B) = \exp(A)\exp(B)$, which plays a central role in the logic that the cluster operators are additively separable.[1,73,96] Modifying an idea from Lindgren,[100] we redefine the multiplication in the exponential to be the vacuum-normal order product rather than the operator product; so for example, we use the multiplication $\{a_r^p a_s^q\} = a_{rs}^{pq}$ rather than $a_r^p a_s^q = a_{rs}^{pq} + \delta_r^q a_s^p$. (In notation such as $\{a_r^p a_s^q\}$, the braces denote redefining multiplication, not a function applied to $a_r^p a_s^q$. The latter approach leads to contradictions of the type discussed in References [101] and [102].) The normal product always commutes for particle-conserving operators and reduces to the usual exponential when we only need excitation operators, as in coupled cluster. While normal ordered exponentials also appear explicitly in the KMHK approach to cumulants[82,83,86,103,104] and in the Mazziotti approach to cumulants,[44,48,84,85,87–89] in those formalisms, normal ordered exponentials do not relate the moment and cumulant generating functions, as in this formalism. We discuss this in detail in Section 2.4.3.

Therefore, our candidate solution to our additive separability problem is given by

$$1 + \mathcal{C} = \{\exp(\mathcal{T})\} \tag{2.9}$$

or equivalently

$$\{\log(1+\mathcal{C})\} = \mathcal{T} \quad . \tag{2.10}$$

We have used the fact that the logarithm and exponential are inverses as long as the product operation commutes because they must be inverses as formal power series.[105–107]

Is the quantity additively separable, as desired? To show that (or rather, when) it is, we follow the standard proof used to show the additive separability of CC amplitudes. Let A and B be two subsystems of a larger system. Then the proof is simply:

$$1 + \mathcal{C}_{A+B} = \{(1+\mathcal{C}_A)(1+\mathcal{C}_B)\} = \{\{\exp(\mathcal{T}_A)\}\{\exp(\mathcal{T}_B)\}\} = \{\exp(\mathcal{T}_A + \mathcal{T}_B)\} \quad . \tag{2.11}$$

We have used the fact that $\exp(A)\exp(B) = \exp(A+B)$ whenever the multiplication commutes, which is guaranteed by our use of normal ordered multiplication, but also the important relation

$$1 + \mathcal{C}_{A+B} = \{(1+\mathcal{C}_A)(1+\mathcal{C}_B)\} \quad . \tag{2.12}$$

(2.12) encodes the requirement that the RDM have *multiplicative separability*.

We say a tensor is multiplicatively separable if the orbitals can be divided into subsets (usually but not necessarily corresponding to orbitals localized on noninteracting subsystems) so that any tensor element factors into a product of tensor elements, each containing only the indices of one subsystem. For example, $\gamma^{pq}_{rs} = \gamma^p_r \gamma^q_s$ if p, r are on a different subsystem from q, s, or $c^{pqr}_{stu} = -\gamma^p_t \gamma^{qr}_{su}$ if p, t are on one subsystem and q, r, s, u on another. This property manifestly requires a family of tensors across different ranks and that all orbitals be assigned to some subsystem. Furthermore, multiplicative separability of a family of tensors with respect to some division into subsystems is not automatic, but must be rigorously proven. If the tensor elements are determined by applying some function (such as a statistical or quantum mechanical expectation value) to a second quantized operator, then the multiplicative separability of the tensor depends on the properties of that function. And if the tensor is not multiplicatively separable, our proof is invalid, and additive separability does not follow.

It can be shown, after straightforward second quantized algebra on (2.6), that (2.12) is satisfied if Ψ_{AB} is an antisymmetrized product of Ψ_A and Ψ_B. *So in that case, the cumulants are additively separable.* However, Ψ_{AB} need not be multiplicatively separable for two reasons. First, the exact target Ψ_{AB} may not have this property, usually because Ψ_{AB} is a "low-spin" eigenstate, but an antisymmetrized product of Ψ_A and Ψ_B will always be a "high-spin" eigenstate. It has been shown theoretically and numerically that cumulants with orbitals from multiple subsystems will not vanish in this case,[82,91,92] and cumulants have even been studied as a way to measure the resulting spin-entanglement.[91] The second reason is that the wavefunctions or reduced density matrices may be computed by an approximation that artificially changes the multiplicative separability structure. Examples of this behavior, even with size-extensive energies, include the orbital unrelaxed density matrices of coupled cluster,[90] the orbital optimized methods studied by Bozkaya and co-workers,[108–111] and the RDM formulation of CEPA given by Mazziotti and related to his parametric RDM method.[25,112] This multiplicative separability structure is preserved in FCI within a complete active space as well as several approximate RDM methods.[28,45,69,70]

We close this subsection by observing that formulas to convert between RDMs and their cumulants can be extracted from (2.9) and (2.10). Some explicit examples are

$$\gamma^p_q = \lambda^p_q \tag{2.13}$$

$$\gamma^{pq}_{rs} = \lambda^{pq}_{rs} + \lambda^p_r \lambda^q_s - \lambda^p_s \lambda^q_r \tag{2.14}$$

$$\lambda^{pq}_{rs} = \gamma^{pq}_{rs} - \gamma^p_r \gamma^q_s + \gamma^p_s \gamma^q_r \tag{2.15}$$

$$\begin{aligned}\gamma^{pqr}_{stu} = {} & \lambda^{pqr}_{stu} + \lambda^p_s \lambda^{qr}_{tu} - \lambda^p_t \lambda^{qr}_{su} + \lambda^p_u \lambda^{qr}_{st} - \lambda^q_s \lambda^{pr}_{tu} + \lambda^q_t \lambda^{pr}_{su} - \lambda^q_u \lambda^{pr}_{st} + \lambda^r_s \lambda^{pq}_{tu} - \lambda^r_t \lambda^{pq}_{su} + \lambda^r_u \lambda^{pq}_{st} \\ & + \lambda^p_s \lambda^q_t \lambda^r_u - \lambda^p_s \lambda^q_u \lambda^r_t - \lambda^p_t \lambda^q_s \lambda^r_u + \lambda^p_t \lambda^q_u \lambda^r_s + \lambda^p_u \lambda^q_s \lambda^r_t - \lambda^p_u \lambda^q_t \lambda^r_s\end{aligned} \tag{2.16}$$

$$\begin{aligned}\lambda^{pqr}_{stu} = {} & \gamma^{pqr}_{stu} - \gamma^p_s \gamma^{qr}_{tu} + \gamma^p_t \gamma^{qr}_{su} - \gamma^p_u \gamma^{qr}_{st} + \gamma^q_s \gamma^{pr}_{tu} - \gamma^q_t \gamma^{pr}_{su} + \gamma^q_u \gamma^{pr}_{st} - \gamma^r_s \gamma^{pq}_{tu} + \gamma^r_t \gamma^{pq}_{su} - \gamma^r_u \gamma^{pq}_{st} \\ & + 2\gamma^p_s \gamma^q_t \gamma^r_u - 2\gamma^p_s \gamma^q_u \gamma^r_t - 2\gamma^p_t \gamma^q_s \gamma^r_u + 2\gamma^p_t \gamma^q_u \gamma^r_s + 2\gamma^p_u \gamma^q_s \gamma^r_t - 2\gamma^p_u \gamma^q_t \gamma^r_s\end{aligned} \tag{2.17}$$

To write the general formula, we need some more notation. Each term corresponds to a way to partition the upper and lower indices onto RDMs or cumulants. These groupings are more abstract

than a product of terms of a particular tensor, and we call each grouping a "fermionic partition". Given a fermionic partition ρ, the associated product of RDM or cumulant elements (with parity factor) is written as $\gamma(\rho)$ or $\lambda(\rho)$, and the number of tensor elements in the product is written as $\#\rho$. So for the fermionic partition $\{{}^{p}_{t}\}\{{}^{qr}_{su}\}$, $\lambda(\{{}^{p}_{t}\}\{{}^{qr}_{su}\}) = -\lambda^{p}_{t}\lambda^{qr}_{su}$ and $\#\{{}^{p}_{t}\}\{{}^{qr}_{su}\} = 2$. Then we have

$$\gamma^{pq\cdots}_{rs\cdots} = \sum_{\rho} \lambda(\rho) \tag{2.18}$$

and

$$\lambda^{pq\cdots}_{rs\cdots} = \sum_{\rho} (-1)^{\#\rho-1}(\#\rho - 1)!\gamma(\rho) \tag{2.19}$$

where summation is over all fermionic partitions. Equation 2.19 is derived in detail in Appendix 2.8.

2.3.2 Combinatorial Nature of Cumulants

Now that we have defined RDM cumulants, we can make some further observations about the definition.

First, the *only* fact specific to RDMs and their cumulants that we used is that they obey (2.12) for non-interacting subsystems with a high-spin wavefunction. Accordingly, precisely the same mechanism defines an additively separable "cumulant" from any tensor that is multiplicatively separable. Our results thus extend to more exotic quantities, such as the reduced transition matrices of Mazziotti[88,89] or the amplitudes of valence universal multireference coupled cluster.[102] Alternately, the familiar coupled cluster expansion can be viewed as a specific case of the general construction of this paper. (By the argument in Section 4.3.1 of Reference [96], coupled cluster amplitudes have the same factorization property that we require of RDMs.) While there have been previous attempts to connect reduced density matrix cumulants and coupled cluster,[51,88–90,113] we do not believe it has been previously observed that near identical "generating functions" can be produced for the two, or that this is a general solution to the problem of converting between multiplicative and additive separability.

Second, our cumulant formulas can be shown to be additively separable just from their polynomial form, even without the explicit appearance of the exponential, if there is some way to separate the orbitals of the RDMs onto noninteracting subsystems. We will follow the argument of Herbert and Harriman.[44] Consider how (2.15) simplifies if *any* factorization of the RDM is assumed. For example, if $\gamma^{pq}_{rs} = \gamma^{p}_{r}\gamma^{q}_{s}$, corresponding to p, r being on one subsystem and q, s on another non-interacting subsystem, (2.15) becomes $\gamma^{p}_{r}\gamma^{q}_{s} - \gamma^{p}_{r}\gamma^{q}_{s} + 0 = 0$. Or if $\gamma^{pq}_{rs} = -\gamma^{p}_{s}\gamma^{q}_{r}$, corresponding to p, s and q, r being on the two subsystems, (2.15) simplifies to $-\gamma^{p}_{s}\gamma^{q}_{r} - 0 + \gamma^{p}_{s}\gamma^{q}_{r} = 0$. Exactly the same logic, but with many more cases to consider, can be used to show the additive separability of (2.17) if the RDMs are multiplicatively separable. This shows the explicit mechanism by which the additive separability of cumulants is achieved: the coefficients of the terms in the cumulants are exactly such that if any RDM factorization occurs, the cumulant vanishes.

This requirement that a cumulant turns a multiplicatively separable quantity into an additively separable quantity can be used to provide an alternate characterization of cumulants. Rather than using

our "generating functions" to define cumulants, we can define them by providing a list of conditions they must satisfy and showing that only one definition is acceptable. In this viewpoint, the generating functions emerge as a clever solution to the problem, but not as the definition themselves.

Our alternate definition mirrors the definition of probabilistic cumulants given by Percus[95] and latter refined by Simon,[114] and can also be adapted to define an additively separable counterpart of any quantity which may have multiplicative separability:

1. **Functional Form**

$$\lambda\binom{pq\cdots}{rs\cdots} = \sum_{\rho} \mu_\rho \gamma(\rho) \tag{2.20}$$

This axiom uses notation introduced at the end of Section 2.3.1. It says that the cumulants are some linear combination of products of RDMs with parity factors, one for each way to split the orbitals in $\binom{pq\cdots}{rs\cdots}$ across multiple RDM elements (the fermionic partitions). To fully define cumulants, the expansion coefficients μ need to be specified. Because each orbital appears in exactly one RDM, orbital invariance is guaranteed.

2. **Normalization** $\mu_{\substack{pq\cdots \\ rs\cdots}} = 1$

This axiom gives the normalization for the cumulants. Without it, we could multiply cumulants by an arbitrary scalar and still get something additively separable.

3. **Additive Separability** If $\gamma\binom{pq\cdots}{rs\cdots}$ is multiplicatively separable with respect to some separation of the orbitals (other orbitals not being relevant), $\lambda\binom{pq\cdots}{rs\cdots}$ is identically zero, for any choice of the unspecified γ.

This axiom specifies the key property that multiplicative separability of the RDMs implies additively separable cumulants, discussed in the previous subsection. This axiom can be used to determine all remaining coefficients from (2.20) by recursing over the number of RDM elements in each term. For a given ρ, factorize all RDM elements according to that partition, and set the coefficient of $\gamma(\rho)$ to 0. You can then solve for the desired coefficient as a sum of the coefficients from partitions with fewer RDM elements, which have already been solved for.

From these axioms, it is possible to define cumulants without any generating functions, but just sophisticated counting. We take this approach in Appendix 2.7, although recognizing that (2.10) leads to the desired form is far more convenient.

What should be abundantly clear at this point is that cumulants are a combinatorial construction to convert multiplicative separability to additive separability. RDM cumulants are just a very important special case. Whatever uses for them RDM theory may have, their definition conveys nothing special about either RDMs or probability theory.

2.4 Generating Functions

Equations (2.9) and (2.10) provide a way to construct a multiplicatively separable quantity from an additively separable one and vice versa. However, we have not yet established why a function should be so useful in solving what is an essence a combinatorial problem, how the differences between RDM cumulants and the probabilistic cumulants should be understood, how the difference between our generating functions and those of the KMHK and Mazziotti approaches should be understood, or what this means for earlier attempts to interpret RDM cumulants probabilistically. We address each of these questions in turn in the following subsections.

2.4.1 Mathematicians' Generating Functions

While RDM cumulant generating functions have been defined numerous times,[44,48,82–87,103,104] as have generating functions for the more general reduced transition matrix cumulants,[88,89] we are aware of no general discussion of generating functions in the chemistry literature. As this is crucial for this research, we provide one, emphasizing the underlying ideas in language accessible to quantum chemists rather than mathematical rigor. We refer readers interested in detailed mathematical treatments of generating functions to References [106], [107], [115], [116], and [117].

Combinatorialists frequently study arrays of numbers. For example, a_v may be the number of connected graphs with v vertices. This sequence can be encoded into a formal power series. A formal power series is a power series in a variable that is associative and commutative, but indeterminate. This variable is called a formal variable. Formal variables cannot be evaluated at specific numbers, and accordingly, questions of convergence do not exist. The formal power series that a sequence is converted into is called a generating function. For example, one can imagine the sequence $\sum_{n=0}^{\infty} a_n x^n$.

Although generating functions have multiple uses, the one most relevant to the present work is that they convert combinatorial problems into algebraic ones. It is possible to define algebraic operations on formal power series that replicate familiar operations on functions and that also automate some combinatorially significant operation on the sequence. We can thus solve a problem algebraically and only afterwards rephrase the result in terms of the original combinatorial problem.

Let us illustrate the combinatorial significance of the familiar algebraic operation of multiplying functions. Suppose that there are a_n ways to put a structure of type A on n objects and b_n ways to put a structure of type B on n objects. Given n objects, how many ways are there to divide them into a structure of type A and structure of type B? If different ways to partition the objects into A and B produce different objects, the answer is $\sum_{m=0}^{n} \binom{n}{m} a_m b_{n-m}$. Now, from the sequences $\{a_n\}$ and $\{b_n\}$, construct the functions $a(x) = \sum_{n=0}^{\infty} a_n \frac{x^n}{n!}$ and $b(x) = \sum_{n=0}^{\infty} b_n \frac{x^n}{n!}$. (The $\frac{1}{n!}$ denominator is optional, and using it means we have exponential generating functions.) If we compute $a(x) * b(x)$, we find the coefficient of $\frac{x^n}{n!}$ is

$\sum_{m=0}^{n} \binom{n}{m} a_m b_{n-m}$. Multiplying exponential generating functions corresponds precisely to our problem of counting labeled structures.

Alternately, if different ways to partition the objects into A and B produce the same object, the answer to our counting problem is $\sum_{m=0}^{n} a_m b_{n-m}$. If we now form the functions $a(x) = \sum_{n=0}^{\infty} a_n x^n$ and $b(x) = \sum_{n=0}^{\infty} b_n x^n$, we find the coefficient of x^n in $a(x) * b(x)$ is the desired $\sum_{m=0}^{n} a_m b_{n-m}$. These generating functions without the $\frac{1}{n!}$ are called ordinary generating functions.

This example illustrates an important principle: the nature of the counting that is of interest determines which kind of generating function is best.

These ideas can be extended to sequences indexed by n natural numbers rather than just one, requiring multivariable functions. The generating functions then use n formal variables x_1 through x_n, and the generating functions are written as $a(x_1, ..., x_n) = \sum_d a_d \prod_{i=1}^{\infty} \frac{x_i^{d_i}}{d_i!}$ for an exponential generating function and $a(x_1, ..., x_n) = \sum_d a_d \prod_{i=1}^{\infty} x_i^{d_i}$ for an ordinary generating function. The counting principles are the same, although the details are more complex.

2.4.2 Probabilistic Cumulants

We are now prepared to address the probabilistic cumulants. We noted in the introduction that multiplicative separable moments turn into additively separable probabilistic cumulants. We may turn this into an abstract definition of probabilistic cumulants, independent of any generating functions, much as we did for RDM cumulants. This will reveal why mirroring probabilistic cumulants leads to useful RDM cumulants.

First, let us write some explicit formulas for probabilistic cumulants, κ, in terms of moments, m.

$$\kappa(X) = m(X) \tag{2.21}$$

$$m(XY) = \kappa(XY) + \kappa(X)\kappa(Y) \tag{2.22}$$

$$\kappa(XY) = m(XY) - m(X)m(Y) \tag{2.23}$$

$$m(XYZ) = \kappa(XYZ) + \kappa(X)\kappa(YZ) + \kappa(Y)\kappa(XZ) + \kappa(Z)\kappa(XY) + \kappa(X)\kappa(Y)\kappa(Z) \tag{2.24}$$

$$\begin{aligned}\kappa(XYZ) = {} & m(XYZ) - m(X)m(YZ) - m(Y)m(XZ) - m(Z)m(XY) \\ & + 2m(X)m(Y)m(Z)\end{aligned} \tag{2.25}$$

These closely parallel the RDM cumulant formulas from (2.13) to (2.17). It is apparent from these examples that we will need to put all of our variables into groups and take products of the moments or cumulants of each group. If one of these groupings is ρ, we will write the corresponding product as $m(\rho)$ or $\kappa(\rho)$ for moments and cumulants, respectively.

We can now write our abstract definition, following Percus[95] and Simon,[114] as

1. **Functional Form**

$$\kappa(XY\cdots) = \sum_{\rho} \mu_{\rho} m(\rho) \tag{2.26}$$

This axiom uses the notation introduced immediately above. It says that the cumulants are some linear combination of products of moments, one for each way to split the variables across different moments (a partition). To fully define cumulants, the expansion coefficients μ need to be specified.

2. **Normalization** $\mu_{XY\ldots} = 1$

This axiom gives the normalization for the cumulants. Without it, we could multiply cumulants by an arbitrary scalar and still get something additively separable.

3. **Additive Separability** If $m(XY\cdots)$ is multiplicatively separable with respect to some separation of the variables, $\kappa(XY\cdots)$ is identically zero, for any choice of the unspecified m.

This axiom specifies the key property that multiplicative separability of the moments implies additively separable of the cumulants. This axiom can be used to determine all remaining coefficients from (2.26) by recursing over the number of moments in each term. For a given ρ, factorize all moments according to that partition, and set the coefficient of $m(\rho)$ to 0. You can then solve for the desired coefficient as a sum of the coefficients from partitions with fewer moments, which have already been solved for.

As before, we may check that the cumulant generating function given by (2.2) satisfies the axioms, confirming that the more familiar generating function and the more abstract axiomatic approach give the same result.

More importantly for our purposes, this definition is nearly identical to that of RDM cumulants earlier. All differences arise from only two sources. First, probabilistic cumulants are polynomials in moments where RDM cumulants are polynomials in RDM elements. Second, the multiplicative separability that matters for probabilistic cumulants is separation of variables, where the multiplicative separability that matters for RDM cumulants is simultaneous separation of creation and annihilation operators, giving rise to different notions of "partitions." This leads us to the reason why cumulants should be so useful both in probability theory and in RDMs: *in both cases, we want to construct a polynomial in something that may be multiplicatively separable that will be additively separable if it is multiplicatively separable*. It is precisely the same combinatorial problem, just arising in different contexts.

This insight was present as early as Reference [83], but it has new significance when rationalizing the different forms of the generating functions. First, the fact that we want to convert multiplicative separability into additive separability is a strong indicator that $\log$ should appear in both cases.

Second, why does the multiplication differ? As discussed in Section 2.4.1, different kinds of generating functions are suited to different counting problems. In both cases, to read off relations of form (2.20) and (2.26) from our generating functions, we want to count how many times each variable or creation/annihilation operator appears in our cumulant of interest, find the corresponding terms, and match the coefficient of that term in those equations. The left-hand side gives a cumulant element, while the

Table 2.1: A comparison of different generating functions of reduced density matrix cumulants.

Descriptor	KMHK Approach[a]	Mazziotti Approach[b]	This Work[c]
Moment Generating Function	$\langle\psi\vert\{\exp(k_q^p a_p^q)\}\vert\psi\rangle$	$\langle\psi\vert\{\exp(J_k a_p^\dagger + J_k^* a_p)\}\vert\psi\rangle$	$1 + \sum \mathcal{C}_{p\ldots}^{q\cdots} a_{q\ldots}^{p\cdots}$
Formal Variable	k_q^p	J_k, J_k^*	a_q^p
Product of Formal Variables	$k_q^p * k_s^r = k_q^p k_s^r \neq -k_s^p k_q^r$	$J_k * J_l = J_k J_l = -J_l J_k$	$\{a_q^p a_s^r\} = a_{qs}^{pr} = -a_{sq}^{pr}$
Particle-conserving variables only?	Yes	No	Yes
Role of a_q^p	Construct RDMs	Construct RDMs	Formal variables
Multiplication in exp/log	$\times_A$	Standard	$\{\}$
Match coefficients of...	Antisym. products of variables	Products of variables	Products of variables
Rank n cumulant needs	n variables	$2n$ variables	n variables

[a] Kutzelnigg, Mukherjee, Hanauer, and Köhn;[82,83,86,103,104] [b] Mazziotti[48,84,87–89] and other reduced density matrix investigators;[44,85] [c] Section 2.3.1 of the present research

right-hand side gives it in terms of products of moments using our multiplication. The multiplication thus governs how the simple starting "counts" of moments can be combined to give "counts" that will add to the final desired term.

For probabilistic cumulants, the standard multiplication of Section 2.4.1 counts this perfectly well. Just correlate the degree of each formal variable t_n with the number of times the random variable X_n appears in the moment.

For RDM cumulants, we must keep separate counts of creation and annihilation operators, and must also count the overall phase factor. For efficiency, we should assume the same number of creation as annihilation operators. It is possible to adapt the formal variable approach to this, and as we shall discuss in Section 2.4.3, this is exactly what the KMHK and Mazziotti approaches to RDM cumulants do. However, quantum chemists already have a multiplication to count this: the normal ordered product of particle-conserving operators. This is the fundamental reason why the normal ordered product must be used rather than the operator product in equations (2.9) and (2.10).

The final difference between the two functions is that an exponential appears in the creation of the moment-generating function (2.1) for probabilistic cumulants, but not in our RDM analogue, (2.7). In brief, this is a simplification that emerges because RDMs do not have to consider repeated orbitals, by antisymmetry. The argument is discussed in Appendix 2.9.

2.4.3 Comparison with Previous Generating Functions

While both the KMHK and Mazziotti approaches provide perfectly legitimate definitions of cumulants, they acquire added complexity by sticking too closely to formal variables. Products of formal variables reflect the factorizations of probabilistic cumulants but not RDM cumulants, so products of formal variables are not an optimal tool for defining RDM cumulants. We now describe how the concepts of our approach in Section 2.3.1 emerge from those previous. The comparison is summarized in Table 2.1.

Both the KMHK and Mazziotti approaches obtain their RDM generating functions by taking the normal ordered exponential of a sum of "minimal" second quantized operators multiplied by formal variables indexed by the "minimal" operator. An expectation value is then taken. This constructs the moment-generating function. For probabilistic moments, where repeated variables exist, this is a very useful device to construct the moment-generating function and much easier to remember than the explicit factorials. However, for our fermionic quantities, we can instead use (2.7), which is an easy generalization of the familiar configuration interaction form (2.4). This is exactly as discussed in Appendix 2.9.

We now consider the two approaches separately.

First is the KMHK approach. As Hanauer and Köhn's presentation uses six different product operations,[82] we comment only on the variant of Kutzelnigg and Mukherjee.[83,86,103,104] In the KMHK approach, each formal variable is indexed by both a creation operator and an annihilation operator. This ensures that each term contains the same number of creation operators as annihilation operators. However, different products may be related by antisymmetry. Namely, $k_r^p k_s^q$ and $-k_s^p k_r^q$ both count the same thing. To resolve this, when extracting terms from the generating functions, the KMHK approach matches coefficients of antisymmetrized products of their formal variables, such as $k_r^p k_s^q - k_s^p k_r^q$, instead of simply matching coefficients of the formal variables. Our formalism avoids this entirely because $\{a_r^p a_s^q\} = -\{a_s^p a_r^q\}$. Instead of the normal ordered logarithm that appears in our formalism, the KMHK approach uses an "antisymmetrized logarithm" to enforce that each product of their formal variables appearing in the Taylor series of $\log(1+X)$ is antisymmetric. In our formalism, this is unnecessary because the formal variables have been replaced with the fermionic second-quantized operators, which are already antisymmetric.

In the Mazziotti approach, each formal variable is indexed by a single operator, creation or annihilation. In that case, the formal variables are ordered in the same way as the creation and annihilation operators used to produce the reduced density matrix. In Mazziotti's moment-generating function, every string of "probe variables" can be replaced with a second-quantized operator to convert to our notation. The anticommutation of the probe variables so $J_p J_q J_s^\dagger J_r^\dagger = -J_q J_p J_s^\dagger J_r^\dagger$ is just the familiar equation in our formalism, $a_{rs}^{pq} = -a_{rs}^{qp}$. That the probe variables are ordered so that the ones associated with creation operators are on the left of those with annihilation operators again is more naturally stated in our formalism as $\{a_r^p a_s^q\} = a_{rs}^{pq}$. In Mazziotti's approach, a traditional exponential is used rather than a normal ordered one. However, the multiplication used by Mazziotti's approach is not that of a second-quantized operator product, but multiplication of formal variables. Further, different orderings of the operator are not treated as distinct, so $J_p J_q J_s^\dagger J_r^\dagger$ and $J_p J_r^\dagger J_q J_s^\dagger$ are treated as the same. This is again the behavior of the familiar normal ordering our formalism uses, $a_{rs}^{pq} = \{a_r^p a_s^q\}$. However, we reiterate that Mazziotti's formalism generates terms with different numbers of creation and annihilation operators that must eventually vanish. This does not occur in our formalism, which is particle-conserving from the start.

So we see that both previous formalisms can be understood in terms of our cumulants.

2.4.4 Probabilities and the RDM Cumulant

The arguments of the preceding sections establish that the cumulants are a fundamentally combinatorially entity that construct an additively separable quantity from a multiplicative separable one. This has

different forms for probabilities compared to RDM cumulants and related quantities because they have different notions of multiplicative separability. Probabilistic cumulants have probabilistic significance only because they are polynomials in expectation values, which themselves have probabilistic significance. Accordingly, we revisit and correct the claims of Hanauer and Köhn[82] that there is a probabilistic interpretation of the RDM cumulant.

Hanauer and Köhn concluded that "in a natural orbital basis, the diagonal elements of λ_n are in fact the covariances of the occupation numbers of n spin orbitals" and stated that a paper by Kong and Valeev[78] made the same conclusion. The actual conclusion of Kong and Valeev was limited to the special cases of λ_2 and λ_3, but conspicuously made no statement for λ_n of higher ranks. For ranks higher than 3, the statement is false.

Hanauer and Köhn correctly claimed that a diagonal RDM element, where the creation and annihilation operators are the same, can be interpreted as the probability that the relevant orbitals are simultaneously occupied. We can thus say $\gamma^p_p = m(p), \gamma^{pq}_{pq} = m(pq)$, and so forth. Let us then take the RDM cumulant, λ, and see if it agrees with the probabilistic cumulant we obtain by regarding RDMs as probabilistic quantities, κ.

For the two-electron case, we have $\lambda^{pq}_{pq} = \gamma^{pq}_{pq} - \gamma^p_p\gamma^q_q + \gamma^p_q\gamma^q_p$ and $\kappa(pq) = m(pq) - m(p)m(q)$. The two cumulants λ and κ disagree by the non-diagonal terms. If we choose our orbitals to be the natural spin orbitals, γ_1 is diagonal by definition, so γ^p_q and γ^q_p vanish, and the two formulas then agree. The same argument shows equality for the λ_3 case. However, for λ_4, the argument fails because the RDM cumulant will contain terms such as $-\gamma^{pq}_{rs}\gamma^{rs}_{pq}$, which cannot be assumed to vanish. The RDM cumulant then disagrees with the probabilistic cumulant of the probabilistic interpretation of the RDM.

This disagreement is unsurprising from the framework of this article. The functional forms for the RDM cumulant, (2.20), and the probabilistic cumulant, (2.26), differ precisely by such terms. These represent valid multiplicative separations for RDMs, which have n creation and n annihilation indices, but not for expectation values of variables, which simply have n variables.

Hanauer and Köhn further attempted to give a probabilistic interpretation for off-diagonal RDMs but struggled to make sense of negative RDM elements. The situation is in fact worse. The second quantized operators of off-diagonal RDMs are non-Hermitian. These quantities may be complex numbers, which cannot be a probability. For example, consider the hydrogen atom RDM element, $\langle p_{+1}| \, a^{p_x}_{p_y} \, |p_{+1}\rangle = \frac{i}{2}$.

While RDM cumulants give some information about orbital occupation, we must reject claims that this information is the same statistical information of probabilistic cumulants. The similarities between RDM cumulants and probabilistic cumulants should be understood on the basis that they solve very similar problems of constructing an additively separable quantity from a multiplicatively separable one using very similar techniques.

2.5 Generalized Normal Ordering

We now shift our perspective entirely to view cumulants from the GNO formalism.[20,65–68] We shall primarily consider why RDM cumulants appear here. In brief, RDM elements appear so that the expectation

values of normal ordered second-quantized operators (which will themselves be RDM elements) vanish. It is then a choice whether to invoke cumulant decomposition or not. The decomposition has several advantages: it makes the contractions additively separable for RDMs corresponding to an antisymmetrized product of wavefunctions, it is a certain generalization of the contraction patterns of single-reference normal ordering, and it crucially simplifies the formula to write a product of GNO operators as a sum of other GNO operators. The latter property has little to do with cumulants in particular but follows from the contraction pattern.

There are many uses of GNO concepts, and we cannot describe all of them here. We refer interested readers to the papers describing the methods that use GNO for the use of many-body residual expressions,[118–120] construction of GNO excitation operators,[68,74,77,121–123] neglect of high-rank cumulants,[75,119,120,124] neglect of high-rank generalized normal order operators,[75,77,118–120,122–124] use of state-averaged reduced density matrices,[119,120,123] forming the zeroth-order Hamiltonian in perturbation theory,[19,68,77,122,123] and elimination of disconnected terms.[41,121]

2.5.1 Wick Expansion

We seek to generalize the familiar single-reference Wick Theorem,[1,73] which says that an arbitrary string of creation and annihilation operators can be expanded into a scalar and a linear combination of operator strings "normal ordered" with respect to Φ, meaning their expectation value for wavefunction Φ is zero. We do so in two steps: we generalize this for vacuum-normal operator strings, and then extend this result to arbitrary operator strings. Our presentation shall follow that of Reference [20]. There is an alternate presentation[65] which requires a detour through unitary coupled cluster theory but does have the GNO operators appear naturally as intermediates. We discuss this proof in relation to cumulants in Appendix 2.10.

First, let us assume a vacuum-normal operator string, where all creation operators are to the left of annihilation operators. In any such expansion, the scalar must be the expectation value of the string because all other terms in the expansion have zero expectation value. If the operator is particle-conserving, this expectation value is an RDM element; otherwise, it is zero.

Now, in the single-reference formalism, we write the scalar term as the sum of all possible "contractions." Contractions take a creation operator and an annihilator operator into an additively separable tensor element, and multiple contractions are allowed. If we want additively separable contractions in GNO, we must perform a cumulant expansion of the RDM, per (2.18), and say that each contraction is a cumulant. Accordingly, the rules for which contractions are allowed are dictated by the possible cumulant patterns in Equation (2.18). Multiple contractions are still allowed, but contractions now may take n creation and n annihilation operators for any n. As usual, there is a sign factor associated with anticommuting operators to bring operators together for a contraction.

Alternatively, we could have started by generalizing the rule that the scalar term is the sum of all possible complete contractions, which takes us to (2.27). If we take the expectation value of both sides and insist that normal-ordered operators have zero expectation value, we conclude that the RDM is the sum of all possible complete contractions. The equation for a rank n operator has exactly the same structure as

the rank n case of (2.18), but with contractions instead of cumulants. *This is why the contraction structure of Reference [20] must have the contractions be cumulants.* It follows immediately that contractions are cumulants, multiple contractions remain allowed, and contractions must be able to take n creation and n annihilation operators. Generalizing this contraction structure was the heart of the approach with convolutions and Hopf algebras by Brouder and coworkers,[125] although they did not recognize the importance of the cumulants.

We could just as easily have not bothered with cumulant decomposition at all but kept contractions as RDMs. We can then no longer have multiple contractions, and the proper way to generalize n repeated contractions from the single-reference Wick theorem is as a single contraction involving n creation and n annihilation operators, yielding an n-RDM element. The same property holds true in the alternate proof discussed in Appendix 2.10.

Writing a creation or annihilation operator as $\hat{q}$, we can write the Wick expansion of a vacuum normal operator as

$$\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_q\hat{q}_s\hat{q}_t\hat{q}_u\ldots = \{\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_q\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} + \sum\{\hat{q}_p\overbrace{\hat{q}_q\hat{q}_r}\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} + \sum\{\hat{q}_p\overbrace{\hat{q}_q\hat{q}_r\hat{q}_s}\hat{q}_t\hat{q}_u\ldots\}$$
$$+ \sum\{\hat{q}_p\overbrace{\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t}\hat{q}_u\ldots\} + \sum\{\hat{q}_p\overbrace{\hat{q}_q\hat{q}_r}\hat{q}_s\overbrace{\hat{q}_t\hat{q}_u}\ldots\} + \sum\{\hat{q}_p\overbrace{\hat{q}_q\hat{q}_r}\hat{q}_s\hat{q}_t\overbrace{\hat{q}_u}\ldots\} + \sum\{\hat{q}_p\overbrace{\hat{q}_q\hat{q}_r\hat{q}_s}\overbrace{\hat{q}_t\hat{q}_u}\ldots\} + \ldots \tag{2.27}$$

where the sums range over all possible contractions, and there can be any number of contractions, and contractions can connect n creation and n annihilation operators for any n. At this point in the argument, contractions are defined by $\overbrace{a^p a_q} = \lambda^p_q$, $\overbrace{a^p a^q a_s a_r} = \lambda^{pq}_{rs}$, and so forth. As usual, there is a permutational sign factor to bring non-adjacent operators in the string together. It is also possible to define a "quasi-normal order" where (2.27) holds, but the contractions are not RDM cumulants. Then it will *not* be true that the normal-ordered operators have zero expectation value with respect to Ψ, as only cumulants have this property. For now, we shall note that (2.27) alone is needed for all the remaining proofs.

Before proceeding to the general case, let us confirm that our procedure defined on operator strings is well-defined on operators. There are two ways by which different strings can refer to the same operator: the use of anticommutation relations and expanding one orbital as a linear combination of others. The only way to use anticommutation relations on a vacuum-normal order string to get another vacuum-normal order string is to anticommute creation and annihilation operators, so we need to check orbital invariance and antisymmetry. Both of these properties can be shown by a straightforward recursion on the minimum of the number of creation operators and the number of annihilation operators, assuming contractions are antisymmetric and orbital invariant. For RDM cumulants, they are.

Now let us define the Ψ-normal Wick expansion of an arbitrary operator by first bringing it into vacuum-normal order and then bringing the resulting operators into Ψ-normal order using (2.27). We are composing two maps that obey the anticommutation relations and are orbital invariant, so our final result obeys the anticommutation relations and is orbital invariant.

Our expansion still has the form of (2.27), but more contractions are possible. First, it is possible to have a contraction if creation operators are not all left of annihilation operators, by reordering them in

the transformation to vacuum-normal ordering and then contracting them. This introduces contractions such as $\overbrace{a^p a_s \vert a^q a_r}^{} = -\lambda^{pq}_{rs}$. Second, the contractions of vacuum-normal ordering must also be accounted for. We do this by adding the Kronecker delta from the vacuum normal contraction to the contraction from applying (2.27) after the vacuum normal ordering step, so we have $\overbrace{a_q a^p} = -\lambda^p_q + \delta^p_q$.

We also note that a Ψ-normal ordered operator is antisymmetric with respect to *any* permutation of the operators in the operator string inside the normal ordering. This property is inherited from the vacuum-normal ordering. This antisymmetry was also emphasized in the context of generalized ordered products by Mukherjee and coworkers.[67]

2.5.2 Extended Generalized Wick Theorem

There is one more reason "why" we choose to use cumulants in GNO, which is that it greatly simplifies the rule for taking products of GNO operators. While it can be expressed with RDMs,[125] the cumulant presentation simplifies the final result and the combinatorics of the proof. Although this is the analogue of what is often called the generalized Wick Theorem, because we are already in Generalized Normal Ordering, we follow Mukherjee,[67] Evangelista,[68] and their coworkers in instead calling it the extended generalized Wick Theorem. The theorem is

$$\{A\}\{B\} = \{AB\} + \sum \{\overbrace{A B}\} \tag{2.28}$$

where the sum is over all repeated contractions, provided each contraction contains at least one operator from both A and B.

The bulk of the work is in deriving a lemma, the formula for a Ψ-normal ordered operator in terms of operator strings. This lemma may be regarded as an inverse to (2.27). The lemma on its own will demonstrate the formal advantages of cumulants in GNO. For pedagogical purposes, we complete the proof of the extended generalized Wick's Theorem from the lemma in Appendix 2.11.

The lemma is

$$\begin{aligned}\{\ldots\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} = \ldots\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u\ldots - \sum \ldots\hat{q}_q\overbrace{\hat{q}_q\hat{q}_r}\hat{q}_s\hat{q}_t\hat{q}_u\ldots - \sum \ldots\hat{q}_r\overbrace{\hat{q}_q\hat{q}_r\hat{q}_s}\hat{q}_t\hat{q}_u\ldots \\ - \sum \ldots\overbrace{\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t}\hat{q}_u\ldots + \sum \ldots\hat{q}_p\overbrace{\hat{q}_q\hat{q}_r\hat{q}_s}\hat{q}_t\hat{q}_u\ldots + \sum \ldots\overbrace{\hat{q}_p\hat{q}_q\hat{q}_r}\hat{q}_s\hat{q}_t\hat{q}_u\ldots - \sum \ldots\overbrace{\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s}\hat{q}_t\hat{q}_u\ldots + \ldots\end{aligned} \tag{2.29}$$

where a term with c contractions has phase $(-1)^c$, and all contraction patterns appear in the sums. We prove this by induction on the minimum of the number of creation operators and annihilation operators, n. In the base case $n = 0$, no contractions are possible, and (2.29) reduces to (2.27).

We proceed to prove the case of $n = k + 1$ if (2.29) holds for all cases from 0 to k. We can solve for the completely normal ordered term in (2.27) to give:

$$\{\ldots\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} = \ldots\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u\ldots - \sum\{\ldots\hat{q}_p\overbrace{\hat{q}_q\hat{q}_r}\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} - \sum\{\ldots\hat{q}_p\overbrace{\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t}\hat{q}_u\ldots\}$$
$$- \sum\{\ldots\overbrace{\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u}\ldots\} - \sum\{\ldots\hat{q}_p\overbrace{\hat{q}_q\hat{q}_r}\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} - \sum\{\ldots\overbrace{\hat{q}_p\hat{q}_q\hat{q}_r}\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} - \sum\{\ldots\hat{q}_p\overbrace{\hat{q}_q\hat{q}_r\hat{q}_s}\hat{q}_t\hat{q}_u\ldots\} - \ldots \tag{2.30}$$

All the normal ordered terms on the right-hand side are previous cases in the induction, so we substitute in (2.29) and collect the terms with t contractions. Given a particular set of t contractions, it can be produced by any term in the right-hand side of (2.30) whose explicit contractions are among those t. The remaining contractions will be supplied by substituting (2.29). Let the number of explicit contractions be denoted o. There are $\binom{t}{o}$ ways to choose which of the t contractions come from the substitution, giving a sign factor of $(-1)^{t-o}$. Thus, the overall coefficient of our set of t contractions is

$$-\sum_{o=1}^{t}(1)^o(-1)^{t-o}\binom{t}{o} = -\big((1-1)^t - (-1)^t\big) = (-1)^t \tag{2.31}$$

by binomial expansion. All terms with a product of t contractions appear with coefficient $(-1)^t$. This proves (2.29).

As first observed by Kong, Nooijen, and Mukherjee,[66] the fact that the contractions are cumulants plays little role in the proof. All that we require is (2.27), from which (2.29) follows and then (2.28). Contractions can be defined in a largely arbitrary manner and still maintain these properties, although care should be taken to ensure that orbital invariance and antisymmetry are preserved. (2.29) and (2.28) are just rearrangements of the contraction pattern of (2.27), however the contractions in (2.27) are defined.

This freedom to change contractions has been used by Evangelista and coworkers[123,126] to define a variant of GNO where the contractions are the "cumulants" of a density matrix for a statistical ensemble of electronic states, for multistate chemistry, and also by Kutzelnigg, Mukherjee, and coworkers to formulate a spinfree GNO by taking contractions as the "cumulants" of a spin-averaged ensemble density matrix.[20,127]

However, let us suppose that contractions are chosen by the rule that the sum of all contractions equals some tensor. Then between postulating that and postulating the contraction structure of (2.27), we are back to the second way to arrive at "contractions are cumulants" outlined in the previous subsection, but now with stronger motivation. By the logic of Section 2.3.1, if the tensor is an RDM or even something else, the contractions will have the property that if the tensor is multiplicatively separable, the contractions are additively separable. This requires no further effort.

2.6 Conclusions

Despite the importance of reduced density matrix cumulants, we believe that cumulant formalisms can be made more accessible by further simplifying conceptual issues surrounding cumulants. This research has striven to do so. In particular:

1. We have provided a simplified definition of reduced density matrix cumulants and a generating function to provide explicit formulas for them, beginning with the familiar exponential relation between configuration interaction amplitudes and coupled cluster amplitudes. Previous approaches[82–84] are shown to reduce to our solution. Of special importance is the fact that our solution is a general prescription to convert between multiplicative and additive separability, which can be of use to novel electronic structure methods.

2. Interpretive issues of cumulants have been resolved. The analogy between RDM cumulants and the probabilistic cumulants is based on the fact that they are both combinatorial objects to solve the problem of converting from multiplicative to additive separability. No further probabilistic meaning of the reduced density matrix cumulants is expected, and arguments to the contrary[82] have been refuted. In addition, our definition of cumulants provides a way to confirm the additive separability of cumulants from their polynomial form and understand why, for some approximate theories, the cumulants are not additively separable. This gives an elementary way to confirm additive separability.

3. We have also presented a brief proof of the Generalized Normal Ordering formalism to explain why cumulants appear as contractions there and make it more accessible for multireference theories, one of the most pressing problems in electronic structure theory. The key theorems are shown to follow from combinatorics applied to the form of allowed contractions in the formalism. In the original Generalized Normal Ordering formalism where normal ordered operators are required to have zero expectation value against some wavefunction, this leads to contractions being cumulants. More general formulations are possible and have even been shown to be quite useful,[20,123,126,127] and we have shown that the contractions will remain additively separable if the expectation value and RDMs is replaced with some other multiplicatively separable tensor.

2.7 Appendix: Cumulants by Low-Level Combinatorics

To illustrate how the $\exp$ and $\log$ functions solve the combinatorial problem given in our axiomatic definition of the RDM cumulant (or any other additively separable quantity), we solve it without generating functions by combining the axioms of Percus[95] and Simon[114] with the Möbius inversion of Speed.[128] In brief, suppose a set where some elements are said to be greater than others, or more precisely, a *partially ordered set*. We denote this abstract "greater than" relation with $\supseteq$. Mathematicians prefer to use $\geq$, but the symbol $\supseteq$ suggests the specific relation we will use. Then given an equation of form

$$\sum_{x:y\supseteq x} f(x) = g(y) \quad , \tag{2.32}$$

Möbius inversion solves for f as a linear combination of the g by

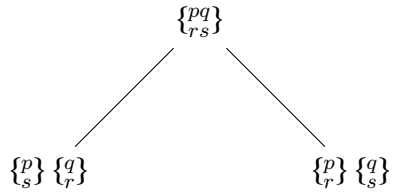


Figure 2.1: The fermionic partitions for a rank-two tensor. A vertical path between two elements ρ and π, where ρ is higher than π, means that $\rho \supseteq \pi$.

$$\sum_{x:y \supseteq x} g(x)\mu(x,y) = f(y) \tag{2.33}$$

where the function μ is determined by the recursion relations

$$\sum_{x:z \supseteq x \supseteq y} \mu(y,x) = \delta_{y,z} \tag{2.34}$$

and

$$\sum_{x:z \supseteq x \supseteq y} \mu(x,z) = \delta_{y,z} \tag{2.35}$$

Equations (2.34) and (2.35) show that the values of μ depend on the set and the rules governing which elements are greater than others.

Readers interested in a detailed mathematical treatment of Möbius inversion are directed to Chapter 16 of reference [129], Chapter 8 of reference [107], Chapter 3 of reference [117], Chapter 3 of reference [130], and reference [131]. We especially recommend reference [129].

We require the idea of fermionic partitions. A fermionic partition is, given n creation indices and n annihilation indices, a way to split them into "blocks" such that each "block" contains as many creation as annihilation indices, and each index appears in exactly one group. For the case of a rank-two quantity, these are shown in Figure 2.1.

We shall use the following facts about the set of fermionic partitions:

1. Given any two fermionic partitions ρ, σ, $\rho \supseteq \sigma$ means that each block of σ is contained in a block of ρ. This $\supseteq$ is a *partial order*, which means that we may use Möbius inversion. Given n creation and annihilation operators, we call the set of all possible fermionic partitions the *fermionic partition lattice*. Figure 2.1 demonstrates this for a rank-two tensor.

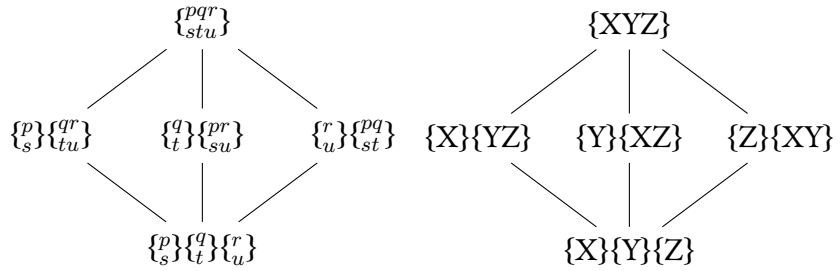


Figure 2.2: The fermionic partitions greater than or equal to $\{^{p}_{s}\}\{^{q}_{t}\}\{^{r}_{u}\}$, and the set of partitions of three objects. A vertical path between two elements ρ and π, where ρ is higher than π, means that $\rho \supseteq \pi$. The two subsets and their order relations are isomorphic.

2. Given any fermionic partition of n creation and annihilation operators, arbitrarily pair up creation and annihilation operators, and assign each pair to one of n distinct symbols. Then any fermionic partitions where each operator in the pair is in the same block can be mapped to a partition of n sets. Furthermore, if all pairs are in the same block for σ, all pairs will also be in the same block for any ρ where $\rho \supseteq \sigma$. By this map between fermionic partitions and set partitions, the set of π where $\rho \supseteq \pi \supseteq \sigma$ has exactly the same $\supseteq$ (partial order) structure as some subset of the set of partitions of n objects, which is known as the *partition lattice*. An example of this is shown in Figure 2.2. By this trick, if we show a statement is true on some subset of the partition lattice, we can show it is true for any "counterpart" of that subset in the fermionic lattice.

3. Suppose $\rho \supseteq \sigma$ and block i of ρ is split into b_i blocks in σ, then

$$\mu(\sigma, \rho) = \prod_i (-1)^{b_i - 1}(b_i - 1)! \quad . \tag{2.36}$$

   The same property holds on the set of fermionic partitions, because the recursions that determine μ, (2.34) and (2.35), depend only on the structure of the partially ordered set, which is the same between the two sets by Point 2.

   This property of the partition lattice is shown in Example 16.17 combined with Theorem 16.4 of Reference [129], proved in two ways in Example 3.10.4 of Reference [116] and Examples 3.3.4 and 3.5.5 of Reference [130], then proved in two more ways in Sections 16 and 18 of Reference [131].

4. Let $\rho \wedge \pi$ denote the partition in the partition lattice whose blocks are obtained by intersecting the blocks of ρ and π. For any σ and for any π other than $\{XY \cdots\}$:

$$\sum_{\rho:\rho\wedge\pi=\sigma} \mu(\rho, \{XY\cdots\}) = 0 \quad . \tag{2.37}$$

This is proven in the course of Theorem 16.5 of reference [129] and by more sophisticated arguments in Proposition 3.5.4 of reference [130] and Corollary 3.9.3 of reference [116].

By the trick of Point 2, a very similar property holds for the fermionic partitions:

$$\sum_{\rho:\rho,\pi\supseteq\sigma,\rho\wedge\pi=\sigma} \mu(\rho, \{{}^{pq\cdots}_{rs\cdots}\}) = 0 \quad . \tag{2.38}$$

Now, suppose a polynomial satisfying the fermionic axioms. It must have the form of (2.20). Consider an arbitrary fermionic partition, π.

For most fermionic partitions, π has multiple blocks. Factorize every $\gamma(\rho)$ in (2.20) so each tensor contains only indices of a single block of π. Given a partition, σ, the new coefficient of $\gamma(\sigma)$ after this factorization by π is

$$\mu_{\sigma,\pi} = \sum_{\rho:\rho,\pi\supseteq\sigma,\rho\wedge\pi=\sigma} \mu_\rho \quad . \tag{2.39}$$

By the third axiom, for any such π, our polynomial is identically zero. Therefore, each coefficient must equal zero.

$$\mu_{\sigma,\pi} = 0 \tag{2.40}$$

Choosing the coefficients c so that (2.40) is satisfied is necessary and sufficient to define our cumulant.

The above discussion has assumed π consists of multiple blocks, so we may apply the connectedness axiom. If π consists of only one block, $\pi = \{{}^{pq\cdots}_{rs\cdots}\}$, and the connectedness axiom does not apply, but $\sum_{\rho\supseteq\pi} \mu_\rho = \mu_\pi = \mu_{\{{}^{pq\cdots}_{rs\cdots}\}} = 1$ by the normalization axiom.

In either case, we require

$$\sum_{\rho\supseteq\pi} \mu_\rho = \delta_{\pi,\{{}^{pq\cdots}_{rs\cdots}\}} \quad . \tag{2.41}$$

But this equation is just (2.35) when $z = \{{}^{pq\cdots}_{rs\cdots}\}$, which is precisely the recursion that determines $\mu(\rho, \{{}^{pq\cdots}_{rs\cdots}\})$. Using (2.36), we may immediately conclude

$$\mu_\sigma = \mu(\rho, \{{}^{pq\cdots}_{rs\cdots}\}) = (-1)^{\#\rho-1}(\#\rho - 1)! \tag{2.42}$$

where $\#\rho$ is the number of blocks of ρ. This is precisely in agreement with (2.18).

While (2.42) is necessary, the connectedness axiom still requires that (2.40) holds. With a formula for the coefficients just derived, (2.40) reduces to

$$\sum_{\rho:\rho,\pi\supseteq\sigma,\rho\wedge\pi=\sigma} \mu(\rho, \{^{pq\cdots}_{rs\cdots}\}) = 0 \quad . \tag{2.43}$$

This equation is merely (2.38) and is thus guaranteed to hold. We have therefore shown a polynomial satisfying the fermionic additively separability axioms exists and is unique, and we have determined its coefficients by (2.42). This polynomial is the probabilistic cumulant.

With Möbius inversion, we can straightforwardly invert our formula to convert multiplicative separability to additive separability and obtain a formula for a multiplicatively separable quantity as a polynomial in additively separable ones. Given fermionic partition π, we may substitute the cumulant formula just found for the cumulants appearing in the product $\lambda(\pi)$. We find

$$\lambda(\pi) = \sum_{\pi\supseteq\rho} \gamma(\rho)\mu(\rho,\pi) \tag{2.44}$$

but this is just (2.33) with $f(y) = \lambda(y)$ and $g(x) = \gamma(x)$. Because (2.33) is equivalent to (2.32), we have

$$\gamma(\pi) = \sum_{\pi\supseteq\rho} \lambda(\rho) \tag{2.45}$$

which is equivalent to relation (2.19). We have now derived the relations between probabilistic moments and cumulants entirely from combinatorics and the axiomatic definition.

The reader may wonder what any of this has to do with the $\exp$ and $\log$ functions of Section 2.3.1. The answer is that taking $\log$ of an exponential generating function precisely corresponds to performing Möbius inversion of the partition lattice, and taking $\exp$ of an exponential generating function undoes the Möbius inversion on the partition lattice, or sums over all partitions. (This is made precise by Theorem 5.1.11 and Example 5.1.13 of Reference [117].) As evidence of this, observe that the Taylor-series expansion coefficients of the $\log$-series are precisely (2.42) when $\#\rho$ is replaced with the degree of the coefficient. We expect a similar relation holds for the set of fermionic patterns and "generating functions" based on the normal ordered exponential.

The use of generating functions entirely avoids this otherwise tedious and non-obvious problem of Möbius inversion.

2.8 Appendix: Explicit Formulas from Generating Functions

For pedagogical purposes, we explicitly derive Equation 2.19 from Equation (2.10).

First, order the orbital indices and restrict the summations in Equations (2.7) and (2.8) so the indices occur in order. This exactly cancels the factorial denominators. Now, choose the cumulant element of interest. This is associated with a second quantized operator. Match the coefficients of this operator on both sides. On the right side, the possible ways to produce this operator using the normal ordered multiplication are given by every way to decompose the second quantized operator, i.e., the fermionic partitions, with an explicit order imposed. If the operator is decomposed into n operators, there are $n!$

possible orders of these operators, so the term will occur $n!$ times. (There will be less than $n!$ orders in the case of repeated operators, but then the original operator would have been zero by antisymmetry.) This term has a coefficient given by the degree n term of the Maclaurin series of $\log(1+x)$, $\frac{(-1)^{n-1}}{n}$. Multiplying this by the $n!$ multiplicity factor gives a final weight of this partition of $(-1)^{n-1}(n-1)!$. Upon summing over all fermionic partitions, this produces Equation 2.19.

Equation 2.18 may be derived from Equation (2.9) by the same reasoning, but instead using the fact that the degree n term of the Maclaurin series of $\exp(x)$ is $\frac{1}{n!}$.

2.9 Appendix: Exponentials in the Moment-Generating Function

Another obvious difference between the generating functions for the additively separable probabilistic (2.2) and fermionic (2.10) quantities is that the probabilistic multiplicatively separable generating function (2.1) uses an exponential that has no counterpart in the "generating function" for the fermionic multiplicatively separable quantity, (2.7). This is due to fermionic antisymmetry eliminating a technicality in the probabilistic cumulants.

For probabilities, it is perfectly legitimate to have a moment with a repeated variable, such as the cumulant $\kappa(XX)$. This cannot occur for fermionic quantities, because any "moments" with a repeated creation index or annihilation index must be zero by antisymmetry. We point out that (2.18) and (2.19) preserve antisymmetry because there is a sign-factor built into the definitions of $\gamma(\rho)$ and $\lambda(\rho)$.

The possibility of repeated variables in a probabilistic cumulant introduces an ambiguity in how we define the probabilistic cumulant. Do we define it by taking the formula for the cumulant given *distinct* variables and substitute in the repeated variables, or do we extract the term from the functions (2.1) and (2.2) with the repeated variables? Ideally, both approaches should produce the same polynomial.

Direct computation shows that when all variables are distinct, encoding the moments m as an ordinary generating function or an exponential generating function produces the same polynomial. However, for repeated variables, the two definitions *differ* using the ordinary generating function. For example, the ordinary generating function produces $\kappa(XX) = m(XX) - \frac{1}{2}m(X)m(X)$ and $\kappa(XY) = m(XY) - m(X)m(Y)$.

The remedy for the case of repeated variables is to choose an exponential generating function for the moment and cumulant generating functions. Taking the logarithm of our moment-generating function is then the composition of exponential generating functions. It is a well-known combinatorial fact that this encodes a sum over all set partitions for a single variable. (See Theorem 5.1.4 of Reference [117].) This interpretation hinges on repeated application of the multiplication of exponential generating functions we discussed in Section 2.4.1. The multivariable generalization of the same argument shows that the use of an exponential generating function maintains the desired sum over partitions structure, whether variables are repeated or not. Thus, we see that the exponential in the moment generating function is only necessary to treat repeated variables, which we do not have in the fermionic case.

2.10 Appendix: Cumulants in Mukherjee's Proof of GNO

The original paper of Mukherjee[65] offered an alternate proof of the GNO formalism in which contractions naturally appear as different connectivity patterns of operators after a similarity transformation by a unitary coupled cluster operator. These connectivity patterns can be shown to be cumulants by summing all possible connectivity patterns together and equating them to an RDM. (The connection between unitary coupled cluster connectivity and cumulants has been further explored in Reference [21].) Products of cumulants arise as products of operators not connected by a contraction, and sign phases arise from permutational phases of operators.

While this provides another motivation to consider cumulants in the context of GNO, the proof works just as well if the distinction between connectivity patterns of similarity-transformed operators is not made, so cumulants do not appear. Separating out connectivity patterns, or equivalently cumulants from the RDMs, is an arbitrary choice in this proof, although one that clearly yields the advantage of additively separable contractions. Not separating contractions based on connectivity patterns leads to a GNO where contractions are RDMs instead of cumulants, but pairs of contractions are not valid, as in Section 2.5.1.

2.11 Appendix: Extended Generalized Wick's Theorem: Remaining Steps

To prove the extended generalized Wick Theorem, we expand the GNO operators on the left side of (2.28) into vacuum normal operators with (2.29), multiply them, and then convert the result back into GNO operators with (2.27). This is similar in concept to the proof of Kong, Nooijen, and Mukherjee,[66] but (2.29) simplifies the proof.

Take two Ψ-normal operators, A and B. The expansion via (2.29) sums over all contractions on only one term, with a sign factor. We call these internal contractions. When we multiply and convert the result back using a Wick expansion, we sum over all possible contractions. This includes contractions of operators from both A and B, called cross-contractions. So the result is a sum over all possible contraction patterns with some coefficient. Let us choose a particular contraction pattern and find its coefficient.

Suppose our contraction pattern has i internal contractions and c cross-contractions. The cross-contractions must occur during the Wick expansion (2.27), but the internal contractions may originate from (2.27) or (2.29). (2.27) always contributes a sign factor of 1, but the terms with n contractions from (2.29) contribute a sign factor of $(-1)^n$. Further, there are $\binom{i}{f}$ ways to choose which f internal contractions come from (2.27). So our total coefficient is

$$\sum_{f=0}^{i} (-1)^f (1) \binom{i}{f} \tag{2.46}$$

We can change the exponent of 1 arbitrarily to $i - f$ to apply a binomial expansion again and get

$$\sum_{f=0}^{i}(-1)^f(1)^{i-f}\binom{i}{f} = (1-1)^i = \begin{cases}1 & i=0\\ 0 & \text{else}\end{cases} \tag{2.47}$$

In other words, all contraction patterns happen exactly once, which contain no internal contractions. This is precisely the Extended Generalized Wick Theorem, (2.28).

Chapter 3

Assessing the Orbital-Optimized Unitary Ansatz for Density Cumulant Theory[1]

[1]Misiewicz, J. P.; Turney, J. M.; Schaefer, H. F.; Sokolov, A. Y. **2020**, Submitted to *J. Chem. Phys.*, November 5, 2020.

3.1 Abstract

The previously proposed ansatz for density cumulant theory that combines orbital-optimization and a parameterization of the 2-electron reduced density matrix cumulant in terms of unitary coupled cluster amplitudes (OUDCT) is studied. Formally, we elucidate the relationship between OUDCT and orbital-optimized unitary coupled cluster theory and show the existence of near-zero denominators in the stationarity conditions for both the exact and some approximate OUDCT methods. We implement methods of the OUDCT ansatz restricted to double excitations for numerical study, up to the fifth commutator in the Baker-Campbell-Hausdorff expansion. We find that methods of the ansatz beyond the previously known ODC-12 method tend to be less accurate for equilibrium properties and less reliable when attempting to describe H_2 dissociation. New developments are needed to formulate more accurate DCT variants.

3.2 Introduction

ODC-12 is the most successful method to date of the density cumulant theory[18,133,134] (DCT) family of electronic structure methods. For a system of o occupied orbitals and v virtual orbitals, ODC-12 has the $\mathcal{O}(o^2v^4)$ scaling of coupled cluster with singles and double excitations[1,135] (CCSD) but is consistently more accurate.[134,136,137] It has a simple, inexpensive analytic gradient theory.[134] It tolerates multireference effects that leave CCSD qualitatively incorrect.[138] For these reasons, there has been interest in extending the success of ODC-12 both to achieve greater accuracy for weakly correlated molecules, and to develop a method able to treat multiconfigurational molecules.[21,34,138]

To date, there has been only one published proposal of density cumulant theory methods going beyond ODC-12 in accuracy.[21] Reference [21] introduced a formally exact ansatz for density cumulant theory and proposed that approximating it may yield the desired improvements to ODC-12. As a proof-of-concept, the authors implemented and benchmarked the ODC-13 method, which adds terms to ODC-12 and is derived from the aforementioned ansatz.

Unfortunately, the ODC-13 method did not improve on the success of the simpler ODC-12. The authors of Reference [21] reported that ODC-13 was less accurate in the weakly correlated regime, as determined by comparison against experimental bond lengths and vibrational frequencies for diatomic molecules. The accuracy of the method across various correlation strengths was assessed by H_2 dissociation. For this system, ODC-13 was less accurate than ODC-12 past 0.9 Å and could not be converged beyond 1.3 Å. Reference [21] observed that a particular exact relationship between two key intermediates of the theory, the 1-electron reduced density matrix (1RDM) and the 2-electron reduced density matrix (2RDM), was not satisfied in ODC-13. The authors suggested that violating that relationship might have caused the "unsatisfactory" performance of ODC-13.

The authors of Reference [21] proposed but did not implement an alternative scheme to approximate their ansatz where that relationship is obeyed. This approximation consists of truncating a Baker-Campbell-Hausdorff (BCH) expansion to a finite number of commutators to obtain one part of the

2RDM while maintaining the aforementioned exact relation between the 1RDM and the 2RDM to determine the rest. As there have been no further studies of any post-ODC-12 methods of this ansatz, it remains untested whether the failure of ODC-13 can be attributed to violations of this relationship or whether the performance of ODC-13 indicates a more general complication in working with the DCT ansatz advanced in Reference [21].

In this article, we study truncations of the orbital-optimized unitary coupled cluster ansatz for DCT (OUDCT) proposed in Reference [21]. We begin in Section 3.3 with a thorough review of the equations of the OUDCT ansatz, which are scattered across multiple papers.[18,21,133,134] During this review, two new *formal* questions about the ansatz arise, namely:

1. The residual equations for the OUDCT stationarity conditions contain terms with near-zero denominators, which all vanish in ODC-12. Do these vanish in the exact OUDCT theory?

2. The similar orbital-optimized variational unitary coupled cluster method can also be approximated by truncations of the BCH expansion to a finite number of commutators. What is the relationship between approximations of that method and OUDCT, truncated at the same degree?

We then turn our attention to numerical studies of the performance of low-degree OUDCT truncations, with only double excitations. The truncation at degree two is the aforementioned ODC-12 method and is our baseline for both accuracy and degree of truncation. After discussing our implementation of the methods in Section 3.4, we perform numerical studies in Section 3.5. We investigate:

3. Do higher-degree truncations of the OUDCT ansatz improve the accuracy for H_2? H_2 is important both as a case where effects of triple and higher-rank cluster operators do not exist, and as a model of variable correlation strength.

4. Do higher-degree truncations of the OUDCT ansatz, restricted to doubles, improve the accuracy for systems with more than two electrons, where triples effects may be important?

The results of our investigation lead us to conclude that OUDCT ansatz truncations that include more commutators than ODC-12, up to five, improve upon ODC-13 for H_2 dissociation, but are still inferior to ODC-12 for moderate bond stretching. For equilibrium properties of weakly correlated molecules with more than two electrons, OUDCT approximations will not improve upon ODC-12 unless unitary cluster operators beyond doubles are accounted for. Further, treating triple unitary cluster operators to four or more commutators in the BCH expansion will lead to singularities in the theory.

3.3 The Orbital-Optimized Unitary Density Cumulant Theory Ansatz

This section provides a self-contained exposition of DCT and the OUDCT ansatz in particular starting from an understanding of electron correlation at the level of Shavitt and Bartlett's text[1] and a loose acquaintance with reduced density matrix (RDM) theory.[139,140] Section 3.3.1 derives the theoretical essentials

of DCT, bypassing the intermediates κ and τ of Reference [18]. The degeneracies in the cumulant partial trace discussed in that section have not been discussed previously. Section 3.3.2 and Section 3.3.3 derive the Variational Unitary Coupled Cluster (VUCC) and Unitary DCT (UDCT) ansätze. The latter should be compared with Reference [21]. Section 3.3.4 discusses the addition of orbital optimization to the VUCC and UDCT ansätze to produce OVUCC and OUDCT, focusing on the implications and advantages of doing so. Orbital optimization was added to DCT in Reference [134]. In this section, we also discuss the possibility of singularities in the cumulant update equations, as these depend not only on the cumulant parameterization but also on the orbitals. Finally, Section 3.3.5 formally analyzes the difference between UDCT and UCC truncated at the same degree.

Throughout this section, we use primed indices to denote a quantity that must be computed in the basis of natural orbitals.

3.3.1 Abstract Density Cumulant Theory

We begin by writing the Hamiltonian in second-quantized form

$$\hat{H} = h_p^q a_q^p + \frac{1}{4}\bar{g}_{pq}^{rs} a_{rs}^{pq} \tag{3.1}$$

where h_p^q is the standard one-electron integral, $\langle\phi_p|\,\hat{h}\,|\phi_q\rangle$, and $\bar{g}_{pq}^{rs}$ is the antisymmetrized electron repulsion integral, $\langle pq|\,|rs\rangle$. We use the notation of Reference [141] for writing the vacuum-normal, particle-conserving second quantized fermionic operators ($a_q^p = a_p^\dagger a_q$ and $a_{rs}^{pq} = a_p^\dagger a_q^\dagger a_s a_r$), and we also use the Einstein summation convention throughout this article.

It follows from (3.1) that the energy expectation value of any normalized wavefunction Ψ may be written as

$$E = h_p^q \gamma_q^p + \frac{1}{4}\bar{g}_{pq}^{rs}\gamma_{rs}^{pq} \tag{3.2}$$

respectively defining the 1-electron RDM (1RDM) and 2-electron RDM (2RDM) with

$$\gamma_q^p = \langle\Psi|\,a_q^p\,|\Psi\rangle \tag{3.3}$$

and

$$\gamma_{rs}^{pq} = \langle\Psi|\,a_{rs}^{pq}\,|\Psi\rangle \quad . \tag{3.4}$$

For exact wavefunctions, γ_{rs}^{pq} is multiplicatively separable, not additively separable, i.e., not size-consistent.[64] We may decompose it into size-consistent tensors with

$$\gamma_{rs}^{pq} = \lambda_{rs}^{pq} + \gamma_r^p\gamma_s^q - \gamma_s^p\gamma_r^q \quad . \tag{3.5}$$

It may be checked manually that if γ_{rs}^{pq} is multiplicatively separable, λ_{rs}^{pq} must be zero.[64] These size-consistent tensors are called RDM cumulants and denoted with λ.[28,64,69,82–85,142] Because the 1RDM equals

its cumulant, we shall usually refer to it with γ, as done in (3.5). When no superscripts or subscripts specify the rank of the tensor, λ shall refer to the 2RDM cumulant, and γ shall refer to the 1RDM.

Substituting (3.5) into (3.2) and using antisymmetry of $\bar{g}$ gives

$$E = (h^q_p + \frac{1}{2}\bar{g}^{qs}_{pr}\gamma^r_s)\gamma^p_q + \frac{1}{4}\bar{g}^{rs}_{pq}\lambda^{pq}_{rs} \quad . \tag{3.6}$$

This is an exact functional of γ and λ. To find the exact ground-state energy, we want to minimize this functional over the set of γ and λ possible given the definitions of (3.3), (3.4), and (3.5). A pair of γ and λ consistent with those equations is said to be pure n-representable.[37,38,143–146] However, the set of pure n-representable γ and λ has a complicated structure, and there is no known parameterization that is necessary, sufficient, and computationally efficient. Accordingly, our strategy will be to take a parameterization that is necessary and sufficient, approximate it for computational efficiency, and vary the amplitudes until the derivative of the energy functional is zero.

At first sight, we need to parameterize both γ and λ. However, for a given λ, the set of γ consistent with it is strongly constrained. While γ is not a function of λ (we will construct a counterexample later in this subsection), the set of possible γ is discrete for all but exceptional λ. This enables us to use implicit differentiation to treat (3.6) as a function of the λ parameters alone for differentiation purposes, so we need only parameterize λ.

We will begin by constraining the set of γ that are consistent with a given λ.[18] For an n-electron system,

$$\gamma^{pr}_{qr} = (n-1)\gamma^p_q \tag{3.7}$$

and

$$\gamma^p_p = n \quad . \tag{3.8}$$

(Equations (3.7) and (3.8) are easily proven by expanding Ψ from (3.3) and (3.4) in terms of Slater determinants.) Inserting (3.5) in (3.7) yields, through straightforward algebra and an invocation of (3.8):

$$d^p_q = (\gamma^2 - \gamma)^p_q \tag{3.9}$$

where

$$d^p_q = \lambda^{pr}_{qr} \quad . \tag{3.10}$$

d is quadratic in the matrix γ. The set of γ consistent with (3.9) for a given d may be characterized as follows: If γ is consistent with Equation (3.9), then express Equation (3.9) in an eigenbasis of γ where eigenvector v_p has eigenvalue $\gamma_{p'}$. The eigenvectors are called the natural spin-orbitals, and the eigenvalues are the natural spin-orbital occupation numbers. Then the right-hand side of Equation (3.9) is a diagonal matrix with entries $(\gamma^2_{p'} - \gamma_{p'})$. It follows that each eigenvectorv_p is also an eigenvector of d with eigenvalues

$\Delta_{p'} = \gamma_{p'}^2 - \gamma_{p'}$. This may be solved to yield

$$\gamma_{p'} = \frac{1 \pm \sqrt{1 + 4\Delta_{p'}}}{2} \quad . \tag{3.11}$$

The choice of $+$ sign is consistent with $\gamma_{p'} \geq \frac{1}{2}$, and the choice of $-$ sign is consistent with $\gamma_{p'} \leq \frac{1}{2}$. These choices are illustrated in Figure 3.1. Therefore, for all γ consistent with Equation (3.9), it is necessary that there exist some eigenbasis of d that is also an eigenbasis of γ with eigenvalues from (3.11). It is clear that the existence of such a d eigenbasis is sufficient to satisfy (3.9) in the chosen eigenbasis, and thus in any basis. Therefore, the set of γ so constructed from d is precisely the set of solutions to (3.9). Equations (3.9) and (3.10) are merely necessary for γ and λ to be pure n-representable, not sufficient, but we shall not need sufficiency.

Equivalently, solutions to (3.9) take the form

$$\gamma = U \begin{bmatrix} \frac{1+\sqrt{1+4\Delta_o}}{2} & 0 \\ 0 & \frac{1-\sqrt{1+4\Delta_v}}{2} \end{bmatrix} U^{-1} \tag{3.12}$$

where the matrix U is some matrix of eigenvectors of d,

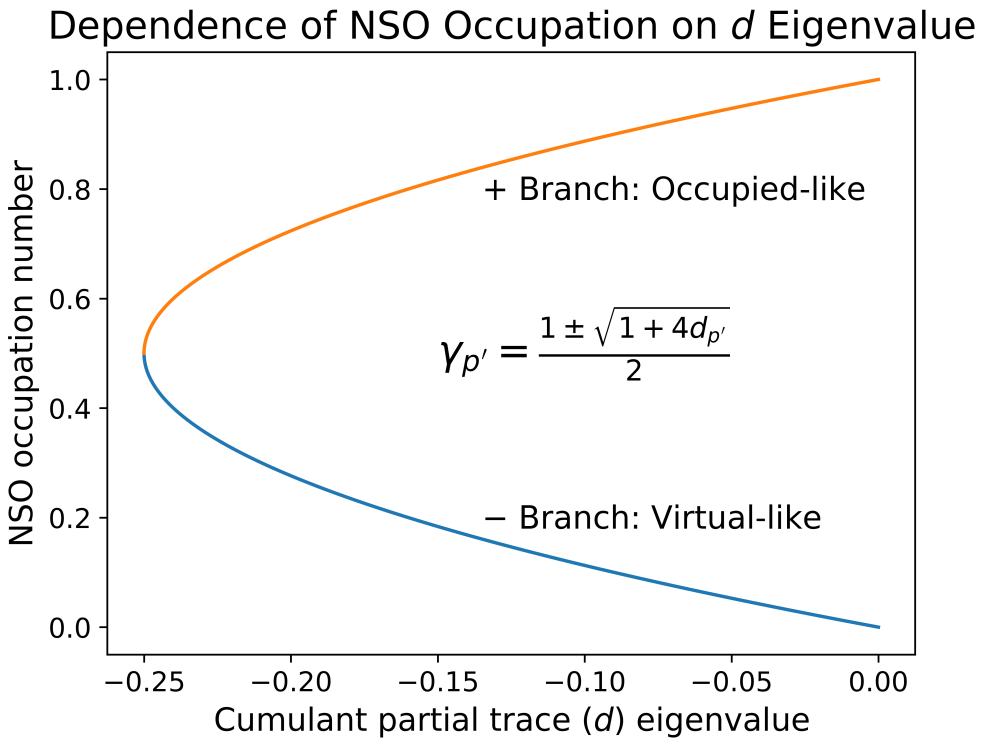
$$\Delta = U^{-1}\, d\, U \tag{3.13}$$

and Δ_o and Δ_v are the occupied and virtual blocks of Δ, the matrix of eigenvalues of d. A natural orbital taking the $+$ solution of (3.11) is equivalent to it being a column of U that is multiplied against the (occupied) $+$ block of (3.12), and analogously for the (virtual) $-$ block.

Depending on the eigenvalue structure of d, the set of possible γ from (3.12) may be either discrete or continuous. If there are no degeneracies in the d matrix, then the eigenvectors of d are unambiguous, and so are the eigenvectors of γ. It remains only to choose whether a given natural spin-orbital occupation number should take the $+$ sign (occupied-like) or the $-$ sign (virtual-like) in (3.11). If the goal is to approximate some electronic state, these can be chosen by comparing the natural spin-orbitals to those of another approximation to the electronic state and choosing the signs to mimic the occupation numbers of the other approximation.[44,147] This other approximation may be a Hartree–Fock computation or a previous solution to (3.9).

However, let us suppose that there is a degeneracy in the d matrix. There remains the discrete freedom in how many of an eigenspace's eigenvectors take the $+$ sign and how many $-$, but there is also a new continuous freedom in partitioning the eigenspaces into $+$ and $-$ eigenvectors. A concrete example of this is a single determinant wavefunction, which has $\lambda = 0$. Then (3.11) implies that the natural orbitals all have occupation number 0 or 1, but the requirement that the wavefunction is a Slater determinant does not determine which orbitals are occupied and which are virtual. Instead, there is a continuous set of possible Slater determinants, as is well-known from the continuous Hartree–Fock problem. This also shows that a pure n-representable λ need not uniquely determine the corresponding γ. This continuous freedom from degeneracies was not considered by previous works that derived (3.11).[18,44,147]

Figure 3.1: The natural spin-orbital (NSO) occupation number $\gamma_{p'}$ as a multi-valued function of the corresponding eigenvalue in the partial trace of the 2RDM cumulant, $d_{p'}$. In general, a $d_{p'}$ eigenvalue is consistent with two possible occupation numbers, one suggesting an occupied orbital and the other suggesting a virtual orbital.



Let us use these results to write γ as a (continuously) differentiable implicit function of λ about some neighborhood of a starting solution to (3.9). If we cast γ in the basis of natural orbitals, we find that

$$\frac{\partial}{\partial d^{p'}_{q'}}\gamma^{p'}_{q'} = \frac{1}{\gamma_{p'} + \gamma_{q'} - 1} \quad . \tag{3.14}$$

This equation has singularities if $\gamma_{p'} + \gamma_{q'} = 1$, which are precisely the cases where $\frac{d}{d\gamma}(\gamma^2 - \gamma)$ fails to be invertible. $\frac{d}{d\gamma}(\gamma^2 - \gamma)$ is the matrix A_x in Theorem 9.28 of Reference [148], so the hypotheses of the implicit function theorem are not satisfied in this case, and implicit differentiation fails.

We may interpret these singularities via the discussion regarding solutions to (3.9). If $p' = q'$ and $\gamma_{p'} + \gamma_{q'} = 1$, then orbital p' is half-occupied, and either choice of sign in (3.11) gives the same result. It is undetermined from (3.9) whether a change in d will cause the occupation number to take the $+$ sign and be slightly more occupied, or to take the $-$ sign and be slightly more virtual.

If $p' \neq q'$ and $\gamma_{p'} + \gamma'_q = 1$, then p' and q' have a common d eigenvalue by (3.9), and we must decide how to split their degeneracy in the d matrix into an occupied and a virtual orbital. Any slight perturbation of the d matrix may break the degeneracy, causing unpredictable changes in how the orbital spaces break into an occupied and a virtual orbital. This costs differentiability, because the eigenvectors are not even continuous with respect to changes in d.

We may now use (3.14) in conjunction with (3.6) and (3.10) to minimize the energy with respect to yet unspecified cumulant parameters. We can explicitly write the derivative of the energy with respect to cumulant parameter t as

$$\frac{\partial E}{\partial t} = \tilde{F}^q_p \frac{\partial d^p_q}{\partial t} + \bar{g}^{rs}_{pq} \frac{\partial \lambda^{pq}_{rs}}{\partial t} \tag{3.15}$$

defining

$$\tilde{F}^{q'}_{p'} = \frac{h^{q'}_{p'} + \bar{g}^{q's'}_{p'r'}\gamma^{r'}_{s'}}{n_{p'} + n_{q'} - 1} \tag{3.16}$$

which must be first computed in the basis of natural spin-orbitals before being transformed back to the original orbital basis in which the cumulant was constructed.[133] It remains only to choose a cumulant parameterization.

We note that the formula $\gamma = \kappa + \tau$ used in the original DCT paper[18] has been entirely eliminated in this presentation. Previous work[149] also presented formulas without this decomposition, but did not discuss them in detail. Contrary to the claims of Reference [18], κ is *not* a variable independent of λ, as the two strongly constrain each other. However, all previous DCT numerical studies[21,70,133,134,136–138,150–152] obeyed this constraint. The new constraint is discussed in Appendix 3.7.

3.3.2 Variational Unitary Coupled Cluster Ansatz

Assume that any wavefunction, Ψ, may be written as

$$|\Psi\rangle = \exp(T - T^\dagger)\,|\Phi\rangle \tag{3.17}$$

for a reference determinant $|\Phi\rangle$ where

$$T = T_1 + T_2 + ... \tag{3.18}$$

and

$$T_n = \left(\frac{1}{n!}\right)^2 t^{ij...}_{ab...} a^{ab...}_{ij...} \quad . \tag{3.19}$$

In other words, it is assumed that the unitary coupled cluster (UCC) ansatz[153–160] is exact. The validity of this assumption has been studied by Evangelista, Chan, and Scuseria.[161]

The energy expectation value of this wavefunction is given by (3.2), where the RDM formulas (3.3) and (3.4) may be written as functions of the amplitudes t:

$$\gamma^p_q(t) = \langle\Phi|\exp(T^\dagger - T)a^p_q \exp(T - T^\dagger)\,|\Phi\rangle \tag{3.20}$$

and

$$\gamma^{pq}_{rs}(t) = \langle\Phi|\exp(T^\dagger - T)a^{pq}_{rs} \exp(T - T^\dagger)\,|\Phi\rangle \quad . \tag{3.21}$$

By using the Baker–Campbell–Hausdorff expansion, (3.20) and (3.21) may be written as

$$\gamma^p_q(t) = \sum_{n=0}^{\infty} \frac{1}{n!} \langle\Phi|\,[\cdot, T - T^\dagger]^n(a^p_q)\,|\Phi\rangle \tag{3.22}$$

and

$$\gamma^{pq}_{rs}(t) = \sum_{n=0}^{\infty} \frac{1}{n!} \langle\Phi|\,[\cdot, T - T^\dagger]^n(a^{pq}_{rs})\,|\Phi\rangle \tag{3.23}$$

where the function $[\cdot, T](H)$ sends H to $[H, T]$.

The variational unitary coupled cluster (VUCC) ansatz consists of approximating the functions (3.22) and (3.23), using those approximations in (3.2) to construct an approximate energy function of the amplitudes t, and taking the energy as the variational minimum of that function. This is equivalent to the more usual definition, where the energy function is defined directly as

$$E(t) = \sum_{n=0}^{\infty} \frac{1}{n!} \langle\Phi|\,[\cdot, T - T^\dagger]^n(H)\,|\Phi\rangle \tag{3.24}$$

but using RDM intermediates will facilitate comparison with DCT.

3.3.3 Unitary Density Cumulant Theory

From (3.5), (3.22) and (3.23), we immediately have an exact function from the amplitudes t to λ. Furthermore, this parameterizes only pure n-representable cumulants, and if the UCC ansatz is exact, this parameterizes all pure n-representable cumulants. We can thus approximate the map from the t amplitudes to λ and use density cumulant theory as developed in Section 3.3.1 to approximate (3.3) and (3.4) and perform the variational unitary coupled cluster of Section 3.3.2. The only source of error is how we approximate the map from t amplitudes to the cumulant.

Constructing the cumulant function by inserting (3.22) and (3.23) into (3.5) will lead to a large cancellation of terms. We can instead equate the connected terms on both sides of (3.23).[21] This is valid because that is the only way to divide the terms of (3.23) into pieces with the additive separability structure of (3.5). Every connected term must be assigned to the cumulant because it cannot arise as a product of disconnected pieces. No disconnected term can be assigned to the cumulant because by the linear independence of monomials in any variables (here the t amplitudes), the cumulant would not be zero as a polynomial in the amplitudes if its orbitals correspond to independent subsystems. Doing this yields the exact relation:[21]

$$\lambda_{rs}^{pq}(t) = \sum_{n=0}^{\infty} \frac{1}{n!} \left\langle \Phi \right| [\cdot, T - T^\dagger]^n (a_{rs}^{pq}) \left| \Phi \right\rangle_C \quad . \tag{3.25}$$

Let us make a few observations about these equations.

1. It is natural to approximate (3.25) by truncating its Taylor series expansion at some degree in the cluster operators T. These degrees in T are what Reference [21] meant by orders in perturbation theory. Although methods of the ansatz can be analyzed in terms of the terms produced upon Møller-Plesset partitioning of the molecular Hamiltonian (MPPT),[133,134] and MPPT played a prominent role in the derivation of the cumulant approximation of ODC-12,[18,19] MPPT is not necessary to formulate the ansatz.

2. All DCT publications[18,70,133,134,136–138,150–152] excluding Reference [21] parameterized the cumulant in terms of parameters t_{ab}^{ij} satisfying $\lambda_{ab}^{ij} = t_{ab}^{ij}$. This can be derived by approximating the UDCT cumulant parameterization (3.25) to two commutators and $T = T_2$. The equation $\lambda_{ab}^{ij} = t_{ab}^{ij}$ can alternatively be interpreted as identifying the parameters as cumulant elements, hence why the parameters were written as λ_{ab}^{ij} in many DCT publications.[18,133,134,137,150,151] With three or more commutators or T_4 in the cluster operators, approximations to (3.25) will no longer be consistent with $\lambda_{ab}^{ij} = t_{ab}^{ij}$, and the amplitudes can no longer be identified with cumulant elements. For the exact ansatz of Reference [21], (3.25) shows the parameters *must* be identified as unitary coupled cluster amplitudes.

3. As UDCT determines the energy by variationally minimizing an approximation to (3.24), it can be regarded as a VUCC method. Specifically, UDCT constructs some number of cumulant diagrams and uses a power series of their partial trace to construct an infinite sum of non-cumulant (1RDM

and products of the 1RDM) terms. The mechanism of this summation is discussed in greater detail in Section 3.3.5.

4. One could approximate (3.25) differently for the purposes of constructing d in (3.11) and of constructing the λ component of (3.23). This was done in the ODC-13 method of Reference [21], which used a degree-four truncation and a degree-three truncation, respectively. Reference [21] blamed truncating to different degrees for the poor performance of ODC-13. None of the other methods implemented in this work use this uneven truncation strategy.

5. Commutator truncations are not the only way to approximate (3.23) and the derived (3.25), although they are widely used.[155,156,162–164] For example, there is the recursive commutator approximation,[124,165–167] where high-rank second quantized operators are projected out of commutators. If only RDMs at the converged amplitudes are necessary, there are also truncations of the inherently projective Bernoulli functional.[168–171]

3.3.4 Orbital-Optimized Unitary Methods

The t amplitudes appearing in (3.19) through (3.25) imply a division of orbitals into occupied and virtual spaces. While most electronic structure methods relying on such a partition choose this division based on Hartree–Fock orbitals, it is possible to vary these orbitals over a computation. There are multiple possible criteria for what the converged orbitals of a computation are.[18,172,173] If we perform VUCC or UDCT with the orbitals that minimize the energy, we call the resulting methods orbital-optimized variational unitary coupled cluster (OVUCC) and orbital-optimized unitary density cumulant theory (OUDCT),[134] respectively. The stationarity conditions are functions of the reduced density matrices,[108] therefore DCT does not need to use (3.14) to compute the derivative of the energy with respect to orbital rotations. Orbital optimized methods are well-studied,[108,111,134,174–180] and orbital-optimized unitary coupled cluster has recently received attention from quantum computing.[181,182] The impact of orbital optimization in density cumulant theory, compared to an alternative orbital convergence criterion,[18] is studied numerically in References [136] and [134].

Because the orbitals are added as parameters, varying all unitary cluster amplitudes would lead to the dimension of the variational space being greater than the dimension of the total space of wavefunctions, guaranteeing a redundancy. To remedy this, the T_1 are set to 0. We may qualitatively think of the T_1 amplitudes as corresponding to orbital rotations, because a unitary cluster operator consisting only of T_1 amplitudes is simply an orbital rotation.[183]

Adding orbital optimization to the unitary transformation of (3.17) is a convenient choice for multiple reasons. First, because the exact unitary coupled cluster energy is a variational upper bound to the energy for any choice of cluster operators, the argument of Köhn and Olsen that orbital optimization costs reproducing the full configuration interaction limit does not apply.[184] Second, eliminating the T_1 amplitudes reduces the number of contractions that need to be considered in (3.25). Third, this means that in the gradient theory, it is not necessary to compute an orbital relaxation term.[134,175] This both makes the analytic gradient theory simple and means there is no need to distinguish between the reduced density

matrices delivered by the theory and "relaxed density matrices" including extra Lagrangian terms. Fourth, these operators do not need to be expanded in an infinite series in the manner of (3.25),[134] so we may completely avoid error due to truncation of an infinite series with these parameters.[21,152]

The fifth reason is subtler and specific to UDCT. Because γ is an implicit function of d, which is in turn a function of the amplitudes t, γ is an implicit function of the amplitudes. When the denominator of (3.14) is not zero, the chain rule gives:

$$\frac{\partial}{\partial t}\gamma^{p'}_{q'} = \frac{1}{\gamma_{p'} + \gamma_{q'} - 1}\frac{\partial}{\partial t}d^{p'}_{q'} \tag{3.26}$$

where t is an arbitrary amplitude, and we are working in the basis of natural spin-orbitals of our current 1RDM. If orbital p' is occupied and q' is virtual, or vice versa, $\gamma_{p'} + \gamma_{q'} - 1 \approx 0$, and the denominator of (3.14) becomes very small, which may produce numerical issues.

This calamity is avoidable. If $\frac{\partial}{\partial t}d^{p'}_{q'} = 0$, then the right side of (3.26) is zero, even if the denominator is very close to zero. For all previously studied DCT models, this is true in the occupied-virtual blocks for any choice of t, so we have

$$\frac{\partial}{\partial t}\gamma^{\mathrm{v}}_{\mathrm{o}} = \frac{\partial}{\partial t}\gamma^{\mathrm{o}}_{\mathrm{v}} = 0 \quad . \tag{3.27}$$

Let us call the orbitals used to define the amplitudes the *reference orbitals*. The origin of (3.27) is that the occupied-virtual and virtual-occupied elements of d are zero for any choice of t. This means occupied natural orbitals are linear combinations of occupied orbitals, and virtual natural orbitals are linear combinations of virtual orbitals. Combining these facts means that after moving to the current natural orbital basis for (3.26), $d^{\mathrm{o}}_{\mathrm{v}}$ and $d^{\mathrm{v}}_{\mathrm{o}}$ remain identically zero even as the cumulant changes. Their derivative must therefore vanish. This implies $\gamma^{\mathrm{v}}_{\mathrm{o}}$ and $\gamma^{\mathrm{o}}_{\mathrm{v}}$ vanish. Intuitively, optimizing the orbitals should account for the otherwise missing correlation in these blocks.

Unfortunately, $d^{\mathrm{o}}_{\mathrm{v}}$ and $d^{\mathrm{v}}_{\mathrm{o}}$ being zero is *not* a general feature of the OUDCT ansatz. To see this, let us borrow an idea from Reference [18] and expand γ in (3.9) by $\kappa + \tau$, where κ is the 1RDM of Φ, and τ is the remainder. Using the Φ-normal operator $\tilde{a}^p_q$, τ may be expressed as:

$$\tau^p_q(t) = \sum_{n=0}^{\infty}\frac{1}{n!}\left\langle\Phi\right|\left[\cdot, T - T^\dagger\right]^n(\tilde{a}^p_q)\left|\Phi\right\rangle \quad . \tag{3.28}$$

The occupied-virtual block of both sides of (3.9) is given by

$$d^i_a = \tau^i_p\tau^p_a \tag{3.29}$$

and we must tell when this is nonzero. If only even rank operators are included in (3.18), then the total excitation rank of terms in (3.28) is odd no matter how many even rank operators are contracted against $\tilde{a}^i_a$, so no complete contractions are possible. Consequently, τ^i_a is zero by (3.28), and d^i_a is zero by (3.29).

But if all operators are present in (3.18), then τ^i_a terms exist and give rise to non-vanishing d^i_a through (3.29). There are d^i_a terms of degree three in the amplitudes, but they vanish when $T_1 = 0$ due to their

dependence on the t_a^i term of τ_a^i. Terms without T_1 amplitudes, and thus nonzero even with optimized orbitals, first appear at degree four due to degree two terms of τ_a^i. The term that is of degree three in T_2 and degree one in T_3 is $d_a^i = (\frac{1}{8} t_{bcd}^{ijk} t_{jk}^{cd})(\frac{1}{2} t_{lm}^{be} t_{ae}^{lm}) + (-\frac{1}{2} t_{lm}^{be} t_{be}^{im})(\frac{1}{8} t_{acd}^{ljk} t_{jk}^{cd})$. While inserting the series expansions of (3.28) into (3.29) can lead to cancellations, we do not observe cancellations in this example. This formula can also be derived directly, albeit tediously, from (3.10). We show this in Appendix 3.7.1.

The implication is that continuing the OUDCT ansatz will eventually lead to the terms with small denominators in (3.26) being multiplied by something that is not identically zero. These small denominators then must be computed, which is likely to lead to numerical problems.

We have tested our results numerically by performing exact orbital-optimized unitary coupled cluster (OUCC) on the Be atom in the cc-pVDZ basis set. We find that the occupied-virtual block of the 1RDM, where orbital spaces are determined by the optimal reference, has a norm of 9.7×10^{-5}. This is nonzero, to machine precision. A commutator expansion of the 1RDM shows that the block is numerically zero to one commutator, but has a norm of 9.5×10^{-5} after the second commutator. As discussed in Section 3.3.5, this is the commutator at which we expect the block to first become nonzero in OUCC, and this is consistent with d_a^i being nonzero at the degree four terms of the cumulant, (3.25).

We close with a technical remark. In the special case that the occupied-virtual block of d is identically zero, we can always choose the natural orbitals such that each natural orbital is obtained by diagonalizing either the occupied block or the virtual block. If we make this choice, then the 1RDM derivative, (3.14), simplifies into a series of equations for the occupied block and a series for the virtual block. This also leads to (3.27), the occupied-virtual block of the 1RDM being zero. This construction is identical with the one from (3.26) in the case that $\gamma_{p'} + \gamma_{q'} \neq 1$. But if $\gamma_{p'} + \gamma_{q'} = 1$, (3.26) is not even defined, but constructing d by diagonalizing the blocks of γ separately remains valid. This block-diagonal procedure also gives a continuous γ, and if some infinitesimal change in d breaks the degeneracy, this is the only choice of γ that will be continuous in the direction of that infinitesimal change.

3.3.5 Comparison of UDCT and UCC Truncations

Suppose that the series (3.25) is evaluated to a certain number of commutators, and the 1RDM is generated from (3.11). Can we conclude that this includes all the terms from evaluating (3.22) to the same number of commutators?

For a general cluster operator, we cannot. Evaluating (3.25) to one commutator gives $d = 0$, which fails to generate the one commutator contribution to γ_a^i, t_a^i. Evaluating (3.25) to two commutators gives a block-diagonal d (by Section 3.3.4), which cannot generate any γ_a^i terms, such as $\frac{1}{8} t_{abc}^{ijk} t_{jk}^{bc}$. Because the latter term does not contain T_1 amplitudes, determining d to degree n does not guarantee that γ is determined to degree n, even for orbital-optimized methods.

To explain this puzzling fact, recall that to construct γ, (3.12) requires the change-of-basis matrix U given by the eigenvectors of d. We may expect that to determine γ to degree n in the amplitudes, we require U to degree n. Unfortunately, determining U to degree n from (3.13) requires d to degree $n + 2$ because d is nonzero only at degree two and greater. In general, determining d to degree $n + 2$ suffices to determine γ to degree n. In Appendix 3.7.1, we explicitly show this is *necessary* for $n = 1$ and $n = 2$, if

no restrictions are put on the cluster operator. If the cluster operator is restricted so $T_1 = 0$, but no other restrictions are imposed, it is also necessary for $n = 2$.

There is an important special case where determining γ from d requires fewer commutators. If U has the same block-diagonal structure as the central matrix of (3.12), then (3.12) simplifies into a single block-diagonal matrix, both blocks of which are power series in d.[18] Then if d is correct to degree n, the power series of γ must be as well.

In this special case, which this paper will focus on, a degree n truncation of OUDCT includes all the degree n terms of OVUCC, plus terms of higher degree in the t amplitudes. It is even possible to identify which terms of higher degree are included in this case, which we shall discuss elsewhere.

3.4 Computational Implementation

To conduct the studies described in Section 3.5, we created a Python program to perform OUDCT and OVUCC computations within a given commutator truncation, a Python program to perform an exact orbital-optimized unitary coupled cluster (OUCC) computation, and a Python program to compare the amplitudes of a truncated OUDCT or OVUCC computation with those determined from a full OUCC computation. Because the equations for truncated unitary theories were already quite complicated,[21] we created a code generator to derive the necessary tensor contractions for the OUDCT and OVUCC computations.

Below, we describe the code and the correctness checks we employed to ensure the accuracy of the results. For further information, the codes are fully available (https://github.com/JonathonMisiewicz/assessing-oudct).

3.4.1 Generation and Implementation of Truncated Orbital-Optimized Unitary Theories

Our code generator first draws all possible fully closed diagrams of the normal ordered forms of (3.20) and (3.21). Diagrams that differ only in the ordering of their operators are considered distinct. Afterwards, diagrams identical by time ordering are collected into a single expression. Diagrams of (3.21) are separated into disconnected diagrams, which are not explicitly used in OUDCT but are explicitly used in OVUCC, and the connected diagrams, which are used in both theories. For OUDCT, the connected 2RDM diagrams are partial traced to obtain d of (3.10) as an explicit function of the amplitudes. The residual equations are obtained by differentiation of the energy expressions. No special code is generated for the orbital optimization, as those expressions are kept in terms of the reduced density matrices.

From orbital and amplitude residuals, update steps to the orbital parameters and amplitudes were computed using a crude diagonal approximation to the exact Hessian giving denominators of signed "orbital energies" as in Møller–Plesset perturbation theory for OVUCC and unsigned diagonal elements of (3.16) for OUDCT, per Section 2.2 of Reference [137]. Direct inversion of the iterative subspace (DIIS)[185] is used to accelerate convergence of the combined vector of orbital amplitudes and t amplitudes. All tensor

contractions use the `opt_einsum` package for efficiency,[186] and all integrals are obtained from a developer version of Psi4 1.4.[187,188] To ensure tight convergence, we required that the norms of the amplitude gradient and orbital gradient were both under 1×10^{-12}. To address convergence problems discussed in Section 3.5.1, we enabled reading in amplitudes and overlap-corrected molecular orbital coefficients from previous computations.

To confirm the accuracy of the generated equations, we performed various checks. To confirm the accuracy of our expressions for the reduced density matrices, we compared our degree-four expressions for (3.25) to those previously published.[21] We also implemented a code for *projective* unitary coupled cluster with Hartree–Fock orbitals and confirmed that our energies match the previously reported energies for the commutator truncations studied.[154] Although the conditions for determining amplitudes differ for projective and variational unitary coupled cluster, the function from amplitudes to energy is the same. Hence, by confirming the correctness of the functional for the projective case, we have confirmed its correctness in the variational case.

To confirm the accuracy of our expressions for the d matrices, we performed OUDCT computations both with our explicit expression and by simply taking the partial trace of (3.10). In both cases, we observed the same energy. To confirm the accuracy of our computed derivatives, we have computed the dipoles for all OVUCC and OUDCT truncations studied both by finite difference and analytically, since both OVUCC and OUDCT automatically deliver relaxed density matrices suitable for property computations, by the Hellmann–Feynmann theorem. If the orbitals or amplitudes do not variationally minimize the energy function, the Hellmann–Feynmann theorem does not apply, and the two dipoles will differ. In all cases, we found that the two matched to ten or more decimal places. Consequently, we have also been able to implement the analytic gradients of these theories.

Excluding ODC-13, all OUDCT methods studied use the same parameterization of the cumulant for the intermediate d (3.10) as for reconstructing the RDM (3.5). As a consequence, the partial trace satisfies the equation $\gamma^{pr}_{qr} = \gamma^{p}_{q}(\gamma^{r}_{r} - 1)$. We have numerically confirmed this for all OUDCT truncations. We note that OUDCT truncations do not necessarily satisfy (3.7) or (3.8), where n is the integer number of electrons, but the OVUCC truncations do. This is because (3.7) and (3.8) are true as polynomials in the unitary coupled cluster amplitudes appearing through (3.20) and (3.21), so the partial trace of each degree in t must be zero. OVUCC either includes all or none of the terms of a given degree, but OUDCT does not, as described in Section 3.3.5.

3.4.2 Exact Orbital-Optimized Unitary Coupled Cluster

We implemented a scheme to obtain the exact OUCC orbitals and amplitudes via projective unitary coupled cluster. (When the cluster operator is not truncated, variational and projective unitary coupled cluster are equivalent. When only T_1 is removed, the same is true of their orbital-optimized variants.) Our algorithm consists of macroiterations and microiterations.

In each macroiteration, we solve the projective UCC equations exactly through the microiterations. This gives us a wavefunction of form $\exp(T - T^\dagger)\,|\Phi\rangle$. If the norm of T_1 is less than 1×10^{-8}, we have

converged to the exact amplitudes and orbitals, and the algorithm terminates. Otherwise, we make a guess to the exact orbitals as $\exp(T_1 - T_1^\dagger)\,|\Phi\rangle$ and proceed to the next macroiteration.

We solve the projective UCC equations in a given one-electron basis set following the prescription of Evangelista.[154] We construct the Hamiltonian, H, and $T - T^\dagger$ in the basis of determinants. We then compute $\exp(T^\dagger - T)H\exp(T - T^\dagger)\,|\Phi\rangle$, where Φ is the reference determinant, via the built-in matrix exponential and matrix multiplication operators of NumPy. If $\exp(T - T^\dagger)\,|\Phi\rangle$ is an exact eigenstate, then

$$\exp(T^\dagger - T)H\exp(T - T^\dagger)\,|\Phi\rangle = E\,|\Phi\rangle \tag{3.30}$$

so we select amplitudes such that the projection of $\exp(T^\dagger - T)H\exp(T - T^\dagger)\,|\Phi\rangle$ onto all excited determinants is zero. We take steps according to the formula

$$\Delta t_A^I = \frac{-r_A^I}{\varepsilon_A^I \phi_A^I} \tag{3.31}$$

where I is equivalent to the occupation vector of the orbitals excited from, A is equivalent to the occupation vector of the orbitals excited to, ε is the sum of virtual orbital energies minus occupied orbtial energies, and ϕ_A^I is the phase factor between the reference determinant and the relevant excited determinant. Convergence of the amplitudes within a given macroiteration is accelerated by DIIS.[185] In all cases, we enforce convergence when the difference of two sides of (3.30) has norm less than 1×10^{-9}. We find that by this point, the energy is converged to within 1×10^{-14} Hartrees. As a final correctness check, the energy is then compared against the full configuration interaction energy from `Ps14`.

3.4.3 Amplitude Comparisons

When comparing amplitudes from exact OUCC and an approximate OUCC, the two amplitudes of the two methods are *not* in the same one-electron basis. To compare these quantities, after constructing them, we move all quantities to the basis of the approximate theory. We then find the difference of the two quantities and compute its Euclidean norm, the square root of the sum of squares of the elements. In the context of matrices, this has also been called the Frobenius norm. This metric is invariant to unitary choices of basis to perform the comparison in, and couples how well the amplitudes match with how well the orbitals match.

3.5 Results and Discussion

In this section, we consider the OUDCT and OVUCC ansätze truncated to $T = T_2$, with between two to five commutators. We call these methods by names such as OUDCTn and OVUCCn, where n denotes the number of commutators. OUDCT2 is also known as ODC-12,[134] and OVUCC2 is also known as OCEPA(0).[109] We shall also consider ODC-13,[21] which cannot be expressed as a single commutator truncation.

Table 3.1: Errors in the equilibrium bond length and harmonic vibrational frequencies of H_2, relative to FCI, for approximate OUDCT and OVUCC methods with $T = T_2$, using the cc-pVDZ basis set.

Molecule	OUDCT2 (ODC-12)	OUDCT3	ODC-13	OUDCT4	OUDCT5	OVUCC2 (OCEPA(0))	OVUCC3	OVUCC4	OVUCC5
r_e (pm)	0.03	−0.10	0.08	0.00	0.00	0.12	−0.03	0.00	0.00
ω (cm^{-1})	−5	21	−20	−1	−1	−25	12	0	1

3.5.1 H_2 Dissociation

The dissociation of H_2 has been previously used to model the performance of DCT over a range of electron correlation strengths.[21,134,152] OUDCT with only a T_2 operator will be exactly OVUCC with only a T_2 operator in the limit of an infinite commutator expansion. Because H_2 is a two-electron system, if UCC is exact, OVUCC with only a T_2 operator will be exact as well. Due to this close relationship between the OVUCC and OUDCT ansätze, we first compute the dissociation curve with the truncated OVUCC ansatz for comparison.

Potential Energy Curves

Previous experience with commutator truncations of projective UCC with Hartree–Fock orbitals suggests that the stronger correlation effects are, the less accurate a given UCC commutator truncation should be.[154]

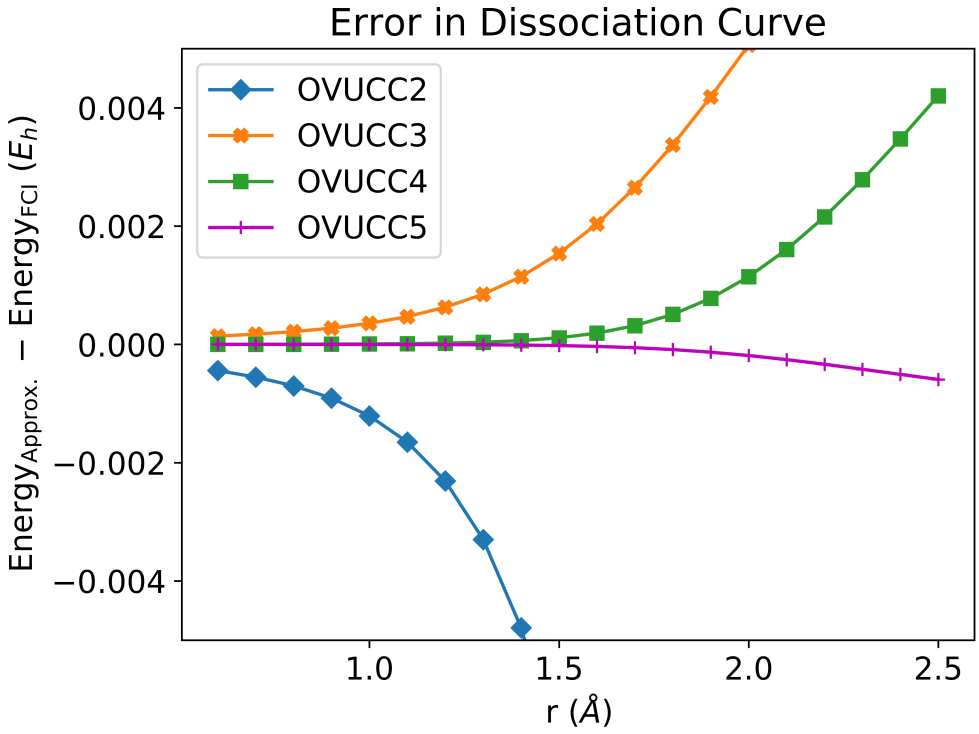
OVUCC illustrates this trend, as well as smooth convergence with respect to the number of commutators. The error in the energy curve for H_2 is shown in Figure 3.2a. For every geometry, adding another commutator decreases the error of the energy compared to FCI. When going from OVUCC2 to OVUCC3, or OVUCC4 to OVUCC5, the decrease is roughly by a factor of five. When going from OVUCC3 to OVUCC4, the decrease is by a factor of 100 in the equilibrium region, but diminishes to about a factor of two by around 2.5 Å. That odd and even rank truncations of VUCC will perform differently was theorized by Kutzelnigg.[141] We observe no convergence problems except for OVUCC2, also known as OCEPA(0).[109] The poor performance of OCEPA(0) for H_2 dissociation has been reported previously[134] and is unsurprising, as singularities are known to appear in CEPA(0) for bond dissociation.[189]

OUDCT displays markedly different behavior across two regimes, shown in Figure 3.2b. For near-equilibrium geometries, with the exception of OUDCT3, we observe improved accuracy as more commutators are added, as shown by the equilibrium geometry and harmonic vibrational frequency in Table (3.1).

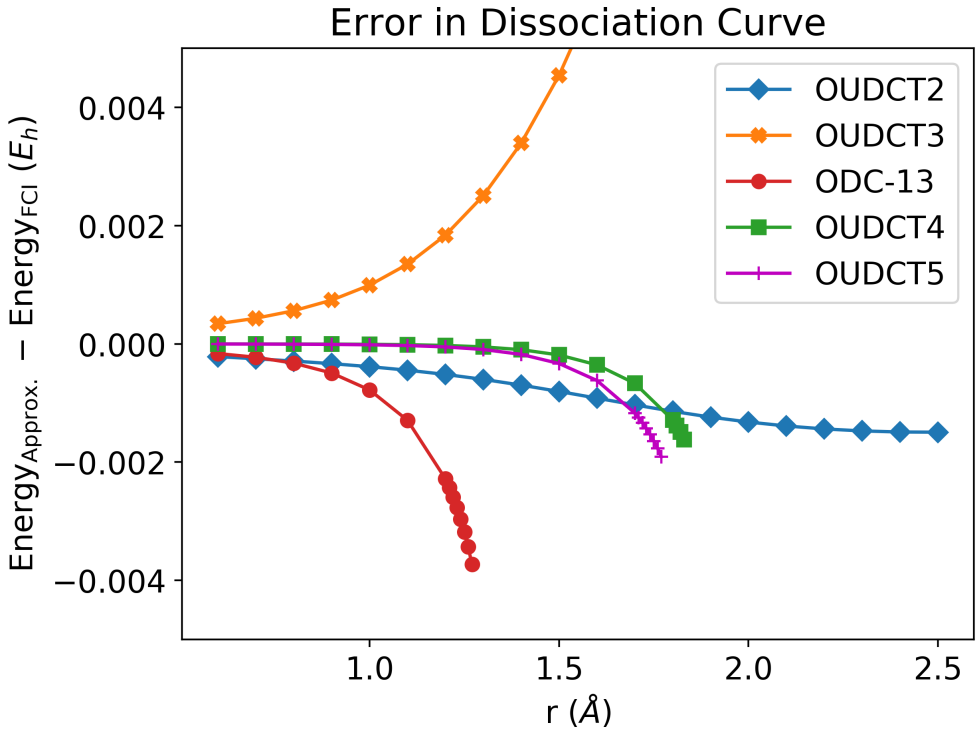
But as the bond stretches, the various OUDCT methods behave dramatically differently. In agreement with previous studies,[134] OUDCT2, also known as ODC-12, has robust performance. In contrast to the other models, its error curve does *not* have an exponential shape. OUDCT3 can be converged, but the energy error increases sharply, and is on the same order of magnitude as the energy errors of OVUCC2. OUDCT4 can only be converged with difficulty after 1.6 Å, and we were not able to converge the equations

Figure 3.2: Dissociation curves of H_2 from 0.6 Å to 2.5 Å computed with low-degree commutator truncations of the OVUCC (a) and OUDCT (b) ansätze in the cc-pVDZ basis set.

(a)



(b)



after 1.8 Å, even reading in the amplitudes and orbitals (after accounting for the change in overlap matrix) from previous computations. OUDCT5 is similar, but with larger energy errors.

ODC-13 also encounters significant error before diverging around 1.3 Å, which was attributed to large violations in the equations (3.8) and $\gamma^{pq}_{pq} = n(n-1)$, which hold for pure n-representable RDMs.[21] OUDCT4 and OUDCT5 follow these equations more closely than the OUDCT2 method by an order of magnitude. While we observe that the partial trace failure of ODC-13 contributes to its poor performance, using more consistent approximations only delays the convergence problems.

Amplitude Residuals

It may seem puzzling that OUDCT2, also known as ODC-12, yields a relatively accurate H_2 dissociation curve, but less severe truncations of the same ansatz lead to more severe errors in dissociation curves. Intuition would suggest that OVUCC2 is already a good approximation to the exact OUDCT ansatz, and better approximations to the ansatz would give better energies. To identify the flaw in this inuition, consider the difference between the exact t amplitudes and the final t amplitudes of the approximate computation as a fraction of the norm of the exact amplitudes, shown in Figure 3.3a for OVUCC and Figure 3.3b OUDCT.

For all OVUCC and most OUDCT truncations, low error in the energies coexist with low error in the amplitudes, compared to the exact OUCC theory. For OVUCC, less severe commutator truncations decrease both errors across the entire curve, but for OUDCT, this decrease only occurs at weakly correlated geometries. For stretched geometries, OUDCT's error is much worse. We must attribute this to OUDCT's partial inclusion of terms of degree higher than the truncation level, as discussed in Section 3.3.5. At weakly correlated geometries, the small value of the amplitudes means these high degree terms are negligible, leading to good accuracy.

Comparing Figures 3.3a and 3.3b, one would expect an energy error curve for OUDCT2 an order of magnitude worse than OVUCC3, let alone OVUCC4 or OVUCC5. This is not the case. In OUDCT2, an accurate H_2 dissociation curve coexists with large errors in the amplitudes, indicating that the static correlation tolerance of OUDCT2 does not result from well-approximating the exact OVUCC ansatz, at least for H_2. This suggests the effect of better approximating the exact OVUCC ansatz will be difficult to predict, in agreement with Section 3.5.1.

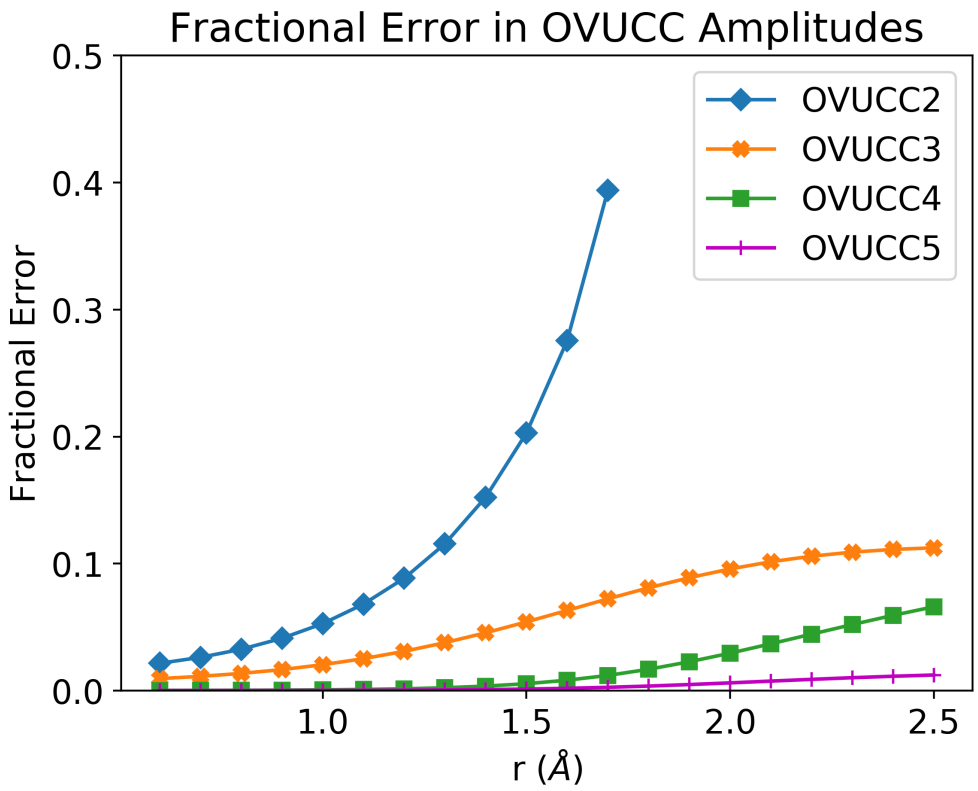
Alternative qualitative explanations for OUDCT2's static correlation tolerance are beyond the scope of this work, but will be explored in the future.

3.5.2 Equilibrium Properties of Diatomics

To assess the performance of OUDCT methods for equilibrium properties of diatomics in systems of more than two electrons, we have computed the equilibrium geometries and harmonic vibrational frequencies of eight diatomics using OUDCT and OVUCC methods with the cluster operator (3.18) truncated to T_2 and the cc-pCVDZ basis set. To exclude non-Born–Oppenheimer effects and basis set convergence, we compare to high level *ab initio* results. Specifically, we compare to properties computed at the

Figure 3.3: The difference between the converged doubles amplitudes for OVUCC (a) and OUDCT (b) theories and the exact unitary T_2 amplitudes as a fraction of the norm of the exact OVUCC amplitudes for H_2 computed with the cc-pVDZ basis set.

(a)



(b)

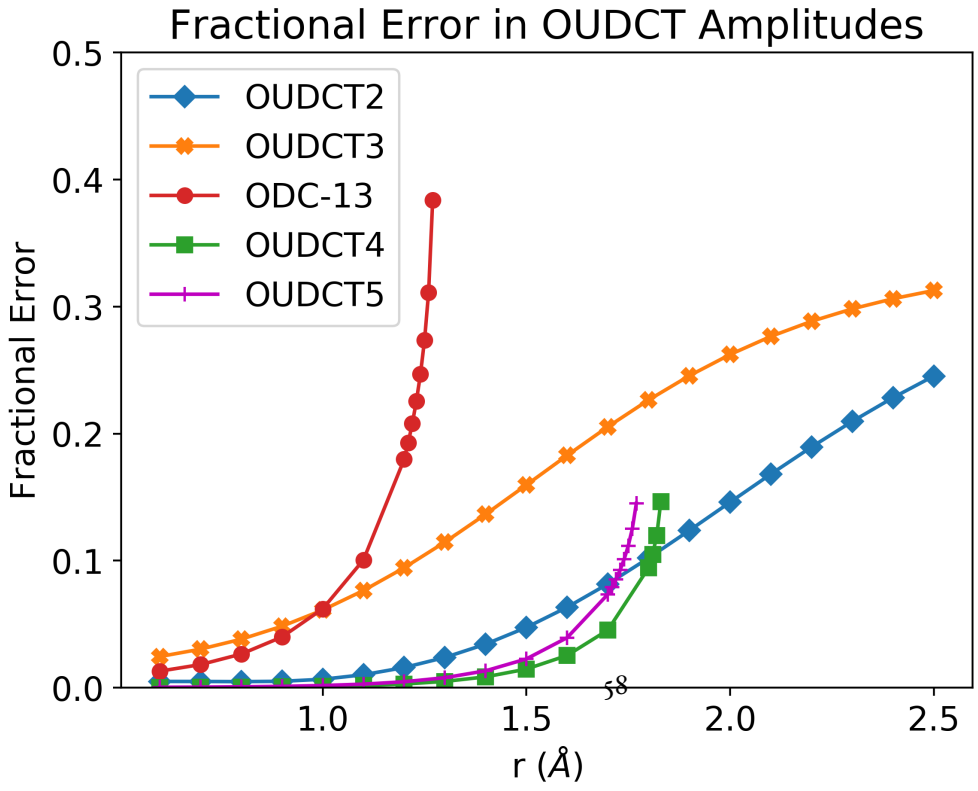


Table 3.2: Errors in the geometries of diatomics (pm), relative to CCSDTQ(P), for approximate OUDCT and OVUCC methods with $T = T_2$, using the cc-pCVDZ basis set. Δ_{abs} denotes the mean absolute error, and Δ_{std} denotes the standard deviation of signed errors.

Molecule	OUDCT$_2$ (ODC-12)	OUDCT$_3$	ODC-13	OUDCT$_4$	OUDCT$_5$	OVUCC$_2$ (OCEPA(0))	OVUCC$_3$	OVUCC$_4$	OVUCC$_5$
N_2	−0.51	−1.00	−0.60	−0.59	−0.61	−0.26	−0.90	−0.60	−0.62
CO	−0.63	−0.92	−0.68	−0.66	−0.68	−0.50	−0.84	−0.66	−0.68
N_2^+	−0.69	−1.36	−0.73	−0.76	−0.82	−0.14	−1.22	−0.78	−0.83
BO	−0.84	−1.10	−0.88	−0.84	−0.86	−0.68	−1.01	−0.84	−0.86
CN	−0.69	−1.45	−0.84	−0.87	−0.91	−0.23	−1.30	−0.88	−0.92
NF	−0.65	−1.41	−0.95	−1.02	−1.02	−0.37	−1.29	−1.03	−1.03
NO	−0.73	−1.32	−0.92	−0.89	−0.91	−0.47	−1.21	−0.90	−0.92
BeO	−1.56	−1.81	−1.50	−1.39	−1.40	−1.31	−1.65	−1.39	−1.44
Δ_{abs}	0.79	1.30	0.89	0.88	0.91	-0.50	1.18	0.89	0.91
Δ_{std}	0.33	0.29	0.27	0.25	0.25	0.37	0.26	0.25	0.25

Table 3.3: Errors in the harmonic frequencies of diatomics (cm^{-1}), relative to CCSDTQ(P), for approximate OUDCT and OVUCC methods with $T = T_2$, using the cc-pCVDZ basis set. Δ_{abs} denotes the mean absolute error, and Δ_{std} denotes the standard deviation of signed errors.

Molecule	OUDCT$_2$ (ODC-12)	OUDCT$_3$	ODC-13	OUDCT$_4$	OUDCT$_5$	OVUCC$_2$ (OCEPA(0))	OVUCC$_3$	OVUCC$_4$	OVUCC$_5$
N_2	56	116	67	66	69	21	105	67	70
CO	67	91	72	68	70	55	85	68	70
N_2^+	50	137	54	73	79	−38	124	75	81
BO	69	88	72	68	70	56	82	69	70
CN	46	106	56	59	63	−1	95	60	64
NF	20	66	40	47	47	3	61	48	47
NO	71	132	92	89	92	43	122	90	93
BeO	55	69	53	47	50	40	61	47	50
Δ_{abs}	54	101	63	65	68	32	92	66	68
Δ_{std}	16	25	15	13	14	31	23	13	14

CCSDTQ(P)/cc-pCVDZ level with MRCC,[190,191] driven using Psi4.[187] The necessary gradients were computed by finite difference of energies. Frequencies for these systems were computed using the DIATOMIC module of Psi4. For the OUDCT and OVUCC methods, we instead computed gradients analytically and frequencies by finite difference of gradients with a five-point stencil.

The errors in the equilibrium geometries are shown in Figure 3.4, and individual data points for equilibrium geometries and harmonic frequencies are given in Tables 4.1 and 3.3, respectively. The ordering of methods in terms of accuracy is consistent across both sets of benchmark data. The best performance is displayed by OVUCC2, more commonly known as OCEPA(0).[109] The mean unsigned error in bond lengths is 0.50 pm, and the same in harmonic vibrational frequencies is 32 cm^{-1}. Second best is OUDCT2, or ODC-12,[134] with respective mean unsigned errors of 0.79 pm and 54 cm^{-1}.

All higher order methods display slightly worse performance, on average. The degree three truncations do exceptionally poorly. The four and five commutator truncations have extremely similar performance. Mean signed geometry errors range from 0.88 to 0.91 pm, and mean unsigned harmonic frequency errors range from 65 to 68 cm^{-1}. The ODC-13 method is also similar with 0.89 pm and 63 cm^{-1} errors, respectively.

We reach two conclusions from this data. First, the performance of ODC-13 for equilibrium properties of diatomic molecules is unrelated to point 4 of Section 3.3.3. The performance difference between the theory where the degree four connected terms of (3.23) are included (OUDCT4) and the theory where they are not (ODC-13) is statistically insignificant.

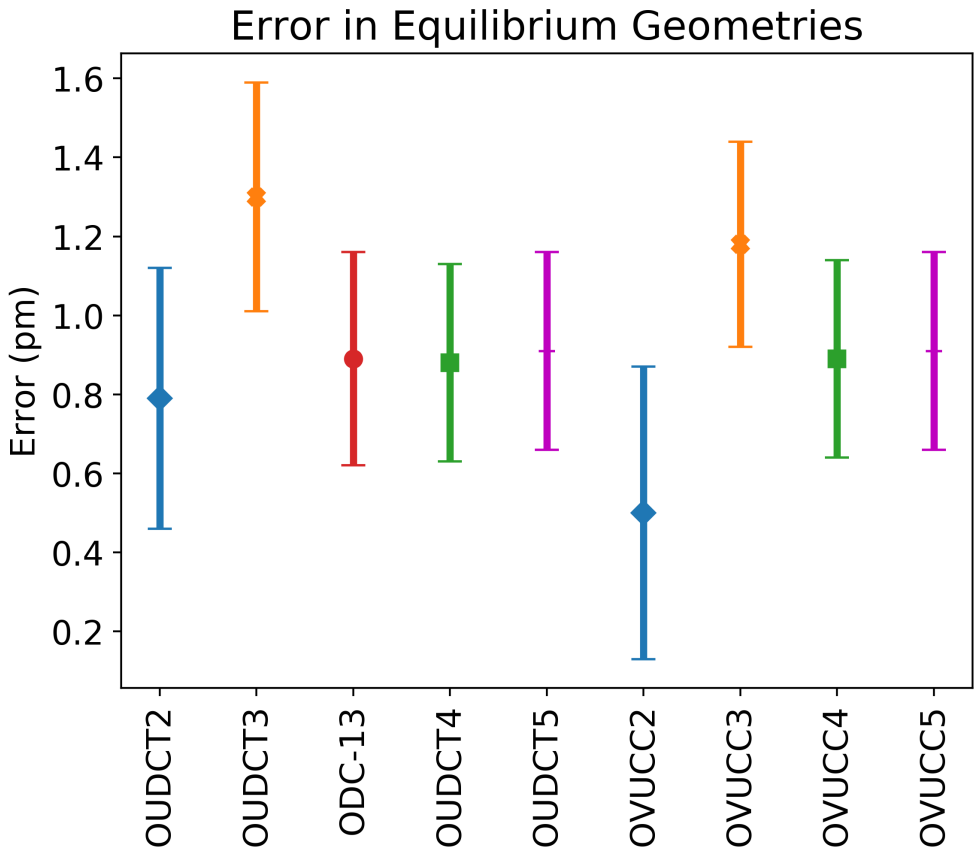
Second, the similarity of these results upon increasing commutator truncations suggest that by four commutators, the equilibrium properties of these systems are well-converged to the exact result with respect to the number of commutators, and the difference between OVUCC and OUDCT is negligible. This is supported by our findings that both energy and amplitudes are well-converged by four or five commutators for H_2 near equilibrium in Section 3.5.1. To outperform OUDCT2, OUDCT5 would need to lower Δ_{abs} by 12 pm and 13 cm^{-1} for equilibrium bond lengths and harmonic frequencies, respectively. Accordingly, we expect that not even the exact OVUCC and OUDCT doubles theories (they are identical) can out-perform OVUCC2 or OUDCT2. This strongly suggests that to improve beyond OVUCC2 and OUDCT2 within orbital-optimized unitary ansätze, it will be necessary to consider cluster operators beyond doubles. To our knowledge, the only studies of unitary cluster operators beyond doubles are the recent work of Li and Evangelista,[192] focused on their driven similarity renormalization group, and the non-iterative λ_3 correction considered within density cumulant theory.[21]

3.6 Conclusions

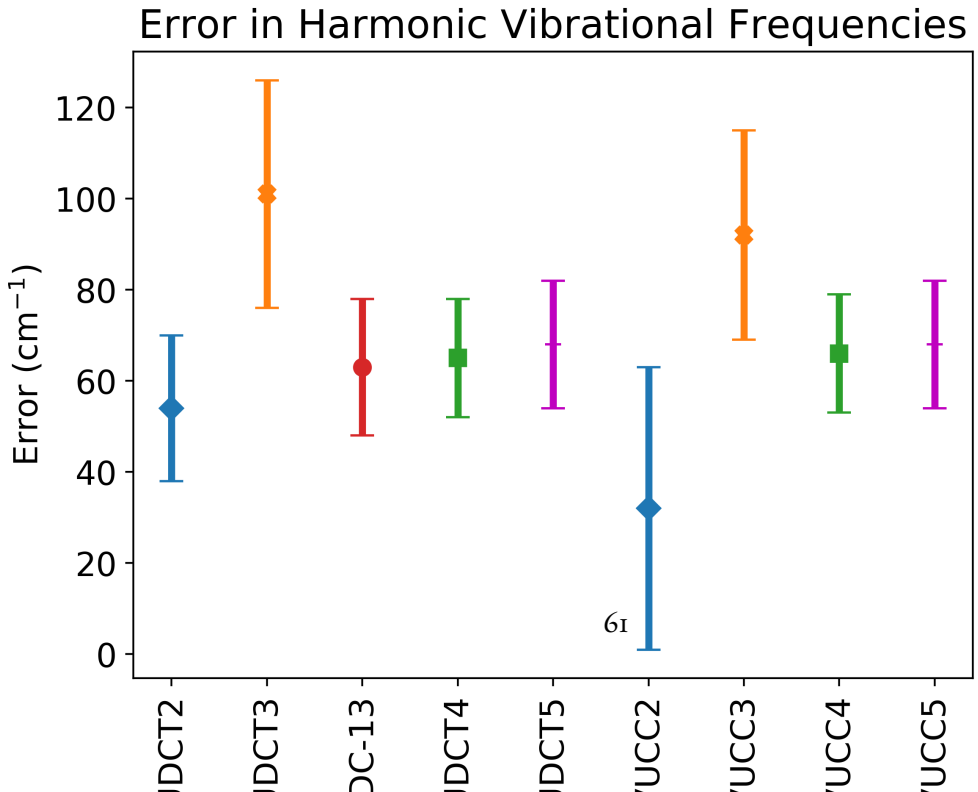
In this article, we have studied the orbital-optimized unitary ansatz for density cumulant theory (OUDCT) both formally, and with numerical simulations of H_2 dissociation and the equilibrium geometries and frequencies of diatomic molecules using low order truncations of the OUDCT ansatz with a cluster operator truncated to double excitations and de-excitations. We have also performed these simulations on analagous

Figure 3.4: The mean absolute error and standard deviation of the signed errors in the geometries (a) and frequencies (b) of diatomics, relative to CCSDTQ(P), for approximate OUDCT and OVUCC methods with $T = T_2$, using the cc-pCVDZ basis set.

(a)



(b)



truncations of the closely related orbital-optimized variational unitary coupled cluster (OVUCC) ansatz. We find that:

1. The DCT ansatz will encounter near-zero denominators in the gradient of the energy with respect to amplitudes if the occupied-virtual and virtual-occupied blocks of the 1-electron reduced density matrix (1RDM) are not identically zero. The OUDCT ansatz does *not* preserve this property once odd-rank cluster operators are added to the ansatz. The terms that cause these problems will first appear at degree four in the Baker–Campbell–Hausdorff expansion of the density cumulant, (3.25). If T_1 is included in the cluster operator, they first appear at degree three.

2. The relationship between the OUDCT and the OVUCC ansatz is complicated by the presence of nonzero occupied-virtual and virtual-occupied blocks of the 1RDM. If these blocks are identically zero, OUDCT truncated to n commutators is OVUCC truncated to n commutators plus 1RDM and disconnected 2RDM terms of degree greater than n in the amplitudes. If these blocks are not identically zero, OUDCT truncated to n commutators will have all 1RDM terms truncated to $n-2$ commutators, but may miss terms at commutators $n-1$ and n.

3. Making less severe truncations of the OUDCT ansatz does not *uniformly* improve the description of the H_2 dissociation curve. While it is strongly improved near equilbrium, the degree four and five theories show worse performance and convergence problems not present for the simple two-commutator truncation, ODC-12, away from equilibrium. The same is not true for OVUCC, where the same truncation procedure improves the entire curve.

4. Making less severe truncations of the OUDCT ansatz with doubles does not improve the description of the equilibrium properties of diatomics. Including the terms from three, four, and five commutators from OUDCT and OVUCC tends to cause a minor loss of accuracy compared to the two-commutator truncations, ODC-12 and OCEPA(0). Based on the rate of convergence with respect to commutator truncation, even the doubles-only OVUCC theory with no commutator truncation is likely inferior to ODC-12 and OCEPA(0).

Let us remark on what these results mean for future developments of DCT. If one decides to develop the theory via the OUDCT ansatz, then to improve the description of molecules at equilibrium, the results of Section 3.5.2 advise against better approximating OVUCC doubles, and in favor of including effects of higher rank cluster operators. Triples seem to be especially important in unitary theories, as in tradiational coupled cluster theory,[192] and the non-iterative λ_3 correction was seen to improve DCT results.[21] However, two special dangers then arise:

1. Triples approximations must avoid near-zero denominators in (3.16). We see three ways to control these singularities. First, the choice of energy-minimizing orbitals while neglecting T_1 could be replaced in favor of the natural orbitals, where the occupied-virtual block of the 1RDM is identically zero. Second, choose the amplitudes non-variationally so that (3.16) and its singularities are irrelevant. Either of these options makes a parameter non-variational and results in a more complicated

and expensive analytic gradient theory. Third, refuse to consider theories where the block-diagonal structure of the 1RDM is compromised during iterations. Such an approach cannot account for the nonzero terms in the occupied-virtual block of the 1RDM and cannot converge to the exact theory. Done perturbatively, the success of the λ_3 correction[21] suggests that this route can still be quite accurate. For iterative approaches, the first terms in the BCH expansion that must be neglected are of degree four and have both doubles and triples. Neglecting this means that degree two terms in the 1RDM are also neglected, as shown in Section 3.3.5. Nonetheless, our unpublished numerical results indicate that including iterative triples to the degree two truncation of the cumulant, (3.25), can still be quite accurate near equilibrium.

2. The cumulant parameterization determines the accuracy of the DCT theory, but the relationship between the degree of truncation of the OUDCT ansatz and the accuracy of the resulting theory is not straightforward. Section 3.5.1 demonstrates that including more commutators in the OUDCT ansatz can make the numerical results significantly less accurate. We expect the relationship to be even more complicated once triples amplitudes are included.

However, if one wishes to improve static correlation tolerance, then the proper description of H_2 is a prerequisite, and this cannot be accomplished by adding triples. Section 3.5.1 makes clear that the static correlation tolerance of ODC-12 does not originate in the method well-approximating the OVUCC ansatz. If one wishes to make a multireference generalization of ODC-12, there is not an obvious feature of ODC-12 that causes its static correlation tolerance and is therefore worth generalizing.

Further theoretical developments in DCT are needed to provide a path to more and more accurate methods. Future work from our group will investigate a new ansatz more suitable for the description of static correlation, and where the occupied-virtual blocks of the 1RDM can be guaranteed to be zero.

3.7 Appendix: Analysis of the κ and τ Decomposition of the 1RDM in DCT

Many earlier DCT papers express the energy as a functional of an idempotent part of the 1RDM, κ, and the cumulant λ,[18,133,134,136,137,150,151] with κ said to be independent of λ.[18,21,136,137,150] Previously reported pure n-representability constraints on the arguments of this functional were incomplete. We first derive the constraints and then analyze previous DCT work in terms of the completed n-representability constraints within this formalism.

The κ, λ formalism decomposes γ as $\kappa+\tau$. κ is defined[18,133] to be the "best idempotent approximation" to γ.[193] That is, κ for an n-electron wavefunction is the 1RDM of a Slater determinant, and its occupied orbitals are the wavefunction's n natural spin-orbitals with the highest occupation numbers. κ, τ, and the cumulant partial trace d then have a common eigenbasis of the natural spin-orbitals. τ can be determined by

$$\tau_{p'} = \frac{1 \pm \sqrt{1 + 4\Delta_{p'}}}{2} - \kappa_{p'} \tag{3.32}$$

where p indexes the eigenvectors, and quantities in the natural spin-orbital basis are denoted with primed indices. $\kappa_{p'}$ is 1 for an occupied natural spin-orbital and 0 otherwise, and $\Delta_{p'}$ refers to a d eigenvalue. Assuming that there are n natural spin-orbitals with occupation number ≥ 0.5 and all others have occupation number ≤ 0.5, (3.32) simplifies to:

$$\tau_{i'} = \frac{-1 + \sqrt{1 + 4\Delta_{i'}}}{2} \tag{3.33}$$

$$\tau_{a'} = \frac{1 - \sqrt{1 + 4\Delta_{a'}}}{2} \tag{3.34}$$

Here, τ depends on both κ and λ by (3.32) and (3.10), respectively. In every case, κ prescribes when to use the $+$ solution of (3.11) and when to use the $-$ solution. κ also prescribes how to resolve degenerate eigenvectors in the d matrix, if any, into occupied and virtual orbitals.

Using (3.6), the energy is then expressed as a functional of κ and λ:[18]

$$E(\kappa, \lambda) = h_p^q(\kappa_q^p + \tau_q^p(\kappa, \lambda)) + \frac{1}{2}\bar{g}_{pq}^{rs}(\kappa_r^p + \tau_r^p(\kappa, \lambda))(\kappa_s^q + \tau_s^q(\kappa, \lambda)) + \frac{1}{4}\bar{g}_{pq}^{rs}\lambda_{rs}^{pq} \tag{3.35}$$

It is now necessary to consider what constraints must be placed on κ and λ. Some are already known.

1. λ must be derived from some wavefunction, that is, be pure n-representable.[18]

2. κ must be derived from some wavefunction, that is, be an idempotent density matrix with trace n.[18]

However, the following have not been previously reported:

3. (3.35) is only defined for pairs of κ, λ derived from *the same* wavefunction. This is a stronger requirement than the above. For example, it was already known[18] that κ and d must share an eigenbasis to satisfy this condition. This has been recognized as crucial in (3.32), but has not been recognized as an *additional* constraint on the parameters of the energy functional.

4. If κ and d have a common eigenbasis, then contrary to previous reports,[18,21,136,137,150] κ and λ are not independent. The set of λ allowed for a given κ depends on κ, and likewise, the set of κ allowed for a given λ depends on λ.

Insisting that (3.35) is variationally minimized with respect to variations of κ unaccompanied by λ variations produces the DCT κ stationarity equation of Equation 22 from Reference [18].

No DCT numerical studies varied κ in this unphysical way.[21,70,133,134,136–138,150–152] In all cases, all variations of κ were coupled to variations of λ so that κ and d computed from λ had a common eigenbasis, consistent with this constraint. To explain the matter, it is convenient to change the variables of (3.35).

First, define:

$$\kappa^p_q(U) = (U^\dagger)^p_{p'}(\kappa')^{p'}_{q'}U^{q'}_q \tag{3.36}$$

where κ' is an arbitrary but fixed idempotent density matrix with trace n, and U is a unitary transformation. Then varying κ so that it remains an idempotent density matrix with trace n is equivalent to varying U subject to it remaining unitary. κ' has always been chosen to be diagonal, so its orbitals do not mix occupied and virtual natural spin-orbitals. Choosing the primed indices to be natural spin-orbitals is consistent with this but not required.

Second, define:[134]

$$\lambda^{pq}_{rs}(U,\lambda') = (U^\dagger)^p_{p'}(U^\dagger)^q_{q'}(\lambda')^{p'q'}_{r's'}U^{r'}_r U^{s'}_s \quad . \tag{3.37}$$

Any wavefunction with cumulant λ will give cumulant λ' after the orbital rotation specified by the matrix U, and vice versa. It follows that for unitary U, λ is pure n-representable if and only if λ' is.

Using this, we define a new energy functional:

$$E(U,\lambda') = E(\kappa(U),\lambda(U,\lambda')) \tag{3.38}$$

These two functionals are related by a change of variables. While they have different functional dependence on their variables, their physical content is the same. However, $E(U,\lambda')$ follows previous DCT publications more closely.[21,70,133,134,136–138,150–152] They parameterized λ' as a finite polynomial in cumulant amplitudes and constructed λ from (3.37).[21,70,133,134,136–138,150–152] They allowed for variations of U that did not vary λ', where variations of κ that did not vary λ were not allowed. This is true of both DC[150] and ODC[134] methods. The difference between the two is their U stationarity condition. DC methods chose U in $E(U,\lambda')$ to make the approximate $E(\kappa,\lambda)$ stationarity with respect to κ, while ODC methods chose U in $E(U,\lambda')$ to make the approximate $E(U,\lambda')$ stationary with respect to U. Although DC methods enforce stationary with respect to κ variations that violate n-representability, the rotations of U used to satisfy that constraint preserve n-representability. Accordingly, the different orbital stationarity condition does not directly affect the n-representability of DC methods.

Let us consider $E(U,\lambda')$'s constraints on its arguments. We now have:

1. λ' must be pure n-representable.
2. U must be a unitary matrix.
3. (3.38) is only defined for λ' that can be derived from a wavefunction that also yields the κ' appearing in (3.36). This implies κ' and λ' have a common eigenbasis. In the typical case that κ' is chosen block-diagonal in the occupied and virtual blocks, this means the same must be true of d.
4. The set of admissible λ' is independent of U. It does depend on κ', but κ' does not vary.

All previous DCT numerical studies[21,70,133,134,136–138,150–152] parameterized λ' with block-diagonal d, although this was not mentioned as a necessary constraint for (3.38).

As discussed in 3.3.4, the general OUDCT ansatz of Reference [21] does not follow this constraint of block-diagonal d. This does not mean that the OUDCT ansatz is inconsistent, only that its orbital rotation is to the *energy minimizing orbitals* rather than the *natural orbitals* from which κ is constructed. Its energy functional is not obtained simply by parameterizing the λ' in (3.37) used in (3.38), but must also modify or bypass the construction of κ and τ in order to determine when to take $+$ or $-$ negative solutions of (3.11).

3.7.1 Appendix: Constructing γ from d

In DCT, the 1RDM γ is constructed from d, the partial trace of the two-body cumulant. In this section, we expand this construction to low degrees in the unitary coupled cluster amplitudes. Our purposes in doing this are to explore the following:

1. Does UDCT's construction of γ match the more straightforward VUCC construction?
2. How does an approximation to d change γ?

Throughout, we shall use the following equations. These determine γ as a function of d in DCT. As used here, they make no reference to the form of d or of γ:

$$\gamma U = U \begin{bmatrix} \frac{1+\sqrt{1+4\Delta_o}}{2} & 0 \\ 0 & \frac{1-\sqrt{1+4\Delta_v}}{2} \end{bmatrix} \tag{3.39}$$

$$U\Delta = dU \tag{3.40}$$

The matrix in (3.39) is a block matrix, with the occupied block followed by the virtual block. All matrices in this section that are written as blocks have this block-diagonal structure. Δ is the diagonal matrix of eigenvalues of d.

To relate d to the expansion of γ, we expand $d = \gamma^2 - \gamma$ in terms of the power series expansion of γ. Matching the terms of degree n produces the following equation:

$$\sum_{i=0}^{n} \gamma_{pr}^{(n-i)} \gamma_{rq}^{(i)} - \gamma_{pq}^{(n)} = d_{pq}^{(n)} \tag{3.41}$$

We emphasize that these equations are true as polynomials, using the exact formulas for d and γ. These equations need not hold in an approximate DCT method.

Lastly, we point out that the exact d matrix satisfies the following equation:

$$d^{(0)} = d^{(1)} = d_{\text{ov}}^{(2)} = d_{\text{vo}}^{(2)} = 0 \tag{3.42}$$

All of these can be shown to be zero by explicitly constructing the relevant cumulant blocks and taking a partial trace. For $d^{(0)}$ and $d^{(1)}$, the relevant cumulant blocks are simply zero, so their partial trace is

zero. The analyses for $d^{(2)}_{\text{ov}}$ and $d^{(2)}_{\text{vo}}$ are nearly identical to each other, so we only show $d^{(2)}_{\text{ov}} = 0$ explicitly. We require the degree two terms of $\lambda^{\text{oo}}_{\text{ov}}$ and $\lambda^{\text{vo}}_{\text{vv}}$. The permissible $\lambda^{\text{oo}}_{\text{ov}}$ diagrams of degree two are exactly those where a rank $n+1$ de-excitation operator contracts with a rank $n+2$ excitation operator, and $n \geq 0$. There are $n+1$ virtual contractions between the operators and n occupied contractions, along with the contractions involving $a^{\text{oo}}_{\text{ov}}$. The permissible $\lambda^{\text{vo}}_{\text{vv}}$ diagrams are similar, but with $n+1$ occupied contractions and n virtual contractions between the operators. The terms of $\lambda^{\text{oo}}_{\text{ov}}$ and $\lambda^{\text{vo}}_{\text{vv}}$ biject naturally, and partial tracing over the two left indices of each pair gives exactly opposite results. Summing these gives zero for each pair, and summing the pairs gives a final $d^{(2)}_{\text{ov}}$ of zero. This cancellation was previously observed for the special case of the cluster operator being restricted to double and triple cluster operators in Reference [21].

(3.42) are the *only* facts specific to VUCC that we require. The analysis of this section of the supplementary material applies to any other ansatz that obeys (3.42).

Degree Zero

The degree zero expansion of (3.39) gives:

$$\gamma^{(0)} U^{(0)} = U^{(0)} \begin{bmatrix} I & 0 \\ 0 & 0 \end{bmatrix} \tag{3.43}$$

This specifies the eigenvalues of γ, but its eigenvectors require $U^{(0)}$. We may attempt to determine this from perturbative analysis of (3.40), but because of (3.42), the degree zero and one equations merely tell us that

$$\Delta^{(0)} = \Delta^{(1)} = 0 \tag{3.44}$$

If we instead expand (3.40) to degree two, we find:

$$U^{(0)} \Delta^{(2)} = d^{(2)} U^{(0)} \tag{3.45}$$

Diagonalization of $d^{(2)}$ determines $U^{(0)}$. Both of these quanities may be simplified if $d^{(2)}$ is block-diagonal in the occupied and virtual blocks.

We now use this result to simplify $d^{(2)}$ and $U^{(0)}$. Given a set of amplitudes, we may transform their indices into the basis of eigenvectors of $d^{(2)}$. Because $d^{(2)}$ is block-diagonal in occupied and virtual blocks, then assuming $d^{(2)}$ is non-degenerate, each eigenvector consists either only of occupied orbitals or only of virtual orbitals. We can now exploit the orbital-invariance of d to rotations within the occupied and virtual subspace to simplify (3.45). Upon transforming our amplitudes and re-computing d, orbital-invariance guarantees that $d^{(2)}$ is already diagonal. This has the pleasant consequences:

$$U^{(0)} = I \tag{3.46}$$

$$d^{(2)} = \Delta^{(2)} \tag{3.47}$$

Furthermore, orbital-invariance implies that we can transform any results expressed as tensors contracted over occupied and virtual orbitals back to the original basis with no change in the forms of our expressions. We will henceforth assume (3.46) and (3.47).

Within this choice, (3.43) becomes

$$\gamma^{(0)} = \begin{bmatrix} I & 0 \\ 0 & 0 \end{bmatrix} \tag{3.48}$$

It is then possible to eliminate the $\gamma^{(0)}$ terms from (3.41). The resulting equations depend on whether the orbital indices are occupied or virtual.

$$\sum_{i=1}^{n-1} \gamma_{ir}^{(n-i)} \gamma_{rj}^{(i)} + \gamma_{ij}^{(n)} = d_{ij}^{(n)} \tag{3.49}$$

$$\sum_{i=1}^{n-1} \gamma_{ar}^{(n-i)} \gamma_{rb}^{(i)} - \gamma_{ab}^{(n)} = d_{ab}^{(n)} \tag{3.50}$$

$$\sum_{i=1}^{n-1} \gamma_{ir}^{(n-i)} \gamma_{ra}^{(i)} = d_{ia}^{(n)} \tag{3.51}$$

$$\sum_{i=1}^{n-1} \gamma_{ar}^{(n-i)} \gamma_{ri}^{(i)} = d_{ai}^{(n)} \tag{3.52}$$

The interested reader may directly compute these equations to various degrees in the unitary coupled cluster amplitudes and confirm them.

Degree One

Expanding (3.39) to degree one gives

$$\gamma^{(1)} = U^{(1)} \begin{bmatrix} I & 0 \\ 0 & 0 \end{bmatrix} - \begin{bmatrix} I & 0 \\ 0 & 0 \end{bmatrix} U^{(1)} \tag{3.53}$$

This equation reduces to

$$\gamma_{ij}^{(1)} = 0 \tag{3.54}$$

$$\gamma_{ab}^{(1)} = 0 \tag{3.55}$$

$$\gamma_{ia}^{(1)} = -U_{ia}^{(1)} \tag{3.56}$$

$$\gamma_{ai}^{(1)} = U_{ai}^{(1)} \tag{3.57}$$

(3.54) and (3.55) are correct and will be correct for any d approximation obeying (3.42). To determine $U^{(1)}$ for (3.56) and (3.57), we expand (3.40) to degree three:

$$\Delta^{(3)} + U^{(1)} \Delta^{(2)} = d^{(3)} + d^{(2)} U^{(1)} \tag{3.58}$$

By taking off-diagonal elements, it follows that:

$$\forall p \neq q : U^{(1)}_{pq} = \frac{d^{(3)}_{pq}}{\Delta^{(2)}_q - \Delta^{(2)}_p} \tag{3.59}$$

The manifest antisymmetry of (3.59) means that because γ is hermitian, (3.56) and (3.57) are equivalent. We proceed only from (3.56), which is:

$$\gamma^{(1)}_{ia} = -\frac{d^{(3)}_{ia}}{\Delta^{(2)}_a - \Delta^{(2)}_i} \quad . \tag{3.60}$$

From this result, it follows that nonzero $d^{(3)}_{ia}$ is equivalent to nonzero $\gamma^{(1)}_{ia}$. We know from the VUCC expansion that $\gamma^{(1)}_{ia} = t^i_a$, which is zero when orbital-optimization is used. Therefore, $d^{(3)}_{ia} = 0$ is not an approximation in OUDCT.

It remains to confirm that (3.60) reproduces the VUCC series when $d^{(3)}_{ia}$ is correct. By invoking (3.51) for $n = 3$ and using the fact that $\gamma^{(1)}$ is zero in the occupied-occupied and virtual-virtual blocks, we find

$$d^{(3)}_{ia} = \gamma^{(1)}_{ib}\gamma^{(2)}_{ba} + \gamma^{(2)}_{ij}\gamma^{(1)}_{ja} \tag{3.61}$$

Upon using the expressions of (3.49) and (3.50) for $n = 2$ alongside (3.47), the previous equation becomes:

$$d^{(3)}_{ia} = \gamma^{(1)}_{ia}(\Delta^{(2)}_i - \Delta^{(2)}_a) \tag{3.62}$$

It follows from (3.60), and (3.62) that

$$\gamma^{(1)}_{ia} = \gamma^{(1)}_{ia} \tag{3.63}$$

as expected. This confirms that having $d^{(3)}_{ia}$ correct is necessary to have $\gamma^{(1)}_{ia}$ correct.

Degree Two

Expanding (3.39) to degree two gives

$$\gamma^{(2)} + \gamma^{(1)}U^{(1)} + \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} U^{(2)} = U^{(2)} \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} + \begin{bmatrix} \Delta^{(2)}_o & 0 \\ 0 & -\Delta^{(2)}_v \end{bmatrix} \tag{3.64}$$

This leads to the equations

$$\gamma^{(2)}_{ij} = \Delta^{(2)}_{ij} - \gamma^{(1)}_{ia}U^{(1)}_{aj} \tag{3.65}$$

$$\gamma^{(2)}_{ab} = -\Delta^{(2)}_{ab} - \gamma^{(1)}_{ai}U^{(1)}_{ib} \tag{3.66}$$

$$\gamma^{(2)}_{ia} = -\gamma^{(1)}_{ib}U^{(1)}_{ba} - U^{(2)}_{ia} \tag{3.67}$$

$$\gamma^{(2)}_{ai} = -\gamma^{(1)}_{aj}U^{(1)}_{ji} + U^{(2)}_{ai} \tag{3.68}$$

(3.65) and (3.66) are just the degree two cases of (3.49) and (3.50) after using (3.47), (3.56), and (3.57). This both proves them and shows that to have these blocks correct to degree two, it is necessary to have d_{ij} to degree two and d_{ia} and its conjugate to degree three. Again, the simple approximation $d_{ia}^{(3)} = 0$ is correct for the orbital-optimized case, but not in general.

We next prove that (3.67) leads to the correct result, but omit the similar analysis for (3.68).

To determine $U^{(2)}$, we expand (3.40) to degree four and take off-diagonal elements, with the result that

$$\forall p \neq q : U_{pq}^{(2)} = \frac{d_{pr}^{(3)} U_{rq}^{(1)} + d_{pq}^{(4)} - U_{pq}^{(1)} \Delta_q^{(3)}}{\Delta_q^{(2)} - \Delta_p^{(2)}} \tag{3.69}$$

In the case where $d_{ia}^{(3)}$ and thus $U^{(1)}$ and $\gamma^{(1)}$ are zero, it is immediate that $d_{ia}^{(4)}$ is necessary to produce a nonzero $\gamma_{ia}^{(2)}$.

Because we do not know diagonal elements of U, we may try to eliminate the U_{aa} terms immediately. Use of (3.60) gives:

$$\gamma_{ia}^{(2)} = -\sum_{b:b\neq a} (\gamma_{ib}^{(1)} U_{ba}^{(1)}) - \frac{\sum_{b:b\neq a} (d_{ib}^{(3)} U_{ba}^{(1)}) + d_{ij}^{(3)} U_{ja}^{(1)} + d_{ia}^{(4)} - U_{ia}^{(1)} \Delta_a^{(3)}}{\Delta_a^{(2)} - \Delta_i^{(2)}} \tag{3.70}$$

We know from (3.51) that

$$d_{ia}^{(4)} = \gamma_{ib}^{(1)} \gamma_{ba}^{(3)} + \gamma_{ib}^{(2)} (\gamma_{ba}^{(2)}) + (\gamma_{ij}^{(2)}) \gamma_{ja}^{(2)} + \gamma_{ij}^{(3)} \gamma_{ja}^{(1)} \tag{3.71}$$

Upon invoking (3.47), (3.49) and (3.50), this becomes:

$$d_{ia}^{(4)} = \gamma_{ib}^{(1)} \gamma_{ba}^{(3)} - \gamma_{ia}^{(2)} \Delta_a^{(2)} + \gamma_{ib}^{(2)} \gamma_{bj}^{(1)} \gamma_{ja}^{(1)} + \Delta_i^{(2)} \gamma_{ia}^{(2)} - \gamma_{ib}^{(1)} \gamma_{bj}^{(1)} \gamma_{ja}^{(2)} + \gamma_{ij}^{(3)} \gamma_{ja}^{(1)} \tag{3.72}$$

So that (3.67) becomes

$$\gamma_{ia}^{(2)} = \gamma_{ia}^{(2)} - \sum_{b:b\neq a} (\gamma_{ib}^{(1)} U_{ba}^{(1)}) - \frac{\sum_{b:b\neq a} (d_{ib}^{(3)} U_{ba}^{(1)}) + d_{ij}^{(3)} U_{ja}^{(1)} + \gamma_{ib}^{(1)} \gamma_{ba}^{(3)} + \gamma_{ib}^{(2)} \gamma_{bj}^{(1)} \gamma_{ja}^{(1)} - \gamma_{ib}^{(1)} \gamma_{bj}^{(1)} \gamma_{ja}^{(2)} + \gamma_{ij}^{(3)} \gamma_{ja}^{(1)} - U_{ia}^{(1)} \Delta_a^{(3)}}{\Delta_a^{(2)} - \Delta_i^{(2)}} \tag{3.73}$$

$$\gamma_{ia}^{(2)} = \gamma_{ia}^{(2)} - \sum_{b:b\neq a} (\gamma_{ib}^{(1)} U_{ba}^{(1)}) - \frac{\sum_{b:b\neq a} (d_{ib}^{(3)} U_{ba}^{(1)}) + \gamma_{ib}^{(1)} \gamma_{ba}^{(3)} + \gamma_{ib}^{(2)} \gamma_{bj}^{(1)} \gamma_{ja}^{(1)} - \gamma_{ib}^{(1)} \gamma_{bj}^{(1)} \gamma_{ja}^{(2)} - (d_{ij}^{(3)} - \gamma_{ij}^{(3)}) \gamma_{ja}^{(1)} - U_{ia}^{(1)} \Delta_a^{(3)}}{\Delta_a^{(2)} - \Delta_i^{(2)}} \tag{3.74}$$

$$\gamma_{ia}^{(2)} = \gamma_{ia}^{(2)} - \sum_{b:b\neq a}(\gamma_{ib}^{(1)}U_{ba}^{(1)}) - \frac{\sum_{b:b\neq a}(d_{ib}^{(3)}U_{ba}^{(1)}) + \gamma_{ib}^{(1)}\gamma_{ba}^{(3)} + \gamma_{ib}^{(2)}\gamma_{bj}^{(1)}\gamma_{ja}^{(1)} - \gamma_{ib}^{(1)}\gamma_{bj}^{(1)}\gamma_{ja}^{(2)} - (\gamma_{ib}^{(1)}\gamma_{bj}^{(2)} + \gamma_{ib}^{(2)}\gamma_{bj}^{(1)})\gamma_{ja}^{(1)} - U_{ia}^{(1)}\Delta_a^{(3)}}{\Delta_a^{(2)} - \Delta_i^{(2)}} \tag{3.75}$$

$$\gamma_{ia}^{(2)} = \gamma_{ia}^{(2)} - \sum_{b:b\neq a}(\gamma_{ib}^{(1)}U_{ba}^{(1)}) - \frac{\sum_{b:b\neq a}(d_{ib}^{(3)}U_{ba}^{(1)}) + \gamma_{ib}^{(1)}\gamma_{ba}^{(3)} - \gamma_{ib}^{(1)}(\gamma_{bj}^{(1)}\gamma_{ja}^{(2)} + \gamma_{bj}^{(2)}\gamma_{ja}^{(1)}) - U_{ia}^{(1)}\Delta_a^{(3)}}{\Delta_a^{(2)} - \Delta_i^{(2)}} \tag{3.76}$$

$$\gamma_{ia}^{(2)} = \gamma_{ia}^{(2)} - \sum_{b:b\neq a}(\gamma_{ib}^{(1)}U_{ba}^{(1)}) - \frac{\sum_{b:b\neq a}(d_{ib}^{(3)}U_{ba}^{(1)}) + \gamma_{ib}^{(1)}\gamma_{ba}^{(3)} - \gamma_{ib}^{(1)}(d_{ba}^{(3)} + \gamma_{ba}^{(3)}) - U_{ia}^{(1)}\Delta_a^{(3)}}{\Delta_a^{(2)} - \Delta_i^{(2)}} \tag{3.77}$$

$$\gamma_{ia}^{(2)} = \gamma_{ia}^{(2)} - \sum_{b:b\neq a}(\gamma_{ib}^{(1)}U_{ba}^{(1)}) - \frac{\sum_{b:b\neq a}(d_{ib}^{(3)}U_{ba}^{(1)}) - \gamma_{ib}^{(1)}d_{ba}^{(3)} - U_{ia}^{(1)}\Delta_a^{(3)}}{\Delta_a^{(2)} - \Delta_i^{(2)}} \tag{3.78}$$

By the degree three expansion of (3.40), $\Delta_a^{(3)} = d_{aa}^{(3)}$, so

$$\gamma_{ia}^{(2)} = \gamma_{ia}^{(2)} - \sum_{b:b\neq a}(\gamma_{ib}^{(1)}U_{ba}^{(1)}) - \frac{\sum_{b:b\neq a}(d_{ib}^{(3)}U_{ba}^{(1)}) - \gamma_{ib}^{(1)}d_{ba}^{(3)} + \gamma_{ia}^{(1)}d_{aa}^{(3)}}{\Delta_a^{(2)} - \Delta_i^{(2)}} \tag{3.79}$$

$$\gamma_{ia}^{(2)} = \gamma_{ia}^{(2)} - \sum_{b:b\neq a}(\gamma_{ib}^{(1)}U_{ba}^{(1)}) - \frac{\sum_{b:b\neq a}(d_{ib}^{(3)}U_{ba}^{(1)}) - \sum_{b:b\neq a}(\gamma_{ib}^{(1)}d_{ba}^{(3)})}{\Delta_a^{(2)} - \Delta_i^{(2)}} \tag{3.80}$$

$$\gamma_{ia}^{(2)} = \gamma_{ia}^{(2)} - \sum_{b:b\neq a}\left(\gamma_{ib}^{(1)}U_{ba}^{(1)} + \frac{d_{ib}^{(3)}U_{ba}^{(1)} - \gamma_{ib}^{(1)}d_{ba}^{(3)}}{\Delta_a^{(2)} - \Delta_i^{(2)}}\right) \tag{3.81}$$

Note that for $a \neq b$

$$\gamma_{ib}^{(1)}U_{ba}^{(1)} - \frac{\gamma_{ib}^{(1)}d_{ba}^{(3)}}{\Delta_a^{(2)} - \Delta_i^{(2)}} = \frac{\gamma_{ib}^{(1)}d_{ba}^{(3)}(\Delta_i^{(2)} - \Delta_b^{(2)})}{(\Delta_a^{(2)} - \Delta_i^{(2)})(\Delta_a^{(2)} - \Delta_b^{(2)})} = \frac{\gamma_{ib}^{(1)}U_{ba}^{(1)}(\Delta_i^{(2)} - \Delta_b^{(2)})}{\Delta_a^{(2)} - \Delta_i^{(2)}} \tag{3.82}$$

so

$$\gamma_{ia}^{(2)} = \gamma_{ia}^{(2)} - \sum_{b:b\neq a} \left(\frac{d_{ib}^{(3)} U_{ba}^{(1)} + \gamma_{ib}^{(1)} U_{ba}^{(1)} (\Delta_i^{(2)} - \Delta_b^{(2)})}{\Delta_a^{(2)} - \Delta_i^{(2)}} \right) = \gamma_{ia}^{(2)} \tag{3.83}$$

This confirms to degree two that the UDCT approach generates the correct γ.

3.7.2 Appendix: Construction of Occupied-Virtual d Elements

The formula for λ_{KA}^{IJ} to degree one in t_3 amplitudes and degree three in t_2 amplitudes is as follows:

$$\begin{aligned}
\lambda_{KA}^{IJ} = &-\frac{1}{3} t_{Aa}^{ij} t_{bcd}^{IJk} t_{ik}^{bc} t_{Kj}^{ad} + \frac{1}{6} t_{Aa}^{ij} t_{bcd}^{IJk} t_{ij}^{bc} t_{Kk}^{ad} - \frac{1}{3} t_{Aa}^{ij} t_{bcd}^{IJk} t_{ik}^{ab} t_{Kj}^{cd} + \frac{1}{6} t_{Aa}^{ij} t_{bcd}^{IJk} t_{ij}^{ab} t_{Kk}^{cd} \\
&- P^{(I/J)} \frac{1}{6} t_{ab}^{Ii} t_{Acd}^{Jjk} t_{ij}^{cd} t_{Kk}^{ab} + P^{(I/J)} \frac{1}{3} t_{ab}^{Ii} t_{Acd}^{Jjk} t_{jk}^{ac} t_{Ki}^{bd} + P^{(I/J)} \frac{2}{3} t_{ab}^{Ii} t_{Acd}^{Jjk} t_{ij}^{ac} t_{Kk}^{bd} - P^{(I/J)} \frac{1}{12} t_{ab}^{Ii} t_{Acd}^{Jjk} t_{jk}^{ab} t_{Ki}^{cd} \\
&- P^{(I/J)} \frac{1}{6} t_{ab}^{Ii} t_{Acd}^{Jjk} t_{ij}^{ab} t_{Kk}^{cd} \\
&- P^{(I/J)} \frac{1}{8} t_{Aa}^{Ii} t_{bcd}^{Jjk} t_{jk}^{bc} t_{Ki}^{ad} - P^{(I/J)} \frac{1}{3} t_{Aa}^{Ii} t_{bcd}^{Jjk} t_{ij}^{bc} t_{Kk}^{ad} - P^{(I/J)} \frac{1}{6} t_{Aa}^{Ii} t_{bcd}^{Jjk} t_{jk}^{ab} t_{Ki}^{cd} - P^{(I/J)} \frac{1}{3} t_{Aa}^{Ii} t_{bcd}^{Jjk} t_{ij}^{ab} t_{Kk}^{cd} \\
&+ \frac{1}{16} t_{ab}^{IJ} t_{Acd}^{ijk} t_{ij}^{cd} t_{Kk}^{ab} - \frac{1}{3} t_{ab}^{IJ} t_{Acd}^{ijk} t_{ij}^{ac} t_{Kk}^{bd} + \frac{1}{12} t_{ab}^{IJ} t_{Acd}^{ijk} t_{ij}^{ab} t_{Kk}^{cd} \\
&+ \frac{1}{12} t_{Aa}^{IJ} t_{ij}^{ab} t_{bcd}^{ijk} t_{Kk}^{cd} + \frac{1}{24} t_{Aa}^{IJ} t_{Ki}^{ab} t_{bcd}^{ijk} t_{jk}^{cd} \\
&- \frac{1}{6} t_{Aab}^{IJi} t_{jk}^{ac} t_{cd}^{jk} t_{bd}^{Ki} - \frac{1}{3} t_{Aab}^{IJi} t_{ij}^{ac} t_{cd}^{jk} t_{bd}^{Kk} + \frac{1}{24} t_{Aab}^{IJi} t_{jk}^{ab} t_{cd}^{jk} t_{cd}^{Ki} + \frac{1}{12} t_{Aab}^{IJi} t_{ij}^{ab} t_{cd}^{jk} t_{cd}^{Kk} + \frac{1}{12} t_{Aab}^{IJi} t_{ij}^{cd} t_{cd}^{jk} t_{Kk}^{ab}
\end{aligned}$$

Likewise, the formula for λ_{BC}^{IA} to the same degrees is

$$\lambda_{BC}^{IA} = -\frac{1}{3}t_{ab}^{Ii}t_{BCc}^{jkl}t_{jk}^{ac}t_{il}^{Ab} + \frac{1}{6}t_{ab}^{Ii}t_{BCc}^{jkl}t_{jk}^{ab}t_{il}^{Ac} - \frac{1}{3}t_{ab}^{Ii}t_{BCc}^{jkl}t_{ij}^{ac}t_{kl}^{Ab} + \frac{1}{6}t_{ab}^{Ii}t_{BCc}^{jkl}t_{ij}^{ab}t_{kl}^{Ac}$$
$$- P^{(A/B)}\frac{1}{6}t_{Ba}^{ij}t_{Cbc}^{Ikl}t_{kl}^{ab}t_{ij}^{Ac} + P^{(A/B)}\frac{1}{3}t_{Ba}^{ij}t_{Cbc}^{Ikl}t_{ik}^{bc}t_{jl}^{Aa} + P^{(A/B)}\frac{2}{3}t_{Ba}^{ij}t_{Cbc}^{Ikl}t_{ik}^{ab}t_{jl}^{Ac} - P^{(A/B)}\frac{1}{12}t_{Ba}^{ij}t_{Cbc}^{Ikl}t_{ij}^{bc}t_{kl}^{Aa}$$
$$- P^{(A/B)}\frac{1}{6}t_{Ba}^{ij}t_{Cbc}^{Ikl}t_{ij}^{ab}t_{kl}^{Ac}$$
$$- P^{(A/B)}\frac{1}{8}t_{Ba}^{Ii}t_{Cbc}^{jkl}t_{jk}^{bc}t_{il}^{Aa} - P^{(A/B)}\frac{1}{3}t_{Ba}^{Ii}t_{Cbc}^{jkl}t_{jk}^{ab}t_{il}^{Ac} - P^{(A/B)}\frac{1}{6}t_{Ba}^{Ii}t_{Cbc}^{jkl}t_{ij}^{bc}t_{kl}^{Aa} - P^{(A/B)}\frac{1}{3}t_{Ba}^{Ii}t_{Cbc}^{jkl}t_{ij}^{ab}t_{kl}^{Ac}$$
$$+ \frac{1}{16}t_{BC}^{ij}t_{abc}^{Ikl}t_{kl}^{ab}t_{ij}^{Ac} - \frac{1}{3}t_{BC}^{ij}t_{abc}^{Ikl}t_{ik}^{ab}t_{jl}^{Ac} + \frac{1}{12}t_{BC}^{ij}t_{abc}^{Ikl}t_{ij}^{ab}t_{kl}^{Ac}$$
$$+ \frac{1}{12}t_{BC}^{Ii}t_{ij}^{ab}t_{abc}^{jkl}t_{kl}^{Ac} + \frac{1}{24}t_{BC}^{Ii}t_{ij}^{Aa}t_{abc}^{jkl}t_{kl}^{bc}$$
$$- \frac{1}{6}t_{BCa}^{Iij}t_{ik}^{bc}t_{bc}^{kl}t_{jl}^{Aa} - \frac{1}{3}t_{BCa}^{Iij}t_{ik}^{ab}t_{bc}^{kl}t_{jl}^{Ac} + \frac{1}{24}t_{BCa}^{Iij}t_{ij}^{bc}t_{bc}^{kl}t_{kl}^{Aa} + \frac{1}{12}t_{BCa}^{Iij}t_{ij}^{ab}t_{bc}^{kl}t_{kl}^{Ac} + \frac{1}{12}t_{BCa}^{Iij}t_{kl}^{ab}t_{bc}^{kl}t_{jl}^{Ac}$$

Upon taking a partial trace of these elements, a massive cancellation occurs, leading to the following formula for the part of d_A^I that is degree one in t_3 and degree three in t_2:

$$d_A^I = \frac{1}{16}t_{ij}^{ab}t_{kl}^{cd}t_{abc}^{Iij}t_{Ad}^{kl} - \frac{1}{16}t_{ij}^{ab}t_{kl}^{cd}t_{Aab}^{ijk}t_{cd}^{Il}$$

This is the same formula determined in the main article. As the above equation is not identically zero, the entire d_A^I is nonzero.

Chapter 4

A Density Cumulant Theory Ansatz from Off-Diagonal Cumulant Elements: λDCT[1]

[1]Misiewicz, J. P.; Turney, J. M.; Schaefer, H. F. **2021**, To be submitted to *J. Chem. Phys.*

4.1 Abstract

We propose a new ansatz for density cumulant theory that combines orbital optimiztion and a parameterization of the 2-electron reduced density matrix cumulant in terms of the off-diagonal elements of the reduced density matrix cumulant, with all upper indices occupied and all lower indices virtual. We show that this ansatz has several desirable properties. It is formally exact, both in orbital-optimized form and otherwise. Crucially, the space of occupied orbitals of the theory is the space of occupied natural orbitals. This gives special significance to the orbitals of the theory and rigorously eliminates the singularities present in the exact theory. It is also shown that the previous ODC-12 method arises naturally in this formalism. We implement the method to degree four in the doubles amplitudes alone. We find it to be slightly less accurate than ODC-12 for equilibrium properties, but it uniformly improves the dissociation curve of H_2 compared to ODC-12. These initial results are highly promising for tolerance of static correlation, though triples must be added to improve equilibrium properties.

4.2 Introduction

Previously,[132] we investigated the orbital-optimized unitary density cumulant theory (OUDCT) ansatz. The OUDCT ansatz constructs the cumulant of a wavefunction from unitary coupled cluster and uses its partial trace, d, to construct the 1RDM of the wavefunction. With the cumulant and the 1RDM, it is possible to construct the 2RDM, and thus to determine the energy. In practice, d will be approximated as some finite polynomial in the unitary coupled cluster amplitudes. We discovered three features about the ansatz that are inconvenient as an approach to converge to an exact theory.

1. The intermediate d is *not* block-diagonal in the occupied and virtual orbital spaces. That is, one *cannot* have orbitals that are both natural orbitals and optimal orbitals in general. This has two disturbing consequences when constructing the 1RDM. First, the fact that an OUDCT method uses a d correct to degree n in the unitary coupled cluster amplitudes only guarantees that the constructed 1RDM is correct to degree $n-2$ in the unitary coupled cluster amplitudes, in the case that d is not block-diagonal. In the special case that d is block-diagonal, then having d correct to degree n provides a 1RDM correct to degree n. Second, the expression for the gradient of the energy with respect to the cumulant parameters involves denominators of the form $\frac{1}{n'_p+n'_q-1}$, where n'_p and n'_q are the occupation numbers of two natural spin-orbitals. In general, cases where one orbital is occupied and the other is virtual produce small denominators, which can lead to singularities. In the special case that d is block-diagonal, all denominators relating an occupied and a virtual orbital are multiplied by zero and disapear from the gradient equations. While choosing natural orbitals will eliminate both of these problems, doing so makes the analytic gradient theory much more complicated.

2. The static correlation tolerance of the method is lost. The ODC-12 method of density cumulant theory is able to describe multireference systems qualitatively correctly, when even CCSD gives

large errors. One of the prototypical static correlation benchmarks of ODC-12 is the dissociation of H_2. When methods of the OUDCT ansatz are applied to H_2, they are significantly improved around equilibrium, where the wavefunction is well-described by a Slater determinant. But along the dissociation coordinate, the performance of OUDCT methods worsen, becoming worse than ODC-12, and eventually leads to convergence failure.

3. Simply including more commutators does not see improved performance for equilibrium performance of diatomic molecules, which is our test set for improved equilibrium properties in general. If anything, including more terms makes the methods slightly worse. Note that unlike coupled cluster, the method does not truncate at some number of commutators. Like coupled cluster, the parameters of the method describe n-body excitations (and de-excitations), so the method has "doubles" parameters. Simply including more commutators while keeping only doubles parameters will not improve the method.

These problems motivate the study of new ansätze for density cumulant theory. The present study investigates such an ansatz. In the ansatz we propose, called $O\lambda$DCT, the fundamental variables of the theory are not unitary coupled cluster amplitudes, but the "off-diagonal" cumulant elements, of the form $\lambda^i_a, \lambda^{ij}_{ab}, \lambda^{ijk}_{abc}$, etc. In Section 4.3, we analyze H_2 dissociation to motivate the ansatz. We perform our formal analysis in 4.4. We also show that the ODC-12 method is consistent with this new ansatz. Where in the OUDCT theory, ODC-12 is at best the degree two approximation when the variables are restricted to doubles, in $O\lambda DCT$, ODC-12 is at best the degree three approximation when the variables are restricted to doubles. We discuss the exactness of the theory and find that it is exact, when the Taylor series converges. We also show that this ansatz is rigorously free of off-diagonal elements of the 1RDM when the variables λ^i_a are chosen zero. Becuase the energy of this method is an upper bound to the full configuration energy within a given basis set, this means that for this theory *the natural orbitals are exactly the optimal orbitals*. In Section 4.5, we present our benchmark results for the degree four approximation of the doubles-only theory. We find that the new ansatz is able to *improve* upon ODC-12's description of H_2 dissociation. For equilibrium properties of diatomics, our new method performs similarly to ODC-12, but with a slight loss of performance. For an improved description of equilibrium properties, it will be necessary to consider triples explicitly.

4.3 A Motivating Example

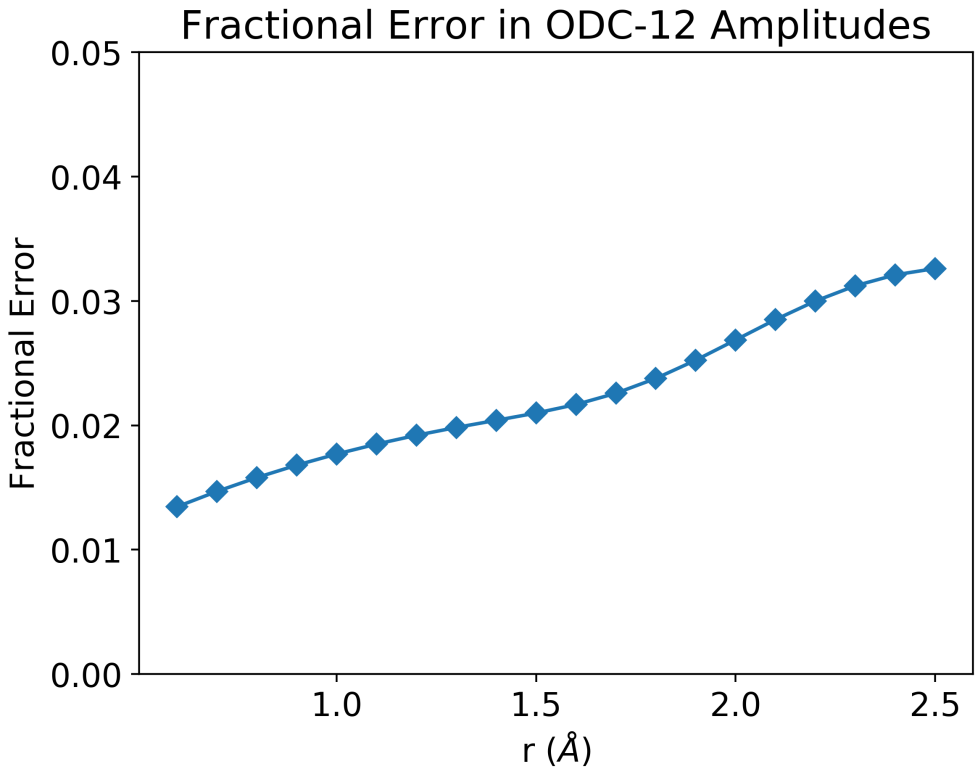
Let us review the ODC-12 method. In ODC-12, the cumulant is parameterized as

$$\lambda^{ij}_{ab} = t^{ij}_{ab} \tag{4.1}$$

$$\lambda^{ij}_{kl} = \frac{1}{2} t^{ij}_{ab} t^{ab}_{kl} \tag{4.2}$$

$$\lambda^{ab}_{cd} = \frac{1}{2} t^{ab}_{ij} t^{ij}_{cd} \tag{4.3}$$

Figure 4.1: The difference between the converged doubles amplitudes for ODC-12 and the exact λ_{ab}^{ij} as a fraction of the norm of the exact λ_{ab}^{ij} for H_2 computed with the cc-pVDZ basis set. Orbitals of λ_{ab}^{ij} are defined to be the natural orbitals.



$$\lambda_{jb}^{ia} = -t_{bc}^{ik} t_{jk}^{ac} \tag{4.4}$$

All cumulant blocks that are not given by the above equations, when combined with antisymmetry and Hermitian conjugation, are zero. In this system of equations, the parameters are identical with the off-diagonal block of the cumulant.

If ODC-12 is reliable across the entire dissociation curve, it is reasonable to suspect that the parameters are a good approximation to λ_{ab}^{ij} across the entire curve. In Figure 4.1, we graph the fractional error in t_{ab}^{ij} compared λ_{ab}^{ij} as computed in the basis of natural orbitals. Even at 2.5 Å, the simple ODC-12 theory has only a 3.2% error in λ_{ab}^{ij}. For comparison, the error against the unitary coupled cluster amplitudes at 2.5 Å is 24.5%. This suggests that the performance of ODC-12 for H_2 dissociation is best understood in comparison to a theory where the amplitudes are the cumulant elements, and the orbitals are either the natural orbitals, or some other set of orbitals close to them.

4.4 Theory

4.4.1 Unitary DCT

For the following discussion, it is convenient to formulate the unitary parameterization of the cumulant in an abstract manner. The reduced density matrices are given by

$$\gamma^{pq\cdots}_{rs\cdots} = \frac{\langle\Psi| a^{pq\cdots}_{rs\cdots} |\Psi\rangle}{\langle\Psi|\,|\Psi\rangle} \quad . \tag{4.5}$$

We now choose a particular ansatz for Ψ such that each term in (4.5) is a product of size-extensive parameters. We can easily infer the size-extensivity behavior of each term by observing the connectedness of the indices. We expect each term to consist of some number of disconnected pieces, where each disconnected piece has the same nonzero number of creation indices and annihilation indices from the original second quantized operator. For example, the unitary approach chooses

$$|\Psi\rangle = \exp(T - T^\dagger)\,|\Phi\rangle \quad . \tag{4.6}$$

The denominator of (4.5) simplifies, and the numerator can be expressed as a Baker-Campbell-Hausdorff series. This means that each commutator is connected to the previous one, so indeed. If $a^{pq\cdots}_{rs\cdots}$ has a size-extensive coefficient tensor, each term would be connected. Instead, we get disconnected terms, each of which was connected to the original $a^{pq\cdots}_{rs\cdots}$.

We can then compare the surviving terms with the cumulant expansion of the RDM elements. The cumulant expansion expresses each RDM exactly as a polynomial in size-extensive pieces. We can then use this size-extensivity analysis to match each term in (4.5) to a product of RDMs in the cumulant expansion. Crucially for our purposes, the cumulant consists of the completely connected terms.

Let us make some observations which were not especially important for the unitary formulation of DCT, but will be for us.

1. This procedure parameterizes cumulants of *any* rank. In unitary DCT, only the rank 2 case was needed.

2. The unitary parameterization is not the only possible wavefunction parameterization. One could instead choose

   $$|\Psi\rangle = \exp(T)\,|\Phi\rangle \tag{4.7}$$

   of variational coupled cluster theory. In this case, the nonzero denominator cancels all unlinked terms in the numerator. This leaves exactly terms with the desired connectivity structure. Because the cumulant expansion is exact, this connectivity structure should always appear for a wavefunction parameterization with size-extensive amplitudes.

3. In both the unitary and the variational parameterization, we have

$$\lambda^{i\cdots}_{a\cdots} = t^{i\cdots}_{a\cdots} + \Omega(t^2) \quad . \tag{4.8}$$

That is, the off-diagonal cumulants consist of the corresponding amplitude plus terms of degree two and greater.

4.4.2 λ DCT

Let us choose a size-extensive wavefunction parameterization satisfying (4.8). Both the variational and unitary coupled cluster parameterizations are examples of this. Our goal is to express the cumulants as functions of the off-diagonal cumulants. This can be accomplished by beginning from our formulas for the cumulants as functions of our wavefunction parameters and repeatedly using (4.8) to replace the wavefunction parameters with cumulant elements and terms of higher degree in the wavefunction parameters.

Let us illustrate this with a toy example, willfully ignoring some important points.

Let us suppose that we have

$$\lambda^{ij}_{kl} = \frac{1}{2} t^{ij}_{ab} t^{ab}_{kl} \tag{4.9}$$

and

$$\lambda^{ij}_{ab} = t^{ij}_{ab} + t^{ijk}_{abc} t^{c}_{k} \quad . \tag{4.10}$$

We can perform substitution of (4.10) into both amplitudes of (4.9) to give

$$\lambda^{ij}_{kl} = \frac{1}{2}(\lambda^{ij}_{ab}\lambda^{ab}_{kl} - t^{ijm}_{abc} t^{c}_{m} \lambda^{ab}_{kl} - \lambda^{ij}_{ab} t^{abc}_{klm} t^{m}_{c} + t^{ijm}_{abc} t^{c}_{m} t^{abd}_{kln} t^{n}_{d}) \quad . \tag{4.11}$$

While we can perform substituion into the remaining terms, it is clear that the terms that are degree two in λ in this toy example are $\frac{1}{2}\lambda^{ij}_{ab}\lambda^{ab}_{kl}$.

Let us make some observations about this procedure:

1. While the toy example had finite polynomials, the full cumulant Maclaurin series will not terminate. If we only desired terms of degree n or lower, then we need not perform substitution on terms of higher than degree than n. No number of substitutions can *reduce* the total degree.

2. Even if one decides to retain terms only with certain excitation ranks, it is *not* justified to exclude those from the outset. For example, suppose that one is interested only in terms of λ^{ij}_{ab} with only T_1 and T_3 amplitudes. One such term has been generated by substitution into (4.10), even though it contains no T_1 or T_3 amplitudes.

3. One would expect the final result, as a power series from the off-diagonal cumulants to the target cumulant elements, to be independent of wavefunction parameterization. However, the wavefunction parameterization does affect the work leading to the final result. For example, in (4.10),

the term $t^{ijk}_{abc}t^c_k$ is in the cumulant of variational coupled cluster. In unitary coupled cluster, the term is instead $\frac{1}{2}t^{ijk}_{abc}t^c_k$. In the true expansion of λ^{ij}_{ab}, the term $t^{ijm}_{abc}t^c_m t^{ab}_{kl}$ occurs with prefactor 1 in variational coupled cluster and prefactor $\frac{1}{2}$ in unitary coupled cluster. In the λ expansion through variational coupled cluster, $\lambda^{ijm}_{abc}t^c_m t^{ab}_{kl}$ has weight $1-1$. In the expansion through unitary coupled cluster, it has weight $\frac{1}{2}-\frac{1}{2}$. Whichever parameterization is chosen, the final term has weight 0.

4. As the preceding point illustrates, these substitutions may cause terms with a nonzero weight to disappear from the final equations.

Formal complications aside, it is clear that this substitution procedure yields a Maclaurin series from the off-diagonal cumulant elements to any desired cumulant element. The radius of convergence of this power series is less clear. We note that this series can be obtained by inverting the map from wavefunction amplitudes to off-diagonal cumulants and then composing with the map from amplitudes to cumulants. The latter map is analytic (at least for variational and unitary coupled cluster) by the properties of the exponential function. The former map is analytic with a nonzero radius of converge by the analyticity of the forward map and the analytic form of the multivariable Lagrange-Bürmann formula. So the radius of convergence is nonzero.

It may be objected that the cumulants of an n-electron system do not vanish after rank n, so this formalism requires variables of infinite rank to describe a system of finitely many electrons. Fortunately, the cumulants that are variables of the theory do truncate. We require our cumulant tensors to be anti-symmetric. If we have only n occupied orbitals but try to form a rank k off-diagonal cumulant for $k > n$, an occupied orbital must be repeated. The cumulant element is then identically zero.

It is possible to identify all the elements of the rank-2 cumulant that are degree four in λ_2 amplitudes and with no cumulants of other ranks. These are given by

$$\lambda^{ij}_{ab} = t^{ij}_{ab} \tag{4.12}$$

$$\lambda^{ij}_{kl} = \frac{1}{2}\lambda^{ij}_{ab}\lambda^{ab}_{kl} + \frac{1}{8}P^{(i/j)}_{(k/l)}\lambda^{im}_{ab}\lambda^{jn}_{cd}\lambda^{ab}_{km}\lambda^{cd}_{kn} + \frac{1}{2}P^{(i/j)}_{(k/l)}\lambda^{im}_{ab}\lambda^{jn}_{cd}\lambda^{ac}_{kn}\lambda^{bd}_{lm} + \frac{1}{2}\lambda^{ij}_{ab}\lambda^{ac}_{mn}\lambda^{mn}_{cd}\lambda^{bd}_{kl} - \frac{1}{8}\lambda^{ij}_{ab}\lambda^{ab}_{mn}\lambda^{mn}_{cd}\lambda^{cd}_{kl} \tag{4.13}$$

$$\lambda^{ab}_{cd} = \frac{1}{2}\lambda^{ab}_{ij}\lambda^{ij}_{cd} + \frac{1}{2}P^{(a/b)}_{(c/d)}\lambda^{ae}_{ij}\lambda^{bf}_{kl}\lambda^{ik}_{cf}\lambda^{jl}_{de} - \frac{1}{8}P^{(a/b)}_{(c/d)}\lambda^{ij}_{ae}\lambda^{Bf}_{kl}\lambda^{cf}_{ij}\lambda^{kl}_{De} + \frac{1}{2}\lambda^{ij}_{ab}\lambda^{ef}_{ik}\lambda^{kl}_{ef}\lambda^{jl}_{cd} - \frac{1}{8}\lambda^{ab}_{ij}\lambda^{mn}_{ab}\lambda^{ab}_{kl}\lambda^{kl}_{cd} \tag{4.14}$$

$$\lambda^{ia}_{jb} = -\lambda^{ik}_{bc}\lambda^{ac}_{jk} + \lambda^{ik}_{bc}\lambda^{cd}_{kl}\lambda^{lm}_{de}\lambda^{ae}_{jm} - \lambda^{kl}_{bc}\lambda^{im}_{de}\lambda^{cd}_{jk}\lambda^{ae}_{lm} - \frac{1}{2}\lambda^{kl}_{bc}\lambda^{im}_{de}\lambda^{de}_{jk}\lambda^{ac}_{lm} - \frac{1}{2}\lambda^{kl}_{bc}\lambda^{im}_{de}\lambda^{cd}_{jm}\lambda^{ae}_{kl} + \frac{1}{2}\lambda^{ik}_{bc}\lambda^{de}_{kl}\lambda^{lm}_{de}\lambda^{ac}_{jm} + \frac{1}{2}\lambda^{ik}_{bc}\lambda^{cd}_{lm}\lambda^{lm}_{de}\lambda^{be}_{jk} \tag{4.15}$$

Observe that no degree three terms are present. This implies that ODC-12 is correct to degree three in the doubles-only theory using an ansatz in terms of cumulants. It is only correct to degree two in the doubles-only theory using an ansatz in terms of unitary coupled cluster amplitudes. Similarly, there are no degree five terms in the ansatz in terms of cumulants, using only doubles.

4.4.3 Orbital Optimization

To formulate the orbital-optimized version of λ DCT, we restrict our amplitudes so that $\lambda_a^i = 0$ is zero and choose the amplitudes to variationally minimize the energy. Two questions arise.

1. Will this procedure converge to the full configuration interaction limit, for a given basis set? This is known not to be the case for conventional coupled cluster.

2. As mentioned in the introduction, we desire that d be block-diagonal in the occupied-virtual blocks. Can we guarantee this with this choice of orbitals? This is known not to be the case with the unitary ansatz for DCT.

The answer to the first question is yes. Because our energy computation proceeds by evaluating the expectation value a wavefunction, the energy is a variational upper bound on the full configuration interaction energy, whatever the value of λ_a^i. It remains to show there is some choice of orbitals where $\lambda_a^i = 0$ is exact. This is given by the natural orbitals, which diagonalize the 1RDM, because λ_a^i is an off-diagonal block of the 1RDM.

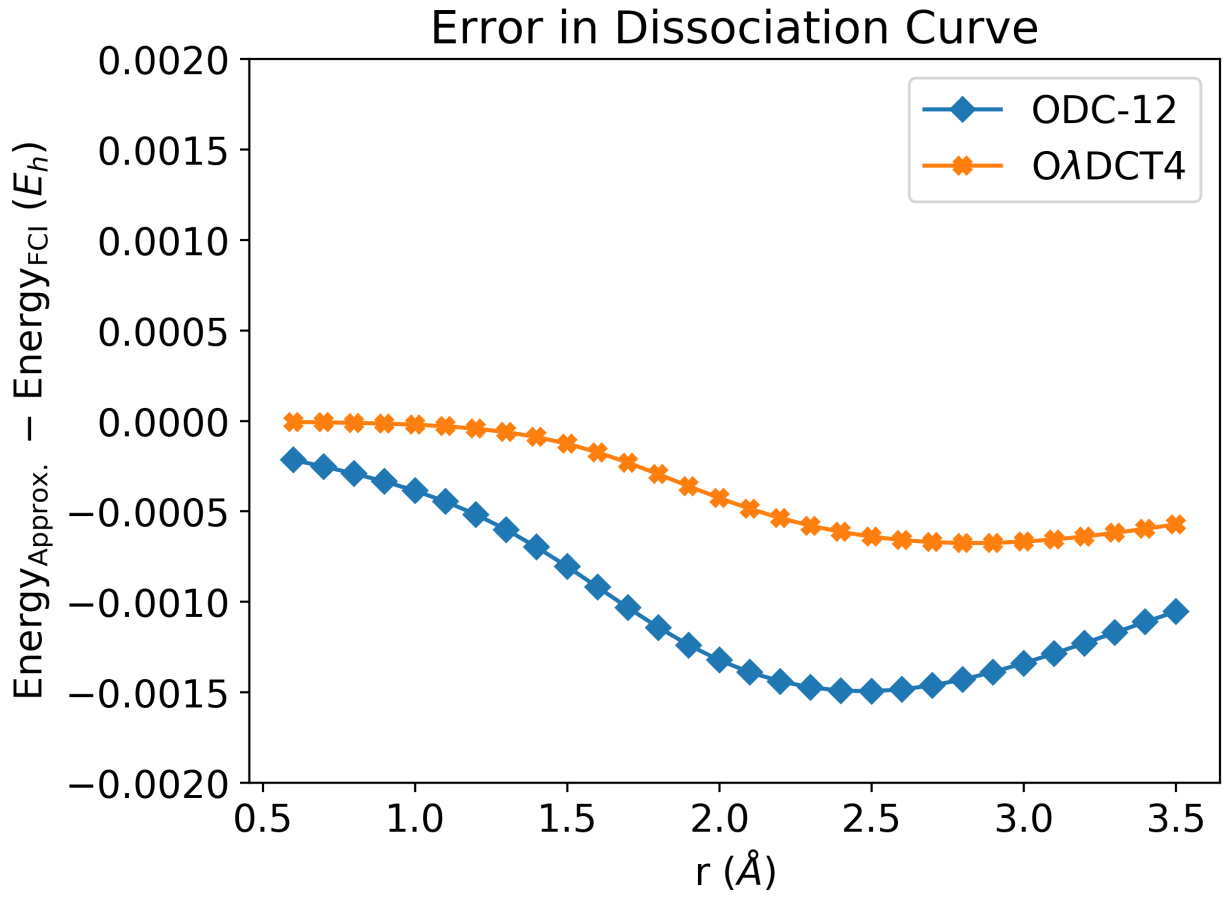
The answer to the second question is yes. While the most direct answer would characterize the terms of the cumulant expansion and take their partial trace, we do not yet have a full characterization of the cumulant terms. Instead, recall that in DCT

$$d_a^i = \gamma_p^i \gamma_a^p - \gamma_a^i = \gamma_b^i \gamma_a^b + \gamma_j^i \gamma_a^j - \gamma_a^i \tag{4.16}$$

The λ DCT ansatz allows us to write both of these as Maclaurin series in terms of the off-diagonal cumulants. Supposing that $\lambda_a^i = 0$, the right-hand side of (4.16) is the zero function. Every term is a Maclaurin series multiplied by $\gamma_a^i = \lambda_a^i$, so every term is zero. It follows that as long as $\lambda_a^i = 0$, $d_a^i = 0$ for any choice of the parameters. This is true in the exact ansatz. Because this must hold degree by degree, this will also be true of any ansatz where for each degree in d_a^i, either all or none of the terms are included. ODC-12 is an example of this, as all terms up to degree t_2^2 are included, and all others are excluded.

We can summarize this by saying that Oλ DCT is exact. It eliminates λ_a^i as variables of the theory, replacing them with the space of occupied natural orbitals. Becuase all parameters variationally minimize the energy, the reduced density matrices automatically delivered by the theory are also the relaxed density matrices needed by response theory.

Figure 4.2: Dissociation curves of H_2 from 0.6 Å to 3.5 Å computed with low-degree commutator truncations of the OλDCT ansatz in the cc-pVDZ basis set.



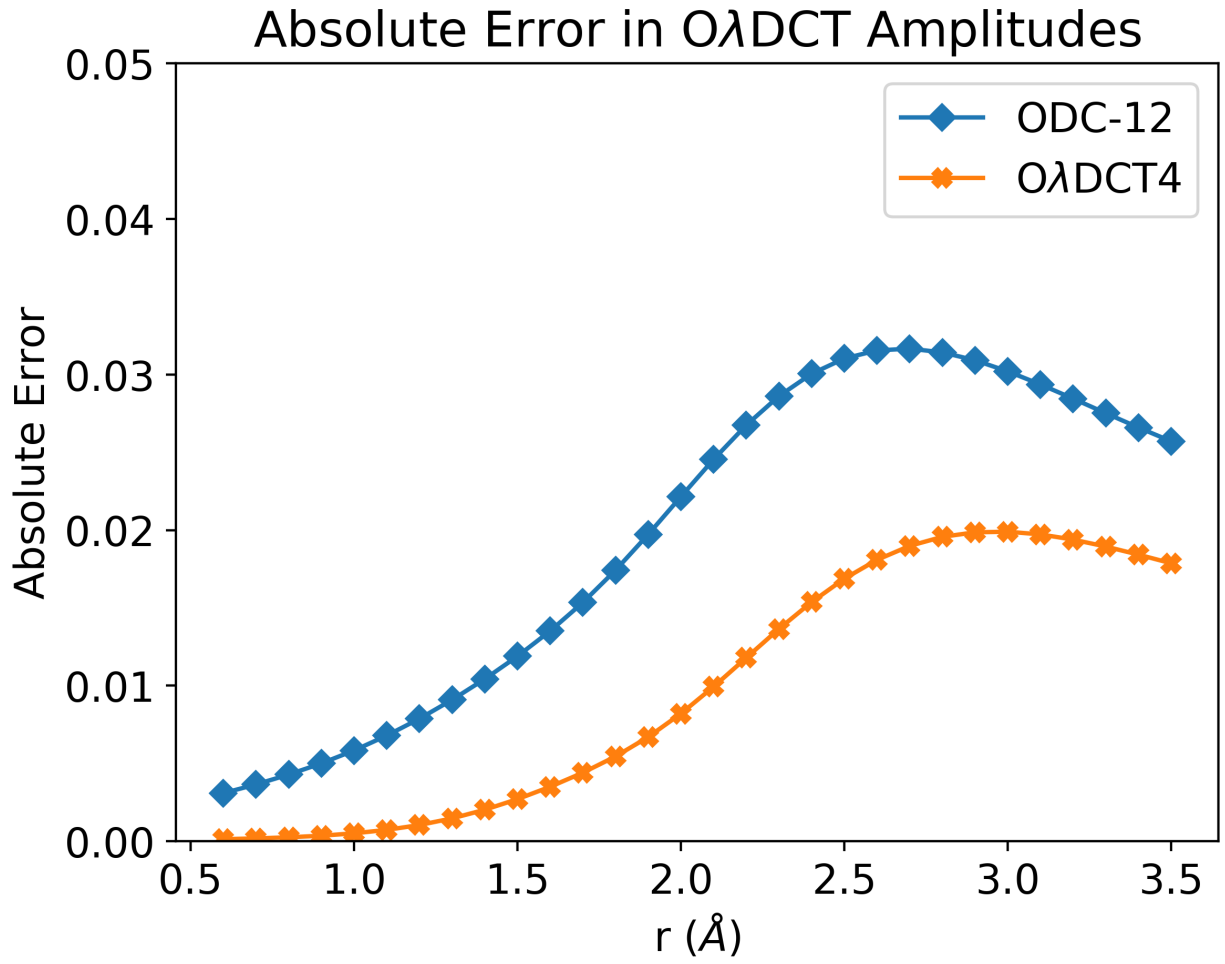
4.5 Benchmarks

We implemented the orbital optimized DCT method using as our λ parameterization equations (4.1) through (4.4). We name this method OλDCT4. We first apply it to H_2 dissociation. The dissociation of H_2 is the simplest possible benchmark of the theory's ability to tolerate static correlation. As a two-electron system, this allows us to assess whether the method is accurately capturing two-electron effects. Afterwards, we apply the method to the equilibrium proprties of diatomics as a first estimate of the applicability of the method to one of the most applications in quantum chemistry.

4.5.1 H_2 Dissociation

First, let us revisit the dissociation of H_2 using ODC-12 and OλDCT4.

Figure 4.3: Error in λ_{ab}^{ij} using the natural orbital basis for H_2 from 0.6 Å to 3.5 Å computed with low-degree commutator truncations of the OλDCT ansatz in the cc-pVDZ basis set.



We observe two things. First, the OλDCT4 method does improve uniformly on the dissociation curve produced by ODC-12. The magnitude of the improvement varies across the curve, but at all points shown reduces the energy error by at least a factor of two. This supports that OλDCT4 is an improvement on ODC-12. Secondly and more curiously, for both curves, the energy error peaks in the range of 2.5 to 2.8 Å after which point, the energy error *decreases* towards dissociation. It may initially be suspected that this is a cancellation of error, but we have graphed the error in the cumulant for both methods along the dissociation curve.

Comparing 4.3 and 4.2, we see that the minimum in energy error roughly corresponds to the minimum in λ error. It would appear, then, that the cumulant approximations become *more* accurate towards dissociation. A reason for this behavior is not immediately obvious to the authors.

Table 4.1: Errors in the geometries (pm) and harmonic frequencies (cm^{-1}) of diatomics (pm), relative to CCSDTQ(P), for ODC-12 and OλDCT4, using the cc-pCVDZ basis set. Δ_{abs} denotes the mean absolute error, and Δ_{std} denotes the standard deviation of signed errors.

Molecule	ODC-12	OλDCT4	ODC-12	OλDCT4
N_2	−0.51	−0.55	56	60
CO	−0.63	−0.63	67	65
N_2^+	−0.69	−0.70	50	65
BO	−0.84	−0.81	69	66
CN	−0.69	−0.79	46	53
NF	−0.65	−0.97	20	44
NO	−0.73	−0.83	71	83
BeO	−1.56	−1.34	55	45
Δ_{abs}	0.79	0.83	54	60
Δ_{std}	0.33	0.25	16	12

We also comment on our decision to end the dissociation curve at 3.5 Å. In our implementation of DCT, we observed convergence difficulties around 2.3 Å when we read it amplitudes and orbitals from the previous steps. These convergence difficulties were associated with large changes in the cumulant, causing its partial trace d to take on an eigenvalue of less than -0.25. When d takes on such an eigenvalue, this corresponds to a natural spinorbital with an occupation number outside the range of 0 and 1. This is clearly unphysical and causes the reconstruction of the 1RDM from d to fail, as the square root of a negative number appears in the equations. To overcome these, we had to reduce our cumulant update step. This strongly suggests that the first-order cumulant step we used is not reliable towards the dissociated limit. This is unsurprising. Towards dissociation, the reconstruction of γ from d becomes highly sensitive on the d eigenvalues, and thus to the cumulant. We recommend that future DCT methods wishing to examine dissociated compounds employ a second order amplitude update algorithm.

4.5.2 Equilibrium Properties of Diatomic Molecules

As in our previous study, to obtain a first estimate on the effectiveness of our new method for equibrium properties, we apply it to the equilibrium properties of diatomics, in particular.

Table 4.1 shows that the two methods have similar performance for both properties, but the simpler ODC-12 method has a slightly smaller Δ_{abs} of 0.04 pm for geometries and 6 cm^{-1} for frequencies. Given that OλDCT4 showed an increase in accuracy for the two-electron case, we hypothesize that this accuracy loss is due to the flexible parameterization of ODC-12 implicitly accounting for effects of other cumulant ranks, such as triples. In this case, triples must be included into the theory to see improvements in accuracy.

4.6 Conclusions

We have proposed a new ansatz for density cumulant theory, in which the variables are the off-diagonal (excitation-type) cumulants and performed initial benchmarks of the method.

Formally, we find that the ansatz has many pleasant properties. It is formally exact. It can be orbital-optimized without costing formal exactness. When it is orbital-optimized, it is variational in all parameters, so the analytic gradients are inexpensive. When it is orbital-optimized, the occupied-virtual blocks of the 1RDM are zero, so the space of occupied orbitals acquires an additional interpretation as the space of occupied natural orbitals. This additionally means that singularities in the cumulant update equations due to the denominator $\frac{1}{n_i+n_a-1}$ no longer exist.

Numerically, we have implemented the simple degree-four truncation of the method, restricted to double cumulants. For equilibrium properties, we see a slight regression in performance compared to ODC-12. This can be attributed to the need to account for triples effects. For H_2 dissociation, the new method is significantly closer to full configuration interaction across the entire curve. This strongly suggests that the ansatz maintains the static correlation tolerance of ODC-12.

For further development, there are three outstanding targets.

1. More extensive benchmarks are necessary, in particular for static correlation tolerance. ODC-12 is known to tolerate static correlation effects which CCSD predicts incorrectly, even qualitatively. That OλDCT4 improves on H_2 dissociation is encouraging, but not sufficient to show that it has good performance for static corrleation in general.

2. Including the degree four, rank-two cumulants decreased the accuracy of the method. To enhance the accuracy of the method for equilibrium properties in the weakly correlated regime, we suspect it will be necessary to explicitly incorporate cumulants of higher rank. That is, the theory needs a triples correction, which must also be derived and benchmarked.

3. Unfortunately, the ansatz as presented here is cumbersome to work with, requiring a sequence of tedious and error-prone substitutions of equations of potentially infinite rank. This it not a viable way to derive corrections at higher degrees. A new formalism is needed to derive the equations, hopefully with the simplicity of the diagramatic techniques used in coupled cluster theory. Such a technique would also be helpful in proving directly form the definition that the d matrix has a block diagonal structure

Work is underway in our group to prove a simpler way to derive the terms of the λDCT ansatz, which will enable further, more sophisticated developments.

Chapter 5

Conclusion

This dissertation provided an extended study of density cumulant theory.

Chapter 2 made the concept of reduced density matrix cumulants, which are foundational to density cumulant theory, more accessible in the literature. It was shown that the reduced density matrices are related to their cumulants by an exponential with second quantized operators, exactly as the configuration interaction amplitudes are related to the coupled cluster amplitudes. Probabilistic interpretations of these quantities are not to be expected. The appearance of second quantized operators does not need to be justified in terms of their properties as operators acting on wavefunctions, but in terms of the combinatorial properties given by their multiplication rules. This combinatorics also explains the appearance of cumulants in the Generalized Normalized Order formalism.

Chapter 3 analyzed the previously proposed Orbital-Optimized Unitary ansatz for Density Cumulant Theory (OUDCT). This study clarified the κ, τ formalism in older Density Cumulant Theory (DCT) literature, especially its complete n-representability conditions. Our analysis of the ansatz uncovered new formal features of the ansatz that would complicate attempts to extend the formalism to triples. Singularities can appear in the cumulant update equations. Determining the crucial d matrix intermediate to degree n does not guarantee that the reconstruction of the 1RDM, γ, is correct to degree n. Both of these features rigorously disappear when the orbitals of the theory are the natural orbitals, but this is inherently at odds with orbital optimization of a unitary ansatz. Our numerical studies also show that this attempt to combine DCT with a unitary ansatz leads to worse performance for H_2 dissociation, sacrificing static correlation tolerance. It was also shown that if one desires to improve the ansatz for equilibrium properties of weakly correlated molecules, triples must be included in the theory.

Chapter 4 provided a new ansatz for density cumulant theory. In this ansatz, the variables of the theory are no longer unitary coupled cluster amplitudes but off-diagonal cumulants. This formalism shares some of the desirable features of the unitary ansatz. It is formally exact and supports orbital optimization. However, in this ansatz, the space of occupied orbitals is identical to the space of occupied natural spin-orbitals, so the orbital-related complications of the unitary ansatz disappear. Furthermore, upon implenting the degree four theory, we observe uniform improvement of the H_2 dissociation curve. This is true both in the energy and the accuracy of the amplitudes. We also identified the reason for non-convergence of more

correlated geometries in previous DCT publications as a flaw in the convergence algorithm, not a failure of the equations themselves. Unfortunately, it remains true in this formalism that for a method of the ansatz to deliver more accurate properties of weakly correlated molecules, triples are necessary.

Let us comment briefly on the future. One important feature of DCT was not addressed in this dissertation, namely, making the existing ODC-12 method more efficient. One way to do this is by implementing the frozen core approximation, in which energetically low-lying orbitals are assumed to be occupied in all determinants, so any amplitudes involving them may be set to zero. This is a standard approximation for non-orbital-optimized methods, but for orbital optimized methods such as ODC-12, the frozen space must be optimized as well. The frozen core approximation with orbital optimized methods has not been benchmarked. In the author's view, this is the priority in terms of efficiency.

A related approximation is the frozen virtual approximation, in which some virtual orbtitals are assumed to be virtual in all determinants, so any amplitudes involving them may be set to zero. This is not a standard approximation, because a way needs to be chosen to identify the virtual orbitals for which this approximation is good. Methods to do this include freezing approximate natural orbitals. This can naturally be done in ODC-12 by optimizing the virtual space. The virtual orbitals frozen are the ones with least impact on the energy.

As discussed in the final chapter, there are two major opportunities for developing more accurate DCT variants. The first is the problem of developing a triples correction, which is needed to improve the precision of the method for weakly correlated geometries. The second is to form a variant of the method that can deal with strong correlation. In both cases, the OλDCT ansatz offers a way forward, but working with the ansatz will be difficult until the formalism for deriving its equations can be automated. In the author's view, this automation is the priority in terms of developing new methods of the ansatz.

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(93) Suppose a set of multiplicatively separable wavefunctions related by a unitary transformation to another set of wavefunctions, which may or may not be multiplicatively separable. The ensemble reduced density matrices of the two are the same. The ensemble reduced density matrix of the multiplicatively separable wavefunctions is multiplicatively separable, which suffices to show the corresponding cumulants are additively separable. The prototypical example of such a case is the spin-uncoupled and spin-coupled systems related by a single M_s block of a Clebsch-Gordan table.

(94) Equation A2 of Ref. [82] is the counterpart of Equation 11b of Ref. [, 83]. These two equations contradict each other: the last two terms of A2 of Ref. [82] correspond to "formal variables" where the creation and annihilation operator correspond to orbitals of different subsystems, and these are missing from Equation 11b of Ref. [83]. The terms should exist by virtue of Equation 3b of Ref. [83]. The missing terms cannot be assumed to be zero because the variables k are formal variables and have no numerical value. Unfortunately, the proof of Ref. [83] is incorrect as written because the crucial Equation 11b is incorrect. The proof can be repaired, which is precisely what Hanauer and Köhn do in Appendix A of Ref. [82]. However, this leads them to a much more complicated analysis. We are not aware of a simpler repair of the original proof of Ref. [83].

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