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Comparison of contracted Schrödinger and coupled-cluster theories

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The theory of the contracted Schrödinger equation (CSE) [D. A. Mazziotti, Phys. Rev. A **57**, 4219 (1998)] is connected with traditional methods of electronic structure including configuration-interaction (CI) and coupled-cluster (CC) theory. We derive a transition contracted Schrödinger equation (TCSE) which depends on the wave function ψ as well as another N-particle function χ through the two-, three-, and four-particle reduced transition matrices (RTMs). By reconstructing the 3 and 4 RTMs approximately from the 2-RTM, the indeterminacy of the equation may be removed. The choice of the reconstruction and the function χ determines whether one obtains the CI, CC, or CSE theory. Through cumulant theory and Grassmann algebra we derive reconstruction formulas for the 3- and 4-RTMs which generalize both the reduced density matrix (RDM) cumulant expansions as well as the exponential ansatz for the CC wave function. This produces a fresh approach to CC theory through RTMs. Two theoretical differences between the CC and the CSE theories are established for energetically nondegenerate states: (i) while the CSE has a single exact solution when the 3- and 4-RDMs are N-representable, the CC equations with N-representable 3- and 4-RTMs have a family of solutions. Thus, N-representability conditions offer a medium for improving the CSE solution but not the CC solution, and (ii) while the 2-RDM for an electronic Hamiltonian reconstructs to unique N-representable 3- and 4-RDMs, the 2-RTM builds to a family of N-representable 3- and 4-RTMs. Hence, renormalized reconstructions beyond the cumulant expansion may be developed for the 2-RDM but not for the 2-RTM without explicit use of the Hamiltonian. In the applications we implement our recently developed reconstruction formula for the 3-RDM which extends beyond the cumulant approximation. Calculations compare the 3-RDM and 3-RTM reconstructions for the molecules LiH, BeH_2, BH_3, and H_2O as well as for systems with more general two-particle interactions. The TCSE offers a unified approach to electronic structure.
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I. INTRODUCTION

The quantum-mechanical wave function of an N-electron system contains much more information than is required to compute the expectation values for most observables. Because the interactions between electrons are pairwise within the Hamiltonian, the energy may be determined exactly through a knowledge of the two-particle reduced density matrix (2-RDM) [1,2]. Unlike the unknown dependence of the energy on the one-particle density in density functional theory (DFT) [3], the dependence of the energy on the 2-RDM is linear. The 2-RDM, however, has not replaced the wave function as the fundamental parameter for many-body calculations because not every two-particle density matrix is derivable from an N-particle wave function. The need for a simple set of necessary and sufficient conditions for ensuring that the 2-RDM may be represented by an N-particle wave function is known as the N-representability problem [4,5].

The contracted Schrödinger equation (CSE) [6–15] has recently offered a new approach to constraining the 2-RDM to be approximately N-representable. An integro-differential version of the CSE was originally derived by Cohen and Frishberg [16] and Nakatsuji [17] in 1976. Harriman presented a matrix formulation in 1979 [18], and Valdemoro gave a second-quantized CSE at the density matrix symposium at Queens University in 1985 [19]. Without additional conditions the CSE, however, cannot be solved for the 2-RDM because the CSE also depends on the 3- and 4-RDMs. In 1993 Valdemoro and her collaborators removed the indeterminacy of the CSE by building the 3- and 4-RDMs approximately from the 2-RDM through the particle-hole duality [13,14]. These formulas were utilized with the CSE by Colmenero and Valdemoro to compute the ground-state energy for beryllium and its isoelectronic sequence [20]. In 1996 Nakatsuji and Yasuda improved Valdemoro's reconstruction functionals for the 3- and 4-RDMs with arguments from the theory of Green's functions and applied these formulas with the CSE to atoms and molecules with as many as fourteen electrons [10,11]. In 1998 we further systematized the reconstruction functionals for RDMs by generating the functionals through the theory of cumulants and Grassmann algebra [6–8]. We also derived a new strategy for improving the 3-RDM functional and applied this technique to solving the CSE for a quasispin model with as many as 50 fermions. Energies were as accurate as those from single-double configuration interaction (SDCI), and the 2-RDMs were an order of magnitude more accurate than SDCI. The CSE converts the N-representability problem for the 2-RDM into a problem involving the reconstruction of the 3- and 4-RDMs from the 2-RDM.

In the present paper the theory of the CSE is connected with standard techniques in electronic structure [21], configuration-interaction (CI) and coupled-cluster (CC) theory [22–24], through the *transition* contracted Schrö-

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dinger equation (TCSE). A generalization of the N-particle density matrix $\psi\psi^*$ is the transition matrix $\chi\psi^*$ involving the two N-particle wave functions χ and ψ. Contraction of the transition matrix produces the reduced transition matrices (RTMs) [1]. We derive the TCSE which by analogy with the CSE depends on the 2-, 3-, and 4-RTMs. The indeterminacy of the TCSE may be removed by building the 3- and 4-RTMs as functionals of the 2-RTMs. Two special cases for χ are considered: (i) when χ equals the exact wave function ψ and (ii) when χ equals a single Slater determinant wave function ψ_{Slater} such as the Hartree-Fock wave function. In the first case the TCSE reduces to the familiar CSE with its RDMs as parameters. The second scenario generates a TCSE whose RTMs may be related to the CI excitation coefficients. From this relationship pure N-representability conditions for these RTMs may be determined. A RTM is pure N representable when it may be defined by two N-particle wave functions χ and ψ through integration of the kernel $\chi\psi^*$ [1]. Unlike the CSE the TCSE with $\chi=\psi_{\mathrm{Slater}}$ has many N-representable solutions including both the SDCI and the exact solutions.

Size-consistent reconstruction functionals for the 3- and 4-RTMs are derivable through the theory of cumulants [7,8,25,26]. A p-RTM is divided into two parts: an unconnected part which may be expressed as antisymmetrized products of lower RTMs and a connected (or cumulant) part. The cumulant portion of the p-RTM vanishes if any of the p particles are statistically independent of the other particles. Using machinery from quantum field theory like generating functionals and Schwinger probes [27] as well as Grassmann algebra [28], we derive all of the unconnected terms for any RTM. Because the connected term of the p-RTM vanishes through the $(p-1)$th order of many-body perturbation theory (MBPT), the unconnected reconstruction formulas for the 3- and 4-RTMs are accurate through the first and second orders of MBPT, respectively. This derivation generalizes the cumulant functionals for RDMs which were presented recently [7,8,26]. By deriving higher transition amplitudes in terms of lower transition amplitudes in coupled-cluster theory with Grassmann algebra, we show that the TCSE with the unconnected reconstruction functionals for the 3,4-RTMs when $\chi=\psi_{\mathrm{Slater}}$ is equivalent to single-double CC (CCSD) theory. More generally, we have that the reconstruction functionals produce RTMs when $\chi=\psi_{\mathrm{Slater}}$ that are N-representable with wave functions equal to the exponential ansatz for ψ in CCs [22,23]. Thus, TCSEs involving higher RTMs may also be derived, and decoupling these RTMs into the appropriate lower RTMs generates TCSE methods that reproduce the various levels of approximation in CC theory from CCSD to full CI for the one-particle basis under consideration. We, therefore, have a new approach to expressing CC theory through RTMs.

Theoretical and practical aspects of moving beyond the accuracy of the unconnected cumulant reconstruction functionals are discussed. Rosina's theorem proves the existence of exact reconstruction of higher RDMs from a nondegenerate ground-state 2-RDM when the underlying but possibly *unknown* Hamiltonian has only one- and two-particle interactions [6,29]. This theorem guarantees that only the 2-RDM is required. We present an explicit formula for building a 3-RDM beyond its cumulant expansion to achieve second-order accuracy in MBPT. This improvement in the 3-RDM formula is important because it makes the accuracy of the 3-RDM consistent with that of the 4-RDM from an unconnected reconstruction. In another paper [9] this correction is shown to be more accurate than the correction proposed by Nakatsuji and Yasuda through the theory of Green's functions [10,11]. A similar improvement for the 3-RTM functional with $\chi=\psi_{\mathrm{Slater}}$ beyond the cumulant expansion does not exist. Unlike the scenario for the 2-RDM we may show that the 2-RTM does not contain enough information to determine the higher RTMs uniquely without detailed information about the Hamiltonian. This represents a significant difference between the CSE and CC theories which may eventually have profound computational consequences. Theoretically, the CSE may be solved for the exact 2-RDM with suitable N-representability or reconstruction constraints, but the CC method cannot determine the correct 2-RTM or transition amplitudes without employing higher RTMs or supplementing the calculation with perturbation theory. Calculations using Hamiltonians with randomly generated two-particle interactions will be employed to illustrate and compare the present implementations of the CSE and CC theories. By connecting the CI, CC, MBPT, and CSE, the TCSE theory offers a fresh approach to unifying the ideas of electronic structure.

II. TRANSITION CSE EQUATIONS

Beginning with the Schrödinger equation, we derive the TCSE which is a generalization of the CSE. The relationship of the TCSE with the configuration interaction is elucidated through RTMs involving both Slater and exact wave functions. In the final section we demonstrate that Nakatsuji's theorem for the CSE is not generally valid for the TCSE.

A. Derivation of the TCSE

A quantum system of N fermions may be described by the Schrödinger equation (SE)

$$H|\psi\rangle=E|\psi\rangle, \tag{1}$$

where the wave function ψ depends on the coordinates for the N particles. In second quantization [30] the Hamiltonian operator may be written as

$$H=\frac{1}{2}\sum_{i_3,i_4;j_3,j_4} {}^2K^{i_3,i_4}_{j_3,j_4} a^\dagger_{i_3} a^\dagger_{i_4} a_{j_4} a_{j_3}, \tag{2}$$

in which ${}^2K$ is the two-particle reduced Hamiltonian. Define the functions $\langle\Phi^{i_1,i_2}_{j_1,j_2}|$ to test the two-electron space,

$$\langle\Phi^{i_1,i_2}_{j_1,j_2}|=\langle\chi|a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1}, \tag{3}$$

where χ is a wave function which may be different from the system's wave function ψ. Forming the inner product of the test functions with the SE yields

$$\langle\chi|a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1} H|\psi\rangle=E\langle\chi|a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1}|\psi\rangle=2E\,{}^2D^{i_1,i_2}_{j_1,j_2}. \tag{4}$$

The symbol ${}^2D^{i_1,i_2}_{j_1,j_2}$ represents the elements of the two-particle *transition* matrix (2-RTM) between the states χ and ψ:

$$ {}^2D^{i_1,i_2}_{j_1,j_2}=\frac{1}{2!}\langle\chi|a^{\dagger}_{i_1}a^{\dagger}_{i_2}a_{j_2}a_{j_1}|\psi\rangle. \tag{5}$$

The general definition for the p-RTM in second quantization is

$$ {}^pD^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p}=\frac{1}{p!}\langle\chi|a^{\dagger}_{i_1}a^{\dagger}_{i_2}\cdots a^{\dagger}_{i_p}a_{j_p}a_{j_{p-1}}\cdots a_{j_1}|\psi\rangle, \tag{6}$$

whose normalization is $N!/(p!(N-p)!)\langle\chi|\psi\rangle$.

Let us replace the Hamiltonian operator in Eq. (4) with its definition in Eq. (2) to obtain

$$\sum_{i_3,i_4,j_3,j_4} {}^2K^{i_3,i_4}_{j_3,j_4}\langle\chi|a^{\dagger}_{i_1}a^{\dagger}_{i_2}a_{j_2}a_{j_1}a^{\dagger}_{i_3}a^{\dagger}_{i_4}a_{i_4}a_{i_3}|\psi\rangle=4E\,{}^2D^{i_1,i_2}_{j_1,j_2}. \tag{7}$$

We then rearrange the creation and annihilation operators on the left-hand side to generate RTMs. This gives us the 2,4-CSE for transition matrices (2,4-TCSE),

$$\sum_{i_3,i_4,j_3,j_4} {}^2K^{i_3,i_4}_{j_3,j_4}R^{i_1,i_2,i_3,i_4}_{j_1,j_2,j_3,j_4}=4E\,{}^2D^{i_1,i_2}_{j_1,j_2}, \tag{8}$$

where

$$\begin{aligned} R^{i_1,i_2,i_3,i_4}_{j_1,j_2,j_3,j_4}={}&4!\,{}^4D^{i_1,i_2,i_3,i_4}_{j_1,j_2,j_3,j_4}\\ &+3!({}^3D^{i_1,i_2,i_3}_{j_2,j_3,j_4}\delta^{i_4}_{j_1}-{}^3D^{i_1,i_2,i_3}_{j_1,j_3,j_4}\delta^{i_4}_{j_2})\\ &+3!({}^3D^{i_1,i_2,i_4}_{j_1,j_3,j_4}\delta^{i_3}_{j_2}-{}^3D^{i_1,i_2,i_4}_{j_2,j_3,j_4}\delta^{i_3}_{j_1})\\ &+2!\,{}^2D^{i_1,i_2}_{j_3,j_4}(\delta^{i_3}_{j_1}\delta^{i_4}_{j_2}-\delta^{i_3}_{j_2}\delta^{i_4}_{j_1}). \end{aligned} \tag{9}$$

While this TCSE becomes the CSE when $\chi=\psi$, the CSEs from previous papers [6,20] may not be converted into the TCSE by replacing the RDMs with RTMs because the rearrangement of the second-quantized operators in these papers use the Hermiticity of the RDMs. A 1,3-TCSE may also be derived by replacing the doubly excited test functions in Eq. (3) with test functions formed by single excitations of the reference wave function χ. Similarly, a 3,5-TCSE and a 4,6-TCSE may be created with test functions using triple and quadruple excitations, respectively. In this paper we use the notation CSE and TCSE to denote the 2,4-CSE and 2,4-TCSE.

B. Relationship with the CI

Two choices for χ will be especially important for bridging the CI, CC, and CSE theories: (i) χ equals the exact wave function ψ, and (ii) χ equals any Slater determinant wave function ψ_{Slater} such as the Hartree-Fock wave function. The first choice produces the CSE in terms of the 2-, 3-, and 4-RDMs. As shown in previous work the CSE alone is indeterminate, but through approximate reconstruction of the 3- and 4-RDMs in terms of the 2-RDM we can solve the CSE for an accurate 2-RDM [6,20]. The second choice, however, generates a TCSE in terms of 2-, 3-, and 4-RTMs between the Slater and the exact ψ wave functions. The exact wave function may be defined as a sum of excitations from the Slater reference. Let $\{o_1,o_2,\ldots\}$ represent the set of occupied Slater orbitals and $\{v_1,v_2,\ldots\}$ represent the set of unoccupied (virtual) Slater orbitals. The wave function ψ may then be written as

$$\begin{aligned} |\psi\rangle=\Bigg(&1+\sum_{v_1,o_1}{}^1c^{v_1}_{o_1}a^{\dagger}_{v_1}a_{o_1}\\ &+\sum_{o_1<o_2,v_1<v_2}{}^2c^{v_1,v_2}_{o_1,o_2}a^{\dagger}_{v_1}a^{\dagger}_{v_2}a_{o_2}a_{o_1}+\cdots\Bigg)|\psi_{\text{Slater}}\rangle. \end{aligned} \tag{10}$$

With this definition $\langle\psi_{\text{Slater}}|\psi\rangle$ equals unity which is known as the intermediate normalization.

Relations between the RTMs in Eq. (6) with $\chi=\psi_{\text{Slater}}$ and the CI coefficients may be derived. If we substitute this configuration-interaction expansion for ψ into the expression for the 1-RTM,

$$ {}^1D^{o_1}_{v_1}=\langle\psi_{\text{Slater}}|a^{\dagger}_{o_1}a_{v_1}|\psi\rangle, \tag{11}$$

we obtain after rearranging the creation and annihilation operators that

$$ {}^1D^{o_1}_{v_1}={}^1c^{v_1}_{o_1}. \tag{12}$$

The other nonzero elements of the 1-RTM are

$$ {}^1D^{o_1}_{o_1}=1, \tag{13}$$

and they ensure that the 1-RTM contracts with the correct normalization N. In general the elements of the p-RTM correspond to p-particle excitation coefficients according to the relationship

$$ {}^pD^{o_1,o_2,\ldots o_p}_{v_1,v_2,\ldots v_p}=\frac{1}{p!}\,{}^pc^{v_1,v_2,\ldots v_p}_{o_1,o_2,\ldots o_p}. \tag{14}$$

As in the case of the 1-RTM, the other nonvanishing elements in the p-RTM correspond to q-particle excitation coefficients with $q<p$:

$$ {}^pD^{o_1,\ldots,o_q,o_{q+1},\ldots,o_p}_{v_1,\ldots,v_q,o_{q+1},\ldots,o_p}=\frac{1}{p!}\,{}^qc^{v_1,v_2,\ldots v_q}_{o_1,o_2,\ldots o_q}. \tag{15}$$

Defining the RTMs in terms of the CI expansion coefficients automatically keeps them N-representable.

Using relations (14) and (15), we can formulate the N-representability conditions on the p-RTM without reference to the CI expansion coefficients. By substituting Eq. (14) into Eq. (15), we obtain (i) the following equations relating elements of the p-RTM to elements of the q-RTM where $q<p$:

$$ {}^pD^{o_1,\ldots,o_q,o_{q+1},\ldots,o_p}_{v_1,\ldots,v_q,o_{q+1},\ldots,o_p}=\frac{q!}{p!}\,{}^qD^{o_1,o_2,\ldots o_q}_{v_1,v_2,\ldots v_q}. \tag{16}$$

The remaining condition (ii) simply stipulates that the elements not defined by Eqs. (14) and (15) must be zero. Unlike the 2-RDM whose necessary and sufficient N-representability conditions remain unknown, the conditions on these special 2-RTMs with $\chi=\psi_{\text{Slater}}$ are very simple and easily applied.

In a CI calculation the expansion of ψ in Eq. (10) is truncated after a certain number of excitations are included by setting the higher expansion coefficients to zero. A CI method with single and double excitations (SDCI) may be produced through the TCSE if we set the elements of the 3- and 4-RTMs, corresponding to the three- and four-particle excitation coefficients in Eq. (14) to zero and enforce the N-representability conditions. Similarly, the CI scheme with p-particle excitations may be formed by deriving the TCSE with the p-, $(p+1)$-, and $(p+2)$-RTMs and setting the elements of the $(p+1)$- and $(p+2)$-RTMs, which correspond to $(p+1)$ and $(p+2)$ excitations, to zero. Hence, the TCSE formalism includes the CI calculations from the SDCI to the full configuration interaction (FCI). The truncated CI approximation, however, is not *size consistent* [21,22] because higher excitations are assumed to vanish. Better strategies for reconstructing the 3- and 4-RTMs will be established in Sec. III A.

C. *N*-representable solutions of the TCSE

If the RDMs in the CSE are pure N-representable, then the CSE may be satisfied if and only if the wave function ψ associated with the representable RDMs satisfies the Schrödinger equation. This theorem was first proved for the integro-differential CSE by Nakatsuji in 1976 [17], and we recently demonstrated the proof for the second-quantized CSE [6]. The proof follows from showing that if the RDMs are pure N-representable, the CSE implies the dispersion condition

$$\langle\psi|H^2|\psi\rangle-\langle\psi|H|\psi\rangle^2=0, \tag{17}$$

which is valid if and only if the SE is satisfied. For the CSE Nakatsuji's theorem guarantees that a solution for a nondegenerate energy in the set of pure N-representable matrices must correspond to a solution of the SE. Hence, approximate reconstruction schemes that satisfy the CSE must yield only approximately N-representable RDMs.

Because the N-representability conditions for the RTMs with $\chi=\psi_{\text{Slater}}$ were derived in Sec. II B, an extension of Nakatsuji's theorem to the TCSE would allow us to solve for the exact 2-, 3-, and 4-RTMs. We can show that if the RTMs are pure N-representable, the TCSE implies the relation

$$\langle\chi|H^2|\psi\rangle-E\langle\chi|H|\psi\rangle=0. \tag{18}$$

Unlike the dispersion condition in Eq. (17), however, this equation does not necessarily imply the SE. Thus, Nakatsuji's theorem cannot be extended to all TCSEs. Since the RTMs for the CI and CC are pure N-representable, an extension of Nakatsuji's theorem to the RTMs would also imply incorrectly that SDCI is not a solution of the TCSE. Satisfaction of the N particle SE in the case of the CSE depends on the strength of the N-representability conditions which may be in the form of reconstruction functionals, but with the TCSE when $\chi=\psi_{\text{Slater}}$ the correspondence with the SE is not limited by N-representability but rather by the accuracy of the test function ψ_{Slater} as an approximation to the correlated wave function ψ.

III. RECONSTRUCTION OF RTMs WITH CUMULANTS

With the theory of cumulants and Grassmann algebra reconstruction functionals for the RTMs are derived. We show that the reconstructed 3- and 4-RTMs for $\chi=\psi_{\text{Slater}}$ are N representable with model wave functions which correspond to the exponential wave functions in coupled-cluster theory [22,23]. In Sec. III C we discuss the theoretical differences in reconstructing from the 2-RDM and the 2-RTM where $\chi=\psi_{\text{Slater}}$ through Rosina's theorem, and in the final section an explicit formula is presented for improving the estimate for the 3-RDM beyond its unconnected cumulant expansion.

A. Derivation of RTM functionals

From the theory of cumulants [7,25] we can derive reconstruction functionals for the *transition* matrices between the N-particle quantum states χ and ψ. We first construct a functional whose derivatives with respect to probe variables generate the RTMs in second quantization. Each derivative of the functional should supply a creation or annihilation operator in the RTM. This constraint leads us to the following exponential form:

$$G(J)=\left\langle \chi\left| O\left[\exp\left(\sum_k J_k a_k^\dagger + J_k^* a_k\right)\right]\right|\psi\right\rangle, \tag{19}$$

where the J_k and its conjugate J_k^* are Schwinger probe variables [7,27]. The Schwinger probes anticommute for fermions, $\{J_k,J_l\}=0$. The symbol J is used to represent the whole set of probe variables $\{J_k\}$. Differentiation of $G(J)$ with respect to the probes causes creation and annihilation operators to accumulate before the exponential. Since the creation and annihilation operators do not commute, a specific ordering must be chosen for which these operators appear before the exponential upon differentiation. To form functionals for RTMs, we define that the creation operators always appear to the left of the annihilation operators regardless of the order in which we differentiate with respect to the probes. Represented by the ordering operator O in the definition of $G(J)$, this ordering process is analogous to the time ordering of the creation and annihilation operators in the theory of Green's functions [27].

Differentiation of $G(J)$ with respect to the Schwinger probes produces the RTMs as follows:

$${}^pD^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p}=\lim_{J\to 0}\frac{1}{p!}\frac{\partial^p G}{\partial J_{i_p}\cdots\partial J_{i_2}\partial J_{i_1}\partial J^*_{j_1}\cdots\partial J^*_{j_{p-1}}\partial J^*_{j_p}} \tag{20}$$

$$=\frac{1}{p!}\langle\chi|a^\dagger_{i_1}a^\dagger_{i_2}\cdots a^\dagger_{i_p}a_{j_p}a_{j_{p-1}}\cdots a_{j_1}|\psi\rangle. \tag{21}$$

The elements of the RTMs are the coefficients of the multivariable Taylor series expansion of $G(J)$ about the point where the Schwinger probes vanish. Hence, $G(J)$ is the *generating functional* for RTMs. Mathematically, the RTMs of the functional $G(J)$ are known as the *moments*. The moment-generating functional $G(J)$ may be used to define another functional $W(J)$, known as the cumulant-generating functional, by the relation

$$G(J)=\exp[W(J)]. \tag{22}$$

Just as the moments are formed from $G(J)$ in Eq. (21), the *cumulants* ${}^{p}\Delta$ are produced from $W(J)$ by

$${}^{p}\Delta^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p}=\lim_{J\to 0}\frac{1}{p!}\,\frac{\partial^{p}W}{\partial J_{i_p}\cdots\partial J_{i_2}\partial J_{i_1}\partial J^{*}_{j_1}\cdots\partial J^{*}_{j_{p-1}}\partial J^{*}_{j_p}}, \tag{23}$$

and the cumulants are defined as the coefficients of the multivariable Taylor series expansion of $W(J)$ about the point where the Schwinger probes vanish. The presentation of another generating functional $W(J)$ in Eq. (22) may seem superfluous. The set of cumulants ${}^{p}\Delta$ with p between 1 and q has the same information as the set of moments ${}^{p}D$ with the same range for p, but the information is expressed differently. This different expression of information will allow us to determine approximate functionals for reconstructing higher RTMs from lower RTMs.

Cumulants have the special property that they vanish if and only if at least one of their particles is statistically independent of the rest [25]. Hence, in a mean-field approximation (Hartree-Fock) where each of the N particles is treated independently all cumulants except ${}^{1}\Delta$ vanish. The p-particle cumulant ${}^{p}\Delta$ represents the part of the p-RTM which cannot be written as an antisymmetrized product of lower RTMs. This allows us to decompose a p-RTM into two pieces: (i) the *unconnected* part ${}^{p}D_{\rm uc}$ that may be written as antisymmetrized products of the lower RTMs, and (ii) the *connected*, or cumulant, part ${}^{p}\Delta$ which may not be expressed as a sum of products of lower RTMs. All the particles of the cumulant are *connected* by the pairwise interactions between the particles. The p-RTM may be written in terms of ${}^{q}\Delta$ for q between 1 and p if we differentiate Eq. (22) with respect to the Schwinger probes as in Eq. (20) and take the limit as the probes approach zero. The derivatives of the generating functional $G(J)$ create the p-RTM, and the differentiation of exp(W) on the right side creates products of elements from the connected RTMs according to Eq. (23). Because the upper and lower indices must permute antisymmetrically in a formula for the elements of the p-RTM, the products between elements of the connected RTMs may be replaced with Grassmann wedge products.

For the 1-RTM we obtain simply that the 1-RTM is equal to ${}^{1}\Delta$ since there cannot be any unconnected terms. In the case of Hartree-Fock wave functions χ and ψ all of the higher RTMs are determined by the 1-RTM since the higher connected RTMs vanish. Reconstruction formulas for the p-RTMs, generated by differentiation of Eq. (22), are summarized for $p\leqslant 4$ in Table I. The p upper and p lower indices of a p-RTM are suppressed for notational convenience. The symbol $\wedge$ indicates the Grassmann wedge product which is determined by summing all of the products generated from the antisymmetric permutation of the upper and lower indices and then dividing by the number of products in the sum [6,28]. The wedge product produces an RTM that is antisymmetric in its upper and lower indices in accordance with the Pauli principle. Right superscripts n indicate that a RDM or its connected part should be wedged with itself n times. The portion of the unconnected 4-RTM which may be written in terms of the 1- and 2-RTMs only is denoted by ${}^{4}D_{\rm uc,p}$. While these formulas are exact, the formulas do not show us how to approximate the connected p-RTM ${}^{p}\Delta$ from a knowledge of the $(p-1)$-RTM.

TABLE I. Reconstruction functionals for RTMs.

$${}^{1}D={}^{1}\Delta$$
$${}^{2}D={}^{1}D\wedge{}^{1}D+{}^{2}\Delta$$
$${}^{3}D={}^{1}D^{3}+3\;{}^{2}\Delta\wedge{}^{1}D+{}^{3}\Delta$$
$${}^{4}D=4\;{}^{3}\Delta\wedge{}^{1}D+{}^{4}D_{\rm uc,p}+{}^{4}\Delta$$
where
$${}^{4}D_{\rm uc,p}={}^{1}D^{4}+6\;{}^{2}\Delta\wedge{}^{1}D^{2}+3\;{}^{2}\Delta\wedge{}^{2}\Delta$$

The reconstruction functionals are significantly renormalized many-body perturbation expansions. Since exact lower RTMs (or guesses to the exact lower RTMs when we are iterating with the TCSE) are used in the functionals, contributions from *all* orders of perturbation theory are incorporated into the reconstructed RTMs. The reconstruction accounts exactly for configurations where at least one particle is statistically isolated from the others. All of the error arises from our imprecise knowledge of ${}^{p}\Delta$. For a Hamiltonian with no more than two-particle interactions the connected p-RTM will have its first nonvanishing term in the $(p-1)$ order of many-body perturbation theory. This follows because the minimum number of pairwise potentials V required to connect p particles completely is $(p-1)$. Thus, as the number of particles p in the reconstructed RTM increases, the accuracy of the functional approximation improves. The unconnected reconstruction formula for the 2-RTM in Table I is equivalent to the Hartree-Fock approximations for χ and ψ since it assumes that the two particles are statistically independent. Correlation corrections first appear in the unconnected 3-RTM functional which is correct through first order of MBPT, and the unconnected 4-RTM functional is correct through second order of MBPT.

B. Relation with coupled-cluster wave functions

Within CC theory the fundamental variables are the transition amplitudes, and yet in the TCSE the RTMs with $\chi=\psi_{\rm Slater}$ are the primary variables. By using Grassmann algebra to express the transition amplitudes for p particles in terms of transition amplitudes for fewer particles, we will elucidate a simple relation between the transition amplitudes and the connected RTMs. It follows that reconstruction formulas for RTMs like those in Table I are equivalent to assuming an exponential ansatz for the wave function as in CC theory [24].

The parametrization of the higher CI coefficients in terms of the lower CI coefficients (or their corresponding transition amplitudes) is accomplished in CC theory by exponentiation of the excitation operators. Thus, the exact CC wave function is written as

$$|\psi_{\rm CC}\rangle = \exp(T)|\psi_{\rm Slater}\rangle, \tag{24}$$

where

$$T = T_1 + T_2 + T_3 + \cdots, \tag{25}$$

$$T_p = \frac{1}{(p!)^2} \sum_{o_1,\ldots,o_p,v_1,\ldots,v_p} {}^p t^{v_1,\ldots,v_p}_{o_1,\ldots,o_p} \times a^\dagger_{v_1}\cdots a^\dagger_{v_p} a_{o_p}\cdots a_{o_1}, \tag{26}$$

and the ${}^p t^{v_1,\ldots,v_p}_{o_1,\ldots,o_p}$ are transition amplitudes. With all excitations included the CC wave function is equivalent to the full CI wave function. Expansion of the exponential yields

$$\exp(T) = 1 + T_1 + \left(T_2 + \frac{1}{2}T_1^2\right) + \left(T_3 + T_1T_2 + \frac{1}{6}T_1^3\right) + \cdots, \tag{27}$$

in which we have collected the terms that correspond to the usual CI excitation operators. We may concisely express the CI expansion coefficients in Eq. (10) in terms of the transition amplitudes ${}^p t^{v_1,\ldots,v_p}_{o_1,\ldots,o_p}$ in Eq. (26) through the use of Grassmann wedge products.

To derive the relationship between the CI coefficients and transition amplitudes, we rewrite the terms in the expanded exponential (27) so that they may be matched with the CI coefficients in Eq. (10). We illustrate this procedure by considering the term T_1^2:

$$T_1^2 = \sum_{o_1,o2,v_1,v_2} ({}^1t^{v_1}_{o_1}\,{}^1t^{v_2}_{o_2}) a^\dagger_{v_1} a_{o_1} a^\dagger_{v_2} a_{o_2}. \tag{28}$$

The second-quantized operators are rearranged to correspond to the ordering in Eq. (10). Replacing the simple product of transition amplitudes in Eq. (28) with a Grassmann wedge product does not alter the expression which must be antisymmetric in its indices:

$$T_1^2 = \sum_{o_1,o2,v_1,v_2} ({}^1t^{v_1}_{o_1} \wedge {}^1t^{v_2}_{o_2}) a^\dagger_{v_1} a^\dagger_{v_2} a_{o_2} a_{o_1}. \tag{29}$$

Each term in the above sum is related to three other terms by antisymmetry of the upper and lower indices. Since we have already antisymmetrized the expansion coefficients with a Grassmann wedge, we can eliminate this redundancy in the summation by restricting the sum as in the CI expansion and multiplying by $(2!)^2$ to obtain

$$T_1^2 = 4 \sum_{o_1<o2,v_1<v_2} ({}^1t^{v_1}_{o_1} \wedge {}^1t^{v_2}_{o_2}) a^\dagger_{v_1} a^\dagger_{v_2} a_{o_2} a_{o_1}. \tag{30}$$

Comparison of Eq. (30) in Eq. (27) with Eq. (10) readily gives us the contribution of this term to the triply excited CI coefficient as $2\,{}^1t^{v_1}_{o_1} \wedge {}^1t^{v_2}_{o_2}$. In the same fashion we find the T_2 contribution to obtain

$${}^2c^{v_1,v_2}_{o_1,o_2} = 2\,{}^1t^{v_1}_{o_1} \wedge {}^1t^{v_2}_{o_2} + {}^2t^{v_1,v_2}_{o_1,o_2} \tag{31}$$

for the doubly excited CI coefficient in terms of the transition amplitudes.

TABLE II. Reconstruction functionals for the expansion coefficients of ψ.

${}^1c = {}^1t$
${}^2c = 2\,{}^1t \wedge {}^1t + {}^2t$
${}^3c = 6\,{}^1t^3 + 9\,{}^2t \wedge {}^1t + {}^3t$
${}^4c = 16\,{}^3t \wedge {}^1t + g({}^1t,{}^2t) + {}^4t$
where
$g({}^1t,{}^2t) = 24\,{}^1t^4 + 72\,{}^2t \wedge {}^1t^2 + 18\,{}^2t \wedge {}^2t$

A similar analysis yields the CI coefficients for triple and quadruple excitations in terms of transition amplitudes. These results are summarized in Table II. Indices are suppressed, but if supplied, the upper and lower indices would represent virtual and occupied orbitals, respectively. As before a right superscript n indicates that a transition amplitude should be wedged with itself n times. The functional $g({}^1t,{}^2t)$ represents those terms which may be expressed without the three- and four-particle transition amplitudes.

Comparison of the functionals for RTMs and CI coefficients in Tables I and II, respectively, reveals that the functionals are identical except for different coefficients. Equation (14) from Sec. II B shows that the CI coefficient ${}^pc$ is related to the p-RTM by a factor of $p!$. Using this relation, we can rewrite Table I to produce the CI coefficients ${}^pc$ as functionals of the connected RTMs. However, in Table II the ${}^pc$ are expressed as functionals of the transition amplitudes ${}^pt$. Both results for ${}^pc$ are valid if and only if

$${}^p\Delta = \frac{1}{p!}\,{}^pt. \tag{32}$$

Hence, the functionals in Tables I and II are equivalent which demonstrates that a cumulant expansion for RTMs with $\chi = \psi_{\rm Slater}$ is the same as the exponential ansatz for the CI coefficients. Similarly, we could prove this result by changing Table II to express the p-RTMs as functionals of the transition amplitudes. Comparison of these functionals with those in Table I would also require Eq. (32).

All of the functionals in both Tables I and II contain connected and unconnected terms and are thereby *exact*. CC approximations to a full CI only include certain connected terms. Equation (32) shows that neglecting the connected portion of a cumulant expansion for a RTM is the same as deleting the corresponding transition amplitude in the exponential ansatz for the wave function; hence, the functionals for RTMs and transition amplitudes remain the same with the introduction of approximations. The equivalence of the unconnected RTM reconstruction with an exponential ansatz for the wave function implies that the unconnected RTMs are pure N-representable. Approximately reconstructing the 3- and 4-RTMs within the TCSE from an N-representable 2-RTM by neglecting ${}^3\Delta$ and ${}^4\Delta$ is the same as building the three- and four-particle CI coefficients in terms of the lower transition amplitudes (${}^1t$ and ${}^2t$) in a single-double CC calculation. Transition CSE methods that are equivalent to the CC at higher orders of approximation may be easily generated by employing higher excitations for the test functions in

TABLE III. Comparison of reconstruction formulas for 3-RDMs and 3-RTMs.

N	r	3-RDM error			3-RTM error	
		Hartree-Fock	Unconnected	Corrected	Hartree-Fock	Unconnected
4	6	5.65×10^{-3}	6.38×10^{-5}	8.43×10^{-8}	4.03×10^{-3}	0
4	12	2.86×10^{-2}	1.46×10^{-3}	4.88×10^{-4}	2.10×10^{-2}	3.52×10^{-4}
5	12	1.48×10^{-2}	6.25×10^{-4}	1.72×10^{-4}	1.07×10^{-2}	1.29×10^{-4}
6	12	8.75×10^{-3}	3.20×10^{-4}	1.09×10^{-4}	7.04×10^{-3}	9.88×10^{-5}
8	12	2.39×10^{-3}	4.61×10^{-5}	2.33×10^{-5}	1.99×10^{-3}	2.25×10^{-5}
10	14	1.31×10^{-3}	2.23×10^{-5}	1.10×10^{-5}	1.03×10^{-3}	8.54×10^{-6}

Eq. (3) and deriving through Eq. (22) cumulant expansions for higher RTMs. With the transition CSE we may formulate CI, CC, or CSE theories. The particular theory obtained and its level of accuracy depends on the choice for the reference wave function χ and the reconstruction strategy.

C. Pure *N*-representable preimages of the RTMs

The preimage of a pure N-representable p-RDM refers to the N-particle wave function ψ whose density matrix contracts to the p-RDM. Similarly, the preimage of a pure N-representable p-RTM is characterized by the two wave functions χ and ψ which define the p-RTM in Eq. (6). Solution of the TCSE introduces the reconstruction problem of building the 3- and 4-RTMs from the 2-RTM. An important question is whether the 2-RTM contains enough information to specify the higher RTMs uniquely. In a previous paper we discussed this question for the case where $\chi=\psi$ through a theorem originally formulated by Rosina at the 1967 conference on RDMs at Queens University [6,29]:

Theorem. If a p-RDM arises from a nondegenerate ground-state wave function from a Hamiltonian with only p-particle interactions, the p-RDM *alone* contains enough information to determine the N-particle preimage uniquely. By *alone* we mean that the p-RDM information is not supplemented by any details concerning the nature of the Hamiltonian's p-particle interactions.

By this theorem a 2-RDM from the nondegenerate ground state of any Hamiltonian in the form of Eq. (2) uniquely determines the N-particle preimage as well as one pure N-representable p-RDM for each p between two and N. There is a one-to-one mapping between the 2-RDM and the N-particle wave function. Rosina's theorem motivates the search in Eqs. (33) and (34) for improving the reconstruction of higher RDMs from the 2-RDM beyond the cumulant expansion.

Rosina's theorem is not true for the 2-RTM with $\chi=\psi_{\rm Slater}$. Unlike the 2-RDM with a unique preimage the 2-RTM reconstructs to many N-particle wave functions ψ including the coupled-cluster wave functions in Eq. (24) with the correct transition amplitudes in T_1 and T_2 but any choice for the transition amplitudes involving more than two particles. When the higher transition amplitudes are chosen to be zero, we have the single-double coupled-cluster preimage. Without employing the Hamiltonian explicitly in the reconstruction the exact preimage for the 2-RTM cannot be distinguished from many other possibilities.

D. Reconstruction of RDMs beyond cumulants

Rosina's theorem motivates the search for reconstruction functionals for RDMs beyond the unconnected cumulant approximations. The iterative solution of the CSE requires us to build the 3- and 4-RDMs from the trial 2-RDM at each iteration until convergence. Building the 3-RDM from the 2-RDM with unconnected part of the cumulant expansion neglects ${}^3\Delta$ which vanishes though first order of MBPT. However, building the 4-RDM from the 3-RDM with unconnected terms neglects ${}^4\Delta$ which vanishes through second order of MBPT. To make the reconstruction of the 3-RDM correct through second order, we must approximate the connected part through second order. Contraction of the unconnected part of the 4-RDM formula ${}^4D_{\rm uc}$ in Table I generates a system of equations for approximating ${}^3\Delta$,

$${}^3\Delta_{\rm app}=\frac{4}{N-3}L_4^3[{}^4D_{\rm uc}({}^1D,{}^2\Delta,{}^3\Delta_{\rm app})]-{}^3D_{\rm uc}, \qquad (33)$$

where L_4^3 is the contraction operator from the four-particle space to the three-particle space and ${}^3D_{\rm uc}$ denotes the unconnected part of the 3-RDM. This system would be exact if we could include the unknown connected 4-RDM. Since the ${}^4\Delta$ vanishes until third order of MBPT, this system of equations produces a ${}^3\Delta_{\rm app}$ which is correct through second order of MBPT. While this contraction condition improves the unconnected approximation for the 3-RDM, the analogous contraction condition for the 3-RTM is always satisfied by the

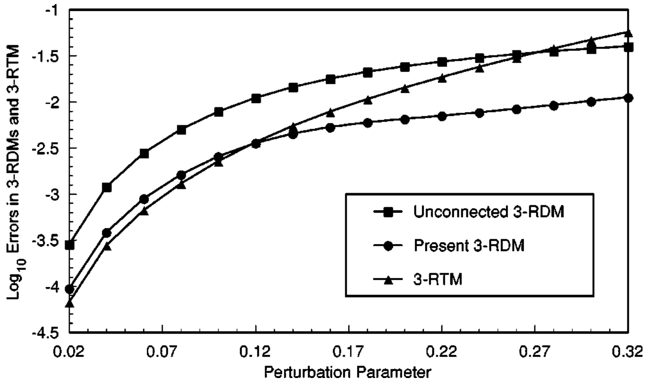

FIG. 1. The errors in 3-RDM and 3-RTM reconstructions are shown as functions of the perturbation parameter λ. The 3-RDM is built with both the unconnected cumulant and the corrected approximations while the 3-RTM is constructed with the unconnected cumulant formula.

TABLE IV. Comparison of 2-RDMs obtained by contracting reconstructed 3-RDMs.

N	r	L_3^2(3-RDM) error			L_3^2(3-RTM) error	
		3-RDM reconstructions			3-RTM reconstructions	
		Hartree-Fock	Unconnected	Corrected	Hartree-Fock	Unconnected
4	6	2.67×10^{-3}	3.01×10^{-5}	3.98×10^{-8}	1.90×10^{-3}	0
4	12	1.35×10^{-2}	6.43×10^{-4}	3.36×10^{-5}	9.89×10^{-3}	0
5	12	8.54×10^{-3}	2.77×10^{-4}	1.36×10^{-5}	6.19×10^{-3}	0
6	12	5.84×10^{-3}	1.34×10^{-4}	6.69×10^{-6}	4.68×10^{-3}	0
8	12	1.95×10^{-3}	1.48×10^{-5}	5.51×10^{-7}	1.63×10^{-3}	0
10	14	1.24×10^{-3}	7.70×10^{-6}	2.72×10^{-7}	9.71×10^{-4}	0

unconnected 3-RTM with $\chi=\psi_{\text{Slater}}$ because its preimage includes an N-particle coupled-cluster wave function with only single- and double-transition amplitudes. Hence, this approximation for the connected 3-RDM illustrates the practical impact of Rosina's theorem for improving RDM reconstruction.

We have recently succeeded in converting the system of equations in Eq. (33) into the following explicit formula for approximating the elements of the connected 3-RDM [9]:

$$ {}^3\Delta_{\text{app}} = \alpha[4L_4^3({}^4D_{\text{uc,p}}) + 9L_3^2({}^3\Delta)\wedge{}^1D - \beta\,{}^3D_{\text{uc}}], \quad (34) $$

where $\alpha=1/(\gamma-3)$, $\beta=N-3$, and

$$ \gamma = \sum_{i\in\{i_1,i_2,i_3,j_1,j_2,j_3\}} {}^1D_i^i . \quad (35) $$

The detailed derivation of this formula is given in [9]. The set of six indices in Eq. (35) contains the upper $\{i_1,i_2,i_3\}$ and lower $\{j_1,j_2,j_3\}$ indices for the specific element of ${}^3\Delta_{\text{app}}$ which we are calculating. All RDMs in this formula must be in the natural orbital basis set which diagonalizes the 1-RDM.

Formally we know that the exact error in this formula is

$$ \text{error in } {}^3\Delta_{\text{app}} = \frac{4}{\gamma-3} L_4^3({}^4\Delta). \quad (36) $$

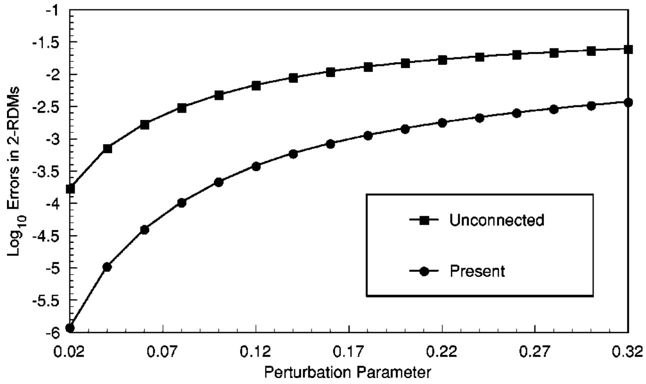

FIG. 2. The errors in the 2-RDMs obtained by contracting the 3-RDM reconstruction formulas are reported as functions of the perturbation parameter λ. The error in the contraction of the unconnected 3-RTM approximation to the 2-RTM is not shown because the contraction is exact.

Since we do not know ${}^4\Delta$, however, we cannot use this formula to obtain an exact answer. Because the connected 4-RDM vanishes until third order of MBPT, this formula for the elements of the connected 3-RDM will be correct through second order of MBPT as long as the denominator in the error expression $\gamma-3$ is not small. However, γ may be close to 3 when three of the six indices correspond to occupied orbitals in the noninteracting limit. Using the Hermitian and antisymmetric properties of the 3-RDM, we may group the elements for which γ is close to 3 into two classes: ${}^3D^{x,x,o}_{x,o,o}$ and ${}^3D^{x,x,x}_{o,o,o}$ where the x's and o's denote occupied and unoccupied orbitals, respectively. For both of these classes we employ the unconnected 3-RDM approximation without correction. All other elements, however, may be corrected with the present formula through second order of MBPT.

IV. APPLICATIONS

Several reconstructions of the 3-RDM with $\chi=\psi$ and the 3-RTM with χ equal to the Hartree-Fock wave function ψ_{HF} are compared through calculations involving random Hamiltonians with general two-particle interactions as well as molecular Hamiltonians for LiH, BeH_2, BH_3, and H_2O. Computations with the random Hamiltonians allow us to vary the strength of the two-particle interactions.

A. Random Hamiltonians

To create a random N-particle Hamiltonian with no more than two-particle interactions, we first choose the elements for a one-particle reduced Hamiltonian ${}^1K$ and a two-particle perturbation ${}^2V$ randomly. The two-particle reduced Hamiltonian ${}^2K$ is then defined by

$$ {}^2K = {}^1K\wedge{}^1I + \lambda\,{}^2V. \quad (37) $$

By wedging the ${}^2K$ with the $(N-2)$-particle identity operator $({}^2K\wedge{}^{N-2}I)$, we create the N-particle Hamiltonian H which we diagonalize with ARPACK [31]. From the wave function we form the exact 1- and 2-RDMs and the exact 1- and 2-RTMs. These matrices are employed to test the reconstruction schemes. Calculations are performed in the natural orbital basis.

Three reconstruction formulas for the 3-RDM are compared in Table III: (i) the Hartree-Fock functional ${}^1D^3$ with the *exact* 1-RDM, (ii) the unconnected portion of the 3-RDM

TABLE V. Comparison of 4-RDMs and 4-RTMs obtained by reconstructing with different 3-RDM and 3-RTM approximations.

N	r	4-RDM error			4-RTM error	
		3-RDM reconstructions			3-RTM reconstructions	
		Hartree-Fock	Unconnected	Corrected	Hartree-Fock	Unconnected
4	6	1.60×10^{-2}	4.42×10^{-4}	6.53×10^{-7}	1.14×10^{-2}	0
4	12	8.12×10^{-2}	9.67×10^{-3}	1.98×10^{-3}	5.94×10^{-2}	1.41×10^{-3}
5	12	2.96×10^{-2}	2.42×10^{-3}	4.90×10^{-4}	2.15×10^{-2}	3.65×10^{-4}
6	12	1.43×10^{-2}	9.14×10^{-4}	2.53×10^{-4}	1.15×10^{-2}	2.28×10^{-4}
8	12	3.03×10^{-3}	9.03×10^{-5}	4.17×10^{-5}	2.53×10^{-3}	4.03×10^{-5}
10	14	1.40×10^{-3}	3.62×10^{-5}	1.66×10^{-5}	1.11×10^{-3}	1.29×10^{-5}

in Table I, and (iii) the present approximation in Eq. (34) for the connected part ${}^3\Delta$ of the reconstruction functional. Two reconstruction methods for the 3-RTM are also reported in Table III: (i) the Hartree-Fock functional ${}^1D^3$ with the *exact* 1-RTM and (ii) the unconnected portion of the 3-RTM in Table I. The error in each 3-RDM or 3-RTM approximation is measured by a least-squares norm, evaluated by summing the squares of the errors in the elements and taking the square root of the result. Calculations are shown in Table III for various particle numbers N and one-particle ranks r with the perturbation parameter $\lambda=0.04$.

From Table III the errors in the unconnected 3-RTMs are half an order of magnitude smaller than the errors in the unconnected 3-RDMs. Hence, the same unconnected functional in Table I yields better 3-RTMs than 3-RDMs. Using the formula in Eq. (34) to move beyond the cumulant approximation produces a corrected 3-RDM that is close to the accuracy of the 3-RTM. It is interesting that while the corrected 3-RDM has many elements calculated through second order of a renormalized MBPT, the 3-RTM which is missing second-order corrections often has a smaller least-squares error. When $r=N+2$, there cannot be any three-particle excitations, and thus, the unconnected 3-RTM formula becomes exact. The present approximation for the 3-RDM also improves when $r=N+2$ because with only two virtual orbitals the elements of the 3-RDM ${}^3D^{x,x,x}_{o,o,o}$, which are not easily corrected through second order, do not occur. Figure 1 presents the 3-RDM and the 3-RTM reconstructions for the perturbation parameter λ in the range $[0.02,0.32]$ and $N=4$ and $r=8$. For small λ, as reported in the tables, the 3-RTM approximation is more accurate than the unconnected 3-RDM, but the corrected 3-RDM is close to the accuracy of the 3-RTM. After $\lambda=0.12$ the 3-RDM is better than the 3-RTM; by $\lambda=0.32$ the error in the 3-RTM, greater than the error in the unconnected 3-RDM, is more than half an order of magnitude larger than the corrected 3-RDM's error.

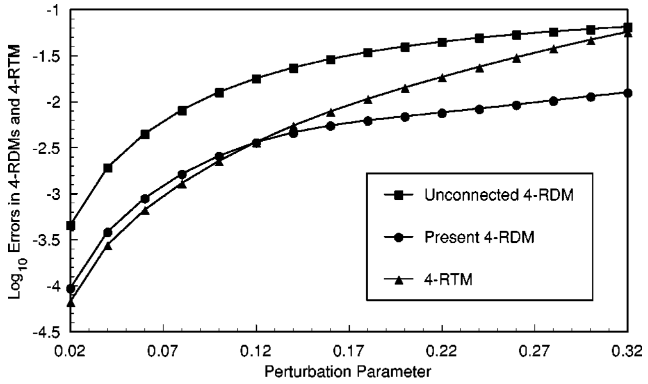

FIG. 3. The errors in the 4-RDMs and 4-RTM obtained by reconstructing with different 3-RDM and 3-RTM approximations are given as functions of the perturbation parameter λ. Both the 4-RDM and the 4-RTM are built with the unconnected cumulant approximation. The results highlight the sensitivity of the 4-RDM and 4-RTM errors to the 3-RDM/3-RTM reconstructions.

By contracting the approximations for the 3-RDMs and 3-RTMs, we obtain 2-RDMs and 2-RTMs whose errors are reported in Table IV. For all cases the contraction of the present 3-RDM is at least an order of magnitude more accurate than the contraction of the unconnected 3-RDM. While the unconnected and corrected estimates for the 3-RDM differ by about half of an order of magnitude for all λ in Fig. 1, the contractions of these 3-RDM estimates differ by two orders of magnitude for small λ and an order of magnitude for large λ as shown in Fig. 2. This dramatic improvement occurs because the elements ${}^3D^{x,x,x}_{o,o,o}$ of the connected 3-RDM which are not easily corrected by Eq. (34) do not contribute to the 2-RDM through contraction. The contraction of the unconnected 3-RTM is exact in Table IV since the unconnected cumulant expansion produces an N-representable 3-RTM. The Hartree-Fock functional for the 3-RTM which is not necessarily N representable does not contract correctly.

Comparison of the 3-RDM and the 3-RTM reconstructions may also be performed by building the 4-RDMs and the 4-RTMs with the unconnected part of the four-particle functional in Table I. The exact 1- and 2-RDMs (or RTMs) are used in the functional for ${}^1D$ and ${}^2D$. Results are reported in Table V for a variety of N and r and $\lambda=0.04$. The 4-RTM from the unconnected 3-RTM is more accurate than the 4-RDM from the unconnected 3-RDM, but the 4-RDM from the corrected 3-RDM is close to the accuracy of the 4-RTM approximation. As with the 3-RTM, when $r=N+2$, the 4-RTM reconstruction becomes exact since three- and four-particle excitations vanish. The errors in the 4-RTM and the 4-RDM built with the corrected 3-RDM cross at $\lambda=0.12$ in Fig. 3 with the 4-RDM approximation becoming significantly better than the 4-RTM estimate for large λ. This is similar to the crossover observed in Fig. 1 for the 3-RDM and the 3-RTM. Comparison of Figs. 1 and 3 also shows that

TABLE VI. Comparison of CSE and CC errors for different 3-RDM and 3-RTM reconstructions.

N	r	${}^2D_{\mathrm{TCSE}}$ error for the CSE $\lvert E_{\mathrm{CSE}}-E_{\mathrm{FCI}}\rvert$			${}^2D_{\mathrm{TCSE}}$ error for the CC $\lvert E_{\mathrm{CC}}-E_{\mathrm{FCI}}\rvert$		E_{FCI}
		3-RDM reconstructions			3-RTM reconstructions		
		Hartree-Fock	Unconnected	Corrected	Hartree-Fock	Unconnected	
4	6	1.60×10^{-3}	4.18×10^{-5}	4.85×10^{-8}	5.95×10^{-4}	0	
		2.71×10^{-2}	2.41×10^{-3}	3.63×10^{-6}	4.78×10^{-5}	0	-171.2288331
4	12	1.13×10^{-2}	4.97×10^{-4}	2.57×10^{-5}	7.16×10^{-3}	7.99×10^{-6}	
		1.27	3.49×10^{-2}	3.96×10^{-3}	2.07×10^{-1}	7.33×10^{-5}	-362.1001722
6	12	5.31×10^{-3}	1.16×10^{-4}	6.70×10^{-6}	3.90×10^{-3}	2.59×10^{-6}	
		5.85×10^{-1}	2.47×10^{-2}	6.90×10^{-4}	1.37×10^{-1}	5.78×10^{-6}	-242.4238873
8	12	1.84×10^{-3}	1.66×10^{-5}	8.37×10^{-7}	1.45×10^{-3}	6.35×10^{-7}	
		1.11×10^{-1}	8.31×10^{-3}	3.53×10^{-5}	3.03×10^{-2}	7.13×10^{-7}	-161.8839847
10	14	1.16×10^{-3}	9.94×10^{-6}	5.04×10^{-7}	8.53×10^{-4}	3.01×10^{-7}	
		8.79×10^{-2}	6.44×10^{-3}	4.28×10^{-5}	3.15×10^{-2}	1.36×10^{-6}	-143.8806157

the gap between the unconnected and corrected 3-RDM reconstructions is larger in the 4-RDM estimate than in the 3-RDM approximation. Therefore, the present correction for the 3-RDM has beneficial effects on both the contraction to the 2-RDM as well as the cumulant reconstruction to the 4-RDM.

An additional criterion for assessing the accuracy of the reconstructed 3,4-RDMs and the 3,4-RTMs is their satisfaction of the CSE and CC equations, respectively. Reconstruction of the RDMs and RTMs is performed as in Tables III–V. In Table VI results are reported for a variety of N and r with $\lambda=0.04$. With the unconnected approximations for the RTMs the TCSE is equivalent to the single-double CC equations. Errors in the TCSE equations are evaluated by a least-squares norm of the matrix ϵ with the following elements

$$\epsilon^{i_1,j_1}_{i_2,j_2}=\frac{2}{N(N-1)}\left({}^2D_{\mathrm{TCSE}}-{}^2D_{\mathrm{exact}}\right), \tag{38}$$

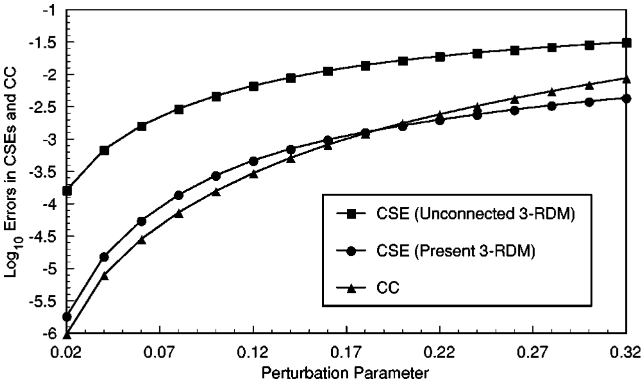

FIG. 4. The errors in the CSE and CC equations are displayed as functions of the perturbation parameter λ for different reconstructions of the 3-RDM/3-RTM. The CSE with the corrected 3-RDM formula outperforms the CSE with the unconnected 3-RDM formula by two orders of magnitude for low λ and an order of magnitude for higher λ. While the CC error is smaller than the CSE for low λ, the CSE with the present 3-RDM has a smaller error for high λ.

where ${}^2D_{\mathrm{TCSE}}$ is determined with the TCSE in Eq. (8),

$$ {}^2D_{\mathrm{TCSE}}=\kappa\sum_{i_3,i_4,j_3,j_4}{}^2K^{i_3,i_4}_{j_3,j_4}R^{i_1,i_2,i_3,i_4}_{j_1,j_2,j_3,j_4}. \tag{39}$$

The constant κ is chosen to adjust the normalization of the resulting matrix to $N(N-1)/2$; this is equivalent to dividing by the $4E$ in Eq. (8). The CC equations are exactly satisfied by the unconnected reconstruction when $r=N+2$ for which the 3- and 4-RTM reconstructions are exact. In Table VI the errors in the CC equations with the unconnected RTMs are much smaller than the errors in the CSE with the unconnected RDMs. The corrected 3-RDM in the CSE, however, yields errors which are close to those from the CC with the unconnected 3-RTM. Energies, computed by taking the trace the 2-RTM ${}^2D_{\mathrm{TCSE}}$ with the reduced Hamiltonian ${}^2K$, are also reported in Table VI. While the CC equations produce the best energies, the CSE with corrected 3-RDM gives energies which are significantly better than those from the CSE with the unconnected 3-RDM reconstruction. For λ larger than 0.20 in Fig. 4 the error in the CSE with the corrected 3-RDM becomes smaller than the error in the CC.

These results reflect the accuracy of the reconstructions, but they do not necessarily indicate that iteratively solving either the TCSE equations from a Hartree-Fock 2-RTM reference or the CSE with a Hartree-Fock 2-RDM reference (CCSD) will yield better results. Within an N-representable set of RDMs the CSE always produces exact results unlike the CC equations which have a family of solutions. Once the N-representability conditions are partially relaxed for the CSE, however, the relative accuracy of the CSE and CC methods is unclear, and we cannot use the accuracy of the reconstructions alone to predict which method will perform better. When the iterative methods for solving the CSE have been better developed, realistic comparisons of the CSE with CC in both accuracy and efficiency will be possible.

B. Molecular Hamiltonians

Reconstruction formulas for the 3-RDM and 3-RTM are compared in Tables VII and VIII for the molecules LiH,

TABLE VII. Comparison of reconstruction formulas for molecular 3-RDMs and 3-RTMs.

System	3-RDM error			3-RTM error	
	Hartree-Fock	Unconnected	Corrected	Hartree-Fock	Unconnected
LiH	6.92×10^{-1}	1.02×10^{-2}	1.72×10^{-3}	5.36×10^{-2}	4.66×10^{-4}
BeH_2	3.09×10^{-1}	2.17×10^{-3}	1.24×10^{-3}	1.69×10^{-2}	8.60×10^{-4}
BH_3	1.77×10^{-1}	7.64×10^{-4}	3.75×10^{-4}	8.23×10^{-3}	2.60×10^{-4}
H_2O	9.24×10^{-2}	2.87×10^{-4}	9.02×10^{-5}	3.81×10^{-3}	4.91×10^{-5}

BeH_2, BH_3, and H_2O. Calculations are performed within an STO-6G basis with geometries from the experimental literature [32]. Errors are computed with the FCI as the reference. Table VII presents the least-squares error in the elements of the 3-RDM and the 3-RTM. As with the random Hamiltonians we perceive that the unconnected functional yields 3-RTMs which are consistently more accurate than the 3-RDMs. The corrected 3-RDMs are significantly better than the unconnected formulas and close to the 3-RTMs in accuracy. Contraction of the 3-RDM and 3-RTM approximations produces 2-RDMs and 2-RTMs whose least-squares errors are reported in Table VIII. The 2-RDMs from the corrected 3-RDMs are between half an order and an order of magnitude more accurate than the 2-RDMs from the unconnected 3-RDMs. The unconnected 3-RTM contracts exactly to the 2-RTM since the reconstruction functionals build the 3-RTM which corresponds to a coupled-cluster wave function with nonvanishing single- and double-transition amplitudes.

V. CONCLUSION

Within the framework of the transition CSE and cumulant theory a unified treatment of the CI, CC, and CSE methods is presented. We derive a relationship between the CI excitation coefficients and the elements of the RTMs where χ is chosen to be any Slater wave function ψ_{Slater}. From these relations a set of necessary and sufficient conditions, independent of the CI coefficients, is generated for constraining the RTMs to be pure N-representable. When the elements of the RTMs which correspond to three- and four-particle excitations are neglected, the solution of the TCSE yields RTMs that are equivalent to the SDCI. Through the theory of cumulants and methods from quantum field theory we determine reconstruction functionals for the RTMs which improve the accuracy of the CI approximation and reestablish size consistency. These RTM formulas represent a renormalized MBPT. We show that these reconstruction functionals for the 3- and 4-RTMs generate N-representable RTMs whose N-particle wave functions ψ are equivalent to those from CCSD. Higher RTMs behave like coupled-cluster wave functions which include more connected excitations. When we choose χ to be the exact wave function ψ, we obtain the CSE which depends on the 2-, 3-, and 4-RDMs. Recent attempts to build the higher RDMs from the 2-RDM have offered a new approach to using the 2-RDM as the fundamental parameter for electron correlation.

Theoretical questions about a reconstruction strategy whose accuracy extends beyond that of the cumulant expansion are addressed. Rosina first demonstrated that a 2-RDM from a nondegenerate, ground-state wave function contains enough information by itself to determine its N-particle preimage as long as the underlying but possibly unknown Hamiltonian has no more than two-particle interactions [29,6]. This justifies the search for improved reconstruction, and we present an explicit formula for calculating second-order corrections for the 3-RDM cumulant functional [9]. Unlike the 2-RDM the 2-RTM with $\chi=\psi_{\mathrm{Slater}}$ does not contain enough information to reconstruct to a unique preimage. Any CI wave function with the appropriate single and double excitations is a candidate for the preimage. Some of these may be eliminated by requiring size consistency. However, there is a significant limitation on building higher RTMs from lower RTMs without additional information about the Hamiltonian. This restricts the degree to which the many-body perturbation expansion may be renormalized within CC theory while a similar theoretical restriction does not exist for the CSE theory whose primary variable is the 2-RDM.

The multiple preimages for the 2-RTM suggest a connection with the one-density of DFT. In DFT the energy is determined from the one-density and the number of electrons by means of a functional which must contain information about the kinetic energy and two-particle interaction terms in the electronic Hamiltonian. By itself the one-density has nu-

TABLE VIII. Comparison of molecular 2-RDMs obtained by contracting reconstructed 3-RDMs.

System	L_3^2(3-RDM) error			L_3^2(3-RTM) error	
	3-RDM reconstructions			3-RTM reconstructions	
	Hartree-Fock	Unconnected	Corrected	Hartree-Fock	Unconnected
LiH	5.69×10^{-1}	4.95×10^{-3}	7.97×10^{-4}	2.53×10^{-2}	0
BeH_2	3.46×10^{-1}	8.42×10^{-4}	1.39×10^{-4}	1.13×10^{-2}	0
BH_3	2.32×10^{-1}	2.99×10^{-4}	3.12×10^{-5}	6.71×10^{-3}	0
H_2O	1.27×10^{-1}	1.28×10^{-4}	1.50×10^{-5}	3.59×10^{-3}	0

merous N-particle preimages including a Slater determinant wave function [33,34]. Recently, DFTs for both the one-density and the 1-RDM have been cast through the adiabatic connection as renormalized MBPTs [35–38]. Because the one-density and the 1-RDM by themselves do not contain enough information to reconstruct the higher RDMs for correlated systems, in the renormalization they like the 2-RTM must be explicitly supplemented with more precise information regarding the two-particle interactions in the Hamiltonian. While a simple and exact reconstruction strategy for the 2-RDM remains unknown, Rosina's existence theorem offers hope for discovering a highly renormalized approach which by using N-representability restrictions may be systematic without relying directly on traditional perturbation theory.

The CC and CSE theories may also be distinguished from an analysis of the relationship of the CSE and the TCSE ($\chi=\psi_{\text{Slater}}$) with the SE. As first shown by Nakatsuji, the CSE may be satisfied with pure N-representable RDMs if and only if the SE holds with the wave function associated with the RDMs [17]. Thus, if the conditions for pure N-representability were known, we could solve the CSE for the ground- and excited-state energies and their 2-RDMs. As we demonstrated, however, the TCSE has multiple solutions for N-representable RTMs which range from SDCI and CCSD to the exact solution. The relative simplicity of the N-representability conditions for the RTMs is complemented by a TCSE that is significantly weaker than the CSE. Within CSE theory improving N-representability offers a mechanism for approaching the exact solution for the 2-RDM, but in CC theory the limitation on accuracy does not depend on the N representability of the RTMs but on their correspondence to a model wave function. In this respect the failure of the RDMs to be N-representable may be perceived as a benefit since the representability provides a means for improvement.

Calculations with random and molecular Hamiltonians indicate that the RTMs reconstruct better than the RDMs with the unconnected functionals; the corrected 3-RDM formula is close to the accuracy of the unconnected 3-RTM. In comparing these reconstructions two issues should be considered: (i) Rosina's theorem indicates that it should be possible to develop better reconstruction strategies for the 3-RDM while the 3-RTM cannot be improved without the Hamiltonian, and (ii) these reconstruction differences do not necessarily reflect the accuracy of solving the CSE and CC equations from an initial 2-RDM–2-RTM guess since the CSE and CC have different characteristics such as correspondence of the CSE with the Schrödinger equation under the conditions of Nakatsuji's theorem. The present paper establishes the foundation for future work to explore the relationship between the CC and CSE in greater computational detail. Before a fair comparison in accuracy and efficiency can be established, however, better iterative methods for solving the CSE need to be developed.

The similarity of the CSE and TCSE suggests the possibility for hybrid schemes. If the 2-, 3-, and 4-RDMs are parametrized in terms of the 2-RTM, we would ensure that they are N-representable. Substitution of these parametrized RDMs into the CSE would then create a system of equations for the 2-RTM. By Nakatsuji's theorem this system would not have a solution, but minimization of a norm for the errors in the CSE would offer a method for optimizing the 2-RTM parameters. The solution would be similar to CCSD, and yet the energy would be an upper bound to the true energy. This CSE-RTM hybrid scheme has connections with the variational formulations for the CC [39]. The CSE might also be useful as a test for measuring the accuracy of RTMs obtained through a CC calculation [40].

In conclusion the TCSE provides a theoretical framework for unifying the CI, CC, and CSE methods. We have connected the expansion coefficients of the CI and the transition amplitudes of the CC with the RTMs and connected RTMs, respectively. These links offer a fresh approach to understanding CC theory within the context of RTM reconstruction. The exponential ansatz for the coupled cluster wave function is shown to be a special case of a generalized cumulant expansion for RTMs. This generalized expansion also includes the RDM reconstruction formulas employed within the context of the CSE. We implemented a recently developed formula for constructing the 3-RDM with an accuracy beyond that of its cumulant expansion. The theorems of Nakatsuji and Rosina, applying only to the CSE and RDMs, respectively, highlight the significant theoretical and potential computational differences between the CC and CSE theories. Through the unifying influence of the TCSE, we obtain a novel perspective on CI and CC calculations as well as a new understanding of the potential role for the CSE within electronic structure.

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