N-electron Slater determinants from nonunitary canonical transformations of fermion operators

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(Received 31 July 2012; revised manuscript received 28 September 2012; published 7 November 2012)

Mean-field methods such as Hartree-Fock (HF) and Hartree-Fock-Bogoliubov (HFB) constitute the building blocks upon which more elaborate many-body theories are based. The HF and HFB wave functions are built out of independent quasiparticles resulting from a unitary linear canonical transformation of the elementary fermion operators. Here, we discuss the possibility of allowing the HF transformation to become nonunitary. The properties of such HF vacua are discussed, as well as the evaluation of matrix elements among such states. We use a simple ansatz to demonstrate that a nonunitary transformation brings additional flexibility that can be exploited in variational approximations to many-fermion wave functions. The action of projection operators on nonunitary-based HF states is also discussed and applied, in a variation-after-projection approach, to the one-dimensional Hubbard model with periodic boundary conditions.

DOI: 10.1103/PhysRevA.86.052102 PACS number(s): 03.65.Ca, 71.27.+a, 74.20.Pq, 71.10.Fd

I. INTRODUCTION

Mean-field methods such as Hartree-Fock (HF) and Hartree-Fock-Bogoliubov (HFB) have become paradigmatic in the description of many-fermion physics. These methods have found a wide range of applications in nuclear structure theory, condensed matter physics, and quantum chemistry. This is not only because they constitute the simplest approximations to the exact many-body wave function, but also because more elaborate correlated approximations usually start from such independent quasiparticle vacua (HF or HFB).

The HFB wave function developed to explain superconductivity relies on the so-called Bogoliubov-Valatin [1,2] transformation, which defines quasiparticle operators as linear combinations of single-fermion creation and annihilation operators. These are then used to form a quasiparticle product state, the HFB wave function. Berezin [3] studied the properties of general linear transformations of fermionic operators within a second-quantized framework. In this sense, one can consider the HF and HFB wave functions as being built out of single quasiparticle operators that result from a linear canonical transformation of the elementary fermion ones.

A canonical transformation is understood in an algebraic framework as that which preserves the Dirac bracket of the phase-space variables in quantum mechanics (the position and momentum operators) [4]. In a second-quantized framework, this corresponds to a transformation that preserves the anticommutation rules of the elementary fermion operators [5]. A linear canonical transformation does not need to be unitary, although Dirac [6] and Weyl [7] showed that unitary transformations are canonical. Standard HF or HFB methods in several fields of many-body physics are usually carried out using a unitary canonical transformation. In this work, we study the possibility of constructing N-particle Slater determinants resulting from nonunitary linear canonical transformations. The extension to HFB determinants will be discussed in a follow-up paper [8].

We note that nonunitary canonical transformations have been discussed in the literature before. They are discussed, for instance, by Blaizot and Ripka [5] in the general context of canonical transformations of second-quantized operators. They have been used by Balian and Berezin [9] in the evaluation of matrix elements between two different Bogoliubov states. Zhang and Tang [10], and later Ma and Zhang [11], have studied the properties of linear canonical transformations of fermion operators, including the nonunitary ones that we have just referred to. We also mention the work of Anderson [4], where the properties of nonunitary canonical transformations have been discussed in a purely algebraic context, without reference to a Hilbert space.

If a single Slater determinant is used as an ansatz for the many-fermion wave function, the full flexibility that a nonunitary canonical transformation affords is not evident because it does not add additional degrees of freedom to those existing in a unitary transformation. On the other hand, one can construct more general ansätze that use the flexibility of such a nonunitary transformation. We discuss here what may be the simplest, two-determinant ansatz that exploits all the degrees of freedom that define a nonunitary transformation for N-particle Slater determinants. This idea has not been explored before in the literature. We here derive all expressions required for the evaluation of matrix elements between nonunitary-based N-particle Slater determinants. We also discuss the variational optimization of states based on a nonunitary (nu)-HF-type canonical transformation.

Our interest in nu-HF-type transformations originated from our recent work on projected HF calculations for molecular systems [12,13] and the two-dimensional (2D) Hubbard Hamiltonian with periodic boundary conditions (PBCs) [14]. The idea of using a symmetry-projected HF state as an approximation to the many-body wave function was proposed by Löwdin [15] as early as 1955. We, building on techniques developed and successfully applied in nuclear physics [5,16–20], have shown that symmetry projection out of the most general HF transformation yields a multireference-type wave function which can account for a very significant part of the electron correlations. We have observed that, the more general the transformation we use (or the more symmetries that

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are broken), the better the resulting projected wave function is able to account for the correlation structure of the true Hamiltonian eigenvector. It is then natural to explore whether a nonunitary canonical transformation, which has more degrees of freedom than the unitary one commonly used, would yield additional flexibility for HF wave functions, in general, and projected HF states, in particular. This work describes our efforts along this line. We show that, indeed, using a nonunitary canonical transformation, one can build more flexible ansätze (based on N-particle Slater determinants) from which additional correlations can be accounted for in variational approximations.

This paper is organized as follows. In Sec. II, we discuss some general properties of linear canonical transformations of fermion operators. We proceed to show in Sec. III how to construct N-particle Slater determinants based on such transformations. Section IV discusses our extension of Thouless' theorem for nonunitary Slater determinants. This is followed by Sec. V, where we use this theorem to derive the form of matrix elements between nonunitary N-particle Slater determinants. In Sec. VI, we introduce a two-determinant ansatz that displays the full flexibility of a nonunitary transformation. We show in Sec. VII how such an ansatz can be used in projected HF approaches. This is followed by an illustrative application of the proposed wave-function ansätze to the one-dimensional (1D) Hubbard Hamiltonian with PBCs in Sec. VIII.

II. CANONICAL TRANSFORMATIONS

We start by introducing a set of fermion annihilation and creation operators $\boldsymbol{c} = \{c_k, c_k^\dagger\}$, which obey the standard anticommutation relations

$$[c_k, c_j]_+ = 0, \quad [c_k^\dagger, c_j^\dagger]_+ = 0, \quad [c_k, c_j^\dagger]_+ = \langle k|j\rangle = \delta_{jk},$$

where $|k\rangle$ ($\langle k|$) is a single-particle ket (bra) state.

We now introduce a new set of fermion operators $\boldsymbol{\beta} = \{\beta_k, \bar{\beta}_k^\dagger\}$, which is related to the original one by the linear transformation

$$\begin{pmatrix} \beta \\ \bar{\beta}^\dagger \end{pmatrix} = \begin{pmatrix} U^\dagger & V^\dagger \\ Y^\mathsf{T} & X^\mathsf{T} \end{pmatrix} \begin{pmatrix} c \\ c^\dagger \end{pmatrix}, \tag{1}$$

where we have arranged the sets of fermion operators $\boldsymbol{c}$ and $\boldsymbol{\beta}$ into single columns. Here, U, V, Y, and X are arbitrary $M \times M$ matrices, where M is the dimension of the single-particle space. For compactness, we write the transformation defined by Eq. (1) as

$$\boldsymbol{\beta} = T\boldsymbol{c}. \tag{2}$$

It should be stressed that we have not enforced the relation $\bar{\beta}^\dagger = (\beta)^\dagger$ in Eq. (1), as this leads to a standard unitary transformation. One can show [5] that the transformation is unitary if the matrix T satifies

$$T^* = \sigma\, T\, \sigma, \tag{3}$$

where the matrix σ is given by

$$\sigma = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{4}$$

Here, Eq. (3) implies $U = X$ and $V = Y$.

We do insist, on the other hand, on making our transformation canonical, which implies preserving the appropriate anticommutation relations, that is,

$$[\beta_k, \beta_j]_+ = 0, \quad [\bar{\beta}_k^\dagger, \bar{\beta}_j^\dagger]_+ = 0, \quad [\beta_k, \bar{\beta}_j^\dagger]_+ = \delta_{jk}.$$

It is not difficult to prove [5] that the transformation T is canonical if it obeys

$$T\, \sigma\, T^\mathsf{T} = \sigma. \tag{5}$$

Using Eq. (5), one can easily deduce the form of the inverse transformation,

$$T^{-1} = \begin{pmatrix} X & V^* \\ Y & U^* \end{pmatrix}. \tag{6}$$

Equation (5) also provides the conditions that the matrices U, V, X, and Y must satisfy for T to define a canonical transformation. Those are given by

$$U^\dagger X + V^\dagger Y = 1, \tag{7a}$$
$$X^\mathsf{T} U^* + Y^\mathsf{T} V^* = 1, \tag{7b}$$
$$U^\dagger V^* + V^\dagger U^* = 0, \tag{7c}$$
$$Y^\mathsf{T} X + X^\mathsf{T} Y = 0. \tag{7d}$$

Note that the matrices $U^\dagger V^*$ and $Y^\mathsf{T} X$ are antisymmetric.

The matrices T form a group (the fermion group described by Ma and Zhang [11]) isomorphic to the group of orthogonal matrices of dimension $2M$ [$O(2M,C)$] [5]. On the other hand, the set of matrices T for which the transformation is unitary forms a group isomorphic to the group of real orthogonal matrices of dimension $2M$ [$O(2M)$]. There are twice as many degrees of freedom in a general nonunitary transformation than in a unitary one.

We close this section by noting that the transformation defined in Eq. (1) is more naturally understood as a linear transformation if one introduces an operator S such that

$$\boldsymbol{\beta} = S\,\boldsymbol{c}\,S^{-1} = T\,\boldsymbol{c}. \tag{8}$$

The form of the operator S has been discussed by Blaizot and Ripka [5], Zhang and Tang [10], and Ma and Zhang [11].

III. N-ELECTRON SLATER DETERMINANTS

In this section, we discuss the construction of N-particle Slater determinants using quasiparticle operators resulting from canonical transformations of the elementary fermion ones. This is discussed in detail by Navon [21], as well as in several textbooks on many-body physics.

In standard (i.e., unitary) HF theory, an N-electron Slater determinant is constructed out of a set N hole creation ($\{b_h^\dagger\}$) and $M - N$ particle annihilation ($\{b_p\}$) operators, each of them resulting from a linear combination of the elementary operators $\{c_k, c_k^\dagger\}$:

$$b_h^\dagger = \sum_j D_{jh}^*\, c_j^\dagger, \tag{9a}$$
$$b_p = \sum_j D_{jp}\, c_j. \tag{9b}$$

Using standard notation, the first N columns in D (which we write as D_h) represent the hole states, while the last $M-N$ columns (which we write as D_p) represent the particle states.

The transformation from the elementary operators to the set of HF operators constructed above can be written as

$$\begin{pmatrix} b_h^\dagger \\ b_p \\ b_h \\ b_p^\dagger \end{pmatrix} = \begin{pmatrix} \mathbf{0}_{N\times M} & D_h^\dagger \\ D_p^{\mathsf{T}} & \mathbf{0}_{(M-N)\times M} \\ D_h^{\mathsf{T}} & \mathbf{0}_{N\times M} \\ \mathbf{0}_{(M-N)\times M} & D_p^\dagger \end{pmatrix} \begin{pmatrix} c \\ c^\dagger \end{pmatrix}, \tag{10}$$

where we have implicitly assumed the transformation to be unitary.

The above transformation is canonical if the HF operators satisfy the (nontrivial) anticommutation relations

$$[b_h, b_{h'}^\dagger]_+ = \delta_{h'h}, \quad [b_p, b_{p'}^\dagger]_+ = \delta_{p'p}, \quad [b_p, b_h^\dagger]_+ = 0.$$

These conditions restrict the form of the matrix D according to

$$[b_h, b_{h'}^\dagger]_+ = \sum_{jk} D_{jh}\, D_{kh'}^*\, \delta_{jk} = (D^\dagger\, D)_{h'h} = \delta_{h'h}, \tag{11a}$$

$$[b_p, b_{p'}^\dagger]_+ = \sum_{jk} D_{jp}\, D_{kp'}^*\, \delta_{jk} = (D^\dagger\, D)_{p'p} = \delta_{p'p}, \tag{11b}$$

$$[b_p, b_h^\dagger]_+ = \sum_{jk} D_{jp}\, D_{kh}^*\, \delta_{jk} = (D^\dagger\, D)_{hp} = 0. \tag{11c}$$

Equation (11a) implies orthonormality of the hole states; Eq. (11b), orthonormality of the particle states; and Eq. (11c) corresponds to orthogonality between hole and particle states. All these conditions are summarized in the requirement $D^\dagger\, D = \mathbf{1}$.

One could allow the HF transformation described previously to become nonunitary by introducing, in addition to the operators described by Eq. (9), another set of hole and particle operators, $\{\bar{b}_h, \bar{b}_p^\dagger\}$, given by

$$\bar{b}_h = \sum_j \bar{D}_{jh}\, c_j, \tag{12a}$$

$$\bar{b}_p^\dagger = \sum_j \bar{D}_{jp}^*\, c_j^\dagger. \tag{12b}$$

A nonunitary transformation can then be built as

$$\begin{pmatrix} b_h^\dagger \\ b_p \\ \bar{b}_h \\ \bar{b}_p^\dagger \end{pmatrix} = \begin{pmatrix} \mathbf{0}_{N\times M} & D_h^\dagger \\ D_p^{\mathsf{T}} & \mathbf{0}_{(M-N)\times M} \\ \bar{D}_h^{\mathsf{T}} & \mathbf{0}_{N\times M} \\ \mathbf{0}_{(M-N)\times M} & \bar{D}_p^\dagger \end{pmatrix} \begin{pmatrix} c \\ c^\dagger \end{pmatrix}. \tag{13}$$

It is a canonical transformation if the (nontrivial) anticommutation relations

$$[b_p, b_h^\dagger]_+ = 0, \quad [\bar{b}_h, \bar{b}_p^\dagger]_+ = 0,$$
$$[\bar{b}_h, b_{h'}^\dagger]_+ = \delta_{h'h}, \quad [b_p, \bar{b}_{p'}^\dagger]_+ = \delta_{p'p}$$

are satisfied. These conditions restrict the form of the matrices D and $\bar{D}$ according to

$$[b_p, b_h^\dagger]_+ = \sum_{jk} D_{jp}\, D_{kh}^*\, \delta_{jk} = (D^\dagger\, D)_{hp} = 0, \tag{14a}$$

$$[\bar{b}_h, \bar{b}_p^\dagger]_+ = \sum_{jk} \bar{D}_{jh}\, \bar{D}_{kp}^*\, \delta_{jk} = (\bar{D}^\dagger\, \bar{D})_{ph} = 0, \tag{14b}$$

$$[\bar{b}_h, b_{h'}^\dagger]_+ = \sum_{jk} \bar{D}_{jh}\, D_{kh'}^*\, \delta_{jk} = (D^\dagger\, \bar{D})_{h'h} = \delta_{h'h}, \tag{14c}$$

$$[b_p, \bar{b}_{p'}^\dagger]_+ = \sum_{jk} D_{jp}\, \bar{D}_{kp'}^*\, \delta_{jk} = (\bar{D}^\dagger\, D)_{p'p} = \delta_{p'p}. \tag{14d}$$

Equations (14a) and (14b) imply orthogonality of the hole and particle states in D and $\bar{D}$. Equations (14c) and (14d) imply a biorthonormality between the hole and the particle orbitals in D and $\bar{D}$. Note that the latter two conditions are satisfied by choosing $\bar{D}^\dagger = D^{-1}$, but the orthogonality among hole and particle states has to be separately imposed.

Let us remark that, if the HF operators $\{b_h^\dagger, b_p, \bar{b}_h, \bar{b}_p^\dagger\}$ define a canonical transformation, the inverse transformation is given by [see Eq. (6)]

$$\begin{pmatrix} c \\ c^\dagger \end{pmatrix} = \begin{pmatrix} \mathbf{0}_{M\times N} & \bar{D}_p^* & D_h^* & \mathbf{0}_{M\times(M-N)} \\ \bar{D}_h & \mathbf{0}_{M\times(M-N)} & \mathbf{0}_{M\times N} & D_p \end{pmatrix} \begin{pmatrix} b_h^\dagger \\ b_p \\ \bar{b}_h \\ \bar{b}_p^\dagger \end{pmatrix}. \tag{15}$$

The biorthonormal Slater determinants $|\Phi\rangle$ and $|\overline{\Phi}\rangle$ are produced when the set of operators $\{b_h^\dagger, \bar{b}_h^\dagger\}$ acts on the bare fermion vacuum $|-\rangle$, i.e.,

$$|\Phi\rangle = \prod_h b_h^\dagger |-\rangle, \tag{16}$$

$$|\overline{\Phi}\rangle = \prod_h \bar{b}_h^\dagger |-\rangle. \tag{17}$$

They satisfy the biorthonormality condition $\langle\overline{\Phi}|\Phi\rangle = 1$.

One can easily show that $|\Phi\rangle$ and $|\overline{\Phi}\rangle$ act as vacua to a certain set of hole or particle states:

$$b_h^\dagger|\Phi\rangle = 0\,\forall\, b_h^\dagger, \quad b_p|\Phi\rangle = 0\,\forall\, b_p,$$
$$\bar{b}_h^\dagger|\overline{\Phi}\rangle = 0\,\forall\, \bar{b}_h^\dagger, \quad \bar{b}_p|\overline{\Phi}\rangle = 0\,\forall\, \bar{b}_p.$$

IV. THOULESS' THEOREM FOR N-ELECTRON SLATER DETERMINANTS

In standard (i.e., unitary) HF, there is a theorem due to Thouless [22] which reads:

Theorem. Given a Slater determinant $|\Phi_0\rangle$ which is a vacuum to the operators $\{b_h^\dagger, b_p\}$, any N-particle Slater determinant $|\Phi_1\rangle$ which is not orthogonal to $|\Phi_0\rangle$ can be written in the form

$$|\Phi_1\rangle = \mathcal{N} \exp\left(\sum_{ph} Z_{ph}\, b_p^\dagger\, b_h\right) |\Phi_0\rangle, \tag{18}$$

where $\mathcal{N} = \langle\Phi_0|\Phi_1\rangle$ is a normalization constant and the coefficients Z_{ph} are uniquely determined. Conversely, any wave function of the form of Eq. (18), where $|\Phi_0\rangle$ is a Slater determinant, is also an N-particle Slater determinant.

For Slater determinants built out of operators resulting from a nonunitary linear canonical transformation, the equivalent theorem reads:

Theorem. Given a Slater determinant $|\Phi_0\rangle$ which is a vacuum to the operators $\{b_h^\dagger, b_p\}$, any N-particle Slater determinant $|\Phi_1\rangle$ which is not orthogonal to $|\overline{\Phi}_0\rangle$ can be written in the form

$$|\Phi_1\rangle = \mathcal{N}\,\exp\left(\sum_{ph} Z_{ph}\,\bar{b}_p^\dagger\,\bar{b}_h\right)|\Phi_0\rangle, \tag{19}$$

where $\mathcal{N} = \langle\overline{\Phi}_0|\Phi_1\rangle$ is a normalization constant and the coefficients Z_{ph} are uniquely determined.

For a proof of the latter theorem we refer the reader to Appendix A of the present work.

V. MATRIX ELEMENTS BETWEEN N-ELECTRON SLATER DETERMINANTS

In this section we obtain the expressions required for the evaluation of matrix elements between arbitrary Slater determinants built out of operators resulting from a nonunitary canonical transformation.

A. Norm overlaps

The overlap between two N-particle Slater determinants of the form $|\Phi_\alpha\rangle = \prod_k \alpha_k^\dagger|-\rangle$ can be obtained by application of Wick's theorem [5] on the bare fermion vacuum. That is,

$$\langle\Phi_\beta|\Phi_\alpha\rangle = \langle-|\beta_N\cdots\beta_1\,\alpha_1^\dagger\cdots\alpha_N^\dagger|-\rangle = \det S, \tag{20}$$

where $S_{ij} = \overbrace{\beta_i\alpha_j^\dagger} = \langle\beta_i|\alpha_j\rangle$. Here, we have used the fact that the contractions $\overbrace{\beta_i\beta_j}$ and $\overbrace{\alpha_i^\dagger\alpha_j^\dagger}$ vanish for HF-type operators.

The overlaps among N-particle Slater determinants become

$$\langle\Phi_0|\Phi_1\rangle = \det{}_N\, D^{0\mathsf{T}}\, D^{1*}, \tag{21a}$$
$$\langle\Phi_0|\overline{\Phi}_1\rangle = \det{}_N\, D^{0\mathsf{T}}\, \bar{D}^{1*}, \tag{21b}$$
$$\langle\overline{\Phi}_0|\Phi_1\rangle = \det{}_N\, \bar{D}^{0\mathsf{T}}\, D^{1*}, \tag{21c}$$
$$\langle\overline{\Phi}_0|\overline{\Phi}_1\rangle = \det{}_N\, \bar{D}^{0\mathsf{T}}\, \bar{D}^{1*}, \tag{21d}$$

where we have used $\det_N$ to denote that the determinant is over the $N\times N$ set of occupied orbitals. Observe that $\langle\Phi_0|\overline{\Phi}_0\rangle = \langle\overline{\Phi}_0|\Phi_0\rangle = 1$, which corresponds to the biorthonormality condition previously described.

B. Operator matrix elements

In deriving the expressions for operator matrix elements, we follow Ring and Schuck [16]. Our aim in this subsection is to evaluate matrix elements of the form

$$\langle\overline{\Phi}_0|c_{l_1}^\dagger\cdots c_{l_p}^\dagger\, c_{k_1}\cdots c_{k_p}|\Phi_1\rangle. \tag{22}$$

The form above is chosen for convenience, but other matrix elements can be derived in the same way described below.

We use Thouless' theorem to write the state $|\Phi_1\rangle$ as

$$|\Phi_1\rangle = \exp(\hat{\mathcal{Z}})|\Phi_0\rangle\langle\overline{\Phi}_0|\Phi_1\rangle, \tag{23}$$

$$\hat{\mathcal{Z}} = \sum_{ph}\mathcal{Z}_{ph}\bar{b}_p^\dagger\bar{b}_h. \tag{24}$$

Here, $\{b_h^\dagger, b_p, \bar{b}_h, \bar{b}_p^\dagger\}$ are defined such that

$$b_h^\dagger|\Phi_0\rangle = 0\,\forall\, b_h^\dagger, \quad b_p|\Phi_0\rangle = 0\,\forall\, b_p,$$
$$\langle\overline{\Phi}_0|\bar{b}_h = 0\,\forall\,\bar{b}_h, \quad \langle\overline{\Phi}_0|\bar{b}_p^\dagger = 0\,\forall\,\bar{b}_p^\dagger.$$

On the other hand, we write the state $\langle\overline{\Phi}_0|$ as

$$\langle\overline{\Phi}_0| = \langle\overline{\Phi}_0|\exp(-\hat{\mathcal{Z}}), \tag{25}$$

where use has been made of the vacuum properties just described.

It then follows that we can evaluate the general matrix element from Eq. (22) as

$$\begin{aligned}
&\langle\overline{\Phi}_0|c_{l_1}^\dagger\cdots c_{l_p}^\dagger\, c_{k_1}\cdots c_{k_p}|\Phi_1\rangle \\
&\quad= \langle\overline{\Phi}_0|\Phi_1\rangle\langle\overline{\Phi}_0|\exp(-\hat{\mathcal{Z}})\,c_{l_1}^\dagger\cdots c_{l_p}^\dagger\, c_{k_1}\cdots c_{k_p}\,\exp(\hat{\mathcal{Z}})|\Phi_0\rangle \\
&\quad= \langle\overline{\Phi}_0|\Phi_1\rangle\langle\overline{\Phi}_0|\tilde{d}_{l_1}\cdots\tilde{d}_{l_p}\,d_{k_1}\cdots d_{k_p}|\Phi_0\rangle,
\end{aligned} \tag{26}$$

where we have introduced the operators

$$\tilde{d}_l = \exp(-\hat{\mathcal{Z}})\,c_l^\dagger\,\exp(\hat{\mathcal{Z}}), \tag{27a}$$
$$d_k = \exp(-\hat{\mathcal{Z}})\,c_k\,\exp(\hat{\mathcal{Z}}). \tag{27b}$$

We now express the operators $\{\tilde{d}_l, d_k\}$ in terms of $\{b_h^\dagger, b_p, \bar{b}_h, \bar{b}_p^\dagger\}$. This is accomplished by using Eq. (15) to write $\{c_j, c_j^\dagger\}$ in terms of $\{b_h^\dagger, b_p, \bar{b}_h, \bar{b}_p^\dagger\}$. It follows that

$$\begin{aligned}
\tilde{d}_l &= \exp(-\hat{\mathcal{Z}})\,c_l^\dagger\,\exp(\hat{\mathcal{Z}}) = c_l^\dagger - [\hat{\mathcal{Z}}, c_l^\dagger] \\
&= \sum_h \bar{D}_{lh}^0\, b_h^\dagger + \sum_p\left(D_{lp}^0 - \sum_h \mathcal{Z}_{ph}\,\bar{D}_{lh}^0\right)\bar{b}_p^\dagger,
\end{aligned} \tag{28}$$

$$\begin{aligned}
d_k &= \exp(-\hat{\mathcal{Z}})\,c_k\,\exp(\hat{\mathcal{Z}}) = c_k - [\hat{\mathcal{Z}}, c_k] \\
&= \sum_h\left(D_{kh}^{0*} + \sum_p \mathcal{Z}_{ph}\,\bar{D}_{kp}^{0*}\right)\bar{b}_h + \sum_p \bar{D}_{kp}^{0*}\, b_p.
\end{aligned} \tag{29}$$

Because $\{\tilde{d}_l, d_k\}$ are given as linear combinations of $\{b_h^\dagger, b_p, \bar{b}_h, \bar{b}_p^\dagger\}$, Wick's theorem [5] can be used to calculate the corresponding matrix elements. The nonvanishing contractions among the operators $\{b_h^\dagger, b_p, \bar{b}_h, \bar{b}_p^\dagger\}$ are given by

$$\overbrace{b_h^\dagger\bar{b}_{h'}} = \delta_{hh'}, \tag{30a}$$
$$\overbrace{b_p\bar{b}_{p'}^\dagger} = \delta_{pp'}. \tag{30b}$$

It follows that the nonvanishing contractions among the operators $\{\tilde{d}_l, d_k\}$ are of the form

$$\begin{aligned}\overbrace{\tilde{d}_l d_k} &= \sum_{hh'} \bar{D}^0_{lh} \left(D^{0*}_{kh'} + \sum_p \mathcal{Z}_{ph'}\, \bar{D}^{0*}_{kp} \right) \delta_{hh'} \\ &= \sum_h \bar{D}^0_{lh}\, D^{0*}_{kh} + \sum_{ph} \bar{D}^0_{lh}\, \mathcal{Z}_{ph}\, \bar{D}^{0*}_{kp}, \qquad (31)\\ \overbrace{d_l \tilde{d}_k} &= \sum_{pp'} \bar{D}^{0*}_{lp} \left(D^0_{kp'} - \sum_h \mathcal{Z}_{p'h}\, \bar{D}^0_{kh} \right) \delta_{pp'} \\ &= \sum_p \bar{D}^{0*}_{lp}\, D^0_{kp} - \sum_{ph} \bar{D}^{0*}_{lp}\, \mathcal{Z}_{ph}\, \bar{D}^0_{kh}. \qquad (32)\end{aligned}$$

The application of Wick's theorem to the operator matrix elements of the form of Eq. (22) leads us to conclude that all such matrix elements can be evaluated in terms of the transition density matrix $\rho^{\bar{0}1}$, given by

$$\begin{aligned}\rho^{\bar{0}1}_{kl} &= \frac{\langle\overline{\Phi}_0|c^\dagger_l\, c_k|\Phi_1\rangle}{\langle\overline{\Phi}_0|\Phi_1\rangle} = \langle\overline{\Phi}_0|\exp(-\hat{\mathcal{Z}})\, c^\dagger_l\, c_k\, \exp(\hat{\mathcal{Z}})|\Phi_0\rangle \\ &= \sum_h \bar{D}^0_{lh}\, D^{0*}_{kh} + \sum_{ph} \bar{D}^0_{lh}\, \mathcal{Z}_{ph}\, \bar{D}^{0*}_{kp}, \qquad (33)\end{aligned}$$

where

$$\begin{aligned}\mathcal{Z}_{ph} &= \sum_{h'} (D^{0\mathsf{T}}\, D^{1*})_{ph'} (\mathcal{L}^{*-1})_{h'h}, \qquad (34)\\ \mathcal{L}_{h'h} &= (\bar{D}^{0\dagger}\, D^1)_{h'h}. \qquad (35)\end{aligned}$$

Here, we have used Eqs. (A2) and (A5) from Appendix A to write the forms of the matrices $\mathcal{Z}$ and $\mathcal{L}$.

C. Evaluation of the energy of a single Slater determinant

As an example of the application of the above equations, let us now consider the evaluation of the energy of a determinant $|\Phi\rangle$. Given a two-body Hamiltonian in the usual second-quantized form Ref. [5],

$$\hat{H} = \sum_{ik} \langle i|\hat{h}|k\rangle\, c^\dagger_i\, c_k + \frac{1}{4} \sum_{ijkl} \langle ij|\hat{v}|kl\rangle\, c^\dagger_i\, c^\dagger_j\, c_l\, c_k, \qquad (36)$$

where $\langle i|\hat{h}|k\rangle$ and $\langle ij|\hat{v}|kl\rangle$ are one-particle and antisymmetrized two-particle integrals, respectively, the energy can be evaluated as

$$\begin{aligned}E &= \frac{\langle\Phi|\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} = \sum_{ik} h_{ik}\, \rho_{ki} + \frac{1}{2} \sum_{ijkl} \langle ij|\hat{v}|kl\rangle\, \rho_{ki}\, \rho_{lj} \\ &= \mathrm{Tr}\left(h\, \rho + \frac{1}{2}\, \Gamma\, \rho \right), \qquad (37)\end{aligned}$$

where

$$\begin{aligned}\rho_{ki} &= \frac{\langle\Phi|c^\dagger_i\, c_k|\Phi\rangle}{\langle\Phi|\Phi\rangle} \\ &= \sum_h D_{ih}\, \bar{D}^*_{kh} + \sum_{ph} D_{ih}\, \bar{\mathcal{Z}}_{ph}\, D^*_{kp}, \qquad (38)\\ \Gamma_{ik} &= \sum_{jl} \langle ij|\hat{v}|kl\rangle\, \rho_{lj}, \qquad (39)\end{aligned}$$

and

$$\begin{aligned}\bar{\mathcal{Z}}_{ph} &= \sum_{h'} (\bar{D}^{\mathsf{T}}\, D^*)_{ph'} (\bar{\mathcal{L}}^{*-1})_{h'h}, \qquad (40)\\ \bar{\mathcal{L}}_{h'h} &= (D^\dagger\, D)_{h'h}. \qquad (41)\end{aligned}$$

It is important to realize that the energy expression [Eq. (37)] has the same form as in standard (i.e., unitary) HF. The difference lies in the form of the density matrix ρ [Eq. (38)], which comes about from the fact that the anticommutation relations satisfied by the HF operators are different.

VI. VARIATIONAL ANSATZ WITH SLATER DETERMINANTS FROM NONUNITARY TRANSFORMATIONS

In this section, we use a simple, two-determinant ansatz that uses the full flexibility of the nu-HF-like transformation of Eq. (13) as part of a variational strategy. Before introducing this ansatz, we note that using a single Slater determinant $|\Phi\rangle$ as a trial wave function, whether resulting from a unitary or a nonunitary canonical transformation, would lead to the same variational energy. An N-particle Slater determinant resulting from a nonunitary canonical transformation is equivalent to an un-normalized Slater determinant in the usual (i.e., unitary) sense. The variational optimization of the energy (taken as the Hamiltonian overlap over the norm overlap) would lead to the same result regardless of the underlying normalization of the determinant.

The two-determinant ansatz that we use is given by

$$\begin{aligned}|\Psi\rangle &= c_1|\Phi\rangle + c_2|\overline{\Phi}\rangle, \\ &\equiv c_1|\Phi_1\rangle + c_2|\Phi_2\rangle, \qquad (42)\end{aligned}$$

where c_1 and c_2 are coefficients to be determined variationally. We have made the identification $|\Phi_1\rangle \equiv |\Phi\rangle$ and $|\Phi_2\rangle \equiv |\overline{\Phi}\rangle$ to simplify our notation below. Observe that for a standard (i.e., unitary) HF transformation, $|\Phi_1\rangle = |\overline{\Phi}\rangle$, which in turn implies $|\Psi\rangle = |\Phi\rangle$.

One could argue that the ansatz of Eq. (42) has the same variational flexibility as that in which $|\Phi_1\rangle$ and $|\Phi_2\rangle$ are two nonorthogonal Slater determinants resulting, each of them, from a standard unitary canonical transformation (see Ref. [23]). Nevertheless, the ansatz we use explicitly results from a single linear canonical transformation of the elementary fermion operators.

The Hamiltonian expectation value associated with the state $|\Psi\rangle$ is given by

$$E = \frac{\sum^2_{\alpha,\beta=1} c^*_\alpha\, c_\beta \langle\Phi_\alpha|\hat{H}|\Phi_\beta\rangle}{\sum^2_{\alpha,\beta=1} c^*_\alpha\, c_\beta \langle\Phi_\alpha|\Phi_\beta\rangle}. \qquad (43)$$

We rewrite the energy above in the form

$$\begin{aligned}E &= \sum_{\alpha,\beta=1}^{2} y_{\alpha\beta} \frac{\langle\Phi_\alpha|\hat{H}|\Phi_\beta\rangle}{\langle\Phi_\alpha|\Phi_\beta\rangle}, \qquad (44)\\ y_{\alpha\beta} &= \frac{c^*_\alpha\, c_\beta \langle\Phi_\alpha|\Phi_\beta\rangle}{\sum^2_{\alpha',\beta'=1} c^*_{\alpha'}\, c_{\beta'} \langle\Phi_{\alpha'}|\Phi_{\beta'}\rangle}. \qquad (45)\end{aligned}$$

The matrix elements appearing in Eqs. (44) and (45) can be evaluated in a straightforward way. The overlap kernels in Eq. (45) are computed as

$$\langle\Phi|\Phi\rangle = \det{}_N\, D^{\mathsf{T}}\, D^*, \tag{46a}$$
$$\langle\overline{\Phi}|\Phi\rangle = \det{}_N\, \bar{D}^{\mathsf{T}}\, D^* = 1, \tag{46b}$$
$$\langle\Phi|\overline{\Phi}\rangle = \det{}_N\, D^{\mathsf{T}}\, \bar{D}^* = 1, \tag{46c}$$
$$\langle\overline{\Phi}|\overline{\Phi}\rangle = \det{}_N\, \bar{D}^{\mathsf{T}}\, \bar{D}^*. \tag{46d}$$

The Hamiltonian kernels are evaluated in terms of transition density matrices as

$$\frac{\langle\Phi_\alpha|\hat{H}|\Phi_\beta\rangle}{\langle\Phi_\alpha|\Phi_\beta\rangle} = \mathrm{Tr}\left(h\,\rho^{\alpha\beta} + \frac{1}{2}\,\Gamma^{\alpha\beta}\,\rho^{\alpha\beta}\right), \tag{47}$$
$$\Gamma^{\alpha\beta}_{ik} = \sum_{jl}\langle ij|\hat{v}|kl\rangle\,\rho^{\alpha\beta}_{lj}. \tag{48}$$

The transition density matrices are in turn given by

$$\rho^{11}_{ki} = \frac{\langle\Phi|c_i^\dagger\, c_k|\Phi\rangle}{\langle\Phi|\Phi\rangle} = \sum_h D_{ih}\,\bar{D}^*_{kh} + \sum_{ph} D_{ih}\,\bar{\mathcal{Z}}_{ph}\,D^*_{kp}, \tag{49a}$$

$$\rho^{21}_{ki} = \frac{\langle\overline{\Phi}|c_i^\dagger\, c_k|\Phi\rangle}{\langle\overline{\Phi}|\Phi\rangle} = \sum_h \bar{D}_{ih}\,D^*_{kh}, \tag{49b}$$

$$\rho^{12}_{ki} = \frac{\langle\Phi|c_i^\dagger\, c_k|\overline{\Phi}\rangle}{\langle\Phi|\overline{\Phi}\rangle} = \sum_h D_{ih}\,\bar{D}^*_{kh}, \tag{49c}$$

$$\rho^{22}_{ki} = \frac{\langle\overline{\Phi}|c_i^\dagger\, c_k|\overline{\Phi}\rangle}{\langle\overline{\Phi}|\overline{\Phi}\rangle} = \sum_h \bar{D}_{ih}\,D^*_{kh} + \sum_{ph} \bar{D}_{ih}\,\mathcal{Z}_{ph}\,\bar{D}^*_{kp}. \tag{49d}$$

Here,

$$\bar{\mathcal{Z}}_{ph} = \sum_{h'}(\bar{D}^{\mathsf{T}}\,D^*)_{ph'}(\bar{\mathcal{L}}^{*-1})_{h'h}, \tag{50a}$$
$$\mathcal{Z}_{ph} = \sum_{h'}(D^{\mathsf{T}}\,\bar{D}^*)_{ph'}(\mathcal{L}^{*-1})_{h'h}, \tag{50b}$$
$$\bar{\mathcal{L}}_{h'h} = (D^\dagger\,D)_{h'h}, \tag{50c}$$
$$\mathcal{L}_{h'h} = (\bar{D}^\dagger\,\bar{D})_{h'h}. \tag{50d}$$

A. Variational optimization of $|\Phi\rangle$

Let us now consider the variational optimization of the wave-function ansatz introduced in Eq. (42). The variational parameters are the coefficients c_1 and c_2 and the orbital coefficients (that is, the matrices D and $\bar{D}$) defining the states $|\Phi\rangle$ and $|\overline{\Phi}\rangle$. The variation has to be carried out subject to the constraint that $\langle\overline{\Phi}|\Phi\rangle = 1$, which is equivalent to saying that $|\Phi\rangle$ and $|\overline{\Phi}\rangle$ are defined by a canonical transformation of the form of Eq. (13).

The variation with respect to the coefficients c_1 and c_2 yields the generalized eigenvalue problem,

$$(\mathbf{H} - E\,\mathbf{N})\,\boldsymbol{c} = 0, \tag{51}$$

with the constraint

$$\boldsymbol{c}^\dagger\,\mathbf{N}\,\boldsymbol{c} = 1, \tag{52}$$

which ensures the orthonormality of the solution. Here, $\boldsymbol{c}$ represents the column of coefficients $\{c_1,c_2\}$, while $\mathbf{H}$ and $\mathbf{N}$ are, respectively, Hamiltonian and overlap matrices given by

$$H_{\alpha\beta} = \langle\Phi_\alpha|\hat{H}|\Phi_\beta\rangle, \tag{53}$$

$$N_{\alpha\beta} = \langle\Phi_\alpha|\Phi_\beta\rangle. \tag{54}$$

It should be stressed that at this level we only keep the lowest energy solution to the generalized eigenvalue problem, in a similar way as in projected-HF methods involving an eigenvalue problem [14].

Let us now consider the variation in the energy with respect to the underlying nu-HF transformation. We have followed the work of Egido and coworkers [24] for this purpose. Let us assume that we are provided a guess for $|\Phi\rangle$ and $|\overline{\Phi}\rangle$, characterized by the set of HF operators $\{b_h^\dagger, b_p, \bar{b}_h, \bar{b}_p^\dagger\}$. We can now parametrize the energy functional around $\{|\Phi\rangle, |\overline{\Phi}\rangle\}$ by allowing for independent Thouless' rotations of both states, characterized by the matrices Z and $\bar{Z}$. That is, we let

$$|\Phi\rangle \to \exp\left(\sum_{ph} Z_{ph}\,\bar{b}_p^\dagger\,\bar{b}_h\right)|\Phi\rangle, \tag{55a}$$

$$|\overline{\Phi}\rangle \to \exp\left(\sum_{ph} \bar{Z}_{ph}\,b_p^\dagger\,b_h\right)|\overline{\Phi}\rangle. \tag{55b}$$

We define the local gradient $\{G,\bar{G}\}$ around $Z = 0$ and $\bar{Z} = 0$ as

$$G_{ph} = -\left.\frac{\partial}{\partial\, Z^*_{ph}}\,E\,[Z,\bar{Z}]\right|_{Z_{ph}=0}, \tag{56a}$$

$$\bar{G}_{ph} = -\left.\frac{\partial}{\partial\, \bar{Z}^*_{ph}}\,E\,[Z,\bar{Z}]\right|_{\bar{Z}_{ph}=0}. \tag{56b}$$

Here, Z_{ph} and Z^*_{ph} are treated as independent variables, and the same is true for $\bar{Z}_{ph}$ and $\bar{Z}^*_{ph}$. The total derivative of the energy then becomes

$$dE = -\sum_{ph}[G_{ph}\,dZ^*_{ph} + \bar{G}_{ph}\,d\bar{Z}^*_{ph} + \text{c.c.}]. \tag{57}$$

Explicit differentiation of the parametrized energy functional leads to the following expressions for the local gradient:

$$G_{ph} = -y_{11}\,\frac{\langle\Phi|\bar{b}_h^\dagger\,\bar{b}_p\,(\hat{H}-E)|\Phi\rangle}{\langle\Phi|\Phi\rangle} - y_{12}\,\frac{\langle\Phi|\bar{b}_h^\dagger\,\bar{b}_p\,(\hat{H}-E)|\overline{\Phi}\rangle}{\langle\Phi|\overline{\Phi}\rangle}, \tag{58a}$$

$$\bar{G}_{ph} = -y_{21}\,\frac{\langle\overline{\Phi}|b_h^\dagger\,b_p\,(\hat{H}-E)|\Phi\rangle}{\langle\overline{\Phi}|\Phi\rangle} - y_{22}\,\frac{\langle\overline{\Phi}|b_h^\dagger\,b_p\,(\hat{H}-E)|\overline{\Phi}\rangle}{\langle\overline{\Phi}|\overline{\Phi}\rangle}, \tag{58b}$$

where E is the energy corresponding to the state $|\Psi\rangle$ from Eq. (42).

The overlap-like matrix elements appearing in Eq. (58) can be evaluated as

$$\frac{\langle\Phi|\bar{b}_h^\dagger\,\bar{b}_p|\Phi\rangle}{\langle\Phi|\Phi\rangle} = \sum_{mn}\bar{D}^*_{mh}\,\bar{D}_{np}\,\rho^{11}_{nm}, \tag{59a}$$

$$\frac{\langle\overline{\Phi}|b_h^\dagger\,b_p|\Phi\rangle}{\langle\overline{\Phi}|\Phi\rangle} = 0, \tag{59b}$$

$$\frac{\langle\Phi|\bar{b}_h^\dagger\,\bar{b}_p|\overline{\Phi}\rangle}{\langle\Phi|\overline{\Phi}\rangle} = 0, \tag{59c}$$

$$\frac{\langle\overline{\Phi}|b_h^\dagger\,b_p|\overline{\Phi}\rangle}{\langle\overline{\Phi}|\overline{\Phi}\rangle} = \sum_{mn}D^*_{mh}\,D_{np}\,\rho^{22}_{nm}. \tag{59d}$$

The Hamiltonian-like matrix elements appearing in Eq. (58) can be evaluated as

$$\frac{\langle\Phi|\bar{b}_h^\dagger\,\bar{b}_p\,\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} = \sum_{mn}\bar{D}^*_{mh}\,\bar{D}_{np}\,\rho^{11}_{nm}\,\frac{\langle\Phi|\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} + \sum_{mn}\sum_{ik} \times \bar{D}^*_{mh}\,\bar{D}_{np}\,\left(h_{ik}+\Gamma^{11}_{ik}\right)\,\rho^{11}_{km}\,\left(\delta_{ni}-\rho^{11}_{ni}\right), \tag{60a}$$

$$\frac{\langle\overline{\Phi}|b_h^\dagger\,b_p\,\hat{H}|\Phi\rangle}{\langle\overline{\Phi}|\Phi\rangle} = \sum_{ik}D^*_{kh}\,D_{ip}\,\left(h_{ik}+\Gamma^{21}_{ik}\right), \tag{60b}$$

$$\frac{\langle\Phi|\bar{b}_h^\dagger\,\bar{b}_p\,\hat{H}|\overline{\Phi}\rangle}{\langle\Phi|\overline{\Phi}\rangle} = \sum_{ik}\bar{D}^*_{kh}\,\bar{D}_{ip}\,\left(h_{ik}+\Gamma^{12}_{ik}\right), \tag{60c}$$

$$\frac{\langle\overline{\Phi}|b_h^\dagger\,b_p\,\hat{H}|\overline{\Phi}\rangle}{\langle\overline{\Phi}|\overline{\Phi}\rangle} = \sum_{mn}D^*_{mh}\,D_{np}\rho^{22}_{nm}\,\frac{\langle\overline{\Phi}|\hat{H}|\overline{\Phi}\rangle}{\langle\overline{\Phi}|\overline{\Phi}\rangle} + \sum_{mn}\sum_{ik}D^*_{mh} \times D_{np}\,\left(h_{ik}+\Gamma^{22}_{ik}\right)\,\rho^{22}_{km}\,\left(\delta_{ni}-\rho^{22}_{ni}\right). \tag{60d}$$

B. Restoration of the biorthonormality condition

Let us assume that, during the optimization process, we started with the states $|\Phi\rangle$ and $|\overline{\Phi}\rangle$ and produced the new states $|\Phi'\rangle$ and $|\overline{\Phi'}\rangle$ by using the Thouless' transformations,

$$|\Phi'\rangle = \mathcal{N}\,\exp\left(\sum_{ph}Z_{ph}\,\bar{b}_p^\dagger\,\bar{b}_h\right)|\Phi\rangle, \tag{61a}$$

$$|\overline{\Phi'}\rangle = \bar{\mathcal{N}}\,\exp\left(\sum_{ph}\bar{Z}_{ph}\,b_p^\dagger\,b_h\right)|\overline{\Phi}\rangle. \tag{61b}$$

Here, the matrices Z and $\bar{Z}$ can be chosen as, for instance,

$$Z_{ph} = \eta\,G_{ph}, \tag{62a}$$

$$\bar{Z}_{ph} = \eta\,\bar{G}_{ph}, \tag{62b}$$

with $\eta \geqslant 0$ being some parameter. We denote by $\{\tilde{d}_h^\dagger,\tilde{d}_p,\tilde{\bar{d}}_h,\tilde{\bar{d}}_p^\dagger\}$ the set of HF operators produced by such transformations [see Eqs. (A6a) and (A6b)],

$$\tilde{d}_h^\dagger = b_h^\dagger + \sum_p Z_{ph}\,\bar{b}_p^\dagger, \tag{63a}$$

$$\tilde{d}_p = b_p - \sum_h Z_{ph}\,\bar{b}_h, \tag{63b}$$

$$\tilde{\bar{d}}_h = \bar{b}_h + \sum_p \bar{Z}^*_{ph}\,b_p, \tag{63c}$$

$$\tilde{\bar{d}}_p^\dagger = \bar{b}_p^\dagger - \sum_h \bar{Z}^*_{ph}\,b_h^\dagger, \tag{63d}$$

where the operators $\{b_h^\dagger,b_p,\bar{b}_h,\bar{b}_p^\dagger\}$ describing states $|\Phi\rangle$ and $|\overline{\Phi}\rangle$ are assumed to satisfy all the appropriate anticommutation relations.

We show in Appendix A that the operators $\{\tilde{d}_h^\dagger,\tilde{d}_p\}$ annihilate the vacuum $|\Phi'\rangle$. Similarly, the operators $\{\tilde{\bar{d}}_h^\dagger,\tilde{\bar{d}}_p\}$ annihilate the vacuum $|\overline{\Phi'}\rangle$. The operators $\{\tilde{d}_h^\dagger,\tilde{d}_p,\tilde{\bar{d}}_h,\tilde{\bar{d}}_p^\dagger\}$ do not, however, satisfy the anticommutation relations given by Eq. (14). In fact, they satisfy

$$[\tilde{d}_p,\tilde{d}_h^\dagger]_+ = 0, \tag{64a}$$

$$[\tilde{\bar{d}}_h,\tilde{\bar{d}}_p^\dagger]_+ = 0 \tag{64b}$$

$$[\tilde{\bar{d}}_h,\tilde{d}_{h'}^\dagger]_+ = (I + Z^{\mathsf{T}}\,\bar{Z}^*)_{h'h}, \tag{64c}$$

$$[\tilde{d}_p,\tilde{\bar{d}}_{p'}^\dagger]_+ = (I + \bar{Z}^*\,Z^{\mathsf{T}})_{p'p}. \tag{64d}$$

We can restore the desired anticommutation relations by performing the transformations

$$d_h^\dagger = \sum_{h'}L^{-1}_{hh'}\,\tilde{d}_{h'}^\dagger, \tag{65a}$$

$$\bar{d}_h = \sum_{h'}\bar{L}^{*-1}_{hh'}\,\tilde{\bar{d}}_{h'}, \tag{65b}$$

$$d_p = \sum_{p'}M^{*-1}_{pp'}\,\tilde{d}_{p'}, \tag{65c}$$

$$\bar{d}_p^\dagger = \sum_{p'}\bar{M}^{-1}_{pp'}\,\tilde{\bar{d}}_{p'}^\dagger \tag{65d}$$

in terms of the lower triangular matrices L, $\bar{L}$, M, and $\bar{M}$ [24].

The anticommutation relations among $\{d_h^\dagger,d_p,\bar{d}_h,\bar{d}_p^\dagger\}$ become

$$[\bar{d}_h,d_{h'}^\dagger]_+ = \sum_{\mu\nu}\bar{L}^{*-1}_{h\mu}\,L^{-1}_{h'\nu}\,(I + Z^{\mathsf{T}}\,\bar{Z}^*)_{\nu\mu} = \delta_{h'h}, \tag{66a}$$

$$[\tilde{d}_p,\tilde{\bar{d}}_{p'}^\dagger]_+ = \sum_{\mu\nu}M^{*-1}_{p\mu}\,\bar{M}^{-1}_{p'\nu}\,(I + \bar{Z}^*\,Z^{\mathsf{T}})_{\nu\mu} = \delta_{p'p}, \tag{66b}$$

which yield the following equations for determining L, $\bar{L}$, M, and $\bar{M}$:

$$I + Z^{\mathsf{T}}\,\bar{Z}^* = L\,\bar{L}^\dagger, \tag{67a}$$

$$I + \bar{Z}^*\,Z^{\mathsf{T}} = \bar{M}\,M^\dagger. \tag{67b}$$

Hence, given the matrices Z and $\bar{Z}$, standard LU decompositions [Eqs. (67a) and (67b)] can be performed to

obtain the matrices L, $\bar{L}$, M, and $\bar{M}$. This is similar to the unitary case, where the only two matrices required (L and M) can be obtained by Cholesky decompositions [14,25].

We remark that if $\bar{Z} = 0$ (or $Z = 0$), then the operators $\{\tilde{d}_h^\dagger, \tilde{d}_p, \tilde{\bar{d}}_h, \tilde{\bar{d}}_p^\dagger\}$ do obey all the required anticommutation relations. In other words, one has to restore the biorthonormality condition only if both $|\Phi\rangle$ and $|\overline{\Phi}\rangle$ are rotated.

C. Global gradient

In order to use gradient-based optimization methods such as the conjugate gradient or quasi-Newton methods (see Refs. [14,19,20,24,25]), one must be able to compute a global gradient. That is, we should be able to compute the gradient of the energy at $|\Psi_1\rangle$ with respect to variations in Z and $\bar{Z}$ defined in terms of the operators $\{b_h^{0\dagger}, b_p^0, \bar{b}_h^0, \bar{b}_p^{0\dagger}\}$ corresponding to the reference state $|\Psi_0\rangle$. Here, we follow Egido *et al.* [24] in deriving the form of the global gradient.

Consider the energy of state $|\Psi_1\rangle$. It is given by

$$E[\Psi_1] = \frac{\sum_{\alpha,\beta=1}^{2} c_\alpha^* c_\beta \langle \Phi_\alpha^1 | \hat{H} | \Phi_\beta^1 \rangle}{\sum_{\alpha,\beta=1}^{2} c_\alpha^* c_\beta \langle \Phi_\alpha^1 | \Phi_\beta^1 \rangle}. \tag{68}$$

Provided that $|\Phi^1\rangle$ and $|\overline{\Phi}^1\rangle$ are nonorthogonal to $\langle\overline{\Phi}^0|$ and $\langle\Phi^0|$, respectively, we can write

$$|\Phi^1\rangle = \mathcal{N} \exp\left(\sum_{ph} Z_{ph}\, \bar{b}_p^{0\dagger}\, \bar{b}_h^0\right) |\Phi^0\rangle, \tag{69a}$$

$$|\overline{\Phi}^1\rangle = \bar{\mathcal{N}} \exp\left(\sum_{ph} \bar{Z}_{ph}\, b_p^{0\dagger}\, b_h^0\right) |\overline{\Phi}^0\rangle, \tag{69b}$$

where $\mathcal{N} = \langle\overline{\Phi}^0|\Phi^1\rangle$ and $\bar{\mathcal{N}} = \langle\Phi^0|\overline{\Phi}^1\rangle$ are normalization constants. Here,

$$Z_{ph} = \sum_{h'} (D^{0\mathsf{T}}\, D^{1*})_{ph'} (\mathcal{L}^{*-1})_{h'h}, \tag{70a}$$

$$\bar{Z}_{ph} = \sum_{h'} (\bar{D}^{0\mathsf{T}}\, \bar{D}^{1*})_{ph'} (\bar{\mathcal{L}}^{*-1})_{h'h}, \tag{70b}$$

$$\mathcal{L}_{h'h} = (\bar{D}^{0\dagger}\, D^1)_{h'h}, \tag{70c}$$

$$\bar{\mathcal{L}}_{h'h} = (D^{0\dagger}\, \bar{D}^1)_{h'h}, \tag{70d}$$

where we have used Eqs. (A2) and (A5) to write Z and $\bar{Z}$ in terms of the matrices of orbital coefficients D^0, $\bar{D}^0$, D^1, and $\bar{D}^1$.

A variation in Z and $\bar{Z}$ leads to a change in energy given by

$$\begin{aligned}\delta E &= \sum_{ph} \left[\frac{\partial E}{\partial Z_{ph}^*}\, \delta Z_{ph}^* + \frac{\partial E}{\partial \bar{Z}_{ph}^*}\, \delta \bar{Z}_{ph}^* \right] + \text{c.c.} \\ &= \sum_{ph} [-\mathcal{G}_{ph}\, \delta Z_{ph}^* - \bar{\mathcal{G}}_{ph}\, \delta \bar{Z}_{ph}^*] + \text{c.c.},\end{aligned} \tag{71}$$

where we have introduced the global gradients $\mathcal{G}$ and $\bar{\mathcal{G}}$ given by

$$\begin{aligned}\mathcal{G}_{ph} = &-y_{11} \frac{\langle \Phi^1 | \bar{b}_h^{0\dagger}\, \bar{b}_p^0\, (\hat{H} - E) | \Phi^1 \rangle}{\langle \Phi^1 | \Phi^1 \rangle} \\ &- y_{12} \frac{\langle \Phi^1 | \bar{b}_h^{0\dagger}\, \bar{b}_p^0\, (\hat{H} - E) | \overline{\Phi}^1 \rangle}{\langle \Phi^1 | \overline{\Phi}^1 \rangle},\end{aligned} \tag{72a}$$

$$\begin{aligned}\bar{\mathcal{G}}_{ph} = &-y_{21} \frac{\langle \overline{\Phi}^1 | b_h^{0\dagger}\, b_p^0\, (\hat{H} - E) | \Phi^1 \rangle}{\langle \overline{\Phi}^1 | \Phi^1 \rangle} \\ &- y_{22} \frac{\langle \overline{\Phi}^1 | b_h^{0\dagger}\, b_p^0\, (\hat{H} - E) | \overline{\Phi}^1 \rangle}{\langle \overline{\Phi}^1 | \overline{\Phi}^1 \rangle}.\end{aligned} \tag{72b}$$

In order to evaluate the matrix elements appearing in the global gradient [Eq. (72)], we need to relate the operators $\{b_h^{0\dagger}, b_p^0, \bar{b}_h^0, \bar{b}_p^{0\dagger}\}$ to the operators $\{b_h^{1\dagger}, b_p^1, \bar{b}_h^1, \bar{b}_p^{1\dagger}\}$. Combining the results in Sec. IV B with Eqs. (A6a) and (A6b), we arrive at

$$b_h^{1\dagger} = \sum_{h'} L_{hh'}^{-1}\, \tilde{b}_{h'}^{0\dagger} = \sum_{h'} L_{hh'}^{-1} \left(b_{h'}^{0\dagger} + \sum_p Z_{ph'}\, \bar{b}_p^{0\dagger} \right), \tag{73a}$$

$$b_p^1 = \sum_{p'} M_{pp'}^{*-1}\, \tilde{b}_{p'}^0 = \sum_{p'} M_{pp'}^{*-1} \left(b_{p'}^0 - \sum_h Z_{p'h}\, \bar{b}_h^0 \right), \tag{73b}$$

$$\bar{b}_h^1 = \sum_{h'} \bar{L}_{hh'}^{*-1}\, \tilde{\bar{b}}_{h'}^0 = \sum_{h'} \bar{L}_{hh'}^{*-1} \left(\bar{b}_{h'}^0 + \sum_p \bar{Z}_{ph'}^*\, b_p^0 \right), \tag{73c}$$

$$\bar{b}_p^{1\dagger} = \sum_{p'} \bar{M}_{pp'}^{-1}\, \tilde{\bar{b}}_{p'}^{0\dagger}, = \sum_{p'} \bar{M}_{pp'}^{-1} \left(\bar{b}_{p'}^{0\dagger} - \sum_h \bar{Z}_{p'h}^*\, b_h^{0\dagger} \right), \tag{73d}$$

where the matrices L, $\bar{L}$, M, and $\bar{M}$ are here determined by the solution to Eqs. (67a) and (67b).

Because the transformation defined by Eqs. (73a)–(73d) is canonical (we have explicitly ensured that anticommutation rules are preserved), we can invert the transformation using Eq. (6) as a reference. We arrive at

$$b_h^{0\dagger} = \sum_{h'} \bar{L}_{h'h}^{*-1}\, b_{h'}^{1\dagger} - \sum_{pp'} Z_{p'h}\, M_{pp'}^{*-1}\, \bar{b}_p^{1\dagger}, \tag{74a}$$

$$b_p^0 = \sum_{p'} \bar{M}_{p'p}^{-1}\, b_{p'}^1 + \sum_{hh'} Z_{ph'}\, L_{hh'}^{-1}\, \bar{b}_h^1, \tag{74b}$$

$$\bar{b}_h^0 = \sum_{h'} L_{h'h}^{-1}\, \bar{b}_{h'}^1 - \sum_{pp'} \bar{Z}_{p'h}^*\, \bar{M}_{pp'}^{-1}\, b_p^1, \tag{74c}$$

$$\bar{b}_p^{0\dagger} = \sum_{p'} M_{p'p}^{*-1}\, \bar{b}_{p'}^{1\dagger} + \sum_{hh'} \bar{Z}_{ph'}^*\, \bar{L}_{hh'}^{*-1} b_h^{1\dagger}. \tag{74d}$$

We now use Eqs. (74a)–(74d) to write the global gradient ($\mathcal{G}$ and $\bar{\mathcal{G}}$) matrix elements in terms of the local gradient

(G and $\bar{G}$) as

$$\mathcal{G}_{ph} = \sum_{p'h'} L^{*-1}_{h'h}\, M^{-1}_{p'p}\, G_{p'h'} = [M^{\mathsf{T}-1}\, G\, L^{*-1}]_{ph}, \quad (75a)$$

$$\bar{\mathcal{G}}_{ph} = \sum_{p'h'} \bar{L}^{*-1}_{h'h}\, \bar{M}^{-1}_{p'p}\, \bar{G}_{p'h'} = [\bar{M}^{\mathsf{T}-1}\, \bar{G}\, \bar{L}^{*-1}]_{ph}. \quad (75b)$$

We close this subsection by noting that one has reached a solution to the variational equations when the local gradient (and, consequently, the global gradient) vanishes, i.e.,

$$\frac{\partial}{\partial\, Z^*_{ph}} E = 0, \quad (76a)$$

$$\frac{\partial}{\partial\, \bar{Z}^*_{ph}} E = 0. \quad (76b)$$

VII. VARIATIONAL ANSATZ WITH PROJECTION OPERATORS

We now turn our attention to states resulting from the action of symmetry-restoring projection operators on symmetry-broken determinants. We start by providing a brief description of the form of the projection operators used. More details can be found in Refs. [5,16,18].

Consider a symmetry group $\hat{G}$, with elements $\{\hat{g}\}$, that commutes with the Hamiltonian. The group can be continuous or discrete, but we assume for simplicity that it is Abelian. A Slater determinant is symmetry broken if

$$\hat{g}|\Phi\rangle \neq |\Phi\rangle, \quad (77)$$

that is, if the determinant is not invariant upon action by the elements $\{\hat{g}\}$. The set of all $\{\hat{g}|\Phi\rangle\}$ is called the Goldstone manifold. The norm and the matrix elements of commuting observables are the same within the Goldstone manifold up to an arbitrary phase factor [5]. It is well known [26] that the symmetry can be restored by diagonalization of the Hamiltonian among the Goldstone manifold.

A projection operator can, in general, be written as

$$\hat{P}^j = \frac{1}{L} \int_L d\theta\, w^j(\theta)\, \hat{R}_\theta, \quad (78)$$

where L is the volume of integration, $\hat{R}_\theta$ is an element of the symmetry group in consideration, the index j labels the eigenvalue restored by means of the projection, and the coefficients $w^j(\theta)$ correspond to the matrix elements of the operator $\hat{R}_\theta$ among the irreducible representations of the group. Evidently, for discrete groups the integration above is replaced by a discrete sum. We drop the label j henceforth for simplicity of notation.

As an example of the projection operators discussed above, S_z projection on a broken-symmetry determinant can be accomplished by

$$\hat{P}^m = \frac{1}{4\pi} \int d\theta\, \exp[i\theta(\hat{S}_z - m)], \quad (79)$$

where an eigenfunction of $\hat{S}_z$ with eigenvalue m is recovered upon the action of the projection operator above.

We work with cases where $\hat{R}_\theta$ are single-particle rotation operators that act on the HF ones according to

$$b^\dagger_k(\theta) \equiv \hat{R}_\theta\, b^\dagger_k \hat{R}^{-1}_\theta = \sum_j D^*_{jk}\, \hat{R}_\theta\, c^\dagger_j \hat{R}^{-1}_\theta = \sum_{ij} R_{ij}(\theta)\, D^*_{jk}\, c^\dagger_i, \quad (80)$$

where $R_{ij}(\theta) = \langle i|\hat{R}_\theta|j\rangle$ is the matrix representation of $\hat{R}_\theta$ in the single-particle basis.

We can now use the variational ansatz introduced in Eq. (42) and put a projection operator in front of it. The proposed wave function becomes

$$\hat{P}|\Psi\rangle = \int d\theta\, w(\theta)[c_1\, \hat{R}_\theta|\Phi\rangle + c_2\, \hat{R}_\theta|\overline{\Phi}\rangle]. \quad (81)$$

The Hamiltonian expectation value of a wave function of the form of Eq. (81) can be written as

$$E[\Psi] = \frac{\langle\Psi|\hat{P}^\dagger\, \hat{H}\, \hat{P}|\Psi\rangle}{\langle\Psi|\hat{P}^\dagger\, \hat{P}|\Psi\rangle} = \frac{\langle\Psi|\hat{H}\, \hat{P}|\Psi\rangle}{\langle\Psi|\hat{P}|\Psi\rangle},$$
$$= \int d\theta\, w(\theta) \sum_{\alpha,\beta=1}^{2} y_{\alpha\beta}(\theta) \frac{\langle\Phi_\alpha|\hat{H}\, \hat{R}_\theta|\Phi_\beta\rangle}{\langle\Phi_\alpha|\hat{R}_\theta|\Phi_\beta\rangle}, \quad (82)$$

$$y_{\alpha\beta}(\theta) = \frac{c^*_\alpha\, c_\beta \langle\Phi_\alpha|\hat{R}_\theta|\Phi_\beta\rangle}{\int d\theta\, w(\theta) \sum_{\alpha',\beta'=1}^{2} c^*_{\alpha'}\, c_{\beta'} \langle\Phi_{\alpha'}|\hat{R}_\theta|\Phi_{\beta'}\rangle}, \quad (83)$$

where we have made the identifications $|\Phi_1\rangle \equiv |\Phi\rangle$ and $|\Phi_2\rangle \equiv |\overline{\Phi}\rangle$. The expressions for the matrix elements appearing in Eqs. (82) and (83) are given in Appendix B.

A. Optimization of the projected ansatz $|\Psi\rangle$

Our task is now to minimize the energy of our ansatz for the projected state [Eq. (82)] with respect to variations in the reference determinants $|\Phi\rangle$ and $|\overline{\Phi}\rangle$. We closely follow the derivation we presented before (Sec. VI A) for the optimization of the unprojected state.

The variation with respect to the coefficients c_1 and c_2 yields a generalized eigenvalue problem similar to the one of Eqs. (51) and (52). In this case, **H** and **N** are 2×2 matrices given by

$$H_{\alpha\beta} = \int d\theta\, w(\theta)\, \langle\Phi_\alpha|\hat{H}\, \hat{R}_\theta|\Phi_\beta\rangle, \quad (84)$$

$$N_{\alpha\beta} = \int d\theta\, w(\theta)\, \langle\Phi_\alpha|\hat{R}_\theta|\Phi_\beta\rangle. \quad (85)$$

Once again, only the lowest-energy solution is used in the variational optimization.

The parametrization of the energy functional with respect to the determinants $|\Phi\rangle$ and $|\overline{\Phi}\rangle$ is done in the same way as was done for the unprojected case [18,24]. That is, we parametrize the energy functional in terms of the Thouless' rotation matrices Z and $\bar{Z}$ acting upon $|\Phi\rangle$ and $|\overline{\Phi}\rangle$, respectively.

The resulting local gradient is derived by using the definitions in Eqs. (56a) and (56b). We arrive at the expressions

$$G_{ph} = \int d\theta\, w(\theta) \left\{ -y_{11}(\theta) \frac{\langle \Phi | \bar{b}_h^\dagger \bar{b}_p (\hat{H} - E) \hat{R}_\theta | \Phi \rangle}{\langle \Phi | \hat{R}_\theta | \Phi \rangle} - y_{12}(\theta) \frac{\langle \Phi | \bar{b}_h^\dagger \bar{b}_p (\hat{H} - E) \hat{R}_\theta | \overline{\Phi} \rangle}{\langle \Phi | \hat{R}_\theta | \overline{\Phi} \rangle} \right\}, \tag{86a}$$

$$\bar{G}_{ph} = \int d\theta\, w(\theta) \left\{ -y_{21}(\theta) \frac{\langle \overline{\Phi} | b_h^\dagger b_p (\hat{H} - E) \hat{R}_\theta | \Phi \rangle}{\langle \overline{\Phi} | \hat{R}_\theta | \Phi \rangle} - y_{22}(\theta) \frac{\langle \overline{\Phi} | b_h^\dagger b_p (\hat{H} - E) \hat{R}_\theta | \overline{\Phi} \rangle}{\langle \overline{\Phi} | \hat{R}_\theta | \overline{\Phi} \rangle} \right\}. \tag{86b}$$

Here, E is the energy corresponding to the state $|\Psi\rangle$ from Eq. (81). The explicit expressions for the matrix elements appearing in Eq. (86) are given in Appendix B. We, finally, note that the relationship between the local gradient and the global gradient is the same as in the unprojected case [see Eq. (75)].

VIII. APPLICATION TO THE ONE-DIMENSIONAL HUBBARD HAMILTONIAN

In this section we present the application of the ansätze discussed previously to the 1D Hubbard Hamiltonian [27] with PBCs. This describes a set of electrons in a lattice according to

$$\hat{H} = -t \sum_{j,\sigma} (c_{j,\sigma}^\dagger c_{j+1,\sigma} + c_{j+1,\sigma}^\dagger c_{j,\sigma}) + U \sum_j c_{j,\uparrow}^\dagger c_{j,\uparrow} c_{j,\downarrow}^\dagger c_{j,\downarrow}. \tag{87}$$

Here, $c_{j,\sigma}^\dagger$ creates an electron on site j of the lattice with $\sigma = \{\uparrow, \downarrow\}$ z-projection of spin. The first term in the Hamiltonian accounts for a negative ($t > 0$) kinetic energy that the electrons gain when they hop from one site to a neighbor. The second term accounts for the ($U > 0$) repulsion that opposite-spin electrons feel when they are in the same site. The lattice used for this Hamiltonian is a finite one with N_s sites. PBCs are assumed, which make the site $N_s + k$ equivalent to the site k. We direct the interested reader to the comprehensive book on the 1D Hubbard Hamiltonian by Essler *et al.* [27]. We also refer the reader to the work of Lieb and Wu [28], where the authors derived a set of equations from which the exact solutions to the 1D Hubbard Hamiltonian of Eq. (87) can be obtained.

The 1D Hubbard Hamiltonian has been extensively studied, and our purpose here is merely to test the flexibility that N-particle Slater determinants constructed in terms of nonunitary canonical transformations bring. In particular, we apply the two-determinant ansätze in Secs. VI and VII (unprojected and projected) to the 1D Hubbard Hamiltonian of Eq. (87). In our symmetry-projected calculations, we have used two different projection operators to demonstrate the feasibility of the approach; more accurate results can be obtained through the simultaneous breaking and restoration of all symmetries in the Hamiltonian. Recent work on the 1D Hubbard Hamiltonian with projected HF approximations has been done by Schmid *et al.* [25] and Tomita [23].

We have performed our calculations with an in-house code using a limited-memory quasi-Newton method for the variational optimization of HF-based states [14,25]. We have selected $U = 4t$ as a representative on-site repulsion, corresponding to a strongly correlated case (U is of the order of the noninteracting bandwidth). Nevertheless, our formalism can be used for any other U value belonging to the weak, intermediate, or strong coupling regimes. For all methods except the restricted HF (RHF), we have constructed an initial guess of the HF transformation such that all symmetries (spin, lattice momentum) are broken. This is sometimes referred to as the generalized HF (GHF) in the quantum chemistry community [29]. We have converged the HF states such that the norm of the gradient is smaller than 10^{-4}. The exact ground-state energies, evaluated by solution to the Lieb-Wu equations from Ref. [28], have been obtained with an in-house MATHEMATICA notebook.

We have used two different projection operators in our calculations: the S_z projection operator of Eq. (79) and the linear momentum (LM) projection operator (equivalent to restoration of C_n symmetry of the lattice [30]) given by

$$\hat{P}^k = \frac{1}{N_s} \sum_{j=1}^{N_s} \exp[i(\hat{p} - k)j], \tag{88}$$

where $\hat{p} = \sum_{k\sigma} k\, c_{k,\sigma}^\dagger c_{k,\sigma}$, with $c_{k,\sigma}^\dagger$ resulting from a discrete Fourier transform of the on-site operators $c_{j,\sigma}^\dagger$, is the LM operator [25]. Only certain values of k with the form $k = 2\pi\xi/N_s$ ($\xi = 0, 1, \ldots, N_s - 1$) are allowed in the projection. For methods involving S_z projection we have chosen to recover states with $\hat{S}_z$ eigenvalue $m = 0$, as it is known that at half-filling the ground state is always a singlet state [31]. For methods involving LM projection we recover states with $k = \pi$ or $k = 0$ for anharmonic ($N_s = 4L$) or harmonic ($N_s = 4L + 2$) lattices, respectively.

Table I shows the total energies predicted by a variety of methods for the ground state of the 1D Hubbard Hamiltonian at half-filling ($N = N_s$, where N is the number of electrons in the system). It is evident from the results in Table I that the nu-HF [defined by Eq. (42)], which uses the full flexibility of a nu-HF transformation, is able to yield lower energies than the standard HF. This was expected, since it is, at the very least, a two-configuration wave function. This remains true in the presence of projection operators (both S_z and LM).

It is less evident that the total correlation energy for the nu-HF, defined here [32] as the difference with respect to the energy of the broken-symmetry HF solution, should tend to a nonzero constant with increasing lattice size. This is the case, as shown in Fig. 1. In fact, the correlation energy tends to a constant for all methods that do not involve LM symmetry breaking and restoration. For the latter methods, the correlation energy per particle increases with lattice size, but it does not reach the ideal $1/N$ behavior as shown in the right panel in Fig. 1. We should stress that, even for those methods for which the correlation energy per particle tends to 0 as $N \to \infty$, the total energy and the wave function itself are different from the broken-symmetry HF solution.

TABLE I. Total energies (in units of t, the hopping parameter) for the ground state of the N_s-site 1D Hubbard model Hamiltonian at half-filling with different approximate methods. We have set $U = 4t$ for all calculations.

N_s	RHF[a]	HF[b]	nu-HF[c]	S_zHF[d]	nu-S_zHF[e]	LMHF[f]	nu-LMHF[g]	Exact[h]
8	−1.656 9	−3.748 6	−3.969 1	−4.163 6	−4.329 0	−3.983 9	−4.463 0	−4.603 5
12	−2.928 2	−5.629 1	−5.849 0	−6.068 1	−6.248 3	−6.051 1	−6.447 0	−6.920 4
16	−4.109 4	−7.505 7	−7.722 4	−7.948 7	−8.118 3	−8.087 4	−8.550 6	−9.214 4
24	−6.383 0	−11.258 5	−11.472 4	−11.703 7	−12.011 3	−12.112 6	−12.648 1	−13.795 8
32	−8.612 7	−15.011 4	−15.224 9	−15.457 5	−15.777 3	−16.101 8	−16.708 9	−18.379 4
48	−13.028 2	−22.517 1	−22.730 5	−22.964 0	−23.291 2	−24.019 6	−24.749 1	−27.552 4
64	−17.421 9	−30.022 7	−30.236 2	−30.470 0	−30.798 9	−31.887 5	−32.718 4	−36.728 7
96	−26.187 4	−45.034 1	−45.247 6	−45.481 8	−45.811 1	−47.532 8	−48.526 3	−55.084 7
128	−34.941 9	−60.045 5	−60.258 9	−60.493 3	−60.822 6	−63.099 8	−64.222 7	−73.442 4
192	−52.440 2	−90.068 2	−90.281 7	−90.516 2	−90.845 3	−94.087 4	−95.413 8	−110.159 4
256	−69.933 0	−120.090 9	−120.304 4	−120.539 0	−120.868 0	−124.947 5	−126.435 1	−146.877 2

[a]Restricted Hartree-Fock, i.e., all symmetries of the Hamiltonian are preserved.
[b]Symmetry-broken Hartree-Fock.
[c]Nonunitary Hartree-Fock, defined by Eq. (42).
[d]S_z-projected Hartree-Fock (with $\hat{S}_z$ eigenvalue $m = 0$).
[e]S_z-projected nonunitary Hartree-Fock, defined by Eq. (81) (with $\hat{S}_z$ eigenvalue $m = 0$).
[f]LM-projected Hartree-Fock (with $\hat{p}$ eigenvalue $k = \pi$).
[g]LM-projected nonunitary Hartree-Fock, defined by Eq. (81) (with $\hat{p}$ eigenvalue $k = \pi$).
[h]Obtained by solution to the Lieb-Wu equations in Ref. [28].

It is noteworthy that simple ansätze such as the nu-HF, S_z-projected nu-HF (nu-S_zHF), and LM-projected nu-HF (LMHF) can be useful to describe finite-size lattices, where they can capture a significant part of the correlation. For $N = 12$, for which the exact ground-state energy is $-6.9204\,t$, the nu-HF recovers 17%, the nu-S_zHF recovers 48%, and the nu-LMHF recovers 63% of the missing correlation energy in the broken-symmetry HF solution. Using both S_z and LM projection (resulting in the nu-LMS_zHF) allows one to recover 96% of the total correlation. Full spin and LM projection may be used to recover even a larger fraction of correlation energy, as has been shown for projected HF methods in small Hubbard 1D or 2D lattices [14,25].

A. Structure of the optimized wave functions

It is interesting to analyze whether the physics behind the character of the broken-symmetry Slater determinants that optimize our (symmetry-projected) wave functions, in both the unitary and the nonunitary cases, is relevant. This has been done in similar contexts in Refs. [23,33], and references therein. We construct the following structure parameters characterizing the nature of a spin-density wave in an arbitrary Slater determinant $|\psi\rangle$:

$$\Delta_1(j) = \left| \frac{\langle\psi|\hat{\mathbf{S}}(j)|\psi\rangle}{\langle\psi|\psi\rangle} \right|^2, \tag{89}$$

$$\Delta_2(j) = (-1)^{j+1} \frac{\langle\psi|\hat{\mathbf{S}}(1)|\psi\rangle}{\langle\psi|\psi\rangle} \cdot \frac{\langle\psi|\hat{\mathbf{S}}(j)|\psi\rangle}{\langle\psi|\psi\rangle}. \tag{90}$$

$\Delta_1(j)$ is a measure of the amplitude of the spin wave at site j, while $\Delta_2(j)$ measures the relative orientation of the spin at site j with respect to the one at site 1, modulated by the expected antiparallel arrangement between neighboring sites.

As an example, we have computed the structure parameters defined by Eqs. (89) and (90) for unitary- and nonunitary-based methods on a 48-site lattice at $U = 4\,t$; they are shown in Fig. 2. The underlying determinants in the nu-HF and nu-S_zHF develop a broad feature in $\Delta_2(j)$, which corresponds to a slight deviation from the antiferromagnetic alignment of spins. On the other hand, the underlying determinants in methods involving LM projection show localized solitons. Previous works [23,33] have connected those localized features in the broken-symmetry Slater determinants with the large quantum fluctuations occurring in 1D Hubbard chains. It is noteworthy that the soliton structure is already present in an LM-projected single-determinant picture. The second determinant included in our nonunitary ansätze displays a soliton structure in a different position in the lattice.

B. Comparison with other two-determinant approaches

The results shown so far indicate that the nu-HF and nu-S_zHF improve upon the HF and S_zHF, respectively. This is due to a combination of the more general canonical transformation being used and the fact that the nu-HF and nu-S_zHF are explicitly constructed as two-determinant configurations.

It is interesting to compare the nonunitary-based ansätze discussed in this paper with other two-determinant ansätze resulting from a *single, unitary canonical transformation*. We have already discussed that more general two-determinant ansätze, where each configuration results from an independent HF transformation, have the same flexibility as the nonunitary approaches considered in this work, something we have verified numerically.

One can think of several ways to construct a two-determinant ansatz based on a single, unitary canonical transformation. Our experience shows that symmetry-projection approaches are very effective in capturing electron

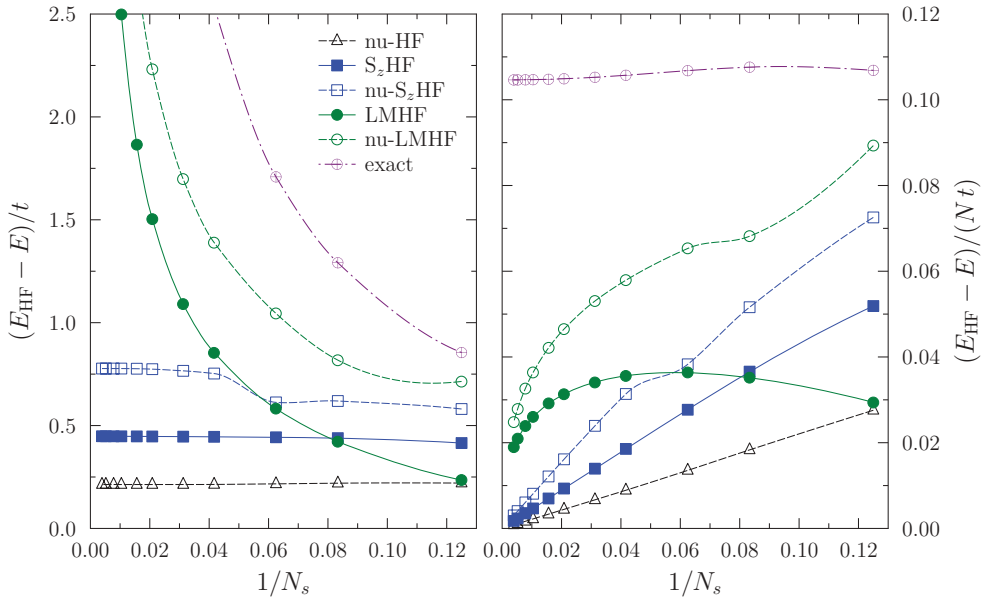

FIG. 1. (Color online) Left: Total correlation energy (in units of t), predicted by several methods for 1D Hubbard model calculations as a function of the number of sites N_s. Right: Corresponding correlation energy per particle. Calculations were performed at half-filling, with $U = 4t$. The correlation energy has been defined with respect to the broken-symmetry HF solution.

correlations. In this sense, several two-element symmetry groups can be used in the 1D periodic Hubbard Hamiltonian to build a two-state Goldstone manifold: the complex-conjugation group built with the elements $\{\hat{I}, \hat{K}\}$, where $\hat{I}$ is the identity operator and $\hat{K}$ is the complex conjugation operator, or the time-reversal group built with the elements $\{\hat{I}, \hat{\Theta}\}$, where $\hat{\Theta} = \exp(i\,\pi\,\hat{S}_y)\,\hat{K}$ is the time-reversal operator. We here consider the complex conjugation group as a representative example. In this subsection, we compare our nonunitary-based ansätze with the complex-conjugation restored HF (KHF) or the complex-conjugation and S_z-projected HF (KS_zHF):

$$|\Psi^{\mathrm{KHF}}\rangle = c_1|\Phi\rangle + c_2\,\hat{K}|\Phi\rangle, \tag{91}$$

$$|\Psi^{\mathrm{KS_zHF}}\rangle = c_1\,\hat{P}^{S_z}|\Phi\rangle + c_2\,\hat{P}^{S_z}\,\hat{K}|\Phi\rangle, \tag{92}$$

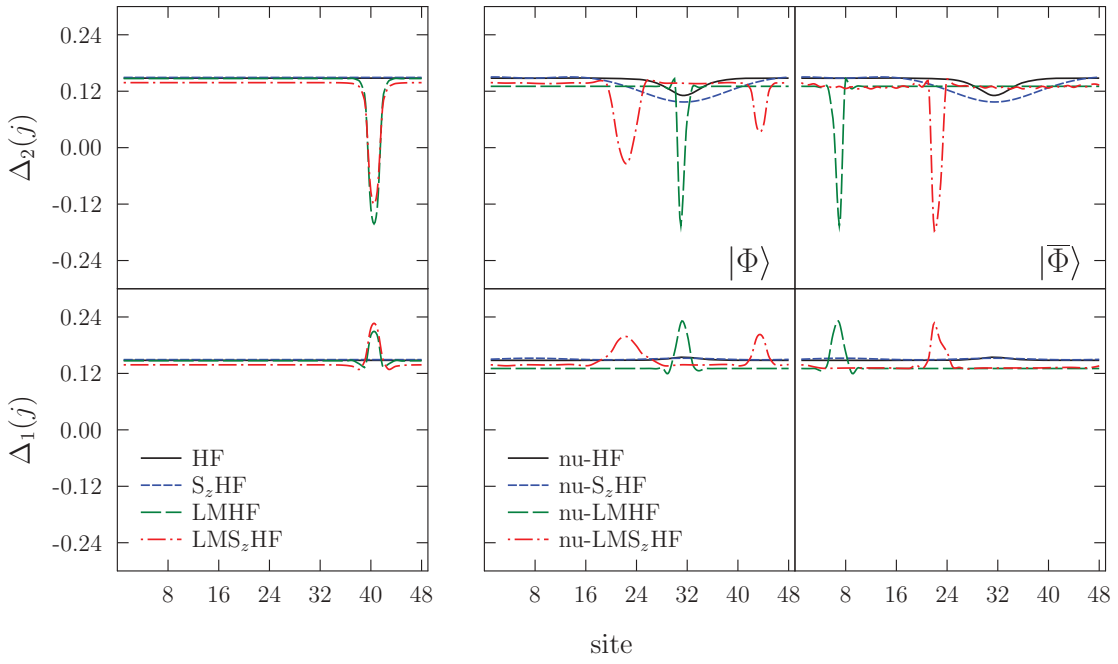

FIG. 2. (Color online) Structure parameters $\Delta_1(j)$ and $\Delta_2(j)$ [defined by Eqs. (89) and (90), respectively] for the broken-symmetry Slater determinants in unitary (left)- and nonunitary (right)-based methods. For the latter, we show the structure parameters for the two determinants $|\Phi\rangle$ and $|\overline{\Phi}\rangle$. The calculations have been performed for a 48-site periodic 1D Hubbard lattice at $U = 4t$. LMS_zHF denotes the simultaneous projection into good S_z and LM quantum numbers.

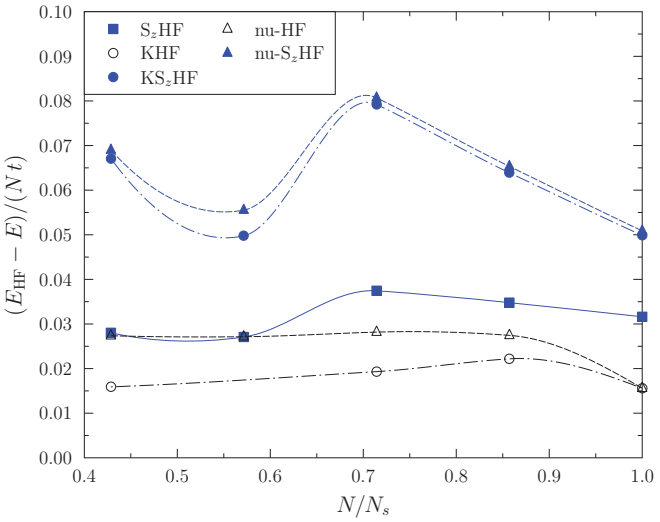

FIG. 3. (Color online) Correlation energy per electron (in units of t), predicted by a variety of approximate methods for a 14-site periodic 1D Hubbard model as a function of N/N_s. The correlation energy has been defined with respect to the broken-symmetry HF solution. We were unable to converge KHF for $N = 8$.

where $|\Phi\rangle$ is an N-particle Slater determinant and $\hat{P}^{S_z}$ is the S_z projection operator (onto $m = 0$).

Figure 3 shows the correlation energy per electron predicted by a variety of approximate methods for a 14-site periodic 1D Hubbard model as a function of the hole filling (N/N_s). It is interesting to note that at half-filling ($N/N_s = 1$) the nu-HF and KHF yield exactly the same correlation energy. In this sense, the full flexibility of the nonunitary transformation is not being exploited in the solution. At other fillings, on the other hand, the nu-HF is able to improve substantially over the KHF. In contrast, the nu-S$_z$HF yields lower energies (or higher correlation energies) at all fillings, even though the improvement is only marginal in some cases.

Overall, there is no guarantee that introducing more flexibility into an approximate wave function will result in lower energies for every system. We have shown, however, that ansätze based on a nonunitary canonical transformation yield lower energies than HF or projected-HF methods. They even yield lower energies than the KHF or projected-KHF solutions in some cases, despite the fact that complex-conjugation projected wave functions are also two-determinant configurations, even though they result from a single, *unitary* canonical transformation.

IX. CONCLUSIONS

The HF and the HFB wave functions constitute the building blocks upon which more elaborate many-body methods rely. They are built out of a set of independent quasiparticles resulting from a linear unitary canonical transformation of elementary fermion operators. In this work, we have explored the possibility of relaxing the unitarity condition within an HF-type formalism in order to have more variational flexibility in the considered wave functions.

The properties of N-particle Slater determinants constructed from a set of HF-type operators resulting from a nonunitary canonical transformation of fermion operators have been discussed. We have derived the corresponding Thouless' theorem for such states, which allowed us to compute matrix elements in an efficient way by application of Wick's theorem [5].

An ansatz based on a single Slater determinant is incapable of utilizing the full flexibility of a nonunitary transformation. We have therefore introduced a two-determinant ansatz, defined by Eq. (42), where all the degrees of freedom of an HF-type nonunitary transformation are used. This, however, is not a limitation of the nonunitary transformation. One could work with other more general ansätze used in many-body theory that utilize an N-particle Slater determinant as a starting point.

Symmetry breaking is commonly used within a HF formalism to access relevant correlations that are otherwise difficult to obtain starting from a symmetry-preserving Slater determinant. In this sense, a nonunitary transformation provides additional degrees of freedom that can be used in the variational problem. A symmetry-broken wave function is, nevertheless, still unphysical; we advocate the use of projection techniques out of a symmetry-broken intrinsic state, within a variation-after-projection approach, to access the relevant correlations resulting from large quantum fluctuations. This can be done, as we have shown in the present work, in combination with a nonunitary canonical transformation, affording even more flexibility than that which a projected HF state based on a unitary HF transformation has. A nonunitary-based projected HF scheme aims to provide an accurate description of a many-particle system with a limited number of configurations, still a far-reaching problem in fields such as nuclear and condensed matter physics as well as in quantum chemistry.

Finally, we note that our formalism can also be used in the optimization of N-particle Slater determinants that are considered as approximations to the left and right eigenvectors of non-Hermitian Hamiltonians. In particular, our work can be directly applied to non-Hermitian Hamiltonians with real eigenvalues, such as those resulting from similarity transformations of a standard Hermitian one.

The extension of this work to the full nonunitary Bogoliubov transformation is possible and will be presented in a forthcoming publication [8].

ACKNOWLEDGMENTS

This work was supported by the US Department of Energy, Office of Basic Energy Sciences (Grant No. DE-FG02-09ER16053), the National Science Foundation (Grant No. CHE-1110884), and the Welch Foundation (Grant No. C-0036).

APPENDIX A: PROOF OF THOULESS' THEOREM

In order to prove the extension to Thouless' theorem stated in Sec. IV, we start by introducing the operators $\{b_h^\dagger, b_p, \bar{b}_h, \bar{b}_p^\dagger\}$ and $\{d_h^\dagger, d_p, \bar{d}_h, \bar{d}_p^\dagger\}$, such that $\{b_h^\dagger, b_p\}$ kill the vacuum $|\Phi_0\rangle$ and $\{\bar{b}_h^\dagger, \bar{b}_p\}$ kill the vacuum $|\overline{\Phi}_0\rangle$, while $\{d_h^\dagger, d_p\}$ annihilate the

vacuum $|\Phi_1\rangle$ and $\{\bar{d}_h^\dagger,\bar{d}_p\}$ annihilate the vacuum $|\overline{\Phi}_1\rangle$. We assume that both sets obey the anticommutation rules defined by Eq. (14). We explicitly write these operators in the form of Eqs. (9) and (12); that is,

$$b_h^\dagger = \sum_j D_{jh}^{0*}\, c_j^\dagger, \quad b_p = \sum_j D_{jp}^{0}\, c_j$$
$$\bar{b}_h = \sum_j \bar{D}_{jh}^{0}\, c_j, \quad \bar{b}_p^\dagger = \sum_j \bar{D}_{jp}^{0*}\, c_j^\dagger,$$
$$d_h^\dagger = \sum_j D_{jh}^{1*}\, c_j^\dagger, \quad d_p = \sum_j D_{jp}^{1}\, c_j,$$
$$\bar{d}_h = \sum_j \bar{D}_{jh}^{1}\, c_j, \quad \bar{d}_p^\dagger = \sum_j \bar{D}_{jp}^{1*}\, c_j^\dagger,$$

where the superscripts to the matrices indicate the state to which the operators correspond.

We can now relate the operators $\{d_h^\dagger,d_p\}$ to the operators $\{b_h^\dagger,b_p\}$ by using the inverse transformation discussed in Eq. (15). We arrive at

$$d_h^\dagger = \sum_{h'} L_{h'h}^*\, b_{h'}^\dagger + \sum_p Y_{ph}^*\, \bar{b}_p^\dagger, \tag{A1a}$$
$$d_p = \sum_{p'} M_{p'p}\, b_{p'} + \sum_h \tilde{Y}_{hp}\, \bar{b}_h, \tag{A1b}$$

where we have set

$$L_{h'h} = (\bar{D}^{0\dagger}\, D^1)_{h'h}, \tag{A2a}$$
$$M_{p'p} = (\bar{D}^{0\dagger}\, D^1)_{p'p}, \tag{A2b}$$
$$Y_{ph} = (D^{0\dagger}\, D^1)_{ph}, \tag{A2c}$$
$$\tilde{Y}_{hp} = (D^{0\dagger}\, D^1)_{hp}. \tag{A2d}$$

We now assume that the $N \times N$ matrix L is invertible, which is only true if $\langle\overline{\Phi}_0|\Phi_1\rangle \neq 0$ [see Eq. (21)]. In such a case, the matrix M is also invertible. We now introduce the operators

$$\tilde{d}_h^\dagger = \sum_{h'} (L^{*-1})_{h'h}\, d_{h'}^\dagger, \tag{A3a}$$
$$\tilde{d}_p = \sum_{p'} (M^{-1})_{p'p}\, d_{p'}. \tag{A3b}$$

Inserting Eq. (A3) into Eq. (A1), we arrive at

$$\tilde{d}_h^\dagger = b_h^\dagger + \sum_p Z_{ph}\, \bar{b}_p^\dagger, \tag{A4a}$$
$$\tilde{d}_p = b_p + \sum_h W_{ph}\, \bar{b}_h, \tag{A4b}$$

where we have set

$$Z_{ph} = \sum_{h'} Y_{ph'}^* (L^{*-1})_{h'h}, \tag{A5a}$$
$$W_{ph} = \sum_{p'} \tilde{Y}_{hp'} (M^{-1})_{p'p}. \tag{A5b}$$

In fact, by computing the anticommutation rules among the operators $\{\tilde{d}_h^\dagger,\tilde{d}_p\}$, one can readily conclude that $W = -Z$. This also implies that if L is invertible, then so is M. The transformed operators become

$$\tilde{d}_h^\dagger = b_h^\dagger + \sum_p Z_{ph}\, \bar{b}_p^\dagger, \tag{A6a}$$
$$\tilde{d}_p = b_p - \sum_h Z_{ph}\, \bar{b}_h. \tag{A6b}$$

We are now in a position to investigate whether the transformed operators, defined by Eqs. (A6a) and (A6b), annihilate the vacuum defined by Eq. (19). We start by evaluating the commutators

$$\left[b_h^\dagger, \exp\left(\sum_{p'h'} Z_{p'h'}\, \bar{b}_{p'}^\dagger\, \bar{b}_{h'}\right)\right] = \left(-\sum_p Z_{ph}\bar{b}_p^\dagger\right) \exp\left(\sum_{p'h'} Z_{p'h'}\, \bar{b}_{p'}^\dagger\, \bar{b}_{h'}\right), \tag{A7a}$$

$$\left[b_p, \exp\left(\sum_{p'h'} Z_{p'h'}\, \bar{b}_{p'}^\dagger\, \bar{b}_{h'}\right)\right] = \left(\sum_h Z_{ph}\bar{b}_h\right) \exp\left(\sum_{p'h'} Z_{p'h'}\, \bar{b}_{p'}^\dagger\, \bar{b}_{h'}\right). \tag{A7b}$$

The operators from Eqs. (A6a) and (A6b) act on the vacuum of Eq. (19) as

$$\tilde{d}_h^\dagger \exp\left(\sum_{ph} Z_{ph}\, \bar{b}_p^\dagger\, \bar{b}_h\right)|\Phi_0\rangle = \left(-\sum_p Z_{ph}\bar{b}_p^\dagger + \sum_p Z_{ph}\bar{b}_p^\dagger\right) \times \exp\left(\sum_{p'h'} Z_{p'h'}\, \bar{b}_{p'}^\dagger\, \bar{b}_{h'}\right)|\Phi_0\rangle = 0, \tag{A8a}$$

$$\tilde{d}_p \exp\left(\sum_{ph} Z_{ph}\, \bar{b}_p^\dagger\, \bar{b}_h\right)|\Phi_0\rangle = \left(\sum_h Z_{ph}\bar{b}_h - \sum_h Z_{ph}\bar{b}_h\right) \times \exp\left(\sum_{p'h'} Z_{p'h'}\, \bar{b}_{p'}^\dagger\, \bar{b}_{h'}\right)|\Phi_0\rangle = 0. \tag{A8b}$$

This essentially completes the proof. $\{\tilde{d}_h^\dagger,\tilde{d}_p\}$ annihilate the right-hand side of Eq. (A6b). The operators $\{d_h^\dagger,d_p\}$ that kill the vacuum $|\Phi_1\rangle$ on the left-hand side of Eq. (A6b) are simple linear combinations of $\{\tilde{d}_h^\dagger,\tilde{d}_p\}$; N-particle Slater determinants built from either sets of operators are the same up to a normalization factor.

APPENDIX B: MATRIX ELEMENTS APPEARING IN PROJECTED STATES

Here, we provide explicit formulas for the matrix elements appearing in the energy expression and in the local gradient from the variational ansatz based on projected states. The overlap kernels appearing in Eq. (83) are evaluated as

$$\langle\Phi|\hat{R}_\theta|\Phi\rangle = \det{}_N\, D^{\mathsf{T}}\, R(\theta)\, D^*, \tag{B1a}$$
$$\langle\overline{\Phi}|\hat{R}_\theta|\Phi\rangle = \det{}_N\, \bar{D}^{\mathsf{T}}\, R(\theta)\, D^*, \tag{B1b}$$
$$\langle\Phi|\hat{R}_\theta|\overline{\Phi}\rangle = \det{}_N\, D^{\mathsf{T}}\, R(\theta)\, \bar{D}^*, \tag{B1c}$$
$$\langle\overline{\Phi}|\hat{R}_\theta|\overline{\Phi}\rangle = \det{}_N\, \bar{D}^{\mathsf{T}}\, R(\theta)\, \bar{D}^*. \tag{B1d}$$

The Hamiltonian kernels appearing in Eq. (82) are evaluated in terms of transition density matrices as

$$\frac{\langle\Phi_\alpha|\hat{H}\,\hat{R}_\theta|\Phi_\beta\rangle}{\langle\Phi_\alpha|\hat{R}_\theta|\Phi_\beta\rangle} = \mathrm{Tr}\left(h\,\rho^{\alpha\beta}(\theta) + \frac{1}{2}\,\Gamma^{\alpha\beta}(\theta)\,\rho^{\alpha\beta}(\theta)\right), \tag{B2}$$
$$\Gamma^{\alpha\beta}_{ik}(\theta) = \sum_{jl}\langle ij|\hat{v}|kl\rangle\,\rho^{\alpha\beta}_{lj}(\theta). \tag{B3}$$

The transition density matrices are in turn given by

$$\rho^{11}_{ki}(\theta) = \frac{\langle\Phi|c_i^\dagger\, c_k\,\hat{R}_\theta|\Phi\rangle}{\langle\Phi|\hat{R}_\theta|\Phi\rangle} = \sum_h D_{ih}\,\bar{D}^*_{kh} + \sum_{ph} D_{ih}\,\mathcal{Z}^{(11)}_{ph}(\theta)\,D^*_{kp}, \tag{B4a}$$

$$\rho^{12}_{ki}(\theta) = \frac{\langle\Phi|c_i^\dagger\, c_k\,\hat{R}_\theta|\overline{\Phi}\rangle}{\langle\Phi|\hat{R}_\theta|\overline{\Phi}\rangle} = \sum_h D_{ih}\,\bar{D}^*_{kh} + \sum_{ph} D_{ih}\,\mathcal{Z}^{(12)}_{ph}(\theta)\,D^*_{kp}, \tag{B4b}$$

$$\rho^{21}_{ki}(\theta) = \frac{\langle\overline{\Phi}|c_i^\dagger\, c_k\,\hat{R}_\theta|\Phi\rangle}{\langle\overline{\Phi}|\hat{R}_\theta|\Phi\rangle} = \sum_h \bar{D}_{ih}\,D^*_{kh} + \sum_{ph} \bar{D}_{ih}\,\mathcal{Z}^{(21)}_{ph}(\theta)\,\bar{D}^*_{kp}, \tag{B4c}$$

$$\rho^{22}_{ki}(\theta) = \frac{\langle\overline{\Phi}|c_i^\dagger\, c_k\,\hat{R}_\theta|\overline{\Phi}\rangle}{\langle\overline{\Phi}|\hat{R}_\theta|\overline{\Phi}\rangle} = \sum_h \bar{D}_{ih}\,D^*_{kh} + \sum_{ph} \bar{D}_{ih}\,\mathcal{Z}^{(22)}_{ph}(\theta)\,\bar{D}^*_{kp}. \tag{B4d}$$

Here,

$$\mathcal{Z}^{(11)}_{ph}(\theta) = \sum_{h'}[\bar{D}^{\mathsf{T}}R(\theta)D^*]_{ph'}[\mathcal{L}^{(11)*-1}(\theta)]_{h'h}, \tag{B5a}$$
$$\mathcal{Z}^{(12)}_{ph}(\theta) = \sum_{h'}[\bar{D}^{\mathsf{T}}R(\theta)\bar{D}^*]_{ph'}[\mathcal{L}^{(12)*-1}(\theta)]_{h'h}, \tag{B5b}$$
$$\mathcal{Z}^{(21)}_{ph}(\theta) = \sum_{h'}[D^{\mathsf{T}}R(\theta)D^*]_{ph'}[\mathcal{L}^{(21)*-1}(\theta)]_{h'h}, \tag{B5c}$$
$$\mathcal{Z}^{(22)}_{ph}(\theta) = \sum_{h'}[D^{\mathsf{T}}R(\theta)\bar{D}^*]_{ph'}[\mathcal{L}^{(22)*-1}(\theta)]_{h'h} \tag{B5d}$$

and

$$\mathcal{L}^{(11)}_{h'h}(\theta) = [D^\dagger R^*(\theta)D]_{h'h}, \tag{B6a}$$
$$\mathcal{L}^{(12)}_{h'h}(\theta) = [D^\dagger R^*(\theta)\bar{D}]_{h'h}, \tag{B6b}$$
$$\mathcal{L}^{(21)}_{h'h}(\theta) = [\bar{D}^\dagger R^*(\theta)D]_{h'h}, \tag{B6c}$$
$$\mathcal{L}^{(22)}_{h'h}(\theta) = [\bar{D}^\dagger R^*(\theta)\bar{D}]_{h'h}. \tag{B6d}$$

The overlap-like matrix elements appearing in the local gradient [Eq. (86)] can be evaluated as

$$\frac{\langle\Phi|\bar{b}_h^\dagger\,\bar{b}_p\,\hat{R}_\theta|\Phi\rangle}{\langle\Phi|\hat{R}_\theta|\Phi\rangle} = \sum_{mn}\bar{D}^*_{mh}\,\bar{D}_{np}\,\rho^{11}_{nm}(\theta), \tag{B7a}$$
$$\frac{\langle\overline{\Phi}|b_h^\dagger\,b_p\,\hat{R}_\theta|\Phi\rangle}{\langle\overline{\Phi}|\hat{R}_\theta|\Phi\rangle} = \sum_{mn}D^*_{mh}\,D_{np}\,\rho^{21}_{nm}(\theta), \tag{B7b}$$
$$\frac{\langle\Phi|\bar{b}_h^\dagger\,\bar{b}_p\,\hat{R}_\theta|\overline{\Phi}\rangle}{\langle\Phi|\hat{R}_\theta|\overline{\Phi}\rangle} = \sum_{mn}\bar{D}^*_{mh}\,\bar{D}_{np}\,\rho^{12}_{nm}(\theta), \tag{B7c}$$
$$\frac{\langle\overline{\Phi}|b_h^\dagger\,b_p\,\hat{R}_\theta|\overline{\Phi}\rangle}{\langle\overline{\Phi}|\hat{R}_\theta|\overline{\Phi}\rangle} = \sum_{mn}D^*_{mh}\,D_{np}\,\rho^{22}_{nm}(\theta). \tag{B7d}$$

Similarly, the Hamiltonian-like matrix elements in Eq. (86) can be evaluated as

$$\frac{\langle\Phi|\bar{b}_h^\dagger\,\bar{b}_p\,\hat{H}\,\hat{R}_\theta|\Phi\rangle}{\langle\Phi|\hat{R}_\theta|\Phi\rangle} = \sum_{mn}\bar{D}^*_{mh}\,\bar{D}_{np}\,\rho^{11}_{nm}(\theta)\,\frac{\langle\Phi|\hat{H}\,\hat{R}_\theta|\Phi\rangle}{\langle\Phi|\hat{R}_\theta|\Phi\rangle} + \sum_{mn}\sum_{ik}\bar{D}^*_{mh}\,\bar{D}_{np}\,\left(h_{ik}+\Gamma^{11}_{ik}(\theta)\right)\times\rho^{11}_{km}(\theta)\,\left(\delta_{ni}-\rho^{11}_{ni}(\theta)\right), \tag{B8a}$$

$$\frac{\langle\overline{\Phi}|b_h^\dagger\,b_p\,\hat{H}\,\hat{R}_\theta|\Phi\rangle}{\langle\overline{\Phi}|\hat{R}_\theta|\Phi\rangle} = \sum_{mn}D^*_{mh}\,D_{np}\,\rho^{21}_{nm}(\theta)\,\frac{\langle\overline{\Phi}|\hat{H}\,\hat{R}_\theta|\Phi\rangle}{\langle\overline{\Phi}|\hat{R}_\theta|\Phi\rangle} + \sum_{mn}\sum_{ik}D^*_{mh}\,D_{np}\,\left(h_{ik}+\Gamma^{21}_{ik}(\theta)\right)\times\rho^{21}_{km}(\theta)\,\left(\delta_{ni}-\rho^{21}_{ni}(\theta)\right), \tag{B8b}$$

$$\frac{\langle\Phi|\bar{b}_h^\dagger\,\bar{b}_p\,\hat{H}\,\hat{R}_\theta|\overline{\Phi}\rangle}{\langle\Phi|\hat{R}_\theta|\overline{\Phi}\rangle} = \sum_{mn}\bar{D}^*_{mh}\,\bar{D}_{np}\,\rho^{12}_{nm}(\theta)\,\frac{\langle\Phi|\hat{H}\,\hat{R}_\theta|\overline{\Phi}\rangle}{\langle\Phi|\hat{R}_\theta|\overline{\Phi}\rangle} + \sum_{mn}\sum_{ik}\bar{D}^*_{mh}\,\bar{D}_{np}\,\left(h_{ik}+\Gamma^{12}_{ik}(\theta)\right)\times\rho^{12}_{km}(\theta)\,\left(\delta_{ni}-\rho^{12}_{ni}(\theta)\right), \tag{B8c}$$

$$\frac{\langle\overline{\Phi}|b_h^\dagger\,b_p\,\hat{H}\,\hat{R}_\theta|\overline{\Phi}\rangle}{\langle\overline{\Phi}|\hat{R}_\theta|\overline{\Phi}\rangle} = \sum_{mn}D^*_{mh}\,D_{np}\,\rho^{22}_{nm}(\theta)\,\frac{\langle\overline{\Phi}|\hat{H}\,\hat{R}_\theta|\overline{\Phi}\rangle}{\langle\overline{\Phi}|\hat{R}_\theta|\overline{\Phi}\rangle} + \sum_{mn}\sum_{ik}D^*_{mh}\,D_{np}\,\left(h_{ik}+\Gamma^{22}_{ik}(\theta)\right)\times\rho^{22}_{km}(\theta)\,\left(\delta_{ni}-\rho^{22}_{ni}(\theta)\right). \tag{B8d}$$

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