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

Jonathon P. Misiewicz, Justin M. Turney, and Henry F. Schaefer III*

Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia, 30602

E-mail: ccq@uga.edu

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.

1 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.[1–5] 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.[6–11] Additive separability of cumulants is a crucial consideration in the derivations of References 12, 13, and Section IIC of 14. 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.[15,16] 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.[17–20]

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.[21–23] Apart from one presentation of the two-body cumulant,[13] 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.[2] 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.[24] The terms can then be related to terms of a perturbation expansion of the reduced density matrices,[25] 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[26] and is now the exclusive formalism used to discuss additive separability of the RDM cumulants.[13,27–31]

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

$$M(t_1, ..., t_n) = \langle \exp(\sum_{i=0}^{N} t_i X_i) \rangle \tag{1}$$

and the cumulant generating function

$$K(t_1, ..., t_n) = \log M(t_1, ..., t_n) \quad . \tag{2}$$

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 (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). 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 (1) and (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[28] but later said it did not apply to the "exclusion-principle violating" cumulants.[32] Kong and Valeev interpreted some RDM cumulant elements as probabilistic correlations of electron occupation, within some restrictive assumptions.[23] Hanauer and Köhn gave the same interpretation with looser assumptions, but could still not provide a definitive probabilistic interpretation for all RDM cumulant elements.[27] 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,[28] and a variant was later made by Hanauer and Köhn.[27] 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 (1) is modified to use a normal ordered product, while the log in the analogue of (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.[29] 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", $t_1, ..., t_n$, are neither real nor complex numbers, but anticommuting numbers. Throughout the literature, it has been typical[13,29,30,33–36] to obtain RDM cumulants by using the exponentiated analogue of (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.[2,23,37] Mukherjee's proof of additive separability further depends on the multiplicative separability of the wavefunction.[2] From this, the fact that cumulants from non-multiplicatively separable wavefunctions, e.g., spin-coupled energy eigenstates, are not additively separable[27,38,39] is expected. However, ensemble averages of such states can still be additively separable.[40] (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.[27,41] (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,[42] 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. 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 A.

In Section 3, 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 3.1 shall review generating functions in detail. Section 3.2 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 3.3, 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 3.4, 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 4. We consider why cumulants appear in the formalism of generalized normal ordering in Section 4 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 Additive Separability from Multiplicative Separability

2.1 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

$$1 + C = \exp(T) \tag{3}$$

where

$$C = \sum_{i,a} \frac{1}{(1!)^2} c^i_a a^a_i + \sum_{i,j,a,b} \frac{1}{(2!)^2} c^{ij}_{ab} a^{ab}_{ij} + ... \tag{4}$$

and

$$T = \sum_{i,a} \frac{1}{(1!)^2} t^i_a a^a_i + \sum_{i,j,a,b} \frac{1}{(2!)^2} t^{ij}_{ab} a^{ab}_{ij} + ... \tag{5}$$

and the operators a^a_i, a^{ab}_{ij}, etc. are the usual second quantized excitation operators of many-fermion theory.[15,16,43]

The excitation operators in (4) and (5) perform two roles. First, they make the left and right hand sides of (3) operators that transform the reference Φ into the target state Ψ.[44] The need for an operator to act on a wavefunction is the usual rationale for the appearance of second quantized operators in (3).[15,16,43,44] For our purposes, this role is irrelevant. Second, equating the coefficients of the operators a^a_i, a^{ab}_{ij}, etc. on each side of (3) gives a c amplitude as a polynomial in the t amplitudes.[44,45] After taking log of (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

$$\gamma^{pq\cdots}_{rs\cdots} = \langle\Psi|\, a^{pq\cdots}_{rs\cdots}\,|\Psi\rangle \quad . \tag{6}$$

Other normalization conventions are known in the RDM literature. This is known as the McWeeny normalization[46] and is especially convenient for our purposes.

Since we want cumulant elements to be additively separable and expressed in terms of RDM elements, replace (4) and (5) with

$$\mathcal{C} = \sum_{p,q} \gamma^q_p a^p_q + \sum_{p,q,r,s} \frac{1}{(2!)^2} \gamma^{rs}_{pq} a^{pq}_{rs} + \ldots \tag{7}$$

and

$$\mathcal{T} = \sum_{p,q} \lambda^q_p a^p_q + \sum_{p,q,r,s} \frac{1}{(2!)^2} \lambda^{rs}_{pq} a^{pq}_{rs} + \ldots \quad . \tag{8}$$

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.[15,16,43] Modifying an idea from Lindgren,[47] 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 $\{a^p_r a^q_s\} = a^{pq}_{rs}$ rather than $a^p_r a^q_s = a^{pq}_{rs} + \delta^q_r a^p_s$. (In notation such as $\{a^p_r a^q_s\}$, the braces denote redefining multiplication, not a function applied to $a^p_r a^q_s$. The latter approach leads to contradictions of the type discussed in References 48 and 49.) 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[27,28,31,50,51] and in the Mazziotti approach to cumulants,[13,29,30,33–36] 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 3.3.

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

$$1 + \mathcal{C} = \{\exp(\mathcal{T})\} \tag{9}$$

or equivalently

$$\{\log(1 + \mathcal{C})\} = \mathcal{T} \quad . \tag{10}$$

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.[52–54]

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:

$$1 + \mathcal{C}_{A+B} = \{(1 + \mathcal{C}_A)(1 + \mathcal{C}_B)\} = \{\{\exp(\mathcal{T}_A)\}\{\exp(\mathcal{T}_B)\}\} = \{\exp(\mathcal{T}_A + \mathcal{T}_B)\} \quad . \tag{11}$$

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

$$1 + \mathcal{C}_{A+B} = \{(1 + \mathcal{C}_A)(1 + \mathcal{C}_B)\} \quad . \tag{12}$$

(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 (6), that (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,[27,38,39] and cumulants have even been studied as a way to measure the resulting spin-entanglement.[38] 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,[37] the orbital optimized methods studied by Bozkaya and co-workers,[55–58] and the RDM formulation of CEPA given by Mazziotti and related to his parametric RDM method.[59,60] This multiplicative separability structure is preserved in FCI within a complete active space as well as several approximate RDM methods.[6–9]

We close this subsection by observing that formulas to convert between RDMs and their cumulants can be extracted from (9) and (10). Some explicit examples are

$$\gamma^p_q = \lambda^p_q \tag{13}$$

$$\gamma^{pq}_{rs} = \lambda^{pq}_{rs} + \lambda^p_r\lambda^q_s - \lambda^p_s\lambda^q_r \tag{14}$$

$$\lambda^{pq}_{rs} = \gamma^{pq}_{rs} - \gamma^p_r\gamma^q_s + \gamma^p_s\gamma^q_r \tag{15}$$

$$\begin{aligned}\gamma^{pqr}_{stu} &= \lambda^{pqr}_{stu} + \lambda^p_s\lambda^{qr}_{tu} - \lambda^p_t\lambda^{qr}_{su} + \lambda^p_u\lambda^{qr}_{st} - \lambda^q_s\lambda^{pr}_{tu} + \lambda^q_t\lambda^{pr}_{su} - \lambda^q_u\lambda^{pr}_{st} + \lambda^r_s\lambda^{pq}_{tu} - \lambda^r_t\lambda^{pq}_{su} + \lambda^r_u\lambda^{pq}_{st} \\ &+ \lambda^p_s\lambda^q_t\lambda^r_u - \lambda^p_s\lambda^q_u\lambda^r_t - \lambda^p_t\lambda^q_s\lambda^r_u + \lambda^p_t\lambda^q_u\lambda^r_s + \lambda^p_u\lambda^q_s\lambda^r_t - \lambda^p_u\lambda^q_t\lambda^r_s\end{aligned} \tag{16}$$

$$\begin{aligned}\lambda^{pqr}_{stu} &= \gamma^{pqr}_{stu} - \gamma^p_s\gamma^{qr}_{tu} + \gamma^p_t\gamma^{qr}_{su} - \gamma^p_u\gamma^{qr}_{st} + \gamma^q_s\gamma^{pr}_{tu} - \gamma^q_t\gamma^{pr}_{su} + \gamma^q_u\gamma^{pr}_{st} - \gamma^r_s\gamma^{pq}_{tu} + \gamma^r_t\gamma^{pq}_{su} - \gamma^r_u\gamma^{pq}_{st} \\ &+ 2\gamma^p_s\gamma^q_t\gamma^r_u - 2\gamma^p_s\gamma^q_u\gamma^r_t - 2\gamma^p_t\gamma^q_s\gamma^r_u + 2\gamma^p_t\gamma^q_u\gamma^r_s + 2\gamma^p_u\gamma^q_s\gamma^r_t - 2\gamma^p_u\gamma^q_t\gamma^r_s\end{aligned} \tag{17}$$

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

$$\gamma^{pq\cdots}_{rs\cdots} = \sum_\rho \lambda(\rho) \tag{18}$$

and

$$\lambda^{pq\cdots}_{rs\cdots} = \sum_\rho (-1)^{\#\rho-1}(\#\rho-1)!\gamma(\rho) \tag{19}$$

where summation is over all fermionic partitions. Equation 19 is derived in detail in Appendix B.

2.2 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 (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[34,35] or the amplitudes of valence universal multireference coupled cluster.[49] 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 43, 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,[22,34,35,37,61] 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.[13] Consider how (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, (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, (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 (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[42] and latter refined by Simon,[62] and can also be adapted to define an additively separable counterpart of any quantity which may have multiplicative separability:

1. **Functional Form**

$$\lambda\binom{pq\cdots}{rs\cdots} = \sum_{\rho} \mu_\rho \gamma(\rho) \tag{20}$$

This axiom uses notation introduced at the end of Section 2.1. 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 (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 A, although recognizing that (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.

3 Generating Functions

Equations (9) and (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.

3.1 Mathematicians' Generating Functions

While RDM cumulant generating functions have been defined numerous times,[13,27–31,33,36,50,51] as have generating functions for the more general reduced transition matrix cumulants,[34,35] 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 53, 54, 63, 64, and 65.

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 $\sum\limits_{n=0}^{\infty} a_v x^v$.

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 $\sum\limits_{m=0}^{n} \binom{n}{m} a_m b_{n-m}$. Now, from the sequences $\{a_n\}$ and $\{b_n\}$, construct the functions $a(x) = \sum\limits_{n=0}^{\infty} a_n \frac{x^n}{n!}$ and $b(x) = \sum\limits_{n=0}^{\infty} b_n \frac{x^n}{n!}$. (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 $\sum\limits_{m=0}^{n} \binom{n}{m} a_m b_{n-m}$. 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.

3.2 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.

$$\kappa(X) = m(X) \tag{21}$$

$$m(XY) = \kappa(XY) + \kappa(X)\kappa(Y) \tag{22}$$

$$\kappa(XY) = m(XY) - m(X)m(Y) \tag{23}$$

$$m(XYZ) = \kappa(XYZ) + \kappa(X)\kappa(YZ) + \kappa(Y)\kappa(XZ) + \kappa(Z)\kappa(XY) + \kappa(X)\kappa(Y)\kappa(Z) \tag{24}$$

$$\begin{aligned} \kappa(XYZ) = {} & m(XYZ) - m(X)m(YZ) - m(Y)m(XZ) - m(Z)m(XY) \\ & + 2m(X)m(Y)m(Z) \end{aligned} \tag{25}$$

These closely parallel the RDM cumulant formulas from (13) to (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[42] and Simon,[62] as

1. **Functional Form**

$$\kappa(XY\cdots) = \sum_\rho \mu_\rho m(\rho) \tag{26}$$

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** $\mu_{XY\cdots} = 1$

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 $m(XY\cdots)$ 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 (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) 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 28, 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 3.1, different kinds of generating functions are suited to different counting problems. In both cases, to read off relations of form (20) and (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 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 3.1 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 3.3, 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 (9) and (10).

The final difference between the two functions is that an exponential appears in the creation of the moment-generating function (1) for probabilistic cumulants, but not in our RDM analogue, (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 C.

3.3 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 2.1 emerge from those previous. The comparison is summarized in Table 1.

Table 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	$\langle\psi\| \{\exp(k^p_q a^q_p)\} \|\psi\rangle$	$\langle\psi\| \{\exp(J_k a^\dagger_p + J^*_k a_p)\} \|\psi\rangle$	$1 + \sum \mathcal{C}^{q\cdots}_{p\cdots} a^{p\cdots}_{q\cdots}$
Formal Variable	k^p_q	J_k, J^*_k	a^p_q
Product of Formal Variables	$k^p_q * k^r_s = k^p_q k^r_s \neq -k^p_s k^r_q$	$J_k * J_l = J_k J_l = -J_l J_k$	$\{a^p_q a^r_s\} = a^{pr}_{qs} = -a^{pr}_{sq}$
Particle-conserving variables only?	Yes	No	Yes
Role of a^p_q	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;[27,28,31,50,51] [b] Mazziotti[29,33–36] and other reduced density matrix investigators;[13,30] [c] Section 2.1 of the present research

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 (7), which is an easy generalization of the familiar configuration interaction form (4). This is exactly as discussed in Appendix C.

We now consider the two approaches separately.

First is the KMHK approach. As Hanauer and Köhn's presentation uses six different product operations,[27] we comment only on the variant of Kutzelnigg and Mukherjee.[28,31,50,51] 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, $k^p_r k^q_s$ and $-k^p_s k^q_r$ 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 $k^p_r k^q_s - k^p_s k^q_r$, instead of simply matching coefficients of the formal variables. Our formalism avoids this entirely because $\{a^p_r a^q_s\} = -\{a^p_s a^q_r\}$. 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 $J_p J_q J^\dagger_s J^\dagger_r = -J_q J_p J^\dagger_s J^\dagger_r$ is just the familiar equation in our formalism, $a^{pq}_{rs} = -a^{qp}_{rs}$. 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 $\{a^p_r a^q_s\} = a^{pq}_{rs}$. 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 $J_p J_q J^\dagger_s J^\dagger_r$ and $J_p J^\dagger_r J_q J^\dagger_s$ are treated as the same. This is again the behavior of the familiar normal ordering our formalism uses, $a^{pq}_{rs} = \{a^p_r a^q_s\}$. 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.

3.4 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[27] 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[23] 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 $\lambda_{pq}^{pq} = \gamma_{pq}^{pq} - \gamma_p^p \gamma_q^q + \gamma_q^p \gamma_p^q$ 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_q^p and γ_p^q 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 $-\gamma_{rs}^{pq}\gamma_{pq}^{rs}$, 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, (20), and the probabilistic cumulant, (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.

4 Generalized Normal Ordering

We now shift our perspective entirely to view cumulants from the GNO formalism.[1–5] 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,[66–68] construction of GNO excitation operators,[5,17,20,69–71] neglect of high-rank cumulants,[18,67,68,72] neglect of high-rank generalized normal order operators,[18,20,66–68,70–72] use of state-averaged reduced density matrices,[67,68,71] forming the zeroth-order Hamiltonian in perturbation theory,[5,20,32,70,71] and elimination of disconnected terms.[12,69]

4.1 Wick Expansion

We seek to generalize the familiar single-reference Wick Theorem,[15,16] 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 1. There is an alternate presentation[2] 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 D.

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 (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 (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 (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 (18), but with contractions instead of cumulants. *This is why the contraction structure of Reference 1 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,[73] 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 D.

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

$$\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_q\hat{q}_s\hat{q}_t\hat{q}_u\ldots = \{\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_q\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} + \sum\{\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} + \sum\{\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u\ldots\}$$
$$+ \sum\{\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} + \sum\{\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} + \sum\{\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} + \sum\{\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u\ldots\} + \ldots \tag{27}$$

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 $a^p a_q = \lambda^p_q$, $a^p a^q a_s a_r = \lambda^{pq}_{rs}$, 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 (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 (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 (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 (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 $\overbracket{a^p a_s a^q a_r} = -\lambda^{pq}_{rs}$. 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 (27) after the vacuum normal ordering step, so we have $\overbracket{a_q a^p} = -\lambda^p_q + \delta^p_q$.

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.[4]

4.2 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,[73] 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,[4] Evangelista,[5] and their coworkers in instead calling it the extended generalized Wick Theorem. The theorem is

$$\{A\}\{B\} = \{AB\} + \sum \{AB\} \tag{28}$$

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 (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 E.

The lemma is

$$\{...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u...\} = ...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u... - \sum ...\hat{q}_q\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u... - \sum ...\hat{q}_r\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u...$$
$$- \sum ...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u... + \sum ...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u... + \sum ...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u... - \sum ...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u... + ... \tag{29}$$

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 (29) reduces to (27).

We proceed to prove the case of $n = k + 1$ if (29) holds for all cases from 0 to k. We can solve for the completely normal ordered term in (27) to give:

$$\{...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u...\} = ...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u... - \sum\{...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u...\} - \sum\{...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u...\}$$
$$- \sum\{...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u...\} - \sum\{...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u...\} - \sum\{...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u...\} - \sum\{...\hat{q}_p\hat{q}_q\hat{q}_r\hat{q}_s\hat{q}_t\hat{q}_u...\} - ... \tag{30}$$

All the normal ordered terms on the right-hand side are previous cases in the induction, so we substitute in (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 (30) whose explicit contractions are among those t. The remaining contractions will be supplied by substituting (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

$$-\sum_{o=1}^{t}(1)^o(-1)^{t-o}\binom{t}{o} = -\big((1-1)^t - (-1)^t\big) = (-1)^t \tag{31}$$

by binomial expansion. All terms with a product of t contractions appear with coefficient $(-1)^t$. This proves (29).

As first observed by Kong, Nooijen, and Mukherjee,[3] the fact that the contractions are cumulants plays little role in the proof. All that we require is (27), from which (29) follows and then (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. (29) and (28) are just rearrangements of the contraction pattern of (27), however the contractions in (27) are defined.

This freedom to change contractions has been used by Evangelista and coworkers[71,74] 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.[1,75]

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 (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 2.1, 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.

5 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[27–29] are shown to reduce to our solution. Of special importance is the fact that this 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 com-

binatorial 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[27] 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 additive separability. 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,[1,71,74,75] 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.

A 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[42] and Simon[62] with the Möbius inversion of Speed.[76] 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

$$\sum_{x:y\supseteq x} f(x) = g(y) \quad , \tag{32}$$

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

$$\sum_{x:y\supseteq x} g(x)\mu(x,y) = f(y) \tag{33}$$

where the function μ is determined by the recursion relations

$$\sum_{x:z\supseteq x\supseteq y} \mu(y,x) = \delta_{y,z} \tag{34}$$

and

$$\sum_{x:z\supseteq x\supseteq y} \mu(x,z) = \delta_{y,z} \tag{35}$$

Equations (34) and (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 77, Chapter 8 of reference 54, Chapter 3 of reference 65, Chapter 3 of reference 78, and reference 79. We especially recommend reference 77.

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 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 1 demonstrates this for a

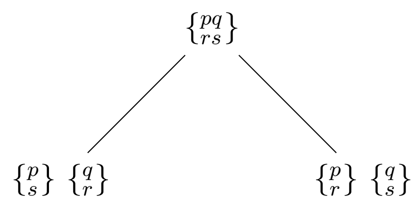

Figure 1: The fermionic partitions for a rank-two tensor. A vertical path between two elements ρ and π, where ρ is higher than π, means that $\rho \supseteq \pi$.

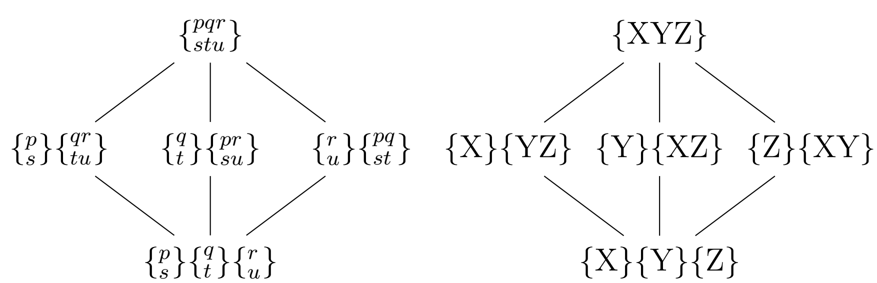

Figure 2: The fermionic partitions greater than or equal to $\{\substack{p\\s}\}\{\substack{q\\t}\}\{\substack{r\\u}\}$, and the set of partitions of three objects. A vertical path between two elements ρ and π, where ρ is higher than π, means that $\rho \supseteq \pi$. The two subsets and their order relations are isomorphic.

rank-two tensor.

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. 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

$$\mu(\sigma, \rho) = \prod_i (-1)^{b_i - 1}(b_i - 1)! \quad . \tag{36}$$

   The same property holds on the set of fermionic partitions, because the recursions that determine μ, (34) and (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 77, proved in two ways in Example 3.10.4 of Reference 64 and Examples 3.3.4 and 3.5.5 of Reference 78, then proved in two more ways in Sections 16 and 18 of Reference 79.

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 $\{XY\cdots\}$:

$$\sum_{\rho : \rho \wedge \pi = \sigma} \mu(\rho, \{XY\cdots\}) = 0 \quad . \tag{37}$$

This is proven in the course of Theorem 16.5 of reference 77 and by more sophisticated arguments in Proposition 3.5.4 of reference 78 and Corollary 3.9.3 of reference 64.

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

$$\sum_{\rho:\rho,\pi\supseteq\sigma,\rho\wedge\pi=\sigma} \mu(\rho,\{{}^{pq\cdots}_{rs\cdots}\}) = 0 \quad . \tag{38}$$

Now, suppose a polynomial satisfying the fermionic axioms. It must have the form of (20). Consider an arbitrary fermionic partition, π.

For most fermionic partitions, π has multiple blocks. Factorize every $\gamma(\rho)$ in (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

$$\mu_{\sigma,\pi} = \sum_{\rho:\rho,\pi\supseteq\sigma,\rho\wedge\pi=\sigma} \mu_\rho \quad . \tag{39}$$

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

$$\mu_{\sigma,\pi} = 0 \tag{40}$$

Choosing the coefficients c so that (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 $\sum\limits_{\rho\supseteq\pi} \mu_\rho = \mu_\pi = \mu_{\{{}^{pq\cdots}_{rs\cdots}\}} = 1$ by the normalization axiom.

In either case, we require

$$\sum_{\rho\supseteq\pi} \mu_\rho = \delta_{\pi,\{{}^{pq\cdots}_{rs\cdots}\}} \quad . \tag{41}$$

But this equation is just (35) when $z = \{{}^{pq\cdots}_{rs\cdots}\}$, which is precisely the recursion that determines $\mu(\rho, \{{}^{pq\cdots}_{rs\cdots}\})$. Using (36), we may immediately conclude

$$\mu_\sigma = \mu(\rho, \{{}^{pq\cdots}_{rs\cdots}\}) = (-1)^{\#\rho - 1}(\#\rho - 1)! \tag{42}$$

where $\#\rho$ is the number of blocks of ρ. This is precisely in agreement with (18).

While (42) is necessary, the connectedness axiom still requires that (40) holds. With a formula for the coefficients just derived, (40) reduces to

$$\sum_{\rho:\rho,\pi\supseteq\sigma,\rho\wedge\pi=\sigma} \mu(\rho, \{{}^{pq\cdots}_{rs\cdots}\}) = 0 \quad . \tag{43}$$

This equation is merely (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 (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

$$\lambda(\pi) = \sum_{\pi\supseteq\rho} \gamma(\rho)\mu(\rho, \pi) \tag{44}$$

but this is just (33) with $f(y) = \lambda(y)$ and $g(x) = \gamma(x)$. Because (33) is equivalent to (32), we have

$$\gamma(\pi) = \sum_{\pi\supseteq\rho} \lambda(\rho) \tag{45}$$

which is equivalent to relation (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 2.1. 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 65.) As evidence of this, observe that the Taylor-series expansion coefficients of the log-series are precisely (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.

B Explicit Formulas from Generating Functions

For pedagogical purposes, we explicitly derive Equation 19 from Equation (10).

First, order the orbital indices and restrict the summations in Equations (7) and (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 19.

Equation 18 may be derived from Equation (9) by the same reasoning, but instead using the fact that the degree n term of the Maclaurin series of $\exp(x)$ is $\frac{1}{n!}$.

C Exponentials in the Moment-Generating Function

Another obvious difference between the generating functions for the additively separable probabilistic (2) and fermionic (10) quantities is that the probabilistic multiplicatively separable generating function (1) uses an exponential that has no counterpart in the "generating function" for the fermionic multiplicatively separable quantity, (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 (18) and (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 (1) and (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 65.) This interpretation hinges on repeated application of the multiplication of exponential generating functions we discussed in Section 3.1. 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.

D Cumulants in Mukherjee's Proof of GNO

The original paper of Mukherjee[2] 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 14.) 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 4.1.

E Extended Generalized Wick's Theorem: Remaining Steps

To prove the extended generalized Wick Theorem, we expand the GNO operators on the left side of (28) into vacuum normal operators with (29), multiply them, and then convert the result back into GNO operators with (27). This is similar in concept to the proof of Kong, Nooijen, and Mukherjee,[3] but (29) simplifies the proof.

Take two Ψ-normal operators, A and B. The expansion via (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 (27), but the internal contractions may originate from (27) or (29). (27) always contributes a sign factor of 1, but the terms with n contractions from (29) contribute a sign factor of $(-1)^n$. Further, there are $\binom{i}{f}$ ways to choose which f internal contractions come from (27). So our total coefficient is

$$\sum_{f=0}^{i}(-1)^f(1)\binom{i}{f} \tag{46}$$

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

$$\sum_{f=0}^{i}(-1)^f(1)^{i-f}\binom{i}{f} = (1-1)^i = \begin{cases} 1 & i=0 \\ 0 & \text{else} \end{cases} \tag{47}$$

In other words, all contraction patterns happen exactly once, which contain no internal contractions. This is precisely the Extended Generalized Wick Theorem, (28).

Acknowledgement

We acknowledge support from the National Science Foundation, Grant No. CHE-1661604. We acknowledge helpful discussions with Professor Andreas Köhn and Dr. Mathias Hanauer regarding the interpretation of Reference 27, with Professor Francesco Evangelista on the generalized normal ordering formalism, and with Dr. Chenyang Li regarding typesetting contractions in generalized normal ordering.

References

(1) Kutzelnigg, W.; Mukherjee, D. Normal order and extended Wick theorem for a multi-configuration reference wave function. *J. Chem. Phys.* **1997**, *107*, 432–449.

(2) Mukherjee, D. Normal ordering and a Wick-like reduction theorem for fermions with respect to a multi-determinantal reference state. *Chem. Phys. Lett.* **1997**, *274*, 561–566.

(3) Kong, L.; Nooijen, M.; Mukherjee, D. An algebraic proof of generalized Wick theorem. *J. Chem. Phys.* **2010**, *132*, 234107.

(4) Sinha, D.; Maitra, R.; Mukherjee, D. Generalized antisymmetric ordered products, generalized normal ordered products, ordered and ordinary cumulants and their use in many electron correlation problem. *Comput. Theor. Chem.* **2013**, *1003*, 62–70.

(5) Li, C.; Evangelista, F. A. Multireference Driven Similarity Renormalization Group: A Second-Order Perturbative Analysis. *J. Chem. Theory Comput.* **2015**, *11*, 2097–2108.

(6) Mazziotti, D. A. Contracted Schrödinger equation: Determining quantum energies and two-particle density matrices without wave functions. *Phys. Rev. A* **1998**, *57*, 4219–4234.

(7) Mazziotti, D. A. Two-Electron Reduced Density Matrix as the Basic Variable in Many-Electron Quantum Chemistry and Physics. *Chem. Rev.* **2011**, *112*, 244–262.

(8) Piris, M.; Ugalde, J. M. Perspective on natural orbital functional theory. *Int. J. Quant. Chem.* **2014**, *114*, 1169–1175.

(9) Peng, R.; Copan, A. V.; Sokolov, A. Y. Simulating X-ray Absorption Spectra with Linear-Response Density Cumulant Theory. *J. Phys. Chem. A* **2019**, *123*, 1840–1850.

(10) Hollett, J. W.; Hosseini, H.; Menzies, C. A cumulant functional for static and dynamic correlation. *J. Chem. Phys.* **2016**, *145*, 084106.

(11) Hollett, J. W.; Loos, P.-F. Capturing static and dynamic correlation with ΔNO-MP2 and ΔNO-CCSD. *J. Chem. Phys.* **2020**, *152*, 014101.

(12) Mukherjee, D.; Kutzelnigg, W. Irreducible Brillouin conditions and contracted Schrödinger equations for n-electron systems. I. The equations satisfied by the density cumulants. *The Journal of Chemical Physics* **2001**, *114*, 2047–2061.

(13) Herbert, J. M.; Harriman, J. E. *Reduced-Density-Matrix Mechanics: With Application to Many-Electron Atoms and Molecules*; John Wiley & Sons, Inc., 2007; pp 261–292.

(14) Sokolov, A. Y.; Schaefer, H. F.; Kutzelnigg, W. Density cumulant functional theory from a unitary transformation: N-representability, three-particle correlation effects, and application to O_4^+. *J. Chem. Phys.* **2014**, *141*, 074111.

(15) Shavitt, I.; Bartlett, R. J. *Many-Body Methods in Chemistry and Physics*; Cambridge University Press, 2009.

(16) Paldus, J. Lecture Notes. University of Nijmegen, Holland. URL: https://www.math.uwaterloo.ca/ paldus/downloads/NijmegenLectures.pdf. Accessed, February 2020.

(17) Mahapatra, U. S.; Datta, B.; Bandyopadhyay, B.; Mukherjee, D. *Advances in Quantum Chemistry*; Elsevier, 1998; pp 163–193.

(18) Neuscamman, E.; Yanai, T.; Chan, G. K.-L. A review of canonical transformation theory. *Int. Rev. Phys. Chem.* **2010**, *29*, 231–271.

(19) Evangelista, F. A. Perspective: Multireference coupled cluster theories of dynamical electron correlation. *J. Chem. Phys.* **2018**, *149*, 030901.

(20) Li, C.; Evangelista, F. A. Multireference Theories of Electron Correlation Based on the Driven Similarity Renormalization Group. *Annu. Rev. Phys. Chem.* **2019**, *70*, 245–273.

(21) Harris, F. E. Cumulant-based approximations to reduced density matrices. *Int. J. Quant. Chem.* **2002**, *90*, 105–113.

(22) Nooijen, M.; Wladyslawski, M.; Hazra, A. Cumulant approach to the direct calculation of reduced density matrices: A critical analysis. *J. Chem. Phys.* **2003**, *118*, 4832–4848.

(23) Kong, L.; Valeev, E. F. A novel interpretation of reduced density matrix and cumulant for electronic structure theories. *J. Chem. Phys.* **2011**, *134*, 214109.

(24) Yasuda, K.; Nakatsuji, H. Direct determination of the quantum-mechanical density matrix using the density equation. II. *Phys. Rev. A* **1997**, *56*, 2648–2657.

(25) Schirmer, J. *Many-Body Methods for Atoms, Molecules and Clusters*; Springer International Publishing, 2018.

(26) Kubo, R. Generalized Cumulant Expansion Method. *J. Phys. Soc. Japan* **1962**, *17*, 1100–1120.

(27) Hanauer, M.; Köhn, A. Meaning and magnitude of the reduced density matrix cumulants. *Chem. Phys.* **2012**, *401*, 50–61.

(28) Kutzelnigg, W.; Mukherjee, D. Cumulant expansion of the reduced density matrices. *J. Chem. Phys.* **1999**, *110*, 2800–2809.

(29) Mazziotti, D. A. Approximate solution for electron correlation through the use of Schwinger probes. *Chem. Phys. Lett.* **1998**, *289*, 419–427.

(30) Ziesche, P. *Mathematical and Computational Chemistry*; Springer US, 2000; pp 33–56.

(31) Kutzelnigg, W. n-Electron problem and its formulation in terms ofk-particle density cumulants. *Int. J. Quant. Chem.* **2003**, *95*, 404–423.

(32) Kutzelnigg, W.; Mukherjee, D. Irreducible Brillouin conditions and contracted Schrödinger equations for n-electron systems. IV. Perturbative analysis. *J. Chem. Phys.* **2004**, *120*, 7350–7368.

(33) Mazziotti, D. A. 3,5-contracted Schrödinger equation: Determining quantum energies and reduced density matrices without wave functions. *Int. J. Quant. Chem.* **1998**, *70*, 557–570.

(34) Mazziotti, D. A. Comparison of contracted Schrödinger and coupled-cluster theories. *Phys. Rev. A* **1999**, *60*, 4396–4408.

(35) Mazziotti, D. A. *Mathematical and Computational Chemistry*; Springer US, 2000; pp 139–163.

(36) Mazziotti, D. A. *Reduced-Density-Matrix Mechanics: With Application to Many-Electron Atoms and Molecules*; John Wiley & Sons, Inc., 2007; pp 165–203.

(37) Korona, T. Two-particle density matrix cumulant of coupled cluster theory. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5698.

(38) Juhász, T.; Mazziotti, D. A. The cumulant two-particle reduced density matrix as a measure of electron correlation and entanglement. *J. Chem. Phys.* **2006**, *125*, 174105.

(39) Harriman, J. E. Reduced-density-matrix cumulants and correlation. *Phys. Rev. A* **2007**, *75*, 032513.

(40) 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.

(41) Equation A2 of Ref. 27 is the counterpart of Equation 11b of Ref. 28. These two equations contradict each other: the last two terms of A2 of Ref. 27 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. 28. The terms should exist by virtue of Equation 3b of Ref. 28. 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. 28 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. 27. However, this leads them to a much more complicated analysis. We are not aware of a simpler repair of the original proof of Ref. 28.

(42) Percus, J. K. Correlation inequalities for Ising spin lattices. *Commun. Math. Phys.* **1975**, *40*, 283–308.

(43) Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic-Structure Theory*; John Wiley & Sons, Ltd, 2000.

(44) Čížek, J. On the Correlation Problem in Atomic and Molecular Systems. Calculation of

Wavefunction Components in Ursell-Type Expansion Using Quantum-Field Theoretical Methods. *J. Chem. Phys.* **1966**, *45*, 4256–4266.

(45) Lehtola, S.; Tubman, N. M.; Whaley, K. B.; Head-Gordon, M. Cluster decomposition of full configuration interaction wave functions: A tool for chemical interpretation of systems with strong correlation. *J. Chem. Phys.* **2017**, *147*, 154105.

(46) McWeeny, R. Some Recent Advances in Density Matrix Theory. *Rev. Mod. Phys.* **1960**, *32*, 335–369.

(47) Lindgren, I. A coupled-cluster approach to the many-body perturbation theory for open-shell systems. *Int. J. Quant. Chem.* **2009**, *14*, 33–58.

(48) Solomon, A. I. Normal Ordering and Abnormal Nonsense. *Found. Phys.* **2009**, *40*, 684–691.

(49) Jeziorski, B.; Paldus, J. Valence universal exponential ansatz and the cluster structure of multireference configuration interaction wave function. *J. Chem. Phys.* **1989**, *90*, 2714–2731.

(50) Kutzelnigg, W.; Mukherjee, D. *Reduced-Density-Matrix Mechanics: With Application to Many-Electron Atoms and Molecules*; John Wiley & Sons, Inc., 2007; pp 293–330.

(51) Kutzelnigg, W. *Explicitly Correlated Wave Functions in Chemistry and Physics*; Springer Netherlands, 2003; pp 3–90.

(52) Stillwell, J. *Naive Lie Theory*; Springer New York, 2008.

(53) Wilf, H. S. *Generatingfunctionology*; Elsevier, 1990.

(54) Cameron, P. J. *Notes on Counting: An Introduction to Enumerative Combinatorics*; Cambridge University Press, 2017.

(55) Bozkaya, U.; Turney, J. M.; Yamaguchi, Y.; Schaefer, H. F.; Sherrill, C. D. Quadratically convergent algorithm for orbital optimization in the orbital-optimized coupled-cluster doubles method and in orbital-optimized second-order Møller-Plesset perturbation theory. *J. Chem. Phys.* **2011**, *135*, 104103.

(56) Bozkaya, U.; Sherrill, C. D. Orbital-optimized coupled-electron pair theory and its analytic gradients: Accurate equilibrium geometries, harmonic vibrational frequencies, and hydrogen transfer reactions. *J. Chem. Phys.* **2013**, *139*, 054104.

(57) Bozkaya, U. Analytic energy gradients for the orbital-optimized third-order Møller–Plesset perturbation theory. *J. Chem. Phys.* **2013**, *139*, 104116.

(58) Bozkaya, U.; Sherrill, C. D. Orbital-optimized MP2.5 and its analytic gradients: Approaching CCSD(T) quality for noncovalent interactions. *J. Chem. Phys.* **2014**, *141*, 204105.

(59) Mazziotti, D. A. Parametrization of the two-electron reduced density matrix for its direct calculation without the many-electron wave function: Generalizations and applications. *Phys. Rev. A* **2010**, *81*, 062515.

(60) DePrince, A. E.; Mazziotti, D. A. Connection of an elementary class of parametric two-electron reduced-density-matrix methods to the coupled electron-pair approximations. *Mol. Phys.* **2012**, *110*, 1917–1925.

(61) Lyakh, D. I.; Bartlett, R. J. Algebraic connectivity analysis in molecular electronic structure theory II: total exponential formulation of second-quantised correlated methods. *Mol. Phys.* **2013**, *112*, 213–260.

(62) Simon, B. *The Statistical Mechanics of Lattice Gases, Volume I (Princeton Legacy Library)*; Princeton University Press, 2016.

(63) Flajolet, P.; Sedgewick, R. *Analytic Combinatorics*; Cambridge University Press, 2009.

(64) Stanley, R. P. *Enumerative Combinatorics*; Cambridge University Press, 2009.

(65) Stanley, R. P.; Fomin, S. *Enumerative Combinatorics*; Cambridge University Press, 1999.

(66) Datta, D.; Kong, L.; Nooijen, M. A state-specific partially internally contracted multireference coupled cluster approach. *J. Chem. Phys.* **2011**, *134*, 214116.

(67) Datta, D.; Nooijen, M. Multireference equation-of-motion coupled cluster theory. *J. Chem. Phys.* **2012**, *137*, 204107.

(68) Demel, O.; Datta, D.; Nooijen, M. Additional global internal contraction in variations of multireference equation of motion coupled cluster theory. *J. Chem. Phys.* **2013**, *138*, 134108.

(69) Hanauer, M.; Köhn, A. Communication: Restoring full size extensivity in internally contracted multireference coupled cluster theory. *The Journal of Chemical Physics* **2012**, *137*, 131103.

(70) Li, C.; Evangelista, F. A. Driven similarity renormalization group: Third-order multireference perturbation theory. *J. Chem. Phys.* **2017**, *146*, 124132.

(71) Li, C.; Evangelista, F. A. Driven similarity renormalization group for excited states: A state-averaged perturbation theory. *J. Chem. Phys.* **2018**, *148*, 124106.

(72) Yanai, T.; Chan, G. K.-L. Canonical transformation theory from extended normal ordering. *J. Chem. Phys.* **2007**, *127*, 104107.

(73) Brouder, C.; Fauser, B.; Frabetti, A.; Oeckl, R. Quantum field theory and Hopf algebra cohomology. *J. Phys. A* **2004**, *37*, 5895–5927.

(74) Li, C.; Lindh, R.; Evangelista, F. A. Dynamically weighted multireference perturbation theory: Combining the advantages of multi-state and state-averaged methods. *J. Chem. Phys.* **2019**, *150*, 144107.

(75) Kutzelnigg, W.; Shamasundar, K.; Mukherjee, D. Spinfree formulation of reduced density matrices, density cumulants and generalised normal ordering. *Molecular Physics* **2010**, *108*, 433–451.

(76) Speed, T. P. Cumulants and Partition Lattices. *Aust. N. Z. J. Stat.* **1983**, *25*, 378–388.

(77) Bóna, M. *A Walk Through Combinatorics*; WORLD SCIENTIFIC, 2016.

(78) Martin, J. L. Lecture Notes. University of Kansas, United States. URL: http://jlmartin.faculty.ku.edu/CombinatoricsNotes.pdf. Accessed, March 2020.

(79) Godsil, C. Lecture Notes. University of Waterloo, Canada. URL: https://arxiv.org/abs/1803.06664v1. Accessed, March 2020.

Graphical TOC Entry

Additively separable

$$1 + C = \{\exp(T)\}; 1 + \gamma = \{\exp(\lambda)\}$$

Multiplicatively separable

$$C = {\tfrac{1}{1!}}^2 c_a^i a_i^a + {\tfrac{1}{2!}}^2 c_{ab}^{ij} a_{ij}^{ab} + ...$$

$$\gamma = {\tfrac{1}{1!}}^2 \gamma_q^p a_p^q + {\tfrac{1}{2!}}^2 \gamma_{rs}^{pq} a_{pq}^{rs} + ...$$