

Towards idempotent reduced density matrices via particle-hole duality: McWeeny's purification and beyond

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Generalizations of McWeeny's purification formula are developed within the formalism of the particle-hole duality from the theory of reduced density matrices. Each of the generalized purification formulas is expressed as a sum of the one-particle reduced density matrix (1-RDM) and a finite series in the product of the one-particle and the one-hole RDMs, a product which vanishes in the limit that the 1-RDM is idempotent. Two categories of purification formulas are explored: (i) formulas which treat the "occupied" and the "virtual" occupation numbers equivalently and (ii) formulas which treat these occupation numbers differently. The latter category includes and extends the purification formulas derived in the context of the 1,2-contracted Schrödinger equation [D. A. Mazziotti, *J. Chem. Phys.* **115**, 8305 (2001)]. While the McWeeny purification minimizes the absolute error in the occupation numbers quadratically, the generalized purification formulas exhibit faster than quadratic convergence of the 1-RDM towards idempotency. Application of these purification formulas in existing algorithms for linear scaling will be explored and discussed including illustrative calculations on sodium wires of length 10, 20, 30, and 40 atoms.

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I. INTRODUCTION

Computation of the electronic structure of large-scale molecules requires algorithms which scale *linearly* with the number N of electrons. Linear-scaling algorithms have been developed within the last decade for semiempirical, tight-binding, Hartree-Fock, and density-functional methods in which the many-electron system is mapped onto a one-electron model [1–11]. Any one-electron reduced Hamiltonian, including a Fock or Kohn-Sham Hamiltonian, has the well-known property that the determinant of its N lowest orbitals is the wave function for the N -particle system. The effective one-electron Hamiltonian from Hartree-Fock or density-functional theory is traditionally diagonalized at each iteration to produce a set of molecular orbitals. However, the process of diagonalization scales as r^3 , where r is the rank of the one-electron basis set. The key to achieving a linear-scaling algorithm for a one-electron model is to compute directly the one-particle reduced density matrix (1-RDM) without determining an orthogonal set of N orbitals.

The main difficulty with using the 1-RDM as the basic variable is that it must be constrained to correspond to an N -particle Slater-determinant wave function. Such constraints are known as N -representability conditions. Fortunately, the ensemble N -representability condition for the 1-RDM was derived by Coleman [12,13]: the eigenvalues of the 1-RDM, normalized to N , must lie in the interval $[0,1]$. Any 1-RDM that derives from an N -particle Slater determinant has the more restrictive condition that its eigenvalues must be zero or one, that is, the 1-RDM must be idempotent. The process of mapping an arbitrary 1-RDM onto an idempotent 1-RDM is known as *purification*. By employing only matrix multiplications, linear-scaling purification formulas

may be designed to converge iteratively to an idempotent 1-RDM. McWeeny derived the most widely employed purification formula [14].

Recently, there has been interest in the following question: can McWeeny's formula be improved in terms of accuracy and efficiency [5,15–17]? Both Kryachko [15] and Holas [16] examined a generalization of McWeeny's formula to higher orders. Kryachko's work overlooked the importance of purifying the occupation numbers associated with the virtual orbitals. Holas corrected Kryachko's work to include both occupied and virtual orbitals, but the analysis of efficiency in comparison with *repeated* applications of McWeeny's formula was inconclusive. We also extended Kryachko's work in another direction by deriving purification formulas, where the occupied and the virtual orbitals are corrected unequally [5]. Very recently, Niklasson [18] independently derived and tested formulas from this second class of generalized McWeeny transformations. In this paper [19] a formalism, known as the *particle-hole duality* [20–26], will be introduced from the field of reduced density matrices [23,27–30] to extend, synthesize, and evaluate efficiently the two classes of generalized purification formulas. Several formulas will be shown to exhibit faster convergence to idempotency with the same number of matrix multiplications as the repeated application of McWeeny's formula.

A quantum system may be equivalently described in terms of the probability of a particle being present or the probability of a particle being absent. The absence of a particle is also called a *hole*. The mathematical equivalence of these two perspectives, which is akin to the equivalence of describing a glass as half empty or half full, is known as the *particle-hole duality*. Every N -particle system may be equally well described by an N -particle wave function or an $(r-N)$ -hole wave function, where r is the rank of the one-particle basis set. Just as integration of the N -particle density matrix over all but one-particle produces the one-particle RDM, integration of the $(r-N)$ -hole density matrix over all

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but one hole produces the one-hole RDM. In the absence of particle interactions the N -particle wave function is, as we previously mentioned, a determinant of the lowest N orbitals, and the $(r-N)$ -hole wave function is a Slater determinant of the remaining $(r-N)$ orbitals. Furthermore, in the interaction-free case, the one-particle RDM and the one-hole RDM are N representable if they are (i) normalized to N and $(r-N)$, respectively, (ii) Hermitian, and (iii) idempotent.

The present exploration of purification differs significantly from previous work, in that we explicitly examine the effect of purification on *both* the one-particle and the one-hole RDMs. The relationship between the 1-particle RDM and the one-hole RDM places an important restriction on the structure of the purification formulas. We reveal the particle-hole structure of both McWeeny's formula and the higher-order generalizations by expressing these formulas directly in terms of the particle and the hole 1-RDMs. Finally, within the framework of the particle-hole notation, purification formulas are derived which converge more efficiently than the McWeeny formula to idempotent RDMs. An extension of Niklasson's trace-correcting algorithm [18] is proposed for using these higher-order formulas to purify one-electron Hamiltonians to their idempotent ground-state 1-RDMs. Application of these purification formulas in existing algorithms for linear scaling will be explored and discussed including illustrative calculations on sodium wires of length 10, 20, 30, and 40 atoms.

II. THEORY

After sketching the salient features of linear scaling with the 1-RDM, we develop in Sec. II B purification formulas from the perspective of the particle-hole duality.

A. Linear-scaling overview

Many useful methods in electronic structure, from the Hartree-Fock method to practical density-functional theory, approximately map the many-electron problem onto one electron. For linear scaling the 1-RDM rather than N orthogonal orbitals must be computed at each self-consistent iteration. Optimization of the energy for the N -electron system may be expressed as

$$E = \min \text{Tr}(KD), \quad (1)$$

where K is the one-electron reduced Hamiltonian and the 1-RDM D is subject to the following N -representability constraints: (i) the trace of the 1-RDM D equals N , (ii) the 1-RDM D is Hermitian, and (iii) the 1-RDM D is idempotent, that is,

$$D - D^2 = 0. \quad (2)$$

Mathematically, we have a constrained optimization problem to be solved.

Practical realization of linear scaling with the 1-RDM occurred when iterative approaches were developed for an efficient solution to the constrained minimization problem. Two broad genres exist for the direct determination of the

1-RDM: (i) gradient-based methods [1–5] and (ii) purification-of-the-Hamiltonian methods [6–8,10]. An example of the gradient-based methods, which we recently developed, is the iterative solution of the 1,2-contracted Schrödinger equation (1,2-CSE) with reconstruction of the 2-RDM from the 1-RDM [5]. The 1,2-CSE suggests the following iterative “gradientlike” update for the 1-RDM,

$$D_{n+1} = D_n + \lambda(\bar{D}_n K D_n + D_n K \bar{D}_n), \quad (3)$$

where $\bar{D}_n (= I - D)$ is the one-hole RDM and I is the identity matrix. While the correction for the 1-RDM is accurate for an idempotent D_n , the new trial 1-RDM D_{n+1} may only be approximately idempotent. Hence, before the next iteration, the trial 1-RDM must be purified. Similar purification is necessary in other gradient-based algorithms.

In the second category of methods a linear mapping of the one-electron reduced Hamiltonian,

$$\tilde{D} = \lambda(\mu I - K) + \gamma I, \quad (4)$$

produces a 1-RDM \tilde{D} , that is, a Hermitian matrix with occupation numbers between 0 and 1 whose appropriate purification can produce the idempotent ground-state 1-RDM for the N -electron system. The parameter λ may be computed from a knowledge of the maximum and minimum eigenvalues of K , the chemical potential μ , and a parameter γ from the purification formula [3]. The technique works because the reduced Hamiltonian and the idempotent 1-RDM share the same eigenfunctions. Only the occupation numbers of K must be corrected through a mapping followed by purification. The need for efficient purification in this approach is of paramount importance. McWeeny's formula is the most commonly used purification [14], and in the following section we explore purification from the perspective of the particle-hole duality.

B. Particle-hole purification

The one-particle and one-hole RDMs satisfy the simple relationship

$$\bar{D} + D = I, \quad (5)$$

where I is the identity matrix of rank r , the total number of orbitals. This relationship is valid for one-particle and one-hole RDMs derived from *any* wave function. If they derive from a determinant wave function, then they must also satisfy the relation

$$\bar{D}D = 0. \quad (6)$$

Satisfaction of Eqs. (5) and (6) is necessary and sufficient for the one-particle and one-hole RDMs to arise from the integration of an N -particle density matrix assembled from a single Slater determinant. Substitution of $\bar{D} = I - D$ from Eq. (5) into Eq. (6) yields the more familiar idempotency condition in Eq. (2). The condition in Eq. (6) expresses succinctly a fundamental property of a noninteracting system, which is that the subspace spanned by the occupied orbitals of D must

be orthogonal to the subspace spanned by the ‘‘occupied’’ orbitals of \bar{D} . If the hole and the particle RDMs are both idempotent, then it follows from Eq. (5) that the unoccupied orbitals of D are the occupied orbitals of \bar{D} and the occupied orbitals of D are the unoccupied orbitals of \bar{D} . In many parts of the paper we will refer to the occupied orbitals and occupation numbers of D as the *particle* orbitals and particle occupation numbers and to the unoccupied orbitals and occupation numbers of D as the *hole* orbitals and hole occupation numbers.

The challenge of purifying a 1-RDM to be N representable with a Slater determinant preimage lies in correcting *both* the particle and the hole occupation numbers. For a given 1-RDM let us denote the maximum error in a particle occupation number by ϵ_p and similarly, the maximum error in a hole occupation number by ϵ_h . Kryachko [15] proposed the following ‘‘high-order’’ iterative purification formulas:

$$P_{0,n-1}(\bar{D}) = \bar{D}^n, \quad (7)$$

where $n \geq 2$. The subscripts on $\bar{P}_{0,n-1}(\bar{D})$ indicate the orders through which the errors in the occupation numbers of the occupied and unoccupied orbitals of \bar{D} , respectively, vanish. The 1-RDM upon *input* and *output* is in its one-hole form. The simplicity of this formula, in comparison with Kryachko’s polynomials in D [15], highlights one advantage of using both particle and hole notations. One iteration of this formula reduces the error in the particle occupation numbers from ϵ_p to ϵ_p^n ; however, as also noted by Holas [16], the error in the hole occupation numbers does not improve, that is, ϵ_h becomes $(1 - \epsilon_h)^n$ which is still $O(\epsilon_h)$. Replacing \bar{D} with D in Eq. (7) yields the formula

$$P_{0,n-1}(D) = D^n, \quad (8)$$

where $n \geq 2$. With the input and the output 1-RDM in its particle form, it is the hole occupation numbers that are improved while the particle occupation numbers remain incorrect to $O(\epsilon_p)$.

In the context of our research on the 1,2-contracted Schrödinger equation [5] we proposed two new purification formulas: (1) the HD formula in which first the particle occupation numbers and then the hole occupation numbers are purified through a nesting of Eqs. (7) and (8) with $n=2$ and (2) the DH formula in which the order for applying particle and hole purification is reversed. Mathematically, the HD and the DH formulas for the one-particle RDM are given by the compositions

$$P_{1,1}^{\text{HD}}(D) = P_{1,2}(I - [P_{1,2}(\bar{D})]) \quad (9)$$

$$= (I - \bar{D}^2)^2 \quad (10)$$

and

$$P_{1,1}^{\text{DH}}(D) = I - P_{1,2}(I - [P_{1,2}(D)]) \quad (11)$$

$$= I - (I - D^2)^2. \quad (12)$$

The formulas are readily interconverted by switching the roles of D and \bar{D} and employing the relationship between D and \bar{D} in Eq. (5). Under the DH formula the errors in the particle and the hole occupation numbers are reduced by the following mappings:

$$\epsilon_h \rightarrow 2\epsilon_h^2 - \epsilon_h^4 \quad (13)$$

and

$$\epsilon_p \rightarrow 4\epsilon_p^2 - 4\epsilon_p^3 + \epsilon_p^4. \quad (14)$$

Importantly, the errors in both the particle and the hole occupations are reduced to second order. However, because we applied the hole purification first, the coefficients of the quadratic error (2 for ϵ_h^2 versus 4 for ϵ_p^2) favor the hole purification. Similarly, the error reductions for the HD formula, obtained by exchanging ϵ_h and ϵ_p in Eqs. (13) and (14), favor the particle purification.

Averaging the DH and the HD purification formulas yields the well-known McWeeny (MW) purification

$$P_{1,1}^{\text{MW}} = \frac{1}{2}(P_{1,1}^{\text{HD}} + P_{1,1}^{\text{DH}}) \quad (15)$$

$$= 3D^2 - 2D^3, \quad (16)$$

where the error in either the particle, ϵ_p or the hole, ϵ_h occupation numbers, which we denote by a generic ϵ , is given by the average of the errors from the HD and the DH formulas

$$\epsilon \rightarrow 3\epsilon^2 - 2\epsilon^3. \quad (17)$$

While the HD and the DH formulas are fourth-order polynomials in D (or \bar{D}), they may be evaluated in *two* matrix multiplications such as the third-order polynomial McWeeny purification [5]. From the traditional expression of the McWeeny formula in Eq. (16) it is difficult to see immediately that the errors in the particle and the hole occupation numbers are treated with equivalent purification.

The *particle-hole symmetry* of the McWeeny purification may be made more manifest by (i) writing the purification as a common correction to the one-particle and the one-hole RDMs and (ii) expressing the MW formula with both the one-particle and the one-hole RDMs. McWeeny’s purification for the one-particle and the one-hole RDMs may be constructed untraditionally through the *addition* of correction terms

$$P_{1,1}^{\text{MW}}(D) = D + \Delta(D) \quad (18)$$

and

$$P_{1,1}^{\text{MW}}(\bar{D}) = \bar{D} + \bar{\Delta}(\bar{D}). \quad (19)$$

For the particles and holes to be purified equivalently, the corrected particle and hole RDMs must satisfy Eq. (5), that is,

$$P_{1,1}^{\text{MW}}(\bar{D}) + P_{1,1}^{\text{MW}}(D) = I. \quad (20)$$

Because D and \bar{D} also satisfy Eq. (5), it follows that

$$\Delta(D) = -\bar{\Delta}(\bar{D}), \quad (21)$$

and, hence, we only need to determine $\Delta(D)$. We now demonstrate that two conditions, satisfied by the McWeeny formula, completely determine the functional forms of $\Delta(D)$: (i) the correction must remove the first-order errors in both the particle and the hole occupation numbers and (ii) from Eq. (21) the correction must change signs upon exchange of the one-particle and the one-hole RDMs. From the first condition it follows that the correction must have one factor of D and one factor of \bar{D} , that is,

$$\Delta = \alpha D \bar{D} \Phi(D, \bar{D}), \quad (22)$$

where α is a scalar and the remainder $\Phi(D, \bar{D})$ is a first-order polynomial in D and \bar{D} . Condition (ii) can only be satisfied if $\Phi(D, \bar{D})$ is a scalar multiple of the difference between the one-particle and the one-hole RDMs, that is, $\Phi(D, \bar{D}) \propto D - \bar{D}$. Substituting this expression into Eq. (22), we find

$$\Delta = \alpha D \bar{D} (D - \bar{D}). \quad (23)$$

The constant α , chosen to cancel the first-order particle and hole errors in the RDM, is unity. Therefore, we have a new particle-hole expression for McWeeny's purification

$$P_{1,1}^{\text{MW}}(D) = D + D \bar{D} (D - \bar{D}). \quad (24)$$

Unlike the standard expression this formulation of the MW purification directly highlights the particle-hole symmetry since exchanging the particle and the hole RDMs gives

$$P_{1,1}^{\text{MW}}(\bar{D}) = \bar{D} - D \bar{D} (D - \bar{D}), \quad (25)$$

where the correction is the same as for the particle matrix except for the sign change.

Building upon the work of Kryachko, Holas derived a higher-order polynomial generalization of McWeeny's formula which corrects the errors in both the particles and the holes through order n . Like the McWeeny formula the Holas hierarchy of purification formula treats the particles and the holes equivalently. While Holas employed the properties of the β function to generate polynomials in D [16], the formulas may be intuitively derived within the framework of the particle and the hole matrices. The first-order Holas formula is equivalent to McWeeny's purification formula. As in our derivation of the McWeeny formula, we derive the second-order Holas formula as a correction to the first-order expression, that is,

$$P_{2,2}^{\text{H}}(D) = P_{1,1}^{\text{MW}}(D) + \Delta(D). \quad (26)$$

The second-order correction Δ is completely determined by two necessary conditions: (i) Δ must remove the second-

order errors in both the particle and the hole occupation numbers of the McWeeny-purified 1-RDM and (ii) Δ must change signs upon exchange of the one-particle and the one-hole RDMs. From the first condition it follows that the correction must *factorize* into two factors of D , two factors of \bar{D} , and a first-order polynomial term. By the second condition this final factor must be a scalar multiple of the difference between the one-particle and the one-hole RDMs. Hence, the correction has the form

$$\Delta(D) = \alpha_2 (D - \bar{D}) D^2 \bar{D}^2, \quad (27)$$

where the constant α_2 , which must be chosen to cancel the second-order errors in the McWeeny purification, equals three. The second-order Holas correction may thus be written as

$$P_{2,2}^{\text{H}}(D) = P_{1,1}^{\text{MW}}(D) + 3(D - \bar{D}) D^2 \bar{D}^2. \quad (28)$$

In general the n th-order purification formulas of Holas may be cast in the particle-hole notation as the 1-RDM *plus* the product of $(D - \bar{D})$ and a power series in $D\bar{D}$,

$$P_{n,n}^{\text{H}} = D + (D - \bar{D}) \sum_{j=1}^n \alpha_j (D\bar{D})^j, \quad (29)$$

where each of the scalars $\alpha_j \in [1, 3, 10, 35, 126, 426, \dots]$ is equal to the negative of the error coefficient for ϵ_p^j in $P_{j-1, j-1}^{\text{H}}$ (note that the error coefficients are negative). Exchanging the particle D and the hole \bar{D} matrices immediately shows that all orders of the formulas treat the particles and the holes equivalently.

Because the particle-hole notation represents the factorization of the purification formula into particle and hole components, it facilitates the design of fast multiplication schemes. For example, this second-order correction may be evaluated in three matrix multiplications:

$$P_{2,2}^{\text{H}}(D) = P_{1,1}^{\text{MW}}(D) + 3YX, \quad (30)$$

where

$$X = D\bar{D}, \quad (31)$$

$$Y = (D - \bar{D})X, \quad (32)$$

$$P_{1,1}^{\text{MW}}(D) = D + Y. \quad (33)$$

At most three matrices need to be stored simultaneously: D , X , and Y . Similarly, the general n th-order formulas may be evaluated efficiently by summing the power series in $D\bar{D}$ in n matrix operations and then multiplying the summed series by the matrix $(D - \bar{D})$ for a total of $(n + 1)$ matrix operations. For any n only four matrices need to be stored simultaneously: D , $D\bar{D}$, the highest power of $D\bar{D}$ computed at a given time in the program, and the accumulated sum of the series in $D\bar{D}$. A higher power in $D\bar{D}$ may be constructed in memory row by row, while the next-to-highest power of $D\bar{D}$

is eliminated from memory row by row. For $n \geq 4$ the computational cost may be further reduced by partitioning the power series in $D\bar{D}$ into separate even and odd series. When n is even, for example, we have

$$P_{n,n}^H = D + (D - \bar{D}) \left\{ \sum_{j=1}^{n/2} \alpha_{2j} (D\bar{D})^{2j} + D\bar{D} \sum_{j=1}^{n/2} \alpha_{2j-1} (D\bar{D})^{2j-2} \right\}, \quad (34)$$

which may be evaluated in a grand total of $(n/2 + 1)$ matrix operations. With this partitioning of the power series for any n a maximum of six matrices need to be stored at the same time: D , $D\bar{D}$, $(D\bar{D})^2$, the highest power of $(D\bar{D})^2$ computed at a given time in the program, the accumulated sum of the even series in $D\bar{D}$, and the accumulated sum of the odd series in $D\bar{D}$. Evaluation of odd orders of purification is slightly less efficient at $(n+1)/2 + 1$ matrix operations for an odd order of n .

Although the Holas formulas correct the errors in the particle and the hole occupation numbers through a higher order than the McWeeny formula, they require additional matrix multiplications. The first-order McWeeny formula as well as the first-order DH and HD formulas require only *two* sparse matrix multiplications each, but the second-order generalized McWeeny formula requires *three* matrix multiplications. How does the efficiency of these higher-order formulas compare with the first-order purifications? To answer this question, one needs to know the order of error correction required for a two-multiplication purification to be as accurate as a higher-order m -multiplication purification if both purification algorithms are permitted to use the same total number of matrix multiplications. For an n th-order formula we define the error of an artificial two-multiplication purification whose $2n$ -times repeated application would generate the error of the n th-order formula applied *twice*. The *effective* error $\chi_{\text{eff}}(\epsilon)$ in the occupation orbitals after one iteration of the ‘‘artificial’’ two-multiplication purification may be computed with the formula

$$\chi_{\text{eff}}(\epsilon) = \beta^p \epsilon^q, \quad (35)$$

where

$$\beta = \alpha^{n+2},$$

$$p = \frac{q-1}{q^m - 1},$$

and

$$q = (n+1)^{2/m}.$$

The symbol α is the error coefficient (or prefactor) of the n th-order purification, $n+1$ is the lowest order of the error in the formula, and the exponent $2/m$ is a ratio of the number of multiplications in one McWeeny purification to the num-

ber of multiplications in one generalized purification. The parameters p and q were determined symbolically with MAPLE 8 [31] so that applying the function χ $2m$ times to an initial error ϵ generates the same final error as applying the n th-order formula *twice* to an initial error ϵ . When $n=1$, $m=2$, and $\alpha=3$, we recover the error in one iteration of the McWeeny formula, that is, $3\epsilon^2$. Using the effective error, we compare in the first four rows of Table I the efficiency of the generalized Holas purification formulas with the well-known McWeeny purification. Only the even-order formulas are presented because they are more efficient than their odd-ordered brethren. We observe that some of the higher-order formulas converge towards an idempotent 1-RDM *faster* than the McWeeny formula with the efficiency peaking at the fourth-order purification which mimics an effective first-order formula with an $O(\epsilon^{2.236})$ error for every two multiplications. Also given in Table I for each formula is the location of the *unstable fixed point* in occupation spectrum $[0,1]$ which determines the boundary after purification between the particle and the hole occupation numbers. The magnitude of the derivative at this fixed point provides a measure for the rate of purification in its vicinity.

The Holas formulas offer one generalization of McWeeny’s purification, while the DH and the HD formulas offer a different generalization in which the particle and the hole corrections are treated unequally. Let us recast the purification $P_{0,n-1}$ in Eq. (8) with $n=2$ as a correction to the one-particle RDM,

$$P_{0,1}(D) = D + \Delta(D). \quad (36)$$

Two properties of Eq. (8) determine the correction within a scalar factor: (i) the correction is a second-order polynomial in D and \bar{D} and (ii) the corrections must vanish in the limit that D and \bar{D} are idempotent. For the second criterion to be true with the quadratic constraint the correction must be proportional to $D\bar{D}$. Specifically, we find that

$$P_{0,1}(D) = D - D\bar{D}. \quad (37)$$

Similarly, the purification $P_{0,1}$ in Eq. (7), which involves squaring the hole matrix, follows from exchanging the particle and the hole matrices,

$$P_{0,1}(\bar{D}) = \bar{D} - D\bar{D}. \quad (38)$$

Unlike the McWeeny formulas for correcting the one-particle and the one-hole RDMs in Eqs. (24) and (25), the corrections in the purification formulas in Eqs. (37) and (38) share the *same sign*. Consequently, the purified particle and hole RDMs deviate from their relation in Eq. (5) by the amount $-2D\bar{D}$. As shown earlier in Eqs. (9) and (11) the composition of these simple, RDM-squaring purification formulas produces the HD and the DH formulas which are correct through first order in both the particles and the holes.

The general formula for purification of the particles and the holes through orders n and $n+1$, respectively, may be readily expressed in particle-hole notation as a perturbation of the Holas formulas in Eq. (29),

TABLE I. For generalized McWeeny purification formulas this table reports the accuracy of the particle and hole occupation numbers per iteration, the number of matrix multiplications per iteration, the location of the unstable fixed point, the derivative at this point, as well as an effective error $\chi_{\text{eff}}(\epsilon)$, that is, the error in the occupation numbers after one iteration of an effective two-multiplication purification. Comparing the $\chi_{\text{eff}}(\epsilon)$, we perceive that several formulas, especially $C_{1,2}(D)$ and $C_{2,3}(D)$, are significantly more efficient than the traditional McWeeny purification.

Purification formulas ^b	Occupation errors ^a			Unstable fixed point		Effective errors $\chi_{\text{eff}}(\epsilon)$	
	Particles	Holes	Matrix multiples	Location	Derivative	Particles	Holes
$P_{1,1}^{\text{MW}}(D)$	$-3\epsilon_p^2$	$3\epsilon_h^2$	2	0.5000	1.500	$3\epsilon_p^2$	$3\epsilon_h^2$
$P_{2,2}^{\text{H}}(D)$	$-10\epsilon_p^3$	$10\epsilon_h^3$	3	0.5000	1.875	$3.5\epsilon_p^{2.080}$	$3.5\epsilon_h^{2.080}$
$P_{4,4}^{\text{H}}(D)$	$-126\epsilon_p^5$	$126\epsilon_h^5$	4	0.5000	2.461	$4.5\epsilon_p^{2.236}$	$4.5\epsilon_h^{2.236}$
$P_{6,6}^{\text{H}}(D)$	$-1716\epsilon_p^7$	$1716\epsilon_h^7$	5	0.5000	2.933	$4.3\epsilon_p^{2.178}$	$4.3\epsilon_h^{2.178}$
$P_{0,1}(D)$	$-2\epsilon_p$	ϵ_h^2	1	N/A	N/A	$4\epsilon_p$	ϵ_h^4
$C_{0,1}(D)$	$-4\epsilon_p^2$	$2\epsilon_h^2$	2	0.6180	1.528	$4\epsilon_p^2$	$2\epsilon_h^2$
$P_{1,2}(D)$	$-6\epsilon_p^2$	$4\epsilon_h^3$	2	0.7676	1.643	$6\epsilon_p^2$	$4\epsilon_h^3$
$C_{1,2}(D)$	$-864\epsilon_p^6$	$96\epsilon_h^6$	4	0.5722	2.825	$5.6\epsilon_p^{2.449}$	$4.2\epsilon_h^{2.449}$
$P_{2,3}(D)$	$-20\epsilon_p^3$	$15\epsilon_h^4$	3	0.6529	2.012	$5.0\epsilon_p^{2.080}$	$3.9\epsilon_h^{2.520}$
$C_{2,3}(D)$	$-2.4 \times 10^6 \epsilon_p^{12}$	$6.8 \times 10^4 \epsilon_h^{12}$	6	0.5528	4.109	$5.1\epsilon_p^{2.289}$	$3.9\epsilon_h^{2.289}$
$P_{3,4}(D)$	$-70\epsilon_p^4$	$56\epsilon_h^5$	4	0.6045	2.313	$4.1\epsilon_p^{2.000}$	$3.5\epsilon_h^{2.236}$
$C_{3,4}(D)$	$-9.4 \times 10^{10} \epsilon_p^{20}$	$6.9 \times 10^8 \epsilon_h^{20}$	8	0.5419	5.388	$4.2\epsilon_p^{2.115}$	$3.4\epsilon_h^{2.115}$

^aThe symbols ϵ_p and ϵ_h represent the maximum errors in the particle and the hole occupation numbers.

^bThe symbols MW and H denote the McWeeny and the Holas purification formulas, respectively.

$$P_{n,n+1}(D) = D + (D - \bar{D}) \sum_{j=1}^n \alpha_j (D\bar{D})^j - \alpha_{n+1} (D\bar{D})^{n+1}, \quad (39)$$

where the scalars $\alpha_j \in [1, 3, 10, 35, 126, 426, \dots]$ are the same as those in Eq. (29). Applying this formula to \bar{D} , which is equivalent to switching D and \bar{D} , produces a purification formula which corrects the particle and the hole occupation numbers through orders $n+1$ and n , respectively. Within the McWeeny and the Holas purification formulas the particle and the hole occupation numbers are treated equivalently because the factor of $(D - \bar{D})$ changes sign when the particle and the hole RDMs are exchanged. Removing the factor of $(D - \bar{D})$ from the last term of $P_{n+1,n+1}^{\text{H}}$ breaks the particle-hole symmetry at the $(n+1)$ th order. While the resulting purification formulas, $P_{n,n+1}(D)$ and $P_{n,n+1}(\bar{D})$, are less accurate than the $(n+1)$ th Holas formula, they may often be evaluated with fewer multiplications which can significantly enhance efficiency. Furthermore, we can compose these complementary formulas to obtain *composite* purification formulas which are correct to the $(n^2 + 3n + 2)$ th order in the particle and the hole occupations,

$$C_{n,n+1}(D) = I - P_{n,n+1}(I - P_{n,n+1}(D)). \quad (40)$$

Selecting D or \bar{D} for the initial purification determines whether the final result slightly favors the particle or the hole occupation numbers. When $n=0$, we obtain the second-order DH formula from Eq. (40), while replacing D with \bar{D} yields the HD formula.

The efficiency of these composite particle-hole formulas is compared with the McWeeny and the Holas formulas in

Table I. Table I reports the accuracy of the particle and hole occupation numbers per iteration, the number of matrix multiplications per iteration, the location of the unstable fixed point, the derivative at this point as well as an effective error $\chi_{\text{eff}}(\epsilon)$, that is, the error in the occupation numbers after one iteration of an effective two-multiplication purification. For the McWeeny and Holas formulas the unstable fixed point occurs at 0.5, while it varies about 0.5 for the purification formulas with a nonsymmetric treatment of the particles and holes. We compute the effective error for the composite formulas by

$$\chi_{\text{eff}}(\epsilon) = \beta^p \epsilon^q, \quad (41)$$

where

$$\beta = \alpha_2 \alpha_1^{n_1+1},$$

$$p = \frac{q-1}{q^m - 1},$$

and

$$q = [(n_1 + 1)(n_2 + 1)]^{1/m}.$$

The parameters α_1 and α_2 are the error coefficients (or pre-factors) in the first and second formulas of the composite purification, $n_1 + 1$ and $n_2 + 1$ are the lowest orders of the errors in the two formulas, and the exponent $1/m$ is a ratio of the number of multiplications (2) in one McWeeny purification to the number of multiplications ($2m$) in one composite purification. Comparisons of the effective errors show that the efficiency peaks for the $n=1$ composite formula with an effective error of $\epsilon^{2.449}$, while the $n=2$ composite formula is also very accurate with an effective error of $\epsilon^{2.289}$. The composite formulas, we note, are more cost effective than the

optimal Holas formula $P_{4,4}^H(D)$ which has an error of $\epsilon^{2.236}$ and, furthermore, the derivatives at the unstable fixed points of the composite formulas tend to be larger than the derivatives in the corresponding Holas formulas. The efficiency of the composite formulas peaks at low n because further improvement, as in the case of the higher-order Holas formulas, is offset by the cost of increasing the number of matrix multiplications.

III. RESULTS AND DISCUSSION

To illustrate the purification formulas, we consider a family of sparse reduced Hamiltonians K with eigenvalues in the interval $[0,1]$. Assume that the lowest occupied and the highest unoccupied states of our target 1-RDM appear in K at $\mu - g/2$ and $\mu + g/2$, where the chemical potential $\mu=0.5$ and g is the band gap. Because the states $\mu - g/2$ and $\mu + g/2$ of the reduced Hamiltonian K require the most purification, the rate of the purification depends not upon the number of states but *only upon the band gap* g between the states $\mu - g/2$ and $\mu + g/2$. The results for a given g , therefore, are representative of any Hamiltonian with that band gap and chemical potential, and hence, *the calculations given below are valid not only for a specific reduced Hamiltonian but for any reduced Hamiltonian with that band gap and chemical potential*. Without defining a specific reduced Hamiltonian, we are able to compute the number of matrix multiplications required for each purification formula by applying the formulas only to the “least idempotent” occupation numbers, $\mu - g/2$ and $\mu + g/2$, respectively, because these occupation numbers require the most matrix multiplications to converge.

Before purification we perform the following mapping to place the chemical potential at the unstable fixed point γ ,

$$\tilde{D} = K + (\gamma - \mu)I. \quad (42)$$

When $\gamma > 0.5$ as for the composite functions, the occupation spectrum of \tilde{D} is no longer in the interval $[0,1]$ but in the interval $[\gamma - 0.5, 1 + (\gamma - 0.5)]$; however, composite purification of the region between 1 and $1 + (\gamma - 0.5)$ still converges rapidly to unity. For three purification formulas, the two composite formulas $C_{1,2}(D)$ and $C_{2,3}(D)$ and the MW purification, Fig. 1 displays the number of sparse matrix multiplications required to purify the occupation numbers to zero or one within 10^{-10} as a function of six different band gaps g . Both composite formulas are consistently more efficient than the McWeeny purification; the formula $C_{1,2}(D)$ decreases the total computational time from 17% to 25%. These savings are consistent with the results obtained by Niklasson [18].

Working with the 1-RDM rather than the wave function Ψ in linear-scaling algorithms necessitates purification for constraining the 1-RDM to be N representable. The two genres for 1-RDM linear scaling, the gradient-based methods and the Hamiltonian-purification methods, use purification in rather different roles. In the gradient-based methods an idempotent 1-RDM is chosen as an initial guess, and then updates of the 1-RDM are computed from gradients of the energy (or iterations of the 1,2-contracted Schrödinger equation [5]).

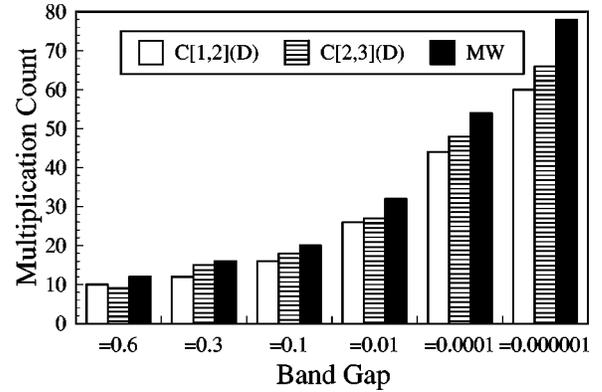


FIG. 1. For three purification formulas, the two composite formulas $C_{1,2}(D)$ and $C_{2,3}(D)$, and the McWeeny (MW) purification, this figure displays the number of sparse matrix multiplications required to purify the occupation numbers to zero or one within 10^{-10} as a function of six different band gaps g . Both composite formulas are consistently more efficient than the McWeeny purification; the formula $C_{1,2}(D)$ decreases the total computational time from 17% to 25%.

The updated 1-RDM is purified between iterations to correct small deviations from idempotency. Daniels and Scuseria [3] report ≈ 28 sparse matrix multiplications per self-consistent-field (SCF) step with four of these multiplications emanating from the McWeeny purification applied twice. Using one $C_{2,3}(D)$ composite purification might reduce the number of multiplications to 26 with a savings of 7%. This increase in efficiency is more modest than the savings in Fig. 1 because much of the computational effort is directed towards computing the gradient and the size of the step along the gradient rather than performing purification.

In the gradient-based method of Li, Nunes, and Daw [1] the McWeeny purification formula has two distinct roles: (i) to correct the 1-RDM for idempotency between iterations as discussed above and (ii) within the energy expression to compute the gradient update of the 1-RDM and an appropriate stepsize along the gradient. An unpublished report [19] indicates that favoring the hole purification by using the DH formula in the energy to compute the 1-RDM gradient may be superior to treating the particles and holes equally with the McWeeny purification. However, using even higher-order purification formulas may not improve upon McWeeny purification in role (ii) because, as Habershon and Manby have demonstrated with the Holas formulas [32], replacing the 1-RDM in the energy expression with a high-order purification formula permits 1-RDMs with a larger purification error to satisfy the energy expression. While the findings of Habershon and Manby imply that more efficient, high-order formulas may not be effective in role (ii), they do not prohibit using efficient Holas or composite purifications effectively in either role (i) of the gradient-based methods or in the Hamiltonian-purification methods.

The primary computational cost in the Hamiltonian-purification methods, in contrast with the gradient techniques, is purification. The eigenvalue range of any reduced Hamiltonian may be mapped onto the interval $[0,1]$ by computing the maximum and minimum eigenvalues with a

TABLE II. Purification Algorithm M. This algorithm differs from method N according to the boldfaced type which controls whether the algorithm attempts a transition to the higher purification formulas $P_{1,2}(D)$ and $P_{1,2}(\bar{D})$.

```

function purify( $N, D_0$ )
while err < tol do
 $H_n = I - D_n$ 
if  $\text{Tr}(D_n) > N$  then
 $D_{n+1} = D_n^2$ 
if  $\text{Tr}(D_{n+1}) < N$  then
 $P_{1,2} = D_n + (D_n - H_n)D_nH_n - 3(D_nH_n)^2$ 
if  $\text{Tr}(P_{1,2}) < N$  then  $D_{n+1} = P_{1,2}$  end if
end if
else if  $\text{Tr}(D_n) < N$  then
 $D_{n+1} = I - H_n^2$ 
if  $\text{Tr}(D_{n+1}) > N$  then
 $P_{1,2} = D_n + (D_n - H_n)D_nH_n + 3(D_nH_n)^2$ 
if  $\text{Tr}(P_{1,2}) < N$  then  $D_{n+1} = P_{1,2}$  end if
end if
end if
err =  $\|D_{n+1} - D_n\|$ 
end do
RETURN( $D_{n+1}$ )
end

```

linear-scaling Lanczos method [10]. When the chemical potential is known, the efficiency of the generalized McWeeny purification formulas in Fig. 1 translates directly into computational savings. In practice, however, the chemical potential must also be either explicitly or implicitly determined during the purification procedure. This identification of the chemical potential increases the computational cost of the procedure. In 1998 Palser and Manolopoulos developed a purification algorithm, based upon McWeeny's formulas, which performs the purification without explicit input of the chemical potential [7]. Another approach to purifying without the chemical potential has recently been developed by Niklasson [18] with the formulas $P_{0,1}(D)$ and $P_{0,1}(\bar{D})$. Because these formulas treat the particle and the holes unequally, they may be applied in a variety of orderings to produce a range of fixed points (chemical potentials) in the interval $[0,1]$. Selecting the ordering of the formulas during purification to converge the trace of the 1-RDM to the number N of electrons automatically and correctly places the chemical potential (fixed point) between the occupation numbers for the occupied and the virtual orbitals.

Extension of Niklasson's algorithm to the higher purification formulas such as $P_{1,2}(D)$ and $P_{1,2}(\bar{D})$ requires some care because compositions of these formulas only yield fixed points in the range $[0.2324, 0.7676]$. An extended algorithm, therefore, must begin with using compositions of the lower-order purification formulas $P_{0,1}(D)$ and $P_{0,1}(\bar{D})$ and then transition to using the higher-order purification formulas $P_{0,1}(D)$ and $P_{0,1}(\bar{D})$. We propose the following extended purification algorithm outlined in Table II. On input the algorithm accepts the number N of electrons and the trial

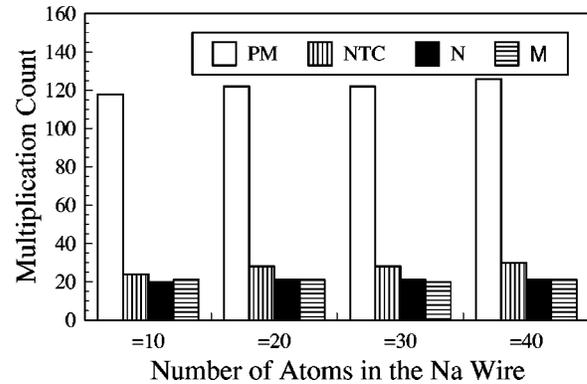


FIG. 2. Performing Hartree-Fock calculations on sodium wires of 10, 20, 30, and 40 atoms, we compare in this figure the purification algorithm (M) with the methods of Palser and Manolopoulos (PM) [7] and Niklasson (N) [18] as well as an algorithm from Niklasson, Tymczak, and Challacombe (NTC) [33]. The number of matrix multiplications in a representative SCF cycle is reported as a function of the purification methodology. Both the M and the N algorithms employ *six times fewer* matrix multiples than the PM method. While both the NTC and the M algorithms extend the N procedure, the M algorithm in this example is as much as 33% more efficient than the NTC method.

1-RDM D_0 which is obtained by mapping the reduced Hamiltonian K with its eigenvalue range $[\epsilon_{\min}, \epsilon_{\max}]$ onto the interval $[0,1]$,

$$D_0 = \frac{1}{\epsilon_{\max} - \epsilon_{\min}} (K - \epsilon_{\min} I), \quad (43)$$

where I is the identity matrix. This algorithm differs from the procedure proposed by Niklasson according to the boldfaced type which controls whether the algorithm attempts a transition to the higher purification formulas $P_{1,2}(D)$ and $P_{1,2}(\bar{D})$. A transition is attempted when the lowered-order purification formulas $P_{0,1}(D)$ and $P_{0,1}(\bar{D})$ are causing the trace of the 1-RDM to fluctuate about N . The new 1-RDM from the higher-order formula is accepted if it continues the fluctuation about N .

Performing Hartree-Fock calculations on sodium wires of 10, 20, 30, and 40 atoms, we compare the purification algorithm (M) with the methods of Palser and Manolopoulos (PM) [7] and Niklasson (N) [18] as well as an algorithm from Niklasson, Tymczak, and Challacombe (NTC) [33] which also extends Niklasson's method to higher-order purification formulas. Electronically each sodium atom is represented by one valence electron through a frozen-core HayWadt basis set [34]. The linear Na wires are defined by a nearest-neighbor bond distance of 3.302 142 3 Å. Using the PC-GAMESS implementation [35] of the GAMESS program for electronic structure [36], we computed the Fock matrices from each iteration of a SCF calculation on the sodium wire. The Fock matrices were then purified with the PM, N, NTC, and M algorithms. In Fig. 2 for each of the sodium wires the number of matrix multiplications in a representative SCF cycle is reported as a function of the purification methodology. Both the M and the N algorithms employ *six times fewer*

matrix multiples than the PM method. The PM method is known to have difficulty for systems with either a low or a high occupancy of the valence orbitals. In practice, difference in computational efficiency between the McWeeny formula and the formulas $P_{n,n+1}$, which treat the particles and holes asymmetrically, can be even more dramatic than shown in Fig. 1 because the asymmetric formulas facilitate purification at a suitable chemical potential for the number N of electrons in the molecular system.

While both the NTC and the M algorithms extend the N procedure, the M algorithm in this example is as much as 33% more efficient than the NTC method. The M technique only evaluates a two-multiplication purification formula when the low-order formulas cause the trace of the 1-RDM to fluctuate about N while the NTC method evaluates a two-multiplication formula at each iteration. The N and M purification methods have the best computational scaling for the 10-, 20-, 30-, and 40-atom Na wires. While the M method employs fewer iterations than the N method, they have a similar number of matrix operations with the N method having one fewer multiplication than M at 10 atoms, and the M method having one fewer multiplication than N at 20 atoms. Further differentiation between the present N and M approaches will require additional molecular examples of varying sizes at high, low, and intermediate valance occupancies as well as scrutiny of computational details such as sparse matrix filling. Because the high-order composite purification formula $C_{2,3}(D)$ converges to an idempotent 1-RDM faster than the lower-order composite purification formula $C_{1,2}$ when the chemical potential is known as in Fig. 1, it is expected that a variant of algorithm M should generally be faster than algorithm N.

IV. CONCLUSIONS

The particle-hole formalism [20–26] from reduced density-matrix theory is applied to the exploration of two classes of generalized McWeeny purification formulas. The first class, including the well-known McWeeny formula, treats the particles and the holes equivalently, while the second class purifies the particles and the holes differently. We derive each of the generalized McWeeny purification formulas as a sum of the 1-RDM and a series expansion in powers of $D\bar{D}$ where the number of terms retained in the series determines the order of the error in the particle and the hole occupation numbers. For McWeeny's formula and its first-

class extensions the series is weighted by a factor of $(D - \bar{D})$ which enforces the particle-hole equivalence. Because the series captures the symmetry of the particles and the holes, it provides an efficient algorithm for fast summation of the formulas with a minimum of sparse matrix multiplications. The second class of generalized purification formulas has a similar particle-hole expansion in powers of $D\bar{D}$ except that the factor of $(D - \bar{D})$ is removed from the final term which breaks the particle-hole symmetry. Application of a particle-biased purification followed by a hole-biased purification produces a composite purification.

The generalized purification formulas from both classes are readily compared with McWeeny's purification through the calculation of an effective error in the occupation numbers, that is, the error from one iteration of an artificial two-multiplication purification which is calibrated to reproduce the error of the generalized formula after an equivalent number of matrix multiplications. Using the effective error as well as a simple application, we show that two of the composite formulas are significantly more efficient than the McWeeny purification. Further improvement is offset by the cost of increasing the number of matrix multiplications. In a second application to sodium wires the higher-order purification formulas are applied to the purification of one-particle Hamiltonians where the chemical potential is not known. For this illustration the proposed algorithm is six times more efficient than the purification method of Palser and Manolopoulos [7] and as much as 33% more efficient than the related algorithm of Niklasson, Tymczak, and Challacombe [33]. The dramatic improvement over the method of Palser and Manolopoulos [7] arises from the ability of the purification formulas $P_{n,n+1}$, which treat the particles and holes differently, to adjust easily to an unknown chemical potential. The particle-hole approach to purification increases our understanding of linear-scaling methods and enhances their computational efficiency for the better quantum-mechanical treatment of large-scale chemical and biological systems.

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