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Contracted Schrödinger equation: Determining quantum energies and two-particle density matrices without wave functions

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The contracted Schrödinger equation (CSE) technique through its direct determination of the two-particle reduced density matrix (2RDM) without the wave function may offer a fresh alternative to traditional many-body quantum calculations. Without additional information the CSE, also known as the density equation, cannot be solved for the 2RDM because it also requires a knowledge of the 4RDM. We provide theoretical foundations through a reconstruction theorem for recent attempts at generating higher RDMs from the 2RDM to remove the indeterminacy of the CSE. With Grassmann algebra a more concise representation for Valdemoro's reconstruction functionals [F. Colmenero, C. Perez del Valle, and C. Valdemoro, Phys. Rev. A **47**, 971 (1993)] is presented. From the perspective of the particle-hole equivalence we obtain Nakatsuji and Yasuda's correction for the 4RDM formula [H. Nakatsuji and K. Yasuda, Phys. Rev. Lett. **76**, 1039 (1996)] as well as a corrective approach for the 3RDM functional. A different reconstruction strategy, the ensemble representability method (ERM), is introduced to build the 3- and 4-RDMs by enforcing four-ensemble representability and contraction conditions. We derive the CSE in second quantization without Valdemoro's matrix contraction mapping and offer the first proof of Nakatsuji's theorem for the second-quantized CSE. Both the functional and ERM reconstruction strategies are employed with the CSE to solve for the energies and the 2RDMs of a quasispin model without wave functions. We elucidate the iterative solution of the CSE through an analogy with the power method for eigenvalue equations. Resulting energies of the CSE methods are comparable to single-double configuration-interaction (SDCI) energies, and the 2RDMs are more accurate by an order of magnitude than those from SDCI. While the CSE has been applied to systems with 14 electrons, we present results for as many as 40 particles. Results indicate that the 2RDM remains accurate as the number of particles increases. We also report a direct determination of excited-state 2RDMs through the CSE. By circumventing the wave function, the CSE presents new possibilities for treating electron correlation.
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I. INTRODUCTION

Knowledge of the two-particle reduced density matrix (2RDM) allows one to calculate the energy and other observables for atomic and molecular systems with an arbitrary number N of electrons. For a quantum system, fully characterized by a single N-particle wave function, the N-particle density matrix ${}^{N}D$ is the kernel of the wave function's projection operator. By integrating the density matrix ${}^{N}D$ over $(N-2)$ particles, we obtain the 2RDM which contains enough information to calculate the expectation values for any operator with only two-particle interactions like the electronic Hamiltonian [1–3]. Although a direct determination of the 2RDM would avoid the difficult calculation of the N-particle wave function and yet still provide us with the most relevant electronic structure information for atoms and molecules, variation of the 2RDM elements to minimize the energy has not been possible because a simple set of N-representability conditions to ensure that the 2RDM represents a realistic N-particle system has not been found [4–13]. Recent theoretical and computational results, however, involving the contracted Schrödinger equation (CSE), also known as the density equation, rekindle the possibility of an accurate method for generating the 2RDM without the wave function [14–20].

The CSE was initially derived in 1976 as an integro-differential equation in the works of Cohen and Frishberg [21] and Nakatsuji [22]. Harriman [23] presented in 1979 a matrix version of the CSE in terms of contraction operators, and in 1985 Valdemoro obtained a matrix formulation of the CSE by contracting the Schrödinger equation to the two-particle space in second quantization [24]. Just as the Schrödinger equation describes the relationship between the N-particle Hamiltonian and its wave function (or density matrix ${}^{N}D$), the CSE connects the two-particle reduced Hamiltonian and the 2RDM. However, because the CSE also depends on the 4RDM, it is indeterminate without additional constraints [23]. We will derive a matrix formulation of the CSE in second quantization without Valdemoro's generalized contraction mapping [18,25,26]. The derivation emphasizes a test function approach which easily generates the contracted equation from the matrix form of the Schrödinger equation. Nakatsuji [22] proved in 1976 that with the assumption of pure N representability [3] a 2RDM and a 4RDM will satisfy the integro-differential version of the CSE if and only if they correspond to an N-particle wave function that satisfies the corresponding Schrödinger equation. We provide a proof of Nakatsuji's theorem [22] for the second-quantized CSE.

Employing the particle-hole equivalence, Valdemoro has derived formulas for reconstructing the 3- and 4RDMs from the 2RDM to remove the indeterminacy of the CSE

[14,15,27]. Recently, Nakatsuji and Yasuda have added an additional term to each of these formulas by considering the decoupling diagrams for Green's functions [19]. Nakatsuji's correction for the 3RDM, involving the solution of a system of equations, requires the Hartree-Fock 1RDM. We achieve a significantly simpler representation for Valdemoro's formulas through the notation of Grassmann algebra [28,29]. Furthermore, we derive Nakatsuji's corrective term for the 4RDM within the framework of the particle-hole equivalence and a new corrective 3RDM term, different from Nakatsuji's but also consistent with the accuracy of the improved 4RDM. Valdemoro and co-workers [16,20] have employed the reconstruction formulas to achieve iterative solutions of the CSE for atoms and molecules with around 4–6 electrons, and more recently, Nakatsuji and Yasuda [19] have used the formulas with their corrections to solve the CSE for molecular systems with four to 14 electrons.

The CSE approach emphasizes the connections between the problems of reconstruction and N-representability. We investigate the reasons why the 2RDM has enough information to build higher RDMs. If the Hamiltonian for an electronic problem is explicitly employed in the reconstruction, the 1-density alone is theoretically sufficient to determine the wave function and hence the higher RDMs through the theorem of Hohenberg and Kohn (HK) [30,31]. However, the reconstruction functionals, employed here as well as in previous work, involve only the 2RDM without any explicit references to the Hamiltonian. Therefore the HK theorem does not directly apply to the reconstruction problem in which we are interested. To demonstrate that the 2RDM is sufficient, we instead will prove and extend an important theorem, originally demonstrated by Rosina [32]. Rosina showed that the ground-state 2RDM for a quantum system completely determines the exact N-particle ground-state wave function *without any specific information about the Hamiltonian* other than it must have no more than two-particle interactions. A consequence of this theorem is that any ground-state electronic 2RDM exactly determines within the ensemble N-representable space a unique series of higher p-RDMs where $2<p\leq N$. These results provide important justification for the functional description of the higher RDMs in terms of the 2RDM.

With the theoretical basis of Rosina's theorem, we propose a new reconstruction scheme, which we call the ensemble representability method (ERM), in which the p-RDM is generated from the 2RDM by imposing contraction and p-ensemble representability conditions. For a p-RDM to be p-representable it must be Hermitian, antisymmetric, and positive semidefinite. Unlike the functional approach that yields a single approximate solution, this method generates a family of solutions that contains the exact solution. Just as the reconstruction functionals act like N-representability conditions, the ensemble representability conditions can also be used to achieve an approximate reconstruction. The ERM will produce more accurate reconstructions as p approaches N, and when $p=N$, the reconstruction becomes exact by Rosina's theorem. The ERM results for $p=4$ are comparable to those from the functional approach. Moreover, the resulting solutions of the CSE with four-ensemble representability are equivalent in accuracy to the 2RDMs produced through the solution of the CSE by Valdemoro's reconstruction formulas with corrections.

Both ERM and functional reconstruction techniques for solving the CSE will be illustrated through a quasispin model, originally used by Lipkin as a benchmark to compare several many-body methods for studying correlation in fermionic systems [33,34]. Results indicate that the methods produce energies equivalent to those from single-double configuration-interaction (SDCI) calculations, and 2RDMs that are an order of magnitude more accurate than those obtained by SDCI. We present results of the method for moderately large numbers N of fermions as well as results on excited states. Unlike most traditional quantum methods which truncate the number of excitations beyond the Hartree-Fock reference state, this method works within a reduced particle space which is equivalent to the full-CI basis. N-representability is approximated for a direct determination of the density matrix.

II. CONTRACTED SCHRÖDINGER EQUATION

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

$$H|\psi_n\rangle = E_n|\psi_n\rangle, \tag{1}$$

in which the wave function ψ_n depends on the coordinates for the N particles. In this section we show that within an N-representable space we may solve for the 2RDM directly through a contraction of the SE to the two-particle space. While the resulting contracted Schrödinger equation cannot be directly solved for the 2RDM without N-representability constraints since the CSE also depends on the 4RDM, approximations of the 4RDM in terms of the 2RDM have recently produced promising results [16,19,20]. Beginning with the SE, we will obtain Valdemoro's form of the CSE in second quantization in a fashion which does not require a knowledge of the generalized matrix contraction mapping (MCM) [16,24–26]. The derivation emphasizes the use of test functions for performing the contraction of the SE to the lower particle space. We will also present a proof of Nakatsuji's theorem [22] for the CSE in second quantization.

A. Derivation in second quantization

Within second quantization [35] the Hamiltonian operator may be expressed as

$$H = \frac{1}{2}\sum_{p,q;s,t} {}^2K^{p,q}_{s,t}\, a^\dagger_p a^\dagger_q a_t a_s\,, \tag{2}$$

where the elements of the two-particle reduced Hamiltonian ${}^2K$ are given by

$${}^2K^{p,q}_{s,t} = (p,s;q,t) + \frac{1}{N-1}(\delta_{q,t}\epsilon_{p,s} + \delta_{p,s}\epsilon_{q,t}). \tag{3}$$

The two-electron repulsion integrals are represented by the Mulliken symbol $(p,s;q,t)$,

$$(p,s;q,t)=\left\langle \phi_p(1)\phi_q(2)\left|\frac{1}{r_{12}}\right|\phi_s(1)\phi_t(2)\right\rangle \tag{4}$$

while one-electron portions of the Hamiltonian are included in the matrix ϵ,

$$\epsilon_{p,s}=-\left\langle \phi_p(1)\left|\frac{\nabla_1^2}{2}+\frac{Z}{r_1}\right|\phi_s(1)\right\rangle . \tag{5}$$

Because the N-particle Hamiltonian (H) contains only two-electron excitations, the expectation value of H yields a formula for the energy involving just the 2RDM,

$$E=\sum_{p,q;s,t} {}^2K_{s,t}^{p,q}\,{}^2D_{s,t}^{p,q}=\mathrm{Tr}({}^2K\,{}^2D), \tag{6}$$

where

$${}^2D_{s,t}^{p,q}=\frac{1}{2!}\langle\psi|a_p^{\dagger}a_q^{\dagger}a_t a_s|\psi\rangle. \tag{7}$$

In general, the p-RDM in second quantization is defined as

$${}^pD_{j_1,j_2,\ldots,j_p}^{i_1,i_2,\ldots,i_p}=\frac{1}{p!}\langle\psi|a_{i_1}^{\dagger}a_{i_2}^{\dagger}\cdots a_{i_p}^{\dagger}a_{j_p}a_{j_{p-1}}\cdots a_{j_1}|\psi\rangle, \tag{8}$$

and the normalization is $N!/[p!(N-p)!]$. Variation of ${}^2D$ to produce the lowest energy will generate the ground-state energy of the reduced Hamiltonian ${}^2K$ which will usually be much lower than the energy of the many-particle Hamiltonian H. To obtain the correct energy E of the N-electron Hamiltonian H, we must impose additional N-representability constraints on the 2RDM to ensure that it is derivable from an antisymmetric N-particle wave function ψ through the integration of its associated density matrix.

To derive the CSE rather than the expectation value, we define functions $\langle\Phi_{k,l}^{i,j}|$ to test the two-electron space

$$\langle\Phi_{k,l}^{i,j}|=\langle\psi|a_i^{\dagger}a_j^{\dagger}a_l a_k . \tag{9}$$

Taking the inner product of the test functions with the SE produces

$$\langle\psi|a_i^{\dagger}a_j^{\dagger}a_l a_k H\psi\rangle=E\langle\psi|a_i^{\dagger}a_j^{\dagger}a_l a_k|\psi\rangle=2E\ {}^2D_{k,l}^{i,j}. \tag{10}$$

If we substitute for the Hamiltonian operator in Eq. (2), we obtain the relation

$$\sum_{p,q,s,t} {}^2K_{s,t}^{p,q}\langle\psi|a_i^{\dagger}a_j^{\dagger}a_l a_k a_p^{\dagger}a_q^{\dagger}a_t a_s|\psi\rangle=4E\ {}^2D_{k,l}^{i,j}. \tag{11}$$

Using a graphical rule [26] to rearrange the creation and annihilation operators on the left-hand side to produce RDMs, we generate Colmenero and Valdemoro's 2,4-CSE [16]

$$({}^2\mathbf{K}\ {}^2\mathbf{D})_{k,l}^{i,j}+3\sum_{p,q,t}({}^2K_{i,t}^{p,q}\ {}^3D_{k,t,l}^{p,q,j}+{}^2K_{j,t}^{p,q}\ {}^3D_{l,t,k}^{p,q,i})$$
$$+6\sum_{p,q,s,t}({}^2K_{s,t}^{p,q}\ {}^4D_{s,t,k,l}^{p,q,i,j})=E\ {}^2D_{k,l}^{i,j}. \tag{12}$$

Evaluation of the first term in the above equation involves multiplying matrices ${}^2\mathbf{K}$ and ${}^2\mathbf{D}$ and then selecting the element of the resulting matrix, specified by the indices. We have derived the 2,4-CSE through test functions rather than the generalized MCM. A 1,3-CSE may also be produced by replacing the doubly excited test functions in Eq. (9) with test functions formed by single excitations of the ground-state wave function. Similarly, a 3,5-CSE and a 4,6-CSE may be created with test functions using triple and quadruple excitations, respectively. Since the 2,4-CSE is the focus of this paper, we will simply refer to it as the CSE.

B. Nakatsuji's theorem

While previous work [16,19] on the CSE has assumed that Nakatsuji's theorem, proven in 1976 for the integro-differential form of the CSE, remains valid for the *second-quantized* CSE, we present a formal proof. Nakatsuji's theorem is the following: if we assume that the density matrices are pure N-representable, then the CSE may be satisfied by a ${}^2D$ and ${}^4D$ if and only if the preimage density matrix ND satisfies the Schrödinger equation. The above derivation clearly proves that the SE implies the CSE. We only need to prove that the CSE implies the SE. The SE equation can be satisfied if and only if

$$\langle\psi|H^2|\psi\rangle-\langle\psi|H|\psi\rangle^2=0, \tag{13}$$

known as the dispersion condition [36]. Multiplying both sides of the CSE in Eq. (11) by the reduced Hamiltonian elements ${}^2K_{k,l}^{i,j}$ and summing over the remaining indices produces

$$\left\langle\psi\left|\left(\frac{1}{2}\sum_{i,j;k,l}{}^2K_{k,l}^{i,j}a_i^{\dagger}a_j^{\dagger}a_l a_k\right)\left(\frac{1}{2}\sum_{p,q;s,t}{}^2K_{s,t}^{p,q}a_p^{\dagger}a_q^{\dagger}a_t a_s\right)\right|\psi\right\rangle$$
$$=E\left(\sum_{i,j;k,l}{}^2K_{k,l}^{i,j}\,{}^2D_{k,l}^{i,j}\right). \tag{14}$$

By Eq. (6) the sum on the right-hand side of the above equation is equal to the energy E, and from Eq. (2) we realize that the sums on the left-hand side are just Hamiltonian operators in the second-quantized notation. Hence, when the 2RDM corresponds to an N-particle wave function ψ, Eq. (14) implies Eq. (13), and the proof of Nakatsuji's theorem is accomplished. Because the Hamiltonian is defined in second quantization, the proof of Nakatsuji's theorem is also valid when the one-particle basis set is incomplete. Recall that the SE with a second-quantized Hamiltonian corresponds to a Hamiltonian eigenvalue equation with the given one-particle basis. Unlike the SE, the CSE only requires the 2- and 4RDMs in the given one-particle basis rather than the full N-particle wave function. While Nakatsuji's theorem holds for the 2,4-CSE, it is not valid for the 1,3-CSE. This foreshadows the advantage of reconstructing from the 2RDM instead of the 1RDM which we will discuss in the context of Rosina's theorem.

III. THEORY OF RECONSTRUCTION

Both Valdemoro and co-workers [16,20] and Nakatsuji and Yasuda [19] have recently solved the CSE by approximating the 4RDM as a functional of the 2RDM. In the first section we derive Valdemoro's approximate reconstruction functionals for the first time in the notation of Grassmann algebra [28,29]. Furthermore, we derive Nakatsuji and Yasuda's recent corrective term for the 4RDM functional through the particle-hole equivalence rather than with Green's function decoupling diagrams and provide a corrective approach for the 3RDM. A central question of the reconstruction problem is whether knowledge of the 2RDM conveys enough information to generate the 4RDM. In the second section we will answer this question through a theorem by Rosina [32] and an extension of the theorem for excited states. We also introduce an approach to reconstruction, the ensemble representability method, in which ensemble 4-representability and contraction conditions are employed to build the 4RDM from the 2RDM without an approximate functional.

A. Reconstruction functionals

Valdemoro's derivation of the 3RDM and 4RDM functionals relies on the relationship between particles and holes. Traditionally, many-body quantum-mechanical systems are described in terms of their particles because there are usually many fewer particles than holes. Within second quantization or Grassmann algebra, however, the Hamiltonian for a many-particle system may also be expressed in terms of the holes. When computing the energy of an N-particle Hamiltonian expressed in holes, we must multiply the hole Hamiltonian $\bar{H}$ by the $(r-N)$-hole matrix ${}^{(r-N)}\bar{D}$ before taking the trace

$$E=\mathrm{Tr}(H\,{}^{N}D)=\mathrm{Tr}(\bar{H}\,{}^{(r-N)}\bar{D}), \tag{15}$$

where r is the rank of the one-particle basis set [37], and the general definition for the p-hole reduced density matrix (p-HRDM) is

$${}^{p}\bar{D}^{j_1,j_2,\ldots,j_p}_{i_1,i_2,\ldots,i_p}=\frac{1}{p!}\langle\psi|a_{j_1}a_{j_2}\cdots a_{j_p}a^{\dagger}_{i_1}a^{\dagger}_{i_2}\cdots a^{\dagger}_{i_p}|\psi\rangle. \tag{16}$$

Normalization of the p-HRDM in second quantization is $(r-N)!/[p!(r-N-p)!]$. As in the particle case, if we use the two-hole reduced Hamiltonian ${}^{2}\bar{K}$, we can express the expectation value with the 2HRDM ${}^{2}\bar{D}$,

$$E=\mathrm{Tr}(\bar{H}\,{}^{(r-N)}\bar{D})=\mathrm{Tr}({}^{2}\bar{K}\,{}^{2}\bar{D}). \tag{17}$$

To directly minimize the energy with respect to parameters in the 2HRDM, we would need to restrict the 2HRDM to the family of $(r-N)$-ensemble representable matrices.

Mathematically, the particle-hole equivalence manifests itself in that the particle and hole matrices exist in dual vector spaces. This means that a p-RDM may be written as a linear functional of the p-HRDM as well as lower HRDMs, and similarly, the p-HRDM may be written as a linear functional of the p-RDM and lower RDMs [38,39]. Valdemoro derives the functional dependence of the p-HRDM on the p-RDM by applying the fermion anticommutation rule

$$a^{\dagger}_{i}a_{j}+a_{j}a^{\dagger}_{i}=\delta_{i,j} \tag{18}$$

to the definition of the p-HRDM in second quantization to convert it to the p-RDM. Taking the expectation value of the above relation, we obtain the linear relationship between the elements of the 1RDM and the 1HRDM,

$${}^{1}D^{i}_{j}+{}^{1}\bar{D}^{j}_{i}={}^{1}I^{i}_{j}. \tag{19}$$

Converting the 2HRDM into a 2RDM produces the expression

$${}^{2}\bar{D}^{j_1,j_2}_{i_1,i_2}=(\delta^{i_1}_{j_1}\delta^{i_2}_{j_2}-\delta^{i_2}_{j_1}\delta^{i_1}_{j_2})/2-{}^{1}D^{i_1}_{j_1}\delta^{i_2}_{j_2}+{}^{1}D^{i_1}_{j_2}\delta^{i_2}_{j_1}+{}^{2}D^{i_1,i_2}_{j_1,j_2}, \tag{20}$$

which contains a sum of three different kinds of terms that have (i) one 2RDM, (ii) one 1RDM multiplying one δ, and (iii) two δs. Equation (20) is just the expectation value of the commutation relation for two fermion particles. The complexity of Eq. (20), compared to Eq. (19), reflects the fact that composite particles do not obey the simple fermion anticommutation relation (18). The deviation of composite particles from Fermi statistics helps to explain why the N-representability problem is much more difficult for the 2RDM than the 1RDM [40–43].

As p increases beyond 2, the derivation becomes unwieldy in second quantization, and Valdemoro relies upon a pictorial approach to simplify the presentation [15]. The relations may be expressed more concisely with wedge (or Grassmann) products from the theory of Grassmann algebra. Additional information about the definition and evaluation of Grassmann products is available in Appendix A. Written completely in this notation, the formula for the 2HRDM will have only three terms

$${}^{2}\bar{D}^{j_1,j_2}_{i_1,i_2}={}^{2}I^{i_1,i_2}_{j_1,j_2}-2\,{}^{1}D^{i_1}_{j_1}\wedge{}^{1}I^{i_2}_{j_2}+{}^{2}D^{i_1,i_2}_{j_1,j_2}, \tag{21}$$

where

$${}^{1}I^{i_1}_{j_1}=\delta^{i_1}_{j_1} \tag{22}$$

and

$${}^{2}I^{i_1,i_2}_{j_1,j_2}={}^{1}I^{i_1}_{j_1}\wedge{}^{1}I^{i_2}_{j_2}. \tag{23}$$

For convenience indices will often be omitted. Similarly, the p-HRDM may be expressed as a sum of $p+1$ wedge products that also correspond to the number of δ functions in each term. For ${}^{3}\bar{D}$ and ${}^{4}\bar{D}$ we have

$${}^{3}\bar{D}={}^{3}I-3\,{}^{1}D\wedge{}^{2}I+3\,{}^{2}D\wedge{}^{1}I-{}^{3}D \tag{24}$$

and

$${}^{4}\bar{D}={}^{4}I-4\,{}^{1}D\wedge{}^{3}I+6\,{}^{2}D\wedge{}^{2}I-4\,{}^{3}D\wedge{}^{1}I+{}^{4}D. \tag{25}$$

These formulas have a predictable structure with alternating signs and coefficients that follow a binomial distribution. In general, the p-HRDM may be expressed as a linear functional of the p-RDM and the lower RDMs,

$${}^{p}\bar{D}={}^{p}I+\sum_{n=1}^{p-1}(-1)^{n}\binom{p}{n}\,{}^{n}D\wedge{}^{(p-n)}I+(-1)^{p}\,{}^{p}D. \tag{26}$$

The linear functional expressing the p-RDM in terms of the p-HRDM and lower HRDMs may be obtained by switching the D and $\bar{D}$ in the above formula. Relation (26) represents the commutation or anticommutation relation (depending on whether p is even or odd, respectively) for two composite particles, each of them consisting of p fermions. While the deviation of the composite particles in Eq. (26) from Fermi statistics is often perceived as the source of difficulty [40–43], Valdemoro utilizes the increased complexity of these relations to develop an approximate reconstruction formula for the p-RDM in terms of lower RDMs.

Using second quantization, Valdemoro realized that these expressions could be rewritten as terms involving only RDMs and other terms involving only HRDMs. By writing ${}^1I$ in terms of ${}^1D$ and ${}^1\bar{D}$ through Eq. (19), the functional for ${}^2\bar{D}$ becomes

$$ {}^2\bar{D} - {}^2D = {}^1\bar{D}\wedge{}^1\bar{D} - {}^1D\wedge{}^1D. \tag{27} $$

To express the higher particle and hole matrices like ${}^qD$ and ${}^q\bar{D}$ where $q>2$ as RDMs and HRDMs, we must perform two sets of substitutions: (i) replace ${}^1I$ with ${}^1D+{}^1\bar{D}$ and (ii) assuming that we have already derived the expressions for the p-RDM as RDMs and HRDMs where $1<p<q$, we want to use these expressions to replace the p-RDMs in terms wedged with HRDMs. This second step causes mixed terms with wedges between HRDMs and RDMs to cancel [14]. For the 3HRDM we find

$$ \begin{aligned} {}^3\bar{D} + {}^3D = {}^1\bar{D}^3 + 3({}^2\bar{D} - {}^1\bar{D}^2)\wedge{}^1\bar{D} + {}^1D^3 \\ + 3({}^2D - {}^1D^2)\wedge{}^1D, \end{aligned} \tag{28} $$

where we have employed the right superscripts to indicate the number of times to wedge a symbol with itself, i.e., ${}^1D^2 = {}^1D\wedge{}^1D$. The right sides of these equations involve only lower RDMs and HRDMs. Because there were no approximations in the substitutions made, the resulting formulas are exact. However, as written, we still need to know the p-HRDM to determine the p-RDM.

Valdemoro then approximates the higher RDM from the lower RDMs by assuming that the RDM on the left may be equated to the formula involving lower RDMs on the right to obtain

$$ {}^2D_{\rm Vald} = {}^1D^2 \tag{29} $$

and

$$ {}^3D_{\rm Vald} = {}^1D^3 + 3({}^2D - {}^1D^2)\wedge{}^1D. \tag{30} $$

Similarly, the 4RDM would be approximated by

$$ {}^4D_{\rm Vald} = {}^1D^4 + 4({}^3D - {}^1D^3)\wedge{}^1D - 6({}^2D - {}^1D^2)\wedge{}^1D^2. \tag{31} $$

If we substitute $\bar{D}$ for D in the above equations, we obtain the analogous reconstruction formulas for the HRDMs. While Valdemoro's formula for the 2RDM in Eq. (29) is just the well-known expression for the 2RDM in the Hartree-Fock limit, the formulas for the 3RDM and 4RDM in Eqs. (30) and (31) possess corrections to their Hartree-Fock expressions ${}^1D^3$ and ${}^1D^4$. When the 2RDM is known, Valdemoro's approximate 3RDM may be constructed with Eq. (30), and then the resulting 3RDM ${}^3D_{\rm Vald}$ as well as the known 2RDM ${}^2D$ may be used in Eq. (31) to build the 4RDM. These reconstruction formulas are approximate because some terms in the p-RDM cancel with those in the p-HRDM and then do not appear within the commutation-anticommutation relations. We have found that these formulas may be obtained more directly from the q-HRDM functionals by approximating the identity operator ${}^1I$ by ${}^1D$ (which is equivalent to setting ${}^1\bar{D}=0$) and setting the q-HRDM to zero, ${}^q\bar{D}=0$. Applying these rules to functionals (21), (24), and (25) generates formulas (29), (30), and (31). This approximation is equivalent to Valdemoro's assumption of a separation of holes and particles and is also valid in the Hartree-Fock limit.

Nakatsuji and Yasuda [19] improved Valdemoro's formula for the 4RDM by finding one of the canceled terms through an analysis of Green's function decoupling diagrams. We now will show that Nakatsuji's correction may also be obtained from the perspective of the particle-hole equivalence. Valdemoro's rewriting of the particle-hole relations provides a powerful mechanism for reconstructing higher RDMs from lower RDMs. We offer here another technique for writing these relations to obtain some of the terms in the p-RDM and p-HRDM that cancel. The exact commutation-anticommutation relations in Eqs. (27) and (28) may be written as

$$ {}^2D - {}^2D_{\rm Vald} = {}^2\bar{D} - {}^2\bar{D}_{\rm Vald} \tag{32} $$

and

$$ {}^3D - {}^3D_{\rm Vald} = -({}^3\bar{D} - {}^3\bar{D}_{\rm Vald}), \tag{33} $$

in which ${}^2D$ and ${}^3D$ represent the exact RDMs. The error in Valdemoro's approximation for the 2RDM must be equal to the error in Valdemoro's approximation for the 2HRDM. Similarly, the error in Valdemoro's approximation for the 3RDM must be the negative of the error in Valdemoro's 3HRDM. Defining the errors in Valdemoro's formulas for the p-RDM and p-HRDM as

$$ {}^p\Delta = {}^pD - {}^pD_{\rm Vald} \tag{34} $$

and

$$ {}^p\bar{\Delta} = {}^p\bar{D} - {}^p\bar{D}_{\rm Vald}, \tag{35} $$

we may write the general, *exact* result for p-RDMs and p-HRDMs,

$$ {}^p\Delta = (-1)^p\ {}^p\bar{\Delta}. \tag{36} $$

With these error matrices Valdemoro's formulas for ${}^3D$ and ${}^4D$ may be rewritten even more concisely as

$$ {}^3D_{\rm Vald} = {}^1D^3 + 3\ {}^2\Delta\wedge{}^1D \tag{37} $$

and

$$ {}^4D_{\rm Vald} = {}^1D^4 + 4\ {}^3\Delta\wedge{}^1D + 6\ {}^2\Delta\wedge{}^1D^2. \tag{38} $$

Replacing the Ds in the above equations with $\overline{D}$ gives us the formulas for $^3\overline{D}$ and $^4\overline{D}$. Note that the coefficient of the last term in Eq. (38) is $+6$ rather than -6 as in Eq. (31) to correct the term $-12\,{}^2\Delta\wedge{}^1D^2$ from $4\,{}^3\Delta\wedge{}^1D$. Formulas (37) and (38) are consistent with the Hartree-Fock (HF) functionals because the Δ terms vanish in the HF limit. While the Δs are wedged with the 1RDM, there are no terms in these formulas where a Δ is wedged with another Δ. A term for the 4RDM which does not appear in Valdemoro's formula but only involves a simple wedge product of lower RDMs and vanishes in the HF limit is

$$k\,{}^2\Delta\wedge{}^2\Delta, \tag{39}$$

where k is a proportionality constant. Similarly, a suitable term for the 4HRDM is

$$k\,{}^2\overline{\Delta}\wedge{}^2\overline{\Delta}. \tag{40}$$

By Eq. (36) with $p=4$ the missing terms in Valdemoro's 4RDM formula *must equal* the missing terms in the 4HRDM formula. This final criterion is satisfied by the corrections in Eqs. (39) and (40) because ${}^2\Delta={}^2\overline{\Delta}$. The proportionality constant k in the correction may be determined by looking at the coefficients in Eqs. (37) and (38). The coefficient for ${}^2\Delta\wedge{}^1D$ in Eq. (37) where ${}^2\Delta$ is a two-particle matrix arises from the three distinct groupings of the particles: {12} {3}, {13} {2}, and {23} {1}. The same argument determines the coefficients in Eq. (38). Finally, we can ascertain that $k=3$ in Eq. (39) from the three distinct groupings of the four quasiparticles: {12} {34}, {13} {24}, and {14} {23}. Calculations with the Lipkin model confirm this choice for k. Combining this correction (39) with the original expression in Eq. (38), we obtain Nakatsuji and Yasuda's improved formula

$${}^4D_{\rm Nakat}={}^1D^4+4\,{}^3\Delta\wedge{}^1D+6\,{}^2\Delta\wedge{}^1D^2+3\,{}^2\Delta\wedge{}^2\Delta \tag{41}$$

for approximating the 4RDM where ${}^2\Delta$ and ${}^3\Delta$ are defined in Eq. (34).

Nakatsuji's correction in Eq. (39) only involves the *known* 2RDM. Hence, it may seem that we can simply determine the 3RDM by Eq. (37) as before, and use this result in Eq. (41) to generate an improved 4RDM. However, this attempt will generally not produce a significant improvement in the 4RDM because the error from the approximate 3RDM will dominate any correction provided by the new 4RDM term. To surmount this problem, we must find a correction for the 3RDM that will make it consistent in accuracy with the improved 4RDM. While Nakatsuji and Yasuda derive a correction for the 3RDM, which involves solving a system of equations and using the 1RDM for Hartree-Fock, we have a different approach for obtaining a suitable correction for the 3RDM directly from the improved 4RDM formula. Contracting the expression for ${}^4D$ in Eq. (41) generates a system of linear equations for a corrected 3RDM ${}^3D_{\rm pres}$ which does not involve the 4RDM,

$$\begin{aligned}{}^3D_{\rm pres}=\frac{4}{N-3}L_4^3[\,&{}^1D^4+4\,{}^3\Delta({}^3D_{\rm pres})\wedge{}^1D+6\,{}^2\Delta\wedge{}^1D^2\\&+3\,{}^2\Delta\wedge{}^2\Delta],\end{aligned} \tag{42}$$

where the contraction operator L denotes the summation required to map the four-particle matrix to a three-particle matrix and the term ${}^3\Delta({}^3D_{\rm pres})$ is calculated by Eq. (34) with ${}^3D_{\rm pres}$ used for the 3RDM. The subscript in ${}^3D_{\rm pres}$ indicates that the resulting 3RDM will be referred to as the present approximation. A system of linear equations rather than a formula for ${}^3D_{\rm pres}$ results because the unknown ${}^3D_{\rm pres}$ appears on both sides. The dependence of ${}^3\Delta$ on the improved 3RDM is denoted by ${}^3\Delta({}^3D_{\rm pres})$. If the 2RDM is known, we can solve for an improved 3RDM from Eq. (42) and then use the result in Eq. (41) to create a more accurate 4RDM. Because of the special relationship between the 3RDM equations and the 4RDM formula, the approximate 4RDM will automatically contract to the approximate 3RDM from which it was made.

B. Ensemble representability method

The reconstruction functionals, which approximate the 3- and 4RDMs in terms of lower RDMs, permit us to solve the CSE iteratively to achieve an accurate 2RDM. By Nakatsuji's theorem, however, other means of enforcing approximate N- representability should also partially remove the indeterminacy of the CSE. Here we discuss a new technique, which we refer to as the ensemble representability method, for performing reconstruction from the 2RDM to the p-RDM through approximate N-representability conditions without an explicit functional. The ERM for reconstruction will involve the *contraction condition* that (i) the p-RDM contract to the 2RDM as well as the *p-ensemble representability* restrictions that the p-RDM be (ii) Hermitian, (iii) antisymmetric, and (iv) positive semidefinite. A family of solutions, including the exact p-RDM, results because these conditions are only necessary for N-representability when $p<N$. The family nature of the solution is an interesting advantage of this approach since at least in principle new necessary constraints may be added to select further for the correct solution. As p approaches N the reconstruction from the 2RDM will become more accurate, and the ERM offers a systematic approach to determining the exact higher RDMs. Extending a result from Rosina, we will prove that when $N=p$ and the Hamiltonian has only two-particle interactions, the ERM will generate an exact p-RDM from a known energetically nondegenerate 2RDM. For four-particle systems the reconstruction functional for the 4RDM, discussed in the preceding section, does not produce exact results. To keep the calculations manageable, we will use the ERM method with $p=4$. Even when N is much larger than four, we will find that four-ensemble representability within the ERM will serve as powerful necessary conditions to generate an accurate 4RDM from a known 2RDM. It is important for us to realize that applying the ERM with the CSE produces a significantly smaller family of solutions than using four-ensemble N-representability with minimization of the energy expectation value. The minimization of the eigenvalue produces the 4RDM associated with the lowest energy of the four-particle reduced Hamiltonian, but the CSE, due to the testing of the two-particle space, does not allow this solution. While offering the possibility of a new approach, the ERM will also help us to better understand the importance of the CSE for finding

an accurate 2RDM and further elucidate the relationship between reconstruction functionals and N-representability.

Proving that the ground-state 2RDM contains enough information to generate the higher RDMs when we enforce ensemble N-representability will help motivate the ERM method and provide theoretical justification for reconstruction functionals for the 3- and 4RDMs in terms of the 2RDM. Previous work [14] on the CSE has appealed to the well-known theorem of Hohenberg and Kohn which demonstrates that the 1-density and the particle number N are theoretically sufficient to determine the ground-state energies and wave functions for atoms and molecules [30,31]. If the 1-density is enough to generate the wave function, it may seem the 1RDM or 2RDM must be more than sufficient to build a unique series of higher RDMs leading to the wave function. However, as we will show, this reasoning is incorrect, because an implicit assumption in the HK theorem is being neglected. The proof that the ground-state 1-density determines the ground and excited wave functions depends on a theoretic construction of the Hamiltonian from the 1-density [44]. For electronic structure problems the particle number N alone completely determines the form of the kinetic energy and electron repulsion terms within the Hamiltonian while the unknown one-particle part of the potential is specified through the given 1-density. Therefore in addition to a knowledge of the particle number N and the 1-density, the theorem of Hohenberg and Kohn implicitly assumes a knowledge of the kinetic and repulsion terms within the Hamiltonian. However, when we construct the higher RDMs from lower RDMs or densities, the Hamiltonian appears in neither the reconstruction formulas nor the restrictions of the ERM. Without more explicit knowledge of the Hamiltonian, the 1-density cannot determine the wave function as it is not difficult to illustrate. Let us consider the 1-density from a wave function which is not a Slater determinant. Both Gilbert [45] and Harriman [46], however, have shown that every 1-density may be represented by an N-particle Slater wave function. Hence, the 1-density clearly corresponds to at least two N-representable wave functions—one Slater wave function and one non-Slater wave function. Furthermore, linear combinations of these pure density matrices yield an infinite family of ensemble N-representable density matrices which contract to the correct 1-density.

Although the 1-density alone is not sufficient to determine the ground-state wave function for an *unknown* Hamiltonian with two-particle interactions, the 2RDM is enough to build the wave function, and the proof of this lies not in the HK theorem but in an important, less famous result, originally discussed by Rosina. Let us consider the 2RDM ${}^{2}D(\psi)$ for the antisymmetric nondegenerate ground state of an N-particle Hamiltonian H with two-particle interactions. By $D^{2}(\psi)$ we indicate the 2RDM from the contraction of a pure density matrix formed with ψ. The 2RDM determines the energy of the eigenstate ψ by Eq. (6). If ${}^{2}D(\psi)$ may be obtained from two antisymmetric wave functions ψ, the ground state will be degenerate since by Eq. (6) they must have the same energy. Because this contradicts the assumption that the ground state is nondegenerate, we have that ${}^{2}D(\psi)$ has only one pure N-representable preimage, ${}^{N}D(\psi)$. Furthermore, because all of the other states of the system have higher energies, minimizing over the larger class of N-ensemble representable matrices will always produce the pure density matrix, corresponding to the ground state. For this reason the ${}^{2}D$ of the ground state also has only one preimage in the larger family of ensemble density matrices. Hence, we have the reconstruction theorem, originally proved by Rosina at the 1967 conference on reduced density matrices at Queen's University [32].

Theorem 1: The 2RDM for the antisymmetric, nondegenerate ground state of an *unspecified* N-particle Hamiltonian H with two-particle interactions has a unique preimage in the set of N-ensemble representable density matrices ${}^{N}D$.

Let us consider the extension of this result to treat excited states and cases where the energies are degenerate. Assume that we know ${}^{2}D(\psi)$ for a nondegenerate excited state of an N-particle Hamiltonian H with two-particle interactions. If ${}^{2}D(\psi)$ reconstructs to two antisymmetric wave functions, the state will be degenerate since the wave functions must have the same energy. Since this contradicts the assumption that the state is nondegenerate, it follows that ${}^{2}D(\psi)$ has only one pure N-representable preimage, ${}^{N}D(\psi)$. Because the excited state cannot be obtained by a direct minimization of the energy, we cannot extend this result to the space of ensemble N-representable density matrices, ${}^{N}D$. We are interested, however, in dealing with excited states that are degenerate for a given energy eigenvalue. The assumption that the state is nondegenerate may be relaxed to the assumption that the given state may be distinguished from each of the other states of the system by at least one two-particle operator ${}^{2}B$. Two different states ψ_1 and ψ_2 have the same expectation values for all two-particle observables ${}^{2}B$ if and only if their corresponding 2RDMs ${}^{2}D(\psi_1)$ and ${}^{2}D(\psi_2)$ are equivalent, ${}^{2}D(\psi_1)={}^{2}D(\psi_2)$. Hence, the new assumption will only remain true if the 2RDM of the state ψ_1 is different from the 2RDM for *all* the other states ψ_i $(i\neq 1)$ of the system. This implies that the 2RDM for the state ψ_1 will have a unique *pure* N-representable preimage ${}^{N}D(\psi_1)$. We express this generalization of the reconstruction theorem as follows.

Theorem 2: If we assume that the given state of an *unspecified* N-particle Hamiltonian H with two-particle interactions may be distinguished from each of the other states of the system by at least one two-particle operator ${}^{2}B$, then the 2RDM for the state will have a unique preimage in the set of *pure* N-representable density matrices ${}^{N}D(\psi)$.

Because the resulting N-particle density matrix may be contracted to the p-RDM when $2<p<N$, a corollary to these theorems is that the 2RDM for electronic problems contains enough information to determine the p-RDM uniquely. Furthermore, these theorems also are true for reconstruction from a q-RDM when the Hamiltonian more generally contains q-particle excitations. Most importantly, these theorems justify the search for reconstruction functionals that build higher RDMs from the 2RDM without reference to the Hamiltonian in the functionals, and they indicate how within the ERM the imposition of p-ensemble representability represents a systematic shrinkage of the p-RDM family as p approaches N. For correlated systems similar justification is not possible for reconstruction schemes based on the 1RDM or 1-density. This elucidates why Valdemoro's formula for the 2RDM in terms of the 1RDM is equivalent to the Hartree-Fock restriction. To move significantly beyond

mean field for the 1RDM, we must incorporate information about the Hamiltonian. Thus the reconstruction problem for the 1-density and 1RDM not only involves preserving the N-representability as higher RDMs are generated but also determining whether the higher RDMs correspond to the Hamiltonian for the system under consideration.

Practical implementation of the ERM for reconstruction of the 4RDM requires us to enforce the four conditions mentioned above: (i) contraction of the 4RDM to the known 2RDM as well as the 4-ensemble representability conditions of (ii) Hermiticity, (iii) antisymmetry, and (iv) positive semidefiniteness. Conditions (ii) and (iii) are easily enforced since they simply require that certain elements of the 4RDM are made equal. In fact a four-particle matrix, fulfilling the first three conditions, may be constructed from a given antisymmetric, two-particle matrix through a linear mapping [47,48]. Restricting the 4RDM to the set of positive semidefinite matrices represents the most difficult condition. A well-known result from linear algebra [49], discussed by Harriman [11] in relation to the N-representability problem, permits us to restrict the 4RDM to the positive semidefinite set by parametrizing it through another real, Hermitian, antisymmetric matrix as follows:

$$^{4}D = RR. \tag{43}$$

Contracting this parametrization over two particles and setting the result to the known 2RDM furnishes us with a set of nonlinear equations for the matrix elements of R,

$$\frac{(N-2)(N-3)}{12}\,{}^{2}D = L_4^2({}^{4}D) = L_4^2(RR), \tag{44}$$

where the contraction operator L denotes the summation required to map the 4RDM to a 2RDM. Because there are more unknown elements of R than nonlinear equations, we may expect to find a family of solutions. This is true for $N>4$. By Rosina's theorem, however, at $N=4$ only one R satisfies these equations, and we obtain the exact 4RDM from the 2RDM. More details for solving these equations will be given when we apply the ERM in the next section.

IV. APPLICATION TO THE LIPKIN MODEL

Two reconstruction techniques have been presented in the preceding section to remove the indeterminacy of the CSE. To explore the accuracy of determining the 2RDM without the wave function through these techniques, we apply them to a quasispin model which was originally employed as a benchmark by Lipkin and co-workers [33,34] to study the correlation of fermions in a variety of many-body methods from perturbation theory to Green's function techniques. The Lipkin model will be described in detail including an important angular momentum analogy that simplifies the calculations by accounting for the system's symmetry. After a discussion of the numerical methods employed for solving the CSE, results will be presented for reconstructing the 3RDM and the 4RDM from a given 2RDM as well as for solving the CSE for the 2RDM with the ERM and functional reconstruction schemes. Results show that the CSE methods produce ground-state energies similar to those from SDCI and density matrices whose elements are about an order of magnitude more accurate than those from SDCI. These trends are illustrated for systems with different numbers of fermions including one system with as many as 40 particles. Finally, we apply the CSE method for the direct determination of excited-state 2RDMs.

A. Description of the model

Consider a quantum system with two energy levels at $-\epsilon/2$ and $+\epsilon/2$, each of which has N degenerate states. By filling each of the N states in the lower level with one fermion, we generate the ground state for a noninteracting N-particle system. The system may be completely characterized by two quantum numbers m and p where m (either -1 or $+1$) denotes the level and p distinguishes the states in each level by ranging from 1 to N. While more than one fermion will possess the same m quantum number, each fermion will always occupy a different state as denoted by *both* quantum numbers m and p. To this noninteracting system, we add a perturbation V which acts to switch two fermions from states in one level to states in the other level. The Hamiltonian for the system is

$$H = \frac{\epsilon}{2}\sum_{m,p} m a_{m,p}^{\dagger} a_{m,p} + V \sum_{p_1,p_2,m} a_{m,p_1}^{\dagger} a_{m,p_2}^{\dagger} a_{-m,p_2} a_{-m,p_1}. \tag{45}$$

The nature of the perturbation in V only allows transitions between states with the same value for p. This implies that the noninteracting ground-state configuration will only mix with configurations in which each of the N fermions has a different quantum number p. Since a fermion may have one of two m values for each of the N values of the quantum number p and yet no two of the N fermions may have the same value of p, there will be 2^N possible configurations. The different configurations of fermions are the basis functions for the system. When V is negligible compared to ϵ, the system populates the lowest level to achieve its minimum energy. The wave function in this case is just the determinant of the one-particle states in the lower level which corresponds to the Hartree-Fock solution for the ground state. When the perturbation V becomes significant, the Hartree-Fock configuration will yield an upper bound on the ground energy. As in configuration interaction for atoms and molecules these approximations to the true wave function and its energy may be improved by including excited configurations. The ground-state wave function will be a linear combination of the possible configurations that delicately balances the self and interaction energies to achieve a minimum total energy.

The probability of finding the system with a given number of fermions in the upper level is independent of the p states that the fermions inhabit. Because of this the number of excited fermions alone determines the probability of the system being found in a certain configuration. Grouping all of the configurations according to the number of excitations, we can reduce the size of the basis set for the Hamiltonian from 2^N configurations to the number of excitations which is only $N+1$. This possible reduction in basis size, arising from the indistinguishability of the p states in the Hamiltonian, may be directly incorporated into the Hamiltonian by writing H in terms of angular momentum operators [33]. For this reason models like this one are often referred to as quasispin models [35]. Using the anticommutation relations for the creation and annihilation operators and the following definitions for the angular momentum operators:

$$J_{+,-}=\sum_{p} a^{\dagger}_{+1,p}a_{-1,p}\,, \quad J_{-,+}=\sum_{p} a^{\dagger}_{-1,p}a_{+1,p}\,, \quad (46)$$

and

$$J_{+,+}=\sum_{p} a^{\dagger}_{+1,p}a_{+1,p} \quad J_{-,-}=\sum_{p} a^{\dagger}_{-1,p}a_{-1,p}\,, \quad (47)$$

where $J_{+,-}$ and $J_{-,+}$ represent one-particle transitions while $J_{+,+}$ and $J_{-,-}$ count the number of particles in the upper and lower levels, respectively, we can write the Hamiltonian as

$$H=\frac{\epsilon}{2}(J_{+,+}-J_{-,-})+V(J^{2}_{+,-}+J^{2}_{-,+}). \quad (48)$$

The z component of the angular momentum is just half of the difference between the number of particles in the upper level and the number in the lower level. Because the H commutes with the square of the total angular momentum J^2, the Hamiltonian partitions into noninteracting submatrices which correspond to the different values of J. The order of each submatrix is $2J+1$. The values of J_z range in each submatrix from $-J$ to $+J$. Since all of the fermions inhabit the lowest level in the unperturbed ground-state configuration, the value for J_z in this case is $-N/2$. This value for J_z, however, only occurs within the largest submatrix of order $N+1$ when $J=N/2$. Thus, to determine the correlated ground state, we only need to consider the $N+1$ configurations in the largest submatrix since other configurations will not mix with the ground state. These $N+1$configurations, as we expect, correspond to exciting a different number of fermions into states of the higher energetic level. In Appendix B we discuss the calculation of the wave functions from the Hamiltonian in Eq. (48) and a procedure that we developed for obtaining the RDMs from the wave functions with a minimum amount of storage. For additional details about the model the reader is referred to the original articles by Lipkin and co-workers [33]. Calculations by Lipkin on this model and the application of N-representability conditions to a similar model by Mihailović and Rosina [34] clearly indicate that the quasispin model presents a challenging problem in correlation despite the feasibility of direct solution. Hence, while the symmetry of the state in each level simplifies the computation, the model faithfully reproduces the difficulty of the electronic correlation problem to provide an excellent benchmark for comparing many-body methods.

B. Numerical methods

Having established the CSE, the reconstruction techniques, and the Lipkin model, we now discuss the methods by which the CSE may be solved for the 2RDM. To use the reconstruction functionals with the CSE, we employ the following self-consistent procedure, similar to the one employed by Colmenero and Valdemoro [16].

(1) Build the 3RDM and 4RDM from an initial guess for the 2RDM (for example, the Hartree-Fock 2RDM).
(2) Substitute the 2-, 3-, and 4RDMS into the left-hand side of the CSE in Eq. (12) to produce a new 2RDM guess multiplied by the energy.
(3) Symmetrize and normalize the 2RDM from the last step to obtain the next guess for the 2RDM. Normalization is equivalent to dividing by the energy.
(4) Repeat steps (1)–(3) until convergence is achieved.

Colmenero and Valdemoro explain the method's convergence through a result from the solution of nonlinear equations [16]. We justify the technique differently by revealing its connection with the power method [49] for finding eigenvalues.

Consider the eigenvalue equation $H\psi_0=E_0\psi_0$. In the power method the trial vector ϕ_0 is multiplied by the matrix H to produce another vector which after normalization becomes the next trial vector ϕ_2. As in the iterative procedure for the CSE, explained above, this process is repeated until convergence is achieved. The method only converges to the eigenvector whose eigenvalue has the maximum absolute value. We can understand this by expanding the initial trial guess ϕ_0 in terms of the actual eigenvectors for the problem

$$\phi_0=a_0\psi_0+a_1\psi_1+a_2\psi_2+\cdots, \quad (49)$$

where the a_i are the expansion coefficients. The $(N+1)$th trial vector ϕ_N arises from acting N times on ϕ_0 with the H matrix and dividing N times by the energy E_0,

$$\phi_N=H^N\phi_0=a_0\psi_0+a_1\left(\frac{E_1}{E_0}\right)^N\psi_1+a_2\left(\frac{E_2}{E_0}\right)^N\psi_2+\cdots\,. \quad (50)$$

As long as the absolute value of E_0 is greater than that of the other eigenvalues, the method will converge linearly towards the true eigenvector ψ_0. Similarly, the iterative solution of the CSE discovers the component of the trial RDM corresponding to the eigenvalue with the largest absolute value.

While we employ the power method to solve the CSE with the reconstruction functionals, a Newton's method is utilized when we reconstruct higher RDMs from known lower RDMs with ERM or solve the CSE through ERM reconstruction. We first examine ERM reconstruction from *known* lower RDMs. As described in Eq. (43) of Sec. III B, the ERM parametrizes the 4RDM in terms of a product of antisymmetric, Hermitian matrices R to preserve four-ensemble representability. By contracting the parametrized 4RDM to the two-particle level as in Eq. (44), subtracting the known 2RDM from this parametrized 2RDM, and setting the resulting matrix F to the zero matrix, we obtain

$$F=\frac{12}{(N-3)(N-2)}L^2_4(RR)-{}^2D=0, \quad (51)$$

whose elements are nonlinear equations that may be solved iteratively for the unknowns in R by a Newton's method. Since there are more elements of R than equations, we have a rectangular Jacobian J [40] whose elements are calculated analytically by

TABLE I. The errors in building the 3- and 4RDMs from a known N-representable 2RDM are reported through four different quantities, described in detail within the table's footnotes. All error measurements involve RDMs normalized to unity. For the 3RDM we examine Valdemoro's reconstruction functional as well as the functional with our correction for the 3RDM. For the 4RDM we present Valdemoro's reconstruction functional, the functional with Yasuda and Nakatsuji's correction, reconstruction by ERM, and finally, reconstruction by ERM with the addition of the CSE condition.

Parameters		3RDM errors		4RDM errors		4RDM errors	
N	$\widetilde{V}$	Valdemoro	Present	Valdemoro	Nakatsuji	ERM	ERM+CSE
4	0.065 80	[a]4.25×10^{-3}	4.26×10^{-4}	1.47×10^{-2}	2.13×10^{-3}	0	0
		[b]1.59×10^{-3}	7.89×10^{-6}	3.27×10^{-2}	3.16×10^{-5}	0	0
		[c]4.25×10^{-3}	8.37×10^{-6}	3.94×10^{-4}	8.37×10^{-6}	0	0
		[d]4.31×10^{-3}	6.50×10^{-5}	1.56×10^{-2}	8.86×10^{-4}	0	0
6	0.040 72	1.28×10^{-3}	1.06×10^{-4}	1.98×10^{-3}	5.33×10^{-4}	1.42×10^{-3}	1.92×10^{-12}
		1.56×10^{-4}	3.46×10^{-7}	4.96×10^{-4}	4.61×10^{-7}	0	0
		1.25×10^{-3}	1.23×10^{-6}	9.08×10^{-5}	1.23×10^{-6}	0	0
		1.32×10^{-3}	1.19×10^{-5}	2.18×10^{-3}	4.72×10^{-5}	0	0
8	0.031 32	6.96×10^{-4}	5.04×10^{-4}	1.01×10^{-3}	2.55×10^{-4}	1.08×10^{-3}	1.23×10^{-8}
		4.16×10^{-5}	5.95×10^{-8}	6.12×10^{-5}	4.76×10^{-8}	0	0
		6.66×10^{-4}	4.39×10^{-7}	5.25×10^{-5}	4.39×10^{-7}	0	0
		7.22×10^{-4}	5.48×10^{-6}	9.22×10^{-4}	1.81×10^{-5}	0	0
15	0.015 00	1.44×10^{-4}	5.80×10^{-6}	2.04×10^{-4}	2.97×10^{-5}	2.47×10^{-4}	1.34×10^{-9}
		2.07×10^{-6}	7.64×10^{-10}	9.33×10^{-7}	2.55×10^{-7}	0	0
		1.35×10^{-4}	2.39×10^{-8}	9.20×10^{-6}	2.39×10^{-8}	0	0
		1.52×10^{-4}	5.40×10^{-7}	1.44×10^{-4}	1.55×10^{-6}	0	0
25	0.009 171	5.21×10^{-5}	1.38×10^{-6}	7.26×10^{-5}	7.10×10^{-6}	1.60×10^{-4}	2.82×10^{-9}
		2.50×10^{-7}	3.68×10^{-11}	5.46×10^{-8}	6.69×10^{-12}	0	0
		4.80×10^{-5}	3.45×10^{-9}	3.55×10^{-6}	3.45×10^{-9}	0	0
		5.55×10^{-5}	1.28×10^{-7}	4.72×10^{-5}	3.45×10^{-7}	0	0

[a] The error in the reconstructed matrix measured by the infinity norm of its deviation from the exact RDM.

[b] The error in the 2RDM determined by contracting the approximate 3- or 4RDM to a 2RDM and then computing the infinity norm of its deviation from the exact 2RDM.

[c] The energy error corresponding to the absolute deviation of the reconstructed RDM's approximate energy from the exact energy.

[d] The error in the positive semidefiniteness of the matrix calculated by adding the squares of its negative eigenvalues and then taking the square root.

$$J_{k,l}^{i,j}=\frac{\partial F_{i,j}}{\partial R_{k,l}}. \tag{52}$$

Although the Jacobian J is singular, a specific Newton direction is chosen by using the singular value decomposition technique to select the direction with the minimal 2-norm [50]. When $N>4$ the elements of R are underdetermined, and a family of reconstructed 4RDMs will result. Since the exact 4RDM must obey the four-ensemble representability and contraction conditions, it will be a member of the resulting family. Newton's method stops after it has located a single member of the family. An analogous procedure may be employed to solve the CSE with ERM reconstruction when the desired 2RDM is *unknown*. Again the 4RDM is parametrized with the elements of R as in Eq. (43). Formulas for the lower RDMs in terms of R are obtained by contracting the 4RDM. All of the RDMs in the CSE in Eq. (12) are replaced with their R matrix parametrizations, and the right-hand side of Eq. (12) is moved to the left side to generate a system of nonlinear equations of the form $F_i=0$. The index i ranges over each of the nonlinear equations represented by the CSE in Eq. (12). These nonlinear equations $F_i=0$ produce a rectangular Jacobian as in Eq. (52) which may be used to solve for the unknowns in R through a Newton's method.

C. Results and discussion

1. Reconstruction results

Applying the techniques described above, we reconstructed the 3RDM and 4RDM from a knowledge of the 2RDM. For the number N of fermions ranging from 4 to 25 the reconstruction errors, measured in four different ways, are reported in Table I for ground states and Table II for excited states. Some errors will be given as the infinity norm of an error matrix. The infinity norm of a matrix is the maximum row sum where the row sum is computed by adding the magnitudes of the elements in a given row. The four reported quantities are (1) the error in the elements of the reconstructed matrix measured by the infinity norm of its deviation from the exact RDM, (2) the error in the 2RDM determined by contracting the approximate 3- or 4RDM to a 2RDM and then computing the infinity norm of its deviation from the exact 2RDM, (3) the energy error corresponding to the absolute deviation of the reconstructed RDM's approximate en-

TABLE II. The errors in building the 3- and 4RDMs from a known excited-state 2RDM are reported through four different quantities, described in detail within the table's footnotes. All error measurements involve RDMs normalized to unity. The level of the excited state is indicated by the subscript on the numbers of particles N. The reconstruction techniques are the same as those tested in Table I.

Parameters		3RDM errors		4RDM errors		4RDM errors	
N	$\tilde{V}$	Valdemoro	Present	Valdemoro	Nakatsuji	ERM	ERM+CSE
4_2	0.065 80	[a]1.66×10^{-1}	5.75×10^{-1}	2.08	1.30	0	0
		[b]4.43×10^{-2}	3.64×10^{-2}	3.75	1.46×10^{-1}	0	0
		[c]1.18×10^{-1}	1.90×10^{-2}	7.18×10^{-2}	1.90×10^{-2}	0	0
		[d]1.09×10^{-1}	3.98×10^{-1}	1.97	5.10×10^{-1}	0	0
10_2	0.040 72	2.19×10^{-2}	6.13×10^{-2}	1.76×10^{-1}	1.74×10^{-1}	5.69×10^{-3}	8.73×10^{-6}
		7.07×10^{-4}	1.49×10^{-4}	1.79×10^{-3}	8.53×10^{-5}	0	0
		1.89×10^{-2}	1.64×10^{-3}	7.80×10^{-3}	1.64×10^{-3}	0	0
		1.48×10^{-2}	3.61×10^{-2}	9.07×10^{-2}	4.62×10^{-2}	0	0
10_3	0.031 32	3.21×10^{-2}	1.69×10^{-1}	4.09×10^{-1}	4.03×10^{-1}	3.81×10^{-2}	4.89×10^{-6}
		9.14×10^{-4}	3.14×10^{-4}	5.29×10^{-3}	1.80×10^{-4}	0	0
		2.44×10^{-2}	2.89×10^{-3}	1.49×10^{-2}	2.89×10^{-3}	0	0
		1.91×10^{-2}	1.10×10^{-1}	2.52×10^{-1}	1.17×10^{-1}	0	0
25_2	0.015 00	3.25×10^{-3}	8.63×10^{-3}	2.58×10^{-2}	2.61×10^{-2}	1.83×10^{-3}	9.26×10^{-10}
		1.60×10^{-5}	1.36×10^{-6}	8.56×10^{-6}	2.47×10^{-7}	0	0
		3.06×10^{-3}	1.22×10^{-4}	9.06×10^{-4}	1.22×10^{-4}	0	0
		2.25×10^{-3}	5.11×10^{-3}	1.12×10^{-2}	7.39×10^{-3}	0	0
25_3	0.009 171	6.01×10^{-3}	2.46×10^{-2}	6.98×10^{-2}	6.99×10^{-2}	7.56×10^{-3}	8.01×10^{-7}
		2.73×10^{-5}	3.55×10^{-6}	3.01×10^{-5}	6.46×10^{-7}	0	0
		5.23×10^{-3}	3.03×10^{-4}	2.47×10^{-3}	3.03×10^{-4}	0	0
		3.85×10^{-3}	1.51×10^{-2}	3.57×10^{-2}	2.01×10^{-2}	0	0

[a] The error in the reconstructed matrix measured by the infinity norm of its deviation from the exact RDM.

[b] The error in the 2RDM determined by contracting the approximate 3- or 4RDM to a 2RDM and then computing the infinity norm of its deviation from the exact 2RDM.

[c] The energy error corresponding to the absolute deviation of the reconstructed RDM's approximate energy from the exact energy.

[d] The error in the positive semidefiniteness of the matrix calculated by adding the squares of its negative eigenvalues and then taking the square root.

ergy from the exact energy, and (4) the error in positive semidefiniteness of the matrix by adding the squares of its negative eigenvalues and then taking the square root. All error measurements are performed with RDMs that are normalized to unity. When reconstructing for excited states, we select as the initial guess the RDM of the energetically closest Hartree-Fock state. There are two parameters in the Lipkin model: the level spacing ϵ and the interaction strength V. To make the energies dimensionless, we perform calculations with the scaled Hamiltonian obtained by dividing the H in Eq. (45) by ϵ. The dimensionless interaction strength $\tilde{V}$ $(=V/\epsilon)$ is chosen for each N to make the ratio of correlation energy to total energy in the Lipkin model consistent with the values reported in the literature for atoms with the corresponding number N of electrons [51,52].

Across all categories in Table I Nakatsuji's correction to Valdemoro's 4RDM and the present correction to Valdemoro's 3RDM significantly improve the accuracy by one or more orders of magnitude. These improvements are consistent with those reported by Nakatsuji for the four-electron Be atom [19]. While Nakatsuji employs the exact 3RDM in his reconstruction results for the 4RDM, we build the 4RDM with the exact 2RDM but a 3RDM obtained by the corrective technique proposed in the present paper. Hence, our implementation of Nakatsuji's improved 4RDM formula actually includes the present 3RDM correction. Building only from the 2RDM is consistent with the reconstruction theorem and our ultimate goal of using these functionals with the CSE which only tests the two-electron space. Table I also gives results for the ERM reconstruction that imposes the four-ensemble representability and contraction conditions. For $N=4$ the ERM produces exact results as expected from Rosina's theorem, and for any N, it yields zero for the last three criteria since the reconstructed 4RDM is forced to have nonnegative eigenvalues and to contract correctly to the known 2RDM. The approximate 4RDM from this scheme shows more deviation from the elements of the exact 4RDM than Nakatsuji's 4RDM. By adding the restriction that the 4RDM must obey the CSE, however, we obtain reconstruction results which are markedly superior to those achieved by the reconstruction functionals. For all methods as N increases, the RDM approximations increase in accuracy.

While the reconstruction results for some excited states at different N values are presented in the same format in Table II, there are several important differences in the data. Accuracy of reconstruction in all categories is significantly less for the given excited states than for the ground state. This is especially pronounced for the reconstruction functionals. Also, the corrections to Valdemoro's functional offer a more nebulous improvement. Although the errors in the energies and 2RDMs decrease with the correction for the 3RDM, the

TABLE III. The CSE and wave function approaches are compared for the calculation of ground-state energies and 2RDMs. Energies are reported first, and then the error in the 2RDM is given as measured by the infinity norm of its deviation from the exact 2RDM. All error measurements involve RDMs normalized to unity. Solutions of the CSE by both the functional and ERM reconstruction methods are presented.

Parameters			CSE approach		Wave function approach		
N	$E_{\text{corr}}/E_{\text{FCI}}\times 100\%$	$\tilde{V}$	Functional	ERM	Hartree-Fock	SDCI	Full CI
4	0.643	0.065 80	−2.012 75	−2.012 95	−2	−2.012 91	−2.012 95
			2.82×10^{-4}	0	3.80×10^{-2}	2.52×10^{-4}	0
6	0.413	0.040 72	−3.012 35	−3.012 53	−3	−3.012 36	−3.012 45
			1.54×10^{-4}	2.78×10^{-5}	2.41×10^{-2}	3.73×10^{-4}	0
8	0.344	0.031 32	−4.013 73	−4.013 94	−4	−4.013 64	−4.013 79
			1.18×10^{-4}	4.11×10^{-5}	1.90×10^{-2}	4.39×10^{-4}	0
10	0.303	0.025 90	−5.015 17	−5.015 40	−5	−5.014 98	−5.015 19
			9.94×10^{-5}	4.73×10^{-5}	1.60×10^{-2}	4.76×10^{-4}	0
15	0.158	0.015 00	−7.511 94	−7.512 02	−7.5	−7.511 74	−7.511 90
			3.74×10^{-5}	1.70×10^{-5}	9.16×10^{-3}	2.56×10^{-4}	0
20	0.126	0.011 46	−10.012 66	−10.012 79	−10	−10.012 40	−10.012 59
			2.75×10^{-5}	2.33×10^{-5}	7.08×10^{-3}	2.28×10^{-4}	0
25	0.102	0.009 171	−12.512 83	−12.512 97	−12.5	−12.512 54	−12.512 74
			2.10×10^{-5}	2.09×10^{-5}	5.69×10^{-3}	1.95×10^{-4}	0
40	0.0647	0.005 730	−20.013 07	−20.013 24	−20	−20.012 72	−20.012 95
			1.22×10^{-5}	1.68×10^{-5}	3.58×10^{-3}	1.33×10^{-4}	0

errors in the 3RDM elements and the positivity actually become worse. Similarly, for the 4RDM the corrections only contribute to fixing the 2RDM and energy errors. This contrasts markedly with the ground-state results in Table I where improvement from the corrections was evident in all categories. For excited states the ERM generates an approximation to the 4RDM that is more accurate in all categories than any functional reconstruction. Again adding to the ERM the CSE, which enforces the correct behavior for the local energy, improves the reconstruction by many orders of magnitude.

2. CSE results

Within the CSE the reconstruction schemes are utilized to determine the 2RDM directly without generating the wave function. These CSE methods will be compared with three standard wave function approaches: Hartree-Fock, single-double configuration interaction, and full configuration interaction (FCI). As an initial guess for the 2RDM in the CSE methods we choose the Hartree-Fock 2RDM. In Table III the energies are reported first and then the error in the 2RDM measured by the infinity norm of its deviation from the exact 2RDM. As in reconstruction these results are for 2RDMs normalized to unity. With the corrective terms the reconstruction functional technique yields energies that are slightly better than SDCI. The energies from the ERM approach, which all happen to be lower than the true energies, fall below the FCI results by about the same amount that the SDCI energies are above them. These trends in energy with N are displayed for the CSE techniques and SDCI in Fig. 1. As noted by Nakatsuji and Yasuda in their calculations, the approximate 2RDMs from the CSE methods are about an order of magnitude better than the 2RDMs from SDCI. This important improvement, illustrated in Fig. 2, may arise from the nonvariational nature of the CSE methods. Additional accuracy for the 2RDM will be very useful when computing expectation values other than the energy. While Yasuda and Nakatsuji solve the CSE for systems with four to 14 electrons [19], our results show that the method remains promising for larger numbers of fermions.

The power method cannot be applied to excited states because it will converge to the state with the maximum absolute eigenvalue. This may explain why Colmenero and Valdemoro's attempt to calculate the excited states of Be with the CSE resulted in the convergence upon the ground state [16]. We also found that the power method would not work for the excited states of the Lipkin model. However, by using the ERM with a Newton's method, we were able to obtain the first excited-state results for the CSE, given in

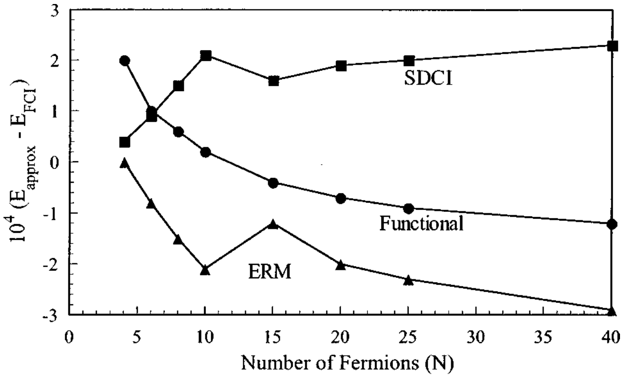

FIG. 1. The approximate energies, produced by the CSE with the ERM and functional reconstruction methods as well as SDCI, are displayed as deviations from the FCI energies. By the variational principle the SDCI energy is always an upper bound to the FCI energy. Both CSE techniques yield energies comparable in error to those from SDCI. Note that all energies are dimensionless.

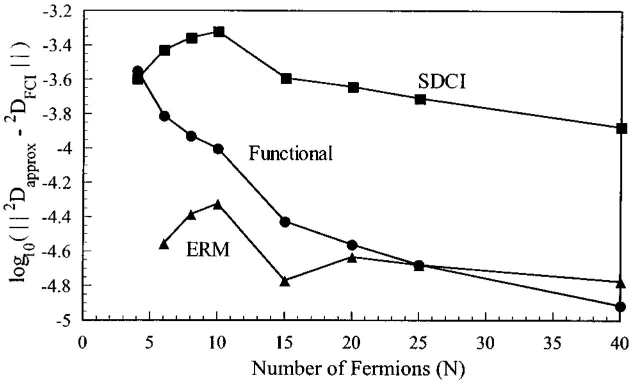

FIG. 2. The logarithmic errors in the approximate 2RDMs, generated by the CSE with the ERM and functional reconstruction methods as well as SDCI, are shown for a range of N. We measure the error in an approximate 2RDM by taking the infinity norm of its deviation from the exact 2RDM. Results indicate that the CSE methods produce 2RDMs which are generally an order of magnitude more accurate than those from SDCI.

Table IV. While the first excited state was procured with an accuracy comparable to the ground state, the second excited state gave energies that were quite lower than those from FCI. The success of the first excited state may be related to the fact that it does not mix with the ground state since they differ in parity. Both states reconstructed with about the same accuracy in Table II, and yet they exhibit quite different accuracy when determined with the CSE.

These calculations show that the CSE may be applied to excited states. Another method for obtaining excited states, already suggested although not computed by Colmenero and Valdemoro [16], would involve directly solving the CSE for the transition RDM between the ground state and an excited state. Reconstruction functionals, similar to those employed for building the ground-state 3- and 4RDMs from the 2RDM, are derivable for the transition RDMs. If a large number of excited states are required, we could follow the 2RDMs for all of the excited states as well as the two-particle transition RDMs (2 T RDMs). Since the 4RDMs and the 4 T RDMs may be resolved with the 2RDMs and the 2 T RDMs, associated with a complete set of eigenstates [34], the CSE would no longer be indeterminate. To solve this set of coupled CSEs for the 2RDMs and 2 T RDMs, we might differentiate the equations with respect to a correlation parameter in the Hamiltonian to produce differential equations for the changes in the RDMs and the energy differences. As in the parametric equations of motion methods for solving the Schrödinger equation [53,54], the energies and the RDMs in the CSEs could be propagated from a known limit like Hartree-Fock to the correlated solution. While furnishing an exact reconstruction, this approach requires calculating with 2RDMs and 2 T RDMs for all the wave functions of the system.

Since the CSE technique may provide a fresh alternative to contemporary wave function calculations, it is important for us to investigate its connections with traditional quantum calculations, especially configuration-interaction methods. In both Hartree-Fock and single-double configuration interaction we are using an incomplete basis set, and hence, we obtain upper bound solutions by the variational principle. In contrast the CSE calculations are performed with a 2RDM that represents the full-CI basis. Forcing the 2- and 4RDMs to be N-representable within the CSE produces the FCI result. When N-representability conditions are not fully applied, the basis set is overcomplete, and variational minimization of the energy from the CSE will yield a lower bound. Although the energies from our solution of the CSE with ERM restrictions gave energies lower than the exact energies, we were not guaranteed lower bounds because we did not minimize the energy. Overcompleteness of the basis arises for correlated systems because, while excitations from the ground state of a Hamiltonian without particle interactions (i.e., HF) are orthogonal, excitations from correlated wave functions are not orthogonal [55]. Related problems occur in other approaches to correlation, including Green's function theory, and require the use of inner projection or Gram-Schmidt orthogonalization [56,57]. Hence, for one-particle Hamiltonians like the one for HF the higher RDMs may be readily reconstructed from the 1RDM. The 2RDM and 3RDM are ${}^1D\wedge{}^1D$ and ${}^1D\wedge{}^1D\wedge{}^1D$, respectively, while in general the p-RDM is ${}^1D^p$ where the right superscript indicates that the 1RDM should be wedged p times with itself. Building higher RDMs from the 2RDM for correlated systems requires a more complicated reconstruction functional. Overcompleteness manifests itself in that commuta-

TABLE IV. The CSE and wave function approaches are compared for the calculation of excited-state energies and 2RDMs. We report the error in the 2RDM as measured by the infinity norm of its deviation from the exact 2RDM. All error measurements involve RDMs normalized to unity. The CSE is solved with the ERM reconstruction technique in which four-ensemble representability and contraction conditions are imposed.

Parameters			CSE+ERM		Hartree-Fock		Full CI
N	$E_{corr}/E_{FCI}\times100\%$	$\tilde{V}$	Energy	2RDM error	Energy	2RDM error	
6_2	1.22	0.040 72	−2.024 58	5.03×10^{-5}	−2	4.59×10^{-2}	−2.024 72
6_3	1.69	0.040 72	−1.023 06	1.58×10^{-3}	−1	3.21×10^{-2}	−1.017 14
8_2	1.02	0.031 32	−3.030 51	8.36×10^{-5}	−3	4.10×10^{-2}	−3.030 80
8_3	1.48	0.031 32	−2.058 12	5.72×10^{-3}	−2	3.75×10^{-2}	−2.030 02
10_2	0.897	0.025 90	−4.035 72	1.15×10^{-4}	−4	3.71×10^{-2}	−4.036 20
10_3	1.34	0.025 90	−3.090 21	8.25×10^{-3}	−3	3.98×10^{-2}	−3.040 85
15_2	0.472	0.015 00	−6.530 36	7.01×10^{-5}	−6.5	3.00×10^{-2}	−6.530 81
15_3	0.735	0.015 00	−5.585 14	5.45×10^{-3}	−5.5	2.33×10^{-2}	−5.540 74

tion and anticommutation relations for composite particles do not obey simple fermion or boson statistics [40,42,43]. While this greater complexity is generally perceived as a hindrance to solving the N-representability problem, Valdemoro uses this complexity to generate the approximate RDMs from the lower RDMs.

V. CONCLUSION

Distinguished from traditional quantum calculations which variationally compute the N-particle wave function in a truncated basis set, the CSE technique solves directly for the 2RDM by combining an approximate reconstruction scheme with the CSE. The given derivation of the second-quantized CSE, reinforcing how the CSE tests the two-electron space, does not require Valdemoro's generalized matrix contraction mapping. We present a formal proof of Nakatsuji's theorem for the second-quantized CSE. By itself the CSE cannot be used to solve for the 2RDM since it also depends on the 4RDM. Recently, however, Valdemoro has overcome this difficulty through a reconstruction scheme for building approximations to the 3- and 4RDMs from the 2RDM. We present a simpler representation for Valdemoro's formulas through the notation of wedge product from the theory of Grassmann algebra. While Nakatsuji has recently obtained a significant correction to Valdemoro's 4RDM from the use of schematic Green's function diagrams, we show that the same correction may also be achieved from the perspective of particle-hole equivalence. A correction for the 3RDM, different from the given in [19] but also consistent with the improved 4RDM, is also derived. We justify the approximation of higher RDMs as functionals of the 2RDM by demonstrating a result, originally proved by Rosina, that the 2RDM for a ground electronic state contains enough information to determine the N-particle ensemble density matrix completely without any information about the Hamiltonian other than that it has no more than two-particle interactions. We extend this result by proving that the 2RDM for any state, distinguishable from the other states of the system by some two-particle operator, uniquely determines a pure density matrix of N particles. This result prepares us for the extension of the CSE method beyond the ground state. In addition to the reconstructive functional approach we present another reconstruction method (ERM) based on imposing four-ensemble representability and contraction conditions.

The CSE with the functional and ERM reconstruction schemes is illustrated through Lipkin's quasispin model. Both schemes produced energies as accurate as SDCI while the resulting 2RDMs had elements that were generally more accurate than those from SDCI by an order of magnitude. This may significantly improve the accuracy of the expectation values for observables of the system other than the energy. We report the first results from applying the CSE method to excited states. While the energies and densities for the excited states were not consistently as good as for the ground state, this approach to excited-state energies may prove useful. Previous calculations have applied the CSE methods to systems with about 14 electrons. Our results with as many as 40 particles confirm that accuracy of the method is maintained with increasing numbers of particles. The success of the CSE method will depend on the efficiency and storage requirements of the algorithms developed to treat electronic systems. Valdemoro has just reported a reconstruction algorithm which avoids storage of the 4RDM [20]. Future research will involve searching for the most efficient and accurate implementations of the CSE techniques for atoms and molecules. Through its direct determination of the 2RDM without the wave function the CSE, coupled with a reconstruction strategy, provides a fresh path towards the calculation of electron correlation.

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APPENDIX A: GRASSMANN PRODUCTS

The Grassmann (or wedge) product of a q-RDM with a $(p-q)$-RDM may be expressed as

$$ {}^{q}D\wedge{}^{(p-q)}D = A_N\,{}^{q}D\otimes{}^{(p-q)}D A_N, \qquad \text{(A1)} $$

where the A_N is the N-particle antisymmetrization operator and $\otimes$ is the tensor product. To utilize this formula in a calculation, we must understand the technique for evaluating wedge products of matrices [47]. Let us first consider the wedge product C of two one-particle matrices, ${}^1A$ and ${}^1B$,

$$ {}^{2}C = {}^{1}A\wedge{}^{1}B. \qquad \text{(A2)} $$

The elements $c^{i,j}_{k,l}$ of the matrix ${}^2C$ may be obtained from a^i_k and b^j_l by summing the distinct products arising from all antisymmetric permutations of the upper indices and all antisymmetric permutations of the lower indices. With the wedge product of one-particle matrices there are only four distinct possibilities

$$ c^{i,j}_{k,l} = a^{i}_{k}\wedge b^{j}_{l} = \tfrac{1}{4}\left(a^{i}_{k}b^{j}_{l} - a^{j}_{k}b^{i}_{l} - a^{i}_{l}b^{j}_{k} + a^{j}_{l}b^{i}_{k}\right). \qquad \text{(A3)} $$

More generally, we can write the elements of the wedge product as

$$ a^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p}\wedge b^{i_{p+1},\ldots,i_N}_{j_{p+1},\ldots,j_N} = \left(\frac{1}{N!}\right)^2 \sum_{\pi,\sigma} \epsilon(\pi)\epsilon(\sigma)\pi\sigma a^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p} b^{i_{p+1},\ldots,i_N}_{j_{p+1},\ldots,j_N}, \qquad \text{(A4)} $$

in which π represents all permutations of the upper indices and σ represents all permutations of the lower indices while the function $\epsilon(\pi)$ returns $+1$ for an even number of transpositions and -1 for an odd number of transpositions. Since both the upper and the lower indices have $N!$ permutations, there are $(N!)^2$ terms in the sum. Hence, normalization requires division by $(N!)^2$. If, however, the elements $a^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p}$ and $b^{i_{p+1},\ldots,i_N}_{j_{p+1},\ldots,j_N}$ are already antisymmetric in their upper and lower indices, only $[N!/(p!q!)]^2$ of the above terms will be distinct. This allows us to decrease the number of numerical operations required for computing the wedge product. For wedge products between matrices with the same number of upper and lower indices we have an important commutation relation

$$ {}^pA^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p}\wedge {}^qB^{i_{p+1},\ldots,i_N}_{j_{p+1},\ldots,j_N} = {}^qB^{i_1,\ldots,i_q}_{j_1,\ldots,j_q}\wedge {}^pA^{i_{q+1},\ldots,i_N}_{j_{q+1},\ldots,j_N} \tag{A5}$$

or without the indices

$$ {}^pA\wedge {}^qB = {}^qB\wedge {}^pA. \tag{A6}$$

If the sum $(p+q)$ is odd, exchanging the p upper indices with q upper indices will produce a minus sign, but this will be canceled by another minus sign produced by exchanging the lower indices. In many cases it will be easier and clearer to write the wedge products as in the second form (A6) without specifying a particular element through indices.

APPENDIX B: CALCULATIONAL DETAILS OF THE LIPKIN MODEL

Wave functions for the Lipkin model are readily obtained by diagonalizing the Hamiltonian in a basis set of the angular momentum states of J_z for $J=N/2$. As the raising and lowering operators of angular momentum, the operators $J_{+,-}$ and $J_{-,+}$ have a well-defined action on the basis functions of J_z. The result of applying the operators $J_{+,+}$ and $J_{-,-}$ may be determined by expressing them directly in terms of J_z. Remember that $2J_z$ gives the difference between the number of fermions in the upper level and the number in the lower level while the total number of fermions is just the sum of the fermions in the upper and lower levels. Hence, the operators $J_{+,+}$ and $J_{-,-}$, which extract the number of particles in the upper and lower levels, respectively, must be related to J_z by

$$ J_{+,+}=N+2J_z \quad \text{and} \quad J_{-,-}=N-2J_z. \tag{B1}$$

Once we have the wave functions, we are interested in obtaining the reduced density matrices. Let us examine the second-quantized definition for the 1RDM

$$ {}^1D^{m_1,p_1}_{m_2,p_2}=\langle\psi|a^\dagger_{m_1,p_1}a_{m_2,p_2}|\psi\rangle. \tag{B2}$$

Transitions between different values of p are forbidden because in the configurations that mix with the noninteracting ground state more than one fermion cannot have the same quantum number p. For this reason the elements of the 1RDM will vanish unless $p_1=p_2$. Furthermore, the value of ${}^1D^{m_1,p}_{m_2,p}$ must be the same for all p since the different states of a level are indistinguishable. We can condense the information in the 1RDM by summing over all values of p to obtain

$$ {}^1C^{m_1}_{m_2}=\sum_p {}^1D^{m_1,p}_{m_2,p} \tag{B3a}$$

$$ =\sum_p \langle\psi|a^\dagger_{m_1,p}a_{m_2,p}|\psi\rangle \tag{B3b}$$

$$ =\langle\psi|J_{m_1,m_2}|\psi\rangle, \tag{B3c}$$

where ${}^1C^{m_1}_{m_2}$ is the condensed 1RDM. Note that if we know ${}^1C^{m_1}_{m_2}$, then we can determine the 1RDM elements for any p since

$$ {}^1D^{m_1,p}_{m_2,p}=\frac{1}{N}C^{m_1}_{m_2}. \tag{B4}$$

By the last two relations the mapping between the condensed 1RDM and the 1RDM is completely defined. The condensed 2RDM has the form

$$ {}^2C^{m_1,m_2}_{m_3,m_4}=\sum_{p_1,p_2} {}^2D^{(m_1,p_1),(m_2,p_2)}_{(m_3,p_1),(m_4,p_2)} \tag{B5a}$$

$$ =\frac{1}{2!}\sum_{p_1,p_2}\langle\psi|a^\dagger_{m_1,p_1}a^\dagger_{m_2,m_2}a_{m_4,p_2}a_{m_3,m_1}|\psi\rangle \tag{B5b}$$

$$ =\frac{1}{2!}(\langle\psi|J_{m_1,m_3}J_{m_2,m_4}|\psi\rangle-\delta_{m_2,m_3}\langle\psi|J_{m_1,m_4}|\psi\rangle). \tag{B5c}$$

Again we have the mapping

$$ {}^2D^{(m_1,p_1),(m_2,p_2)}_{(m_3,p_1),(m_4,p_2)}=\frac{1}{N(N-1)}{}^2C^{m_1,m_2}_{m_3,m_4}, \tag{B6}$$

where now the factor involves division by $N(N-1)$ since the 2RDM vanishes if $p_1=p_2$. From the antisymmetry of the 2RDM we also have

$$ {}^2D^{(m_1,p_1),(m_2,p_2)}_{(m_3,p_2),(m_4,p_1)}=\frac{-1}{N(N-1)}{}^2C^{m_1,m_2}_{m_4,m_3}, \tag{B7}$$

As with the 1RDM, these formulas provide a complete mapping between the condensed 2RDM and the true 2RDM. In a similar fashion we obtain the higher RDMs.

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