$N$-electron Slater determinants from non-unitary canonical transformations of fermion operators

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Abstract

Mean-field methods such as Hartree–Fock (HF) or Hartree–Fock–Bogoliubov (HFB) constitute the building blocks upon which more elaborate many-body theories are based on. The HF and HFB wavefunctions are built out of independent quasi-particles resulting from a unitary linear canonical transformation of the elementary fermion operators. Here, we discuss the possibility of allowing the HF transformation to become non-unitary. 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 non-unitary transformation brings additional flexibility that can be exploited in variational approximations to many-fermion wavefunctions. The action of projection operators on non-unitary based HF states is also discussed and applied to the one-dimensional Hubbard model with periodic boundary conditions.
I. INTRODUCTION

Mean-field methods such as Hartree–Fock (HF) or 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 wavefunction, but also because more elaborate correlated approximations usually start from such independent quasi-particle vacua (HF or HFB).

The HFB wavefunction developed to explain superconductivity relies on the so-called Bogoliubov-Valatin \cite{1, 2} transformation, which defines quasi-particle operators as linear combinations of single-fermion creation and annihilation operators. These are then used to form a quasi-particle product state, the HFB wavefunction. Berezin \cite{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 wavefunctions as being built out of single quasi-particle 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) \cite{4}. In a second-quantized framework, this corresponds to a transformation that preserves the anti-commutation rules of the elementary fermion operators \cite{5}. A linear canonical transformation does not need to be unitary, although Dirac \cite{6} and Weyl \cite{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 non-unitary linear canonical transformations. The extension to HFB determinants will be discussed in a follow-up paper \cite{8}.

We note that non-unitary canonical transformations have been discussed in the literature before. They are discussed, for instance, by Blaizot and Ripka \cite{5} in the general context of canonical transformations of second-quantized operators. They have been used by Balian and Berezin \cite{9} in the evaluation of matrix elements between two different Bogoliubov states. Zhang and Tang \cite{10}, and later Ma and Zhang \cite{11}, have studied the properties of linear canonical transformations of fermion operators, including the non-unitary ones that we have just referred to. We also mention the work of Anderson \cite{4}, where the properties of non-unitary 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 wavefunction, the full flexibility that a non-unitary 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 non-unitary transformation. We discuss here what may be the simplest, two-determinant ansatz that exploits all the degrees of freedom that define a non-unitary 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 non-unitary based \( N \)-particle Slater determinants. We also discuss the variational optimization of states based on a non-unitary HF-type canonical transformation.

Our interest in non-unitary HF-type transformations originated from our recent work on projected HF calculations for molecular systems \cite{12, 13} and the two-dimensional Hubbard Hamiltonian with periodic boundary conditions (PBC) \cite{14}. The idea of using a symmetry-projected HF state as an approximation to the many-body wavefunction was proposed by Löwdin \cite{15} as early as 1955. We, building on techniques developed and successfully applied in nuclear physics \cite{5, 16–20}, have shown that symmetry-projection out of the most general HF transformation yields a multi-reference type wavefunction 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 are broken), the better the resulting projected wavefunction is able to account for the correlation structure of the true Hamiltonian eigenvector. It is then natural to explore whether a non-unitary canonical transformation, which has more degrees of freedom than the unitary one commonly used, would yield additional flexibility for HF wavefunctions in general, and projected HF states in particular. This work describes our efforts along this line. We show that, indeed, using a non-unitary 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 section II, we discuss some general properties of linear canonical transformations of fermion operators. We proceed to show in section III how to construct \( N \)-particle Slater determinants based on such transformations. Section IV discusses our extension of Thouless’ theorem for non-unitary Slater determinants. This is followed by section V where we use this theorem to derive the form of matrix elements between non-unitary \( N \)-particle Slater determinants. In section VI we introduce a two-determinant ansatz that displays the full flexibility of a non-unitary transformation. We show in section VII how such an ansatz can be used in projected HF approaches. This is followed by an illustrative application of the proposed
wavefunction ansätze to the one-dimensional Hubbard Hamiltonian with PBC in section VIII.

II. CANONICAL TRANSFORMATIONS

We start by introducing a set of fermion annihilation and creation operators $c = \{c_k, c_k^\dagger\}$, which obey the standard anti-commutation 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 $\beta = \{\beta_k, \beta_k^\dagger\}$, which is related to the original one by the linear transformation

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

where we have arranged the sets of fermion operators $c$ and $\beta$ 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

$$\beta = Tc.$$  \hspace{1cm} (2)

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

$$T^* = \sigma T \sigma,$$  \hspace{1cm} (3)

where the matrix $\sigma$ is given by

$$\sigma = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$  \hspace{1cm} (4)

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

We do insist, on the other hand, in making our transformation canonical, which implies preserving the appropriate anti-commutation relations, that is,

$$[\beta_k, \beta_j]_+ = 0, \quad [\beta_k^\dagger, \beta_j^\dagger]_+ = 0, \quad [\beta_k, \beta_j^\dagger]_+ = \delta_{jk}.$$
It is not difficult to prove that the transformation $T$ is canonical if it obeys

$$T \sigma T^\dagger = \sigma,$$  \hfill (5)

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

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

$$U^\dagger X + V^\dagger Y = 1,$$ \hfill (7a)
$$X^T U^* + Y^T V^* = 1,$$ \hfill (7b)
$$U^\dagger V^* + V^\dagger U^* = 0,$$ \hfill (7c)
$$Y^T X + X^T Y = 0.$$ \hfill (7d)

Note that the matrices $U^\dagger V^*$ and $Y^T X$ are anti-symmetric.

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 form a group isomorphic to the group of real orthogonal matrices of dimension $2M \ [O(2M)]$. There are twice as many degrees of freedom in choosing a general non-unitary 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

$$\beta = S c S^{-1} = T c.$$ \hfill (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 quasi-particle operators resulting from canonical transformations of the elementary fermion ones. This is discussed in detail by Navon [21], as well as in several textbooks in many-body physics.
In standard (i.e. unitary) HF theory, an $N$-electron Slater determinant is constructed out of a set $N$ hole creation ($\{b^\dagger_h\}$) and $M - N$ particle annihilation ($\{b_p\}$) operators, each of them resulting from a linear combination of the elementary operators $\{c_k, c_k^\dagger\}$:

\begin{align}
    b^\dagger_h &= \sum_j D^*_{jh} c_j^\dagger, \\
    b_p &= \sum_j D_{jp} c_j.
\end{align}

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

\[
\begin{pmatrix}
    b^\dagger_h \\
    b_p \\
    b_h \\
    b^\dagger_p
\end{pmatrix} =
\begin{pmatrix}
    0_{N \times M} & D_h^\dagger \\
    D_p^\top & 0_{(M-N) \times M}
\end{pmatrix}
\begin{pmatrix}
    c \\
    c^\dagger
\end{pmatrix},
\]

where we have implicitly assumed the transformation to be unitary.

The above transformation is canonical if the HF operators satisfy the (non-trivial) anticommutation relations

\begin{align}
    [b_h, b^\dagger_{h'}]_+ &= \delta_{h'h}, \\
    [b_p, b^\dagger_{p'}]_+ &= \delta_{p'p}, \\
    [b_p, b^\dagger_h]_+ &= 0.
\end{align}

These conditions restrict the form of the matrix $D$ according to

\begin{align}
    [b_h, b^\dagger_{h'}]_+ &= \sum_j D_{jh} D^*_{k'h'} \delta_{jk} = \left(D^\dagger D\right)_{h'h} = \delta_{h'h}, \\
    [b_p, b^\dagger_{p'}]_+ &= \sum_j D_{jp} D^*_{k'p'} \delta_{jk} = \left(D^\dagger D\right)_{p'p} = \delta_{p'p}, \\
    [b_p, b^\dagger_h]_+ &= \sum_j D_{jp} D^*_{kh} \delta_{jk} = \left(D^\dagger D\right)_{hp} = 0.
\end{align}

The first equation implies orthonormality of the hole states, the second one orthonormality of the particle states, and the last one corresponds to orthogonality between hole and particle states. All these conditions are summarized in the requirement $D^\dagger D = 1$.

One could allow the HF transformation described previously to become non-unitary 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

\[\bar{b}_h = \sum_j \bar{D}_{jh} c_j, \quad \bar{b}_p^\dagger = \sum_j \bar{D}_{jp}^* c_j^\dagger,\]

(12a)

(12b)

A non-unitary transformation can then be built as

\[
\begin{pmatrix}
\bar{b}_h^\dagger \\
\bar{b}_p \\
\bar{b}_h \\
\bar{b}_p^\dagger
\end{pmatrix} =
\begin{pmatrix}
0_{N \times M} & D_h^\dagger \\
D_p^\dagger & 0_{(M-N) \times M} \\
\bar{D}_h^\dagger & 0_{M \times N} \\
0_{(M-N) \times M} & \bar{D}_p^\dagger
\end{pmatrix}
\begin{pmatrix}
\bar{c} \\
c^\dagger
\end{pmatrix}.
\]

(13)

It is a canonical transformation if the (non-trivial) anti-commutation relations

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

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

\[
\begin{align}
[\bar{b}_p, \bar{b}_h^\dagger]_+ & = \sum_{jk} D_{jp} D_{kjh}^* \delta_{jk} = (D^\dagger \bar{D})_{bp} = 0, \\
[\bar{b}_h, \bar{b}_p^\dagger]_+ & = \sum_{jk} \bar{D}_{jh} \bar{D}_{kp}^* \delta_{jk} = (\bar{D}^\dagger \bar{D})_{ph} = 0, \\
[\bar{b}_h, \bar{b}_h^\dagger]_+ & = \sum_{jk} \bar{D}_{jh} \bar{D}_{kjh'}^* \delta_{jk} = (\bar{D}^\dagger \bar{D})_{h'lh} = \delta_{h'h}, \\
[\bar{b}_p, \bar{b}_p^\dagger]_+ & = \sum_{jk} D_{jp} \bar{D}_{kp'}^* \delta_{jk} = (D^\dagger \bar{D})_{p'p} = \delta_{p'p}.
\end{align}
\]

(14a)

(14b)

(14c)

(14d)

The first two equations imply orthogonality of the hole and particle states in \(D\) and \(\bar{D}\). The last two equations imply a bi-orthonormality between the hole and particle orbitals in \(D\) and \(\bar{D}\). Note that the last 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 \{\bar{b}_h^\dagger, \bar{b}_p, \bar{b}_h, \bar{b}_p^\dagger\} define a canonical transformation, the inverse transformation is given by (see Eq. (f))

\[
\begin{pmatrix}
\bar{c} \\
c^\dagger
\end{pmatrix} =
\begin{pmatrix}
0_{M \times N} & \bar{D}_p^* & \bar{D}_h^* & 0_{M \times (M-N)} \\
\bar{D}_h & 0_{M \times (M-N)} & \bar{D}_h & 0_{M \times N}
\end{pmatrix}
\begin{pmatrix}
\bar{b}_h^\dagger \\
b_p \\
b_h \\
\bar{b}_p^\dagger
\end{pmatrix}.
\]

(15)
The bi-orthonormal Slater determinants $|\Phi\rangle$ and $|\Phi\rangle$ are produced when the set of operators 
\{\hat{b}^\dagger, \hat{b}\} act on the bare fermion vacuum $|-\rangle$, \textit{i.e.},
\begin{align}
|\Phi\rangle &= \prod_h \hat{b}^\dagger \hat{b} |-\rangle, \\
|\Phi\rangle &= \prod_h \hat{\bar{b}}^\dagger \hat{\bar{b}} |-\rangle.
\end{align}

They satisfy the bi-orthonormality condition $\langle \Phi | \Phi \rangle = 1$.

One can easily show that $|\Phi\rangle$ and $|\Phi\rangle$ act as vacua to a certain set of hole or particle states:
\begin{align*}
\hat{b}^\dagger_h |\Phi\rangle &= 0 \quad \forall \quad \hat{b}^\dagger_h, \\
\hat{\bar{b}}^\dagger_h |\Phi\rangle &= 0 \quad \forall \quad \hat{\bar{b}}^\dagger_h.
\end{align*}

IV. THOULESS’ THEOREM FOR $N$-ELECTRON SLATER DETERMINANTS

In standard (\textit{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 
\{\hat{b}^\dagger, \hat{b}\}, any $N$-particle Slater determinant $|\Phi_1\rangle$ which is not orthogonal to $|\Phi_0\rangle$ can be written in the form

\begin{equation}
|\Phi_1\rangle = \mathcal{N} \exp \left( \sum_{ph} Z_{ph} \hat{b}^\dagger_p \hat{b}_h \right) |\Phi_0\rangle,
\end{equation}

where $\mathcal{N} = \langle \Phi_0 | \Phi_1 \rangle$ is a normalization constant and the coefficients $Z_{ph}$ are uniquely determined. Conversely, any wavefunction 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 non-unitary linear canonical transformation, the equivalent theorem reads

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

\begin{equation}
|\Phi_1\rangle = \mathcal{N} \exp \left( \sum_{ph} Z_{ph} \hat{\bar{b}}^\dagger_p \hat{\bar{b}}_h \right) |\Phi_0\rangle,
\end{equation}

where $\mathcal{N} = \langle \Phi_0 | \Phi_1 \rangle$ is a normalization constant and the coefficients $Z_{ph}$ are uniquely determined.

For a proof of this last 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 non-unitary 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,

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

(20)

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

The overlaps among $N$-particle Slater determinants become

$$\langle \Phi_0 | \Phi_1 \rangle = \det_N D^{0T} D_{1\dagger},$$

(21a)

$$\langle \Phi_0 | \bar{\Phi}_1 \rangle = \det_N \bar{D}^{0T} \bar{D}_{1\dagger},$$

(21b)

$$\langle \bar{\Phi}_0 | \Phi_1 \rangle = \det_D \bar{D}^{0T} D_{1\dagger},$$

(21c)

$$\langle \bar{\Phi}_0 | \bar{\Phi}_1 \rangle = \det_D \bar{D}^{0T} \bar{D}_{1\dagger},$$

(21d)

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

B. Operator matrix elements

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

$$\langle \bar{\Phi}_0 | c_{i_1}^\dagger \cdots c_{i_p}^\dagger c_{k_1} \cdots c_{k_p} | \Phi_1 \rangle.$$

(22)

The form above is chosen for convenience, but other matrix elements can be derived in the same way described below.
We shall use Thouless' theorem to write the state $|\Phi_1\rangle$ as

$$|\Phi_1\rangle = \exp(\hat{Z})|\Phi_0\rangle\langle\Phi_0|\Phi_1\rangle,$$

(23)

$$\hat{Z} = \sum_{ph} Z_{ph}\bar{b}_p^\dagger b_h.$$

(24)

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

$$b_h^\dagger|\Phi_0\rangle = 0 \quad \forall \quad b_h^\dagger, \quad b_p|\Phi_0\rangle = 0 \quad \forall \quad b_p,$$

$$\langle\Phi_0|\bar{b}_h = 0 \quad \forall \quad \bar{b}_h, \quad \langle\Phi_0|\bar{b}_p = 0 \quad \forall \quad \bar{b}_p.$$

On the other hand, we write the state $\langle\Phi_0|$ as

$$\langle\Phi_0| = \langle\Phi_0|\exp(-\hat{Z}),$$

(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

$$\langle\Phi_0|c_{l_1}^\dagger \cdots c_{l_p}^\dagger c_{k_1} \cdots c_{k_p}|\Phi_1\rangle = \langle\Phi_0|\Phi_1\rangle\langle\Phi_0|\exp(-\hat{Z})c_{l_1}^\dagger \cdots c_{l_p}^\dagger c_{k_1} \cdots c_{k_p}\exp(\hat{Z})|\Phi_0\rangle$$

$$= \langle\Phi_0|\Phi_1\rangle\langle\Phi_0|\bar{d}_{l_1} \cdots \bar{d}_{l_p} d_{k_1} \cdots d_{k_p}|\Phi_0\rangle,$$

(26)

where we have introduced the operators

$$\bar{d}_l = \exp(-\hat{Z})c_l^\dagger \exp(\hat{Z}),$$

(27a)

$$d_k = \exp(-\hat{Z})c_k \exp(\hat{Z}).$$

(27b)

We now express the operators $\{\bar{d}_l, d_k\}$ 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

$$\bar{d}_l = \exp(-\hat{Z})c_l^\dagger \exp(\hat{Z}) = c_l^\dagger + \left[\hat{Z}, c_l^\dagger\right]$$

$$= \sum_{h} D_{lh}^0 b_h^\dagger + \sum_{p} \left(D_{lp}^0 - \sum_{h} Z_{ph} \bar{D}_{lh}^0\right) \bar{b}_p^\dagger,$$

(28)

$$d_k = \exp(-\hat{Z})c_k \exp(\hat{Z}) = c_k - \left[\hat{Z}, c_k\right]$$

$$= \sum_{h} \left(D_{kh}^{0*} + \sum_{p} Z_{ph} \bar{D}_{kp}^{0*}\right) \bar{b}_h + \sum_{p} \bar{D}_{kp}^{0*} b_p.$$

(29)

Because $\{\bar{d}_l, d_k\}$ 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 non-vanishing contractions among the
operators \( \{b_h^\dagger, bp, \bar{b}_h, \bar{b}_p^\dagger\} \) are given by

\[
\begin{align*}
    b_h^\dagger b_{h'} &= \delta_{hh'}, \\
    b_p^\dagger b_{p'} &= \delta_{pp'}.
\end{align*}
\]

(30a) (30b)

It follows that the non-vanishing contractions among the operators \( \{\tilde{d}_l, d_k\} \) are of the form

\[
\begin{align*}
    \tilde{d}_l^\dagger d_k &= \sum_{hh'} D_{lh}^0 \left( D_{kh'}^{0*} + \sum_p Z_{ph} \bar{D}_{kp}^0 \right) \delta_{hh'} \\
    &= \sum_h D_{lh}^0 D_{kh}^{0*} + \sum_{ph} D_{lh}^0 Z_{ph} \bar{D}_{kp}^0, \\
\end{align*}
\]

(31)

\[
\begin{align*}
    d_l d_k &= \sum_{pp'} D_{lp}^{0*} \left( D_{kp}^0 - \sum_h Z_{ph} D_{kh}^0 \right) \delta_{pp'} \\
    &= \sum_p D_{lp}^{0*} D_{kp}^0 - \sum_{ph} D_{lp}^{0*} Z_{ph} \bar{D}_{kp}^0.
\end{align*}
\]

(32)

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 \( \rho_{01} \), given by

\[
\begin{align*}
    \rho_{01}^{01} &= \frac{\langle \Phi_0 | c_k^\dagger c_l | \Phi_1 \rangle}{\langle \Phi_0 | \Phi_1 \rangle} = \langle \Phi_0 | \exp(-\hat{Z}) c_l^\dagger c_k \exp(\hat{Z}) | \Phi_0 \rangle \\
    &= \sum_h D_{lh}^0 D_{kh}^{0*} + \sum_{ph} D_{lh}^0 Z_{ph} \bar{D}_{kp}^0,
\end{align*}
\]

(33)

where

\[
Z_{ph} = \sum_{h'} \left( D^{0T} D^{1*} \right)_{ph'} \left( \mathcal{L}^{*-1} \right)_{h'h},
\]

(34)

\[
\mathcal{L}_{h'h} = \left( D_{1h}^{0*} D_{1h} \right)_{h'h}.
\]

(35)

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

\[
\hat{H} = \sum_{ik} \langle \hat{i} | \hat{h} | \hat{k} \rangle c_{i}^\dagger c_k + \frac{1}{4} \sum_{ijkl} \langle \hat{i} \hat{j} | \hat{v} | \hat{k} \hat{l} \rangle c_{i}^\dagger c_{j}^\dagger c_{l} c_{k},
\]

(36)
where $\langle i | \hat{h} | k \rangle$ and $\langle ij | \hat{v} | kl \rangle$ are one- and anti-symmetrized two-particle integrals, respectively, the energy can be evaluated as

$$E = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

$$= \sum_{ik} h_{ik} \rho_{ki} + \frac{1}{2} \sum_{ijkl} \langle ij | \hat{v} | kl \rangle \rho_{ki} \rho_{lj}$$

$$= \text{Tr} \left( h \rho + \frac{1}{2} \Gamma \rho \right), \quad (37)$$

where

$$\rho_{ki} = \frac{\langle \Phi | c_i^+ c_k | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

$$= \sum_h D_{ih} \bar{D}_{kh}^* + \sum_{ph} D_{ih} \bar{Z}_{ph} D_{kp}^*, \quad (38)$$

$$\Gamma_{ik} = \sum_{jl} \langle ij | \hat{v} | kl \rangle \rho_{lj}, \quad (39)$$

and

$$\bar{Z}_{ph} = \sum_{h'} \left( \bar{D}^\dagger D^* \right)_{ph'} \left( \bar{\mathcal{L}}^{*-1} \right)_{h'h}, \quad (40)$$

$$\bar{\mathcal{L}}_{h'h} = \left( D^\dagger D \right)_{h'h}. \quad (41)$$

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 $\rho$ (Eq. 38), which comes about from the fact that the anti-commutation relations satisfied by the HF operators are different.

VI. VARIATIONAL ANSATZ WITH SLATER DETERMINANTS FROM NON-UNITARY TRANSFORMATIONS

In this section, we use a simple, two-determinant ansatz that uses the full flexibility of the non-unitary HF-like transformation of Eq. 13 as part of a variational strategy.

Before introducing such ansatz, we note that using a single Slater determinant $|\Phi\rangle$ as a trial wavefunction, whether resulting from a unitary or a non-unitary canonical transformation, would lead to the same variational energy. An $N$-particle Slater determinant resulting from a non-unitary 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

\[ |\Psi\rangle = c_1|\Phi_1\rangle + c_2|\Phi_2\rangle, \]

\[ \equiv c_1|\Phi_1\rangle + c_2|\Phi_2\rangle, \] (42)

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, \( |\Phi_1\rangle = |\Phi\rangle \), 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 non-orthogonal Slater determinants resulting, each of them, from a standard unitary canonical transformation (see Ref. [27]). 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

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

We rewrite the energy above in the form

\[ E = \sum_{\alpha,\beta=1}^{2} y_{\alpha\beta} \frac{\langle \Phi_\alpha | \hat{H} | \Phi_\beta \rangle}{\langle \Phi_\alpha | \Phi_\beta \rangle}, \] (44)

\[ y_{\alpha\beta} = \frac{c^*_\alpha c_\beta \langle \Phi_\alpha | \Phi_\beta \rangle}{\sum_{\alpha',\beta'=1}^{2} c^*_{\alpha'} c_{\beta'} \langle \Phi_{\alpha'} | \Phi_{\beta'} \rangle}. \] (45)

The matrix elements appearing in Eqs. 44 and 45 can be evaluated in a straight-forward way. The overlap kernels in Eq. 45 are computed as

\[ \langle \Phi | \Phi \rangle = \det_N D^T D^*, \] (46a)

\[ \langle \overline{\Phi} | \Phi \rangle = \det_N D^T D^* = 1, \] (46b)

\[ \langle \Phi | \overline{\Phi} \rangle = \det_N D^T \overline{D}^* = 1, \] (46c)

\[ \langle \overline{\Phi} | \overline{\Phi} \rangle = \det_N \overline{D}^T \overline{D}^*. \] (46d)

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

\[ \frac{\langle \Phi_\alpha | \hat{H} | \Phi_\beta \rangle}{\langle \Phi_\alpha | \Phi_\beta \rangle} = \text{Tr} \left( h \rho^{\alpha\beta} + \frac{1}{2} I^{\alpha\beta} \right), \] (47)

\[ \Gamma^{\alpha\beta}_{ik} = \sum_{jl} \langle ij | \hat{v} | kl \rangle \rho^{\alpha\beta}_{lj}. \] (48)
The transition density matrices are in turn given by

\[ \rho_{ki} = \left( \frac{\langle \Phi | c_i^\dagger c_k | \Phi \rangle}{\langle \Phi | \Phi \rangle} \right) = \sum_h D_{ih} \bar{D}_{kh}^\ast + \sum_{ph} D_{ih} \bar{Z}_{ph} D_{kp}^\ast, \]  

(49a)

\[ \rho_{ki} = \left( \frac{\langle \Phi | c_i^\dagger c_k | \Phi \rangle}{\langle \Phi | \Phi \rangle} \right) = \sum_h \bar{D}_{ih} D_{kh}^\ast, \]  

(49b)

\[ \rho_{ki} = \left( \frac{\langle \Phi | c_i^\dagger c_k | \Phi \rangle}{\langle \Phi | \Phi \rangle} \right) = \sum_h D_{ih} \bar{D}_{kh}^\ast, \]  

(49c)

\[ \rho_{ki} = \left( \frac{\langle \Phi | c_i^\dagger c_k | \Phi \rangle}{\langle \Phi | \Phi \rangle} \right) = \sum_h \bar{D}_{ih} D_{kh}^\ast + \sum_{ph} \bar{D}_{ih} \bar{Z}_{ph} D_{kp}^\ast, \]  

(49d)

Here,

\[ \bar{Z}_{ph} = \sum_{h'} \left( \bar{D}^\dagger D \right)_{ph'} \left( \bar{L}^{\ast -1} \right)_{h'h}, \]  

(50a)

\[ Z_{ph} = \sum_{h'} \left( D^\dagger D \right)_{ph'} \left( L^{\ast -1} \right)_{h'h}, \]  

(50b)

\[ \bar{L}_{h'h} = \left( \bar{D}^\dagger \bar{D} \right)_{h'h}, \]  

(50c)

\[ L_{h'h} = \left( \bar{D}^\dagger \bar{D} \right)_{h'h}. \]  

(50d)

### A. Variational optimization of \(|\Phi\rangle\)

Let us now consider the variational optimization of the wavefunction 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 \(|\bar{\Phi}\rangle\). The variation has to be carried out subject to the constraint that \(\langle \Phi | \Phi \rangle = 1\), which is equivalent to saying that \(|\Phi\rangle\) and \(|\bar{\Phi}\rangle\) 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

\[ (H - E N) c = 0, \]  

(51)

with the constraint

\[ c^\dagger N c = 1, \]  

(52)

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

\[ H_{\alpha\beta} = \langle \Phi_\alpha | \hat{H} | \Phi_\beta \rangle, \]  

(53)

\[ N_{\alpha\beta} = \langle \Phi_\alpha | \Phi_\beta \rangle. \]  

(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 non-unitary HF transformation. We have followed the work of Egido and coworkers [23] for this purpose. Let us assume that we are provided a guess for $|\Psi\rangle$ and $|\Phi\rangle$, 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 $\{|\Phi\rangle, |\Phi\rangle\}$ by allowing for independent Thouless’ rotations of both states, characterized by the matrices $Z$ and $\bar{Z}$. That is, we let

$$ |\Phi\rangle \rightarrow \exp \left( \sum_{ph} Z_{ph} b_p^\dagger \bar{b}_h \right) |\Phi\rangle, \quad (55a) $$

$$ |\Phi\rangle \rightarrow \exp \left( \sum_{ph} \bar{Z}_{ph} b_p^\dagger \bar{b}_h \right) |\Phi\rangle. \quad (55b) $$

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

$$ G_{ph} = - \frac{\partial}{\partial Z_{ph}} E[Z, \bar{Z}] \bigg|_{Z_{ph}=0}, \quad (56a) $$

$$ \bar{G}_{ph} = - \frac{\partial}{\partial \bar{Z}_{ph}^*} E[Z, \bar{Z}] \bigg|_{\bar{Z}_{ph}=0}. \quad (56b) $$

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

$$ dE = - \sum_{ph} [G_{ph} dZ_{ph}^* + \bar{G}_{ph} d\bar{Z}_{ph}^* + \text{c.c.}] \ . \quad (57) $$

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

$$ G_{ph} = - y_{11} \frac{\langle \Phi | b_h^\dagger b_p \left( \hat{H} - E \right) |\Phi\rangle}{\langle \Phi | \Phi \rangle} - y_{12} \frac{\langle \Phi | \bar{b}_h^\dagger b_p \left( \hat{H} - E \right) |\Phi\rangle}{\langle \Phi | \Phi \rangle}, \quad (58a) $$

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

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
\[
\langle \Phi | \bar{b} \dagger h \bar{b} p | \Phi \rangle \langle \Phi | \Phi \rangle = \sum_{mn} D_{mn}^* D_{np} \rho_{nm}^{11},
\]
(59a)
\[
\langle \Phi | \bar{b} \dagger p | \Phi \rangle = 0,
\]
(59b)
\[
\langle \Phi | \bar{b} \dagger h \bar{b} p | \Phi \rangle = 0,
\]
(59c)
\[
\langle \Phi | \bar{b} \dagger p | \Phi \rangle \langle \Phi | \Phi \rangle = \sum_{mn} D_{mn}^* D_{np} \rho_{nm}^{22}.
\]
(59d)

The Hamiltonian-like matrix elements appearing in Eq. 58 can be evaluated as
\[
\langle \Phi | \bar{b} \dagger h \bar{b} p \hat{H} | \Phi \rangle \langle \Phi | \Phi \rangle = \sum_{mn} D_{mn}^* D_{np} \rho_{nm}^{11} \langle \Phi | \hat{H} | \Phi \rangle \langle \Phi | \Phi \rangle + \sum_{mn} \sum_{ik} D_{mh}^* D_{np} \left( h_{ik} + \Gamma_{ik}^{11} \right) \rho_{km}^{11} \left( \delta_{ni} - \rho_{ni}^{11} \right),
\]
(60a)
\[
\langle \Phi | \bar{b} \dagger h \bar{b} p \hat{H} | \Phi \rangle \langle \Phi | \Phi \rangle = \sum_{ik} D_{kh}^* D_{ip} \left( h_{ik} + \Gamma_{ik}^{21} \right),
\]
(60b)
\[
\langle \Phi | \bar{b} \dagger h \bar{b} p \hat{H} | \Phi \rangle \langle \Phi | \Phi \rangle = \sum_{ik} D_{kh}^* D_{ip} \left( h_{ik} + \Gamma_{ik}^{12} \right),
\]
(60c)
\[
\langle \Phi | \bar{b} \dagger p \hat{H} | \Phi \rangle \langle \Phi | \Phi \rangle = \sum_{mn} D_{mh}^* D_{np} \rho_{nm}^{22} \langle \Phi | \hat{H} | \Phi \rangle \langle \Phi | \Phi \rangle + \sum_{mn} \sum_{ik} D_{mh}^* D_{np} \left( h_{ik} + \Gamma_{ik}^{22} \right) \rho_{km}^{22} \left( \delta_{ni} - \rho_{ni}^{22} \right).
\]
(60d)

B. Restoration of the bi-orthonormality condition

Let us assume that, during the optimization process, we started with the states \( |\Phi\rangle \) and \( |\Phi^\prime\rangle \) and produced the new states \( |\Phi^\prime\rangle \) and \( |\bar{\Phi}\rangle \) by using the Thouless’ transformations
\[
|\Phi^\prime\rangle = \mathcal{N} \exp \left( \sum_{ph} Z_{ph} \bar{b}_p \dagger \bar{b}_h \right) |\bar{\Phi}\rangle,
\]
(61a)
\[
|\bar{\Phi}\rangle = \mathcal{N} \exp \left( \sum_{ph} \bar{Z}_{ph} b_p \dagger b_h \right) |\bar{\Phi}\rangle.
\]
(61b)

Here, the matrices \( Z \) and \( \bar{Z} \) can be chosen as, for instance,
\[
Z_{ph} = \eta G_{ph},
\]
(62a)
\[
\bar{Z}_{ph} = \eta \bar{G}_{ph},
\]
(62b)

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

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

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

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

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

where the operators \( \{ b_h^\dagger, b_p, \tilde{b}_h, \tilde{b}_p^\dagger \} \) describing the states \(| \Phi \rangle \) and \(| \bar{\Phi} \rangle \) are assumed to satisfy all the appropriate anti-commutation relations.

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

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

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

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

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

We can restore the desired anti-commutation relations by performing the transformations

\[
d_h^\dagger = \sum_{h'} L_{h'h'}^{-1} \tilde{d}_h^\dagger, \tag{65a}
\]

\[
\tilde{d}_h = \sum_{h'} L_{h'h'}^{-1} \tilde{\bar{d}}_h', \tag{65b}
\]

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

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

in terms of the lower triangular matrices \( L, \tilde{L}, M, \) and \( \tilde{M} \).

The anti-commutation relations among \( \{ d_h^\dagger, d_p, \tilde{d}_h, \tilde{d}_p^\dagger \} \) become

\[
[\tilde{d}_h, d_h^\dagger]_+ = \sum_{\mu \nu} L_{h'\mu}^{-1} L_{h'h}^{-1} \left( I + Z^T \tilde{Z}^* \right)_{\nu \mu} = \delta_{h'h}, \tag{66a}
\]

\[
[\tilde{d}_p, d_p^\dagger]_+ = \sum_{\mu \nu} \tilde{M}_{pp'}^{-1} \tilde{M}_{p'\nu}^{-1} \left( I + \tilde{Z}^* Z^T \right)_{\nu \mu} = \delta_{p'p}. \tag{66b}
\]
which yield the following equations for determining $L$, $\bar{L}$, $M$, and $\bar{M}$:

\[ I + Z^T \bar{Z}^* = L \bar{L}^\dagger, \]  
\[ (67a) \]
\[ I + \bar{Z}^* Z^T = \bar{M} M^\dagger. \]  
\[ (67b) \]

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 \[14, 24\].

We remark that if $\bar{Z} = 0$ (or $Z = 0$), then the operators \{\(\tilde{d}_h^\dagger\tilde{h}, \tilde{d}_p^\dagger\tilde{p}, \tilde{d}_h^{\bar{\dagger}}\tilde{h}, \tilde{d}_p^{\bar{\dagger}}\tilde{p}\)} do obey all the required anti-commutation relations. In other words, one has to restore the bi-orthonormality condition only if both $|\Phi\rangle$ and $|\bar{\Phi}\rangle$ 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, 23, and 24), 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 \{\(b_{h_0}^{\dagger}, b_0^0, \bar{b}_{h_0}^{\dagger}, b_0^0\)} corresponding to the reference state $|\Psi_0\rangle$. Here, we follow Egido et al. \[23\] in deriving the form of the global gradient.

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

\[ E[\Psi_1] = \frac{\sum_{\alpha,\beta=1}^2 c_\alpha^* c_\beta \langle \tilde{\Phi}_{\alpha}^1 | \hat{H} | \tilde{\Phi}_{\beta}^1 \rangle}{\sum_{\alpha,\beta=1}^2 c_\alpha^* c_\beta \langle \tilde{\Phi}_{\alpha}^1 | \tilde{\Phi}_{\beta}^1 \rangle}. \]  
\[ (68) \]

Provided that $|\Phi^1\rangle$ and $|\bar{\Phi}^1\rangle$ are non-orthogonal to $\langle \Phi^0 \rangle$ and $\langle \Phi^0 \rangle$, respectively, we can write

\[ |\Phi^1\rangle = N \exp \left( \sum_{ph} Z_{ph} b_{p}^{0\dagger} b_h^0 \right) |\Phi^0\rangle, \]  
\[ (69a) \]
\[ |\bar{\Phi}^1\rangle = \bar{N} \exp \left( \sum_{ph} \bar{Z}_{ph} \bar{b}_{p}^{0\dagger} b_h^0 \right) |\bar{\Phi}^0\rangle, \]  
\[ (69b) \]
where we have introduced the global gradients $G$ and $\tilde{G}$ given by

$$G_{ph} = -y_{11} \frac{\langle \Phi^1 | \tilde{b}_h^{01} \tilde{b}_p^0 \left( \hat{H} - E \right) | \Phi^1 \rangle}{\langle \Phi^1 | \Phi^1 \rangle} - y_{12} \frac{\langle \Phi^1 | \tilde{b}_h^{01} \tilde{b}_p^0 \left( \hat{H} - E \right) | \tilde{\Phi}^1 \rangle}{\langle \Phi^1 | \tilde{\Phi}^1 \rangle},$$

$$\tilde{G}_{ph} = -y_{21} \frac{\langle \tilde{\Phi}^1 | \tilde{b}_h^{01} \tilde{b}_p^0 \left( \hat{H} - E \right) | \Phi^1 \rangle}{\langle \Phi^1 | \Phi^1 \rangle} - y_{22} \frac{\langle \tilde{\Phi}^1 | \tilde{b}_h^{01} \tilde{b}_p^0 \left( \hat{H} - E \right) | \tilde{\Phi}^1 \rangle}{\langle \tilde{\Phi}^1 | \tilde{\Phi}^1 \rangle}.$$  

In order to evaluate the matrix elements appearing in the global gradient (Eq. 72), we need to relate the operators $\{ \tilde{b}_h^{01}, \tilde{b}_p^0, \tilde{b}_h^{01}, \tilde{b}_p^{01} \}$ to the operators $\{ b_h^{11}, b_p^1, \tilde{b}_h^{11}, \tilde{b}_p^{11} \}$. Combining the results of the previous subsection with Eqs. [A6a] and [A6b], we arrive at

$$b_h^{11} = \sum_{h'} M_{hh'}^{-1} \tilde{b}_h^{01},$$

$$b_p^1 = \sum_{p'} \tilde{L}_{hp}^{-1} \tilde{b}_p^0 = \sum_{p'} \tilde{L}_{hp}^{-1} \left( \tilde{b}_p^0 - \sum_h \tilde{Z}_{ph}^* b_h^0 \right),$$

$$\tilde{b}_h^{11} = \sum_{h'} \tilde{L}_{hh'}^{-1} \tilde{b}_h^{01},$$

$$\tilde{b}_p^{11} = \sum_{p'} \tilde{M}_{pp'}^{-1} \tilde{b}_{p'}^0 = \sum_{p'} \tilde{M}_{pp'}^{-1} \left( \tilde{b}_{p'}^0 - \sum_h \tilde{Z}_{ph}^* b_h^0 \right),$$

where the matrices $L, \tilde{L}, M, \tilde{M}$ are here determined by the solution to Eqs. [72a] and [72b]
Because the transformation defined by Eqs. 73a–73d is canonical (we have explicitly ensured that anti-commutation rules are preserved), we can invert the transformation using Eq. 6 as a reference. We arrive at

\[ b_{0}^h = \sum_{h'} \bar{L}_{h'h}^{-1} b_{h'}^1 \]  
\[ b_{0}^p = \sum_{p'} \bar{M}_{p'p}^{-1} b_{p'}^1 + \sum_{hh'} Z_{p'h} L_{h'h}^{-1} \bar{b}_{h}^1, \]  
\[ b_{0}^h = \sum_{h'} Z_{p'h}^* M_{p'p}^{-1} b_{p'}^1, \]  
\[ b_{0}^p = \sum_{p'} M_{p'p}^{-1} \bar{b}_{p'}^1 + \sum_{hh'} Z_{p'h}^* \bar{L}_{h'h}^{-1} \bar{b}_{h}^1. \]  

(74a) (74b) (74c) (74d)

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

\[ G_{ph} = \sum_{p'h'} L_{h'h}^{-1} M_{p'p}^{-1} G_{p'h'} \left[ M_{pp'} L_{h'h}^{-1} \right]_{ph}, \]  
\[ \bar{G}_{ph} = \sum_{p'h'} L_{h'h}^{-1} M_{p'p}^{-1} \bar{G}_{p'h'} \left[ \bar{M}_{pp'} \bar{L}_{h'h}^{-1} \right]_{ph}. \]  

(75a) (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.,

\[ \frac{\partial}{\partial Z_{ph}^*} E = 0, \]  
\[ \frac{\partial}{\partial Z_{ph}} E = 0. \]  

(76a) (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, or 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 shall assume for simplicity that it is Abelian. A Slater determinant is symmetry broken if

\[ \hat{g}|\Phi\rangle \neq |\Phi\rangle, \]  

(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 \[25\] that the symmetry can be restored by diagonalization of the Hamiltonian among the Goldstone manifold.

A projection operator can, in general, be written as

\[ \hat{P}_j = \frac{1}{L} \int_L d\theta \ w^j(\theta) \hat{R}_\theta, \]  

(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 shall 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

\[ \hat{P}_m = \frac{1}{4\pi} \int d\theta \ \exp \left[ i\theta \left( \hat{S}_z - m \right) \right], \]  

(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

\[ b^\dagger_k(\theta) \equiv \hat{R}_\theta b^\dagger_k \hat{R}_\theta^{-1} = \sum_j D^*_j k c^\dagger_j \hat{R}_\theta^{-1} = \sum_{ij} R_{ij}(\theta) D^*_j c^\dagger_i, \]  

(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 wavefunction becomes

\[ \hat{P} |\Psi\rangle = \int d\theta \ w(\theta) \left[ c_1 \hat{R}_\theta |\Phi\rangle + c_2 \hat{R}_\theta |\Phi\rangle \right]. \]  

(81)

The Hamiltonian expectation value of a wavefunction of the form of Eq. \[81\] can be written as

\[ E[\Psi] = \frac{\langle \Psi | \hat{P}^\dagger \hat{H} \hat{P} |\Psi\rangle}{\langle \Psi | \hat{P}^\dagger \hat{P} |\Psi\rangle} = \frac{\langle \Psi | \hat{H} \hat{P} |\Psi\rangle}{\langle \Psi | \hat{P} |\Psi\rangle}, \]  

(82)

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

(83)
where we have made the identifications $|\Phi_1\rangle \equiv |\Phi\rangle$ and $|\Phi_2\rangle \equiv |\Phi\rangle$. 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 $|\Phi\rangle$. We will closely follow the derivation we presented before (section VII 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 $2 \times 2$ matrices given by

\begin{align}
H_{\alpha\beta} &= \int d\theta w(\theta) \langle \Phi_\alpha | \hat{H} \hat{R}_\theta | \Phi_\beta \rangle, \\
N_{\alpha\beta} &= \int d\theta w(\theta) \langle \Phi_\alpha | \hat{R}_\theta | \Phi_\beta \rangle.
\end{align}

(84)

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 $|\Phi\rangle$ is done in the same way as it was done for the unprojected case [18, 23]. That is, we parametrize the energy functional in terms of the Thouless’ rotation matrices $Z$ and $\bar{Z}$ acting upon $|\Phi\rangle$ and $|\Phi\rangle$, respectively.

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

\begin{align}
G_{ph} &= \int d\theta w(\theta) \left\{ -y_{11}(\theta) \frac{\langle \Phi | \hat{b}_h^\dagger b_p \left( \hat{H} - E \right) \hat{R}_\theta | \Phi \rangle}{\langle \Phi | \hat{R}_\theta | \Phi \rangle} - y_{12}(\theta) \frac{\langle \Phi | \hat{b}_h^\dagger b_p \left( \hat{H} - E \right) \hat{R}_\theta | \Phi \rangle}{\langle \Phi | \hat{R}_\theta | \Phi \rangle} \right\}, \\
\bar{G}_{ph} &= \int d\theta w(\theta) \left\{ -y_{21}(\theta) \frac{\langle \Phi | \hat{b}_h^\dagger b_p \left( \hat{H} - E \right) \hat{R}_\theta | \Phi \rangle}{\langle \Phi | \hat{R}_\theta | \Phi \rangle} - y_{22}(\theta) \frac{\langle \Phi | \hat{b}_h^\dagger b_p \left( \hat{H} - E \right) \hat{R}_\theta | \Phi \rangle}{\langle \Phi | \hat{R}_\theta | \Phi \rangle} \right\}.
\end{align}

(86a)

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 as part of 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 one-dimensional Hubbard Hamiltonian [26] with PBC. This describes a set of electrons in a lattice
according to

\[ \hat{H} = -t \sum_{j,\sigma} \left( c_{j,\sigma}^\dagger c_{j+1,\sigma} + c_{j+1,\sigma}^\dagger c_{j,\sigma} \right) + U \sum_j c_{j,\uparrow}^\dagger c_{j,\uparrow} c_{j,\downarrow}^\dagger c_{j,\downarrow}. \]

(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. Periodic boundary conditions are assumed, which make the site \( N_s + k \) equivalent to the site \( k \).

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 non-unitary canonical transformations bring. With this in mind, ours should be regarded as a proof of feasibility for calculations in finite many-fermion systems based on non-unitary HF transformations. We point the interested reader to the comprehensive book on the 1D Hubbard Hamiltonian by Essler et al. \[26\]. Recent work on the 1D Hubbard Hamiltonian with projected HF approximations has been done by Schmid et al. \[24\] and Tomita \[27\]. We also note that Lieb and Wu \[28\] devised a set of equations from which the exact eigenvalues of the 1D Hubbard Hamiltonian of Eq. 87 can be obtained.

We have applied the methods described in the preceding sections to the 1D-Hubbard Hamiltonian. Our calculations have been performed with an in-house code using the conjugate-gradient method described here and in Ref. 23 for the variational optimization of HF-based states (see also Refs. 24 and 14). We have selected \( U = 4t \) as a representative on-site repulsion, corresponding to a strongly correlated case \((U\) is of the order of the non-interacting 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 generalized HF (GHF) in the literature \[29\]. We have converged the HF states such that the norm of the gradient is smaller than \( 10^{-5} \). 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 \[30\]. The exact ground state energies, evaluated by solution to the Lieb–Wu equations from Ref. 28, have been obtained with an in-house \textit{Mathematica} notebook.

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

| $N$ | RHF$^a$ | HF$^b$ | mu-HF$^c$ | $S_z$HF$^d$ | mu-$S_z$HF$^e$ | exact$^f$ |
|-----|---------|--------|-----------|------------|----------------|-----------|
| 8   | -1.656854 | -3.748562 | -3.969123 | -4.163645 | -4.342058 | -4.6035   |
| 12  | -2.928203 | -5.629064 | -5.848959 | -6.068077 | -6.316985 | -6.9204   |
| 16  | -4.109358 | -7.505674 | -7.722392 | -7.948679 | -8.231962 | -9.2144   |
| 24  | -6.383016 | -11.258526 | -11.472354 | -11.703719 | -12.011295 | -13.7958  |
| 32  | -8.612682 | -15.011368 | -15.224875 | -15.457467 | -15.777256 | -18.3794  |
| 48  | -13.028207 | -22.517052 | -22.730518 | -22.963973 | -23.291156 | -27.5524  |
| 64  | -17.421870 | -30.022735 | -30.236201 | -30.470037 | -30.798938 | -36.7287  |
| 96  | -26.187360 | -45.034103 | -45.247569 | -45.481765 | -45.811121 | -55.0847  |
| 128 | -34.941935 | -60.045471 | -60.258936 | -60.493305 | -60.825554 | -73.4424  |
| 192 | -52.440176 | -90.068206 | -90.281672 | -90.516208 | -90.845293 | -110.1594 |
| 256 | -69.932961 | -120.090941 | -120.304407 | -120.539025 | -120.868029 | -146.8772 |

$^a$ Restricted Hartree–Fock, i.e., all symmetries of the Hamiltonian are preserved.
$^b$ Symmetry-broken Hartree–Fock.
$^c$ Non-unitary Hartree–Fock, defined by Eq. 22.
$^d$ $S_z$-projected Hartree–Fock (with $\hat{S}_z$ eigenvalue $m = 0$).
$^e$ $S_z$-projected non-unitary Hartree–Fock, defined by Eq. 81 (with $\hat{S}_z$ eigenvalue $m = 0$).
$^f$ Obtained by solution to the Lieb–Wu equations of Ref. 28.

Hubbard Hamiltonian at half-filling ($N = N_s$, where $N$ is the number of electrons in the system). It is evident from the results shown in Table I that nu-HF (defined by Eq. 22), which uses the full flexibility of a non-unitary HF transformation, is able to yield lower energies than standard HF. This was expected, since it is at the very least a two-configuration wavefunction. Similarly, nu-$S_z$HF (defined by Eq. 81) yields lower energies than standard $S_z$-projected HF.

It is less evident that the total correlation energy, defined here as the difference with respect to the energy of the broken-symmetry HF solution, should tend to a non-zero constant with increasing lattice size. This is the case, as shown in Fig. 1. In any case, the correlation energy per particle predicted by all approximate methods considered in Table I goes to zero as $N \to \infty$. This is a reflection of the limited flexibility that the projected HF and the non-unitary based ansätze still have. Note, however, that even if the energy per particle becomes the same as $N \to \infty$, the total energy and the wavefunction itself are different from the symmetry broken HF solution.

It is interesting to observe that simple ansätze such as nu-HF or nu-$S_z$HF can be useful to
FIG. 1. Total correlation energy (in units of $t$), predicted by $S_z$HF and the non-unitary based ansätze, for 1D Hubbard model calculations as a function of the number of sites $N_s$. The calculations were performed at half-filling, with $U = 4t$. The correlation energy has been defined with respect to the broken-symmetry HF solution.

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 $-6.9204t$, nu-HF recovers 17%, $S_z$HF recovers 34%, and nu-$S_z$HF recovers 53% of the missing correlation energy in the broken-symmetry HF solution. Full spin and linear momentum projection may be used to recover even a larger fraction of correlation energy, as has been shown for projected HF methods in small size Hubbard 1D or 2D lattices [14, 24].
Comparison with other two-determinant approaches

The results shown so far indicate that nu-HF and nu-S₂HF improve upon HF and S₂HF, respectively. This is due to a combination of the more general canonical transformation being used and the fact that nu-HF and nu-S₂HF are explicitly constructed as two-determinant configurations.

It is interesting to compare the non-unitary 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 non-unitary 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 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 \( \{I, \hat{K}\} \), where \( \hat{I} \) is the identity operator and \( \hat{K} \) is the complex conjugation operator, the time-reversal group built with the elements \( \{I, \hat{\Theta}\} \), where \( \hat{\Theta} = \exp(i \pi \hat{S}_y) \hat{K} \) is the time-reversal operator, or the \( C_2 \) group for even lattices built with the elements \( \{\hat{I}, \hat{C}_{N_s/2}\} \), where \( \hat{C}_{N_s/2} \) is the operator performing a 180-degree rotation of the lattice.

We here consider the complex conjugation group as a representative example. In this subsection, we compare our non-unitary based ansätze with KHF, or complex-conjugation restored HF, and KS₂HF, or complex-conjugation and S₂-projected HF:

\[
|\Psi^{\text{KHF}}\rangle = c_1 |\Phi\rangle + c_2 \hat{K} |\Phi\rangle, \tag{88}
\]

\[
|\Psi^{\text{KS}_2\text{HF}}\rangle = c_1 \hat{P}^{S_z} |\Phi\rangle + c_2 \hat{P}^{S_z} \hat{K} |\Phi\rangle, \tag{89}
\]

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

Figure 2 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 \( (N/N_s = 1) \) nu-HF and KHF yield exactly the same correlation energy. In this sense, the full flexibility of the non-unitary transformation is not being exploited in the solution. At other fillings, on the other hand, nu-HF is able to improve substantially over KHF. In contrast, nu-S₂HF yields lower energies (or larger 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 wavefunction
FIG. 2. 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 $N = 8$.

will result in lower energies for every system. We have shown, however, that ans"atze based on a non-unitary canonical transformation yield lower energies than HF or projected-HF methods. They even yield lower energies than KHF or projected-KHF solutions in some cases, despite the fact that complex-conjugation projected wavefunctions are also two-determinant configurations, even if they result from a single, unitary canonical transformation.

IX. CONCLUSIONS

The HF and the HFB wavefunctions constitute the building blocks upon which more elaborate many-body methods rely. They are built out of a set of independent quasi-particles 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 a HF-type formalism in order to have more variational flexibility in the considered wavefunctions.

The properties of $N$-particle Slater determinants constructed from a set of HF-type operators resulting from a non-unitary 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.

An ansatz based on a single Slater determinant is incapable of utilizing the full flexibility of a non-unitary transformation. We have therefore introduced a two-determinant ansatz, defined by Eq. 42, where all the degrees of freedom of a HF-type non-unitary transformation are used. This, however, is not a limitation of the non-unitary 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 non-unitary transformation provides additional degrees of freedom that can be used in the variational problem. A symmetry-broken wavefunction 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 non-unitary canonical transformation, affording even more flexibility than that which a projected HF state based on a unitary HF transformation has. A non-unitary 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 non-unitary Bogoliubov transformation is possible and will be presented in a forthcoming publication.
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Appendix A: Proof of Thouless’ theorem

In order to prove the extension to Thouless’ theorem stated in section IV, we start by introducing the operators 
\[ \{ \hat{b}^\dagger_h, b_p, \overline{b}_h, \overline{b}^\dagger_p \} \] and \[ \{ \hat{d}^\dagger_h, d_p, \overline{d}_h, \overline{d}^\dagger_p \} \], such that \( \{ \hat{b}^\dagger_h, b_p \} \) kill the vacuum \( |\Phi_0\rangle \) and \( \{ \overline{b}_h, \overline{b}^\dagger_p \} \) kill the vacuum \( |\overline{\Phi}_0\rangle \), while \( \{ \hat{d}^\dagger_h, d_p \} \) annihilate the vacuum \( |\Phi_1\rangle \) and \( \{ \overline{d}_h, \overline{d}^\dagger_p \} \) annihilate the vacuum \( |\overline{\Phi}_1\rangle \). We assume that both sets obey the anti-commutation rules defined by Eq. 14. We explicitly write these operators in the form of Eqs. 9 and 12; that is,
\[
\hat{b}^\dagger_h = \sum_j D^0_{jh} c_j^\dagger, \quad \hat{b}_h = \sum_j D^0_{jh}^* c_j, \quad \overline{b}^\dagger_p = \sum_j D^0_{jp} c_j^\dagger, \quad \overline{b}_p = \sum_j D^0_{jp}^* c_j,
\]
\[
\hat{d}^\dagger_h = \sum_j D^1_{jh} c_j^\dagger, \quad \hat{d}_h = \sum_j D^1_{jh}^* c_j, \quad \overline{d}^\dagger_p = \sum_j D^1_{jp} c_j^\dagger, \quad \overline{d}_p = \sum_j D^1_{jp}^* c_j,
\]
where the superscripts on the matrices indicate the state to which the operators correspond.

We can now relate the operators \( \{ \hat{d}^\dagger_h, d_p \} \) to the operators \( \{ \hat{b}^\dagger_h, b_p \} \) by using the inverse transformation discussed in Eq. 15. We arrive at
\[
\hat{d}^\dagger_h = \sum_{h'} L^*_{h'h} \hat{b}^\dagger_{h'} + \sum_p Y^*_{ph} \overline{b}_p^\dagger, \quad \hat{d}_h = \sum_{h'} \tilde{L}_{h'p} \hat{b}_p + \sum_p \tilde{Y}_{hp} \overline{b}_h, \quad \text{(A1a)}
\]
\[
d_p = \sum_{p'} M_{p'p} \hat{b}_{p'} + \sum_h \tilde{Y}_{hp} \overline{b}_h, \quad \text{(A1b)}
\]
where we have set
\[
L^*_{h'h} = \left( \tilde{D}^{0\dagger} D^1 \right)_{h'h}, \quad \text{(A2a)}
\]
\[
M_{p'p} = \left( \tilde{D}^{0\dagger} D^1 \right)_{p'p}, \quad \text{(A2b)}
\]
\[
Y_{ph} = \left( D^{0\dagger} D^1 \right)_{ph}, \quad \text{(A2c)}
\]
\[
\tilde{Y}_{hp} = \left( D^{0\dagger} D^1 \right)_{hp}. \quad \text{(A2d)}
\]
We now assume that the $N \times N$ matrix $L$ is invertible, which is only true if $\langle \Phi_0 | \Phi_1 \rangle \neq 0$ (see Eq. 21). In such a case, the matrix $M$ is also invertible. We now introduce the operators

$$d_h^\dagger = \sum_{h'} (L^{s-1})_{h'h} d_{h'}^\dagger,$$

(A3a)

$$\tilde{d}_p = \sum_{p'} (M^{-1})_{p'p} d_{p'}.$$

(A3b)

Inserting Eq. A3 into Eq. A1 we arrive at

$$d_h^\dagger = b_h^\dagger + \sum_p Z_{ph} \tilde{b}_p^\dagger,$$

(A4a)

$$\tilde{d}_p = b_p + \sum_h W_{ph} \tilde{b}_h,$$

(A4b)

where we have set

$$Z_{ph} = \sum_{h'} Y_{ph'}^* (L^{s-1})_{h'h},$$

(A5a)

$$W_{ph} = \sum_{p'} \bar{Y}_{hp'} (M^{-1})_{p'p}.$$  

(A5b)

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

$$d_h^\dagger = b_h^\dagger + \sum_p Z_{ph} \tilde{b}_p^\dagger,$$

(A6a)

$$\tilde{d}_p = b_p - \sum_h Z_{ph} \tilde{b}_h.$$  

(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

$$\left[ b_h^\dagger, \exp \left( \sum_{p' h'} Z_{p'h'} b_{p'}^\dagger b_{h'} \right) \right] = \left( -\sum_p Z_{ph} b_p^\dagger \right) \exp \left( \sum_{p' h'} Z_{p'h'} b_{p'}^\dagger b_{h'} \right),$$

(A7a)

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

(A7b)

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

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

(A8a)

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

(A8b)
This essentially completes the proof. \( \{ \tilde{d}^\dagger_h, \tilde{d}_p \} \) annihilate the r.h.s. of Eq. [A6b] The operators \( \{ d^\dagger_h, d_p \} \) that kill the vacuum \( |\Phi_1\rangle \) on the l.h.s. of Eq. [A6b] are simple linear combinations of \( \{ \tilde{d}^\dagger_h, \tilde{d}_p \} \); \( N \)-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. [B3] are evaluated as

\[
\langle \Phi|\tilde{R}_\theta|\Phi \rangle = \det_N D^T R(\theta) D^*, \tag{B1a}
\]

\[
\langle \Phi|\tilde{R}_\theta|\Phi \rangle = \det_N \tilde{D}^T R(\theta) \tilde{D}^*, \tag{B1b}
\]

\[
\langle \Phi|\tilde{R}_\theta|\Phi \rangle = \det_N D^T R(\theta) \tilde{D}^*, \tag{B1c}
\]

\[
\langle \Phi|\tilde{R}_\theta|\Phi \rangle = \det_N \tilde{D}^T R(\theta) \tilde{D}^*. \tag{B1d}
\]

The Hamiltonian kernels appearing in Eq. [B2] are evaluated in terms of transition density matrices as

\[
\frac{\langle \Phi_\alpha|\hat{H} \tilde{R}_\theta|\Phi_\beta \rangle}{\langle \Phi_\alpha|\tilde{R}_\theta|\Phi_\beta \rangle} = \text{Tr} \left( h \rho^{\alpha\beta}(\theta) + \frac{1}{2} \Gamma^{\alpha\beta}(\theta) \rho^\alpha(\theta) \right), \tag{B2}
\]

\[
\Gamma^{\alpha\beta}_{ik}(\theta) = \sum_{jl} \langle ij|\hat{v}|kl \rangle \rho_{ij}^{\alpha\beta}(\theta). \tag{B3}
\]

The transition density matrices are in turn given by

\[
\rho_{ki}^{11}(\theta) = \frac{\langle \Phi|c_i^\dagger \tilde{c}_k \hat{R}_\theta|\Phi \rangle}{\langle \Phi|\hat{R}_\theta|\Phi \rangle} = \sum_h D_{ih} \tilde{D}_{kh}^* + \sum_{ph} D_{ih} \bar{Z}_{ph}^{(11)}(\theta) D_{kp}^*, \tag{B4a}
\]

\[
\rho_{ki}^{12}(\theta) = \frac{\langle \Phi|c_i^\dagger \tilde{c}_k \hat{R}_\theta|\Phi \rangle}{\langle \Phi|\hat{R}_\theta|\Phi \rangle} = \sum_h D_{ih} \tilde{D}_{kh}^* + \sum_{ph} D_{ih} \bar{Z}_{ph}^{(12)}(\theta) D_{kp}^*, \tag{B4b}
\]

\[
\rho_{ki}^{21}(\theta) = \frac{\langle \Phi|c_i^\dagger \tilde{c}_k \hat{R}_\theta|\Phi \rangle}{\langle \Phi|\hat{R}_\theta|\Phi \rangle} = \sum_h \tilde{D}_{ih} D_{kh}^* + \sum_{ph} \bar{D}_{ih} \bar{Z}_{ph}^{(21)}(\theta) \tilde{D}_{kp}^*, \tag{B4c}
\]

\[
\rho_{ki}^{22}(\theta) = \frac{\langle \Phi|c_i^\dagger \tilde{c}_k \hat{R}_\theta|\Phi \rangle}{\langle \Phi|\hat{R}_\theta|\Phi \rangle} = \sum_h \tilde{D}_{ih} D_{kh}^* + \sum_{ph} \bar{D}_{ih} \bar{Z}_{ph}^{(22)}(\theta) \tilde{D}_{kp}^*. \tag{B4d}
\]
Here,

\[
Z^{(11)}_{ph}(\theta) = \sum_{h'} \left( \bar{D}^\top \mathcal{R}(\theta) D^* \right)_{ph'} \left( \mathcal{L}^{(11)*-1}(\theta) \right)_{h'h}, \tag{B5a}
\]

\[
Z^{(12)}_{ph}(\theta) = \sum_{h'} \left( \bar{D}^\top \mathcal{R}(\theta) \bar{D}^* \right)_{ph'} \left( \mathcal{L}^{(12)*-1}(\theta) \right)_{h'h}, \tag{B5b}
\]

\[
Z^{(21)}_{ph}(\theta) = \sum_{h'} \left( D^\top \mathcal{R}(\theta) D^* \right)_{ph'} \left( \mathcal{L}^{(21)*-1}(\theta) \right)_{h'h}, \tag{B5c}
\]

\[
Z^{(22)}_{ph}(\theta) = \sum_{h'} \left( D^\top \mathcal{R}(\theta) \bar{D}^* \right)_{ph'} \left( \mathcal{L}^{(22)*-1}(\theta) \right)_{h'h}, \tag{B5d}
\]

and

\[
\mathcal{L}^{(11)}_{h'h}(\theta) = \left( D^\dagger R^*(\theta) D \right)_{h'h}, \tag{B6a}
\]

\[
\mathcal{L}^{(12)}_{h'h}(\theta) = \left( D^\dagger R^*(\theta) \bar{D} \right)_{h'h}, \tag{B6b}
\]

\[
\mathcal{L}^{(21)}_{h'h}(\theta) = \left( \bar{D}^\dagger R^*(\theta) D \right)_{h'h}, \tag{B6c}
\]

\[
\mathcal{L}^{(22)}_{h'h}(\theta) = \left( \bar{D}^\dagger R^*(\theta) \bar{D} \right)_{h'h}. \tag{B6d}
\]

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

\[
\langle \Phi | \hat{b}^\dagger_{h} \hat{b}_{p} \hat{R}_{\theta} | \Phi \rangle = \sum_{mn} \bar{D}^*_{mh} \bar{D}_{np} \rho_{nm}^{11}(\theta), \tag{B7a}
\]

\[
\langle \Phi | \hat{b}^\dagger_{h} \hat{b}_{p} \hat{R}_{\theta} | \Phi \rangle = \sum_{mn} D^*_{mh} D_{np} \rho_{nm}^{21}(\theta), \tag{B7b}
\]

\[
\langle \Phi | \hat{b}^\dagger_{h} \hat{b}_{p} \hat{R}_{\theta} | \Phi \rangle = \sum_{mn} \bar{D}^*_{mh} \bar{D}_{np} \rho_{nm}^{12}(\theta), \tag{B7c}
\]

\[
\langle \Phi | \hat{b}^\dagger_{h} \hat{b}_{p} \hat{R}_{\theta} | \Phi \rangle = \sum_{mn} D^*_{mh} D_{np} \rho_{nm}^{22}(\theta). \tag{B7d}
\]
Similarly, the Hamiltonian-like matrix elements in Eq. \[86\] can be evaluated as

\[
\frac{\langle \Phi \mid \hat{b}_p^\dagger \hat{b}_p \hat{H} \hat{R}_\theta \mid \Phi \rangle}{\langle \Phi \mid \hat{R}_\theta \mid \Phi \rangle} = \sum_{mn} \bar{D}_{mh} \bar{D}_{np} \rho_{nm}^{11}(\theta) \frac{\langle \Phi \mid \hat{H} \hat{R}_\theta \mid \Phi \rangle}{\langle \Phi \mid \hat{R}_\theta \mid \Phi \rangle} + \sum_{mn \ ik} \bar{D}_{mh} \bar{D}_{np} \left( h_{ik} + \Gamma_{1k}^{11}(\theta) \right) \rho_{ik}^{11}(\theta) \left( \delta_{ni} - \rho_{ni}^{11}(\theta) \right), \tag{B8a}
\]

\[
\frac{\langle \Phi \mid \hat{b}_p^\dagger \hat{b}_p \hat{H} \hat{R}_\theta \mid \Phi \rangle}{\langle \Phi \mid \hat{R}_\theta \mid \Phi \rangle} = \sum_{mn} D_{mh} D_{np} \rho_{nm}^{21}(\theta) \frac{\langle \Phi \mid \hat{H} \hat{R}_\theta \mid \Phi \rangle}{\langle \Phi \mid \hat{R}_\theta \mid \Phi \rangle} + \sum_{mn \ ik} D_{mh} D_{np} \left( h_{ik} + \Gamma_{1k}^{21}(\theta) \right) \rho_{ik}^{21}(\theta) \left( \delta_{ni} - \rho_{ni}^{21}(\theta) \right), \tag{B8b}
\]

\[
\frac{\langle \Phi \mid \hat{b}_p^\dagger \hat{b}_p \hat{H} \hat{R}_\theta \mid \Phi \rangle}{\langle \Phi \mid \hat{R}_\theta \mid \Phi \rangle} = \sum_{mn} \bar{D}_{mh} \bar{D}_{np} \rho_{km}^{12}(\theta) \frac{\langle \Phi \mid \hat{H} \hat{R}_\theta \mid \Phi \rangle}{\langle \Phi \mid \hat{R}_\theta \mid \Phi \rangle} + \sum_{mn \ ik} \bar{D}_{mh} \bar{D}_{np} \left( h_{ik} + \Gamma_{ik}^{12}(\theta) \right) \rho_{ik}^{12}(\theta) \left( \delta_{ni} - \rho_{ni}^{12}(\theta) \right), \tag{B8c}
\]

\[
\frac{\langle \Phi \mid \hat{b}_p^\dagger \hat{b}_p \hat{H} \hat{R}_\theta \mid \Phi \rangle}{\langle \Phi \mid \hat{R}_\theta \mid \Phi \rangle} = \sum_{mn} D_{mh} D_{np} \rho_{km}^{22}(\theta) \frac{\langle \Phi \mid \hat{H} \hat{R}_\theta \mid \Phi \rangle}{\langle \Phi \mid \hat{R}_\theta \mid \Phi \rangle} + \sum_{mn \ ik} D_{mh} D_{np} \left( h_{ik} + \Gamma_{ik}^{22}(\theta) \right) \rho_{ik}^{22}(\theta) \left( \delta_{ni} - \rho_{ni}^{22}(\theta) \right). \tag{B8d}
\]

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[31] Note that this definition is not the one suggested by Löwdin [15] and commonly used in quantum chemistry, in which the correlation energy is defined with respect to the symmetry-preserving RHF solution.