Flexible Ansatz for N-body Configuration Interaction

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Abstract

We present a Flexible Ansatz for N-body Configuration Interaction (FANCI) that includes any multideterminant wavefunction. This ansatz is a generalization of the Configuration Interaction (CI) wavefunction, where the coefficients are replaced by a specified function of certain parameters. By making an appropriate choice for this function, we can reproduce popular wavefunction structures like CI, Coupled-Cluster, Tensor Network States, and geminal-product wavefunctions. The universality of this framework suggests a programming structure that allows for the easy construction and optimization of arbitrary wavefunctions. Here, we will discuss the structures of the FANCI framework and its implications for wavefunction properties, particularly accuracy, cost, and size-consistency. We demonstrate the flexibility of this framework by reconstructing popular wavefunction ans"atsze and modifying them to construct novel wavefunction forms. FANCI provides a powerful framework for exploring, developing, and testing new wavefunction forms.

Keywords: multi-reference quantum chemistry; projected Schrödinger equation, antisymmetric geminal product, coupled cluster, tensor network, wavefunction ansätze

1. Introduction

In this paper, we focus on electronic systems, whose Hamiltonian can be written as

\[ \hat{H}_{\text{elec}} = \sum_{ij} h_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \] (1)

where \( h_{ij} \) and \( g_{ijkl} \) are the one- and two-electron integrals and \( a_i^\dagger \) (\( a_i \)) creates (annihilates) the \( i^{\text{th}} \) spin-orbital. The exact solutions to the electronic Hamiltonian can be written as a linear
combination of all possible \(N\)-electron basis functions (Slater determinants) formed from the given set of spin-orbitals. This is the Full Configuration Interaction (FCI) wavefunction\[^1\]:

\[
|\Psi_{\text{FCI}}\rangle = \sum_{m}^{(2K)/N} C_{m} |m\rangle
\]

where \(2K\) is the number of spin-orbitals, \(N\) is the number of electrons, and \(C_{m}\) is the coefficient of the Slater determinant \(|m\rangle\). We can think of \(m\) as an occupation vector that specifies which of the \(2K\) spin-orbitals are occupied to construct the \(N\)-electron basis functions. The number of parameters for the FCI wavefunction scales combinatorially with the number of orbitals and electrons, so brute-force direct calculations of the FCI wavefunctions are restricted to small systems with small basis sets.

Various approximations can be made to the Schrödinger equation to bring down its cost: (1) simplify the Hamiltonian, (2) find alternative algorithms, and (3) parameterize the FCI wavefunction\[^2, 3, 4, 5, 6, 7, 8, 9, 10\]. In this article, we focus on the parameterization of the FCI wavefunction.

The simplest approximation to the FCI wavefunction involves explicitly selecting (or truncating) the Slater determinants that contribute to the wavefunction. Such wavefunctions are broadly termed selected Configuration Interaction (CI) wavefunctions:

\[
|\Psi_{\text{CI}}\rangle = \sum_{m \in S} C_{m} |m\rangle
\]

where \(S\) is a subset of the Slater determinants within the given basis. The Slater determinants can be selected by seniority, such as the doubly occupied CI (DOCI) wavefunction\[^11, 12, 13, 14, 15\], or by excitation-level relative to a reference Slater determinant, such as CI singles and doubles (CISD) wavefunction\[^23\]. Alternatively, we can select all (or many) of the Slater determinants in a given set of orbitals. This leads to active-space methods like CASSCF\[^24\], RASSCF\[^25\], and MCSCF\[^26\]. Finally, if the orbitals are localized, the Slater determinants that embody chemically intuitive concepts can be linearly combined to construct Valence Bond (VB) structures\[^27, 28, 29, 30, 31\]. This leads to VBCI methods. While there are many variants of the CI wavefunction, most are not size-consistent and choosing an efficient set of orbitals/determinants is molecule and geometry dependent. For truly strongly-correlated systems, which have myriad Slater determinants with small yet significant contributions, selected CI methods generally fail.

Alternatively, the FCI wavefunction can be approximated by an alternative form (ansatz), such as a nonlinear function of parameters that are not simply the coefficients of the Slater determinants.
For example, the Coupled-Cluster (CC) wavefunction parameterizes the CI wavefunction using an exponential ansatz:

$$\Psi_{CC} = \exp \left( \sum_i a_i \hat{E}_i + \sum_{i<j} a_a a_b \hat{E}_{ij} + \ldots \right) \Phi_{HF}$$

$$= \exp \left( \sum_{1,a} t^a_{i,a} \hat{E}_i^{a} \right) \Phi_{HF}$$

(4)

where $\hat{E}_i^a$ is an excitation operator that excites electrons from a set of occupied orbitals $i$ to a set of virtual orbitals $a$, $t^a_{i,a}$ is the associated coefficient/amplitude, and $\tilde{S}_E$ is the set of allowed excitation operators. Just as in CI wavefunctions, the complexity of the wavefunction (and the number of parameters) can be controlled by truncating the set of excitation operators used.

Tensor Product State (TPS) wavefunctions are expressed with respect to parameters that describe the correlations between spatial orbitals of different states (occupations):

$$\Psi_{TPS} = \sum_{n_1 \ldots n_K} \ldots \sum_{i_{12} \ldots i_{1K}} (M_1)^{n_1}_{i_{12} \ldots i_{1K}} (M_2)^{n_2}_{i_{12} \ldots i_{2K}} \ldots (M_K)^{n_K}_{i_{1K} \ldots i_{K-1K}} |n_1 \ldots n_K\rangle$$

(5)

where $n_j$ is the occupation of the $j^{th}$ spatial orbital, $i_{jk}$ is an auxiliary index that represents the correlation of $j^{th}$ orbital with the $k^{th}$ orbital, and $M_j$ is a tensor that describes the correlation between the $j^{th}$ orbital and the other orbitals. Each tensor is connected to others by at least one auxiliary index, meaning that the correlation between orbitals is represented by tensor contraction on the auxiliary indices. The specific auxiliary indices used in the tensor-contraction control the correlations that the wavefunction explicitly captures and thereby the complexity of the wavefunction. The Matrix Product State (MPS) wavefunction simplifies the TPS wavefunction by only correlating the orbitals that are adjacent to each other in an ordered list:

$$\Psi_{MPS} = \sum_{n_1,n_2,\ldots,n_{K-1},n_K} \ldots \sum_{i_{12} \ldots i_{1K}} (M_1)^{n_1}_{i_{12}} (M_2)^{n_2}_{i_{12}i_{23}} \ldots (M_K)^{n_K}_{i_{K-1K}} |n_1 n_2 \ldots n_{K-1} n_K\rangle$$

(6)

MPS wavefunctions are usually optimized using the Density Matrix Renormalization Group (DMRG) algorithm.
While MPS and TPS wavefunctions describe, in essence, the contribution of each orbital to the wavefunction, the Antisymmetrized Product of Geminals (APG) wavefunction describes the contribution of each electron pair (geminal) to the wavefunction:

\[
|\Psi_{\text{APG}}\rangle = \frac{N}{2} \prod_{p=1}^{N/2} G_p^\dagger |0\rangle
\]

where \(G_p^\dagger\) is the creation operator of the \(p\)th geminal and \(C_{p;ij} a_i^\dagger a_j^\dagger |0\rangle\) is the contribution of the \(i\)th and \(j\)th spin-orbitals to the \(p\)th geminal. Again, the complexity and the accuracy of this wavefunction can be controlled by limiting the number of terms in the wavefunction. For example, we can choose a set of orbital pairs that contribute to the wavefunction. The Antisymmetrized Product of Interacting Geminals (APIG) wavefunctions and its variants only use spin-orbital pairs from the same spatial orbital:

\[
|\Psi_{\text{APIG}}\rangle = \frac{N}{2} \prod_{p=1}^{N/2} G_p^\dagger |0\rangle
\]

where \(a_i^\dagger\) and \(a_i^\dagger\) are the creation operators of the alpha and beta spin-orbitals corresponding to the \(i\)th spatial orbital.

Each of these wavefunction ansätze seems to be fundamentally different in its nomenclature, structure, and computation. Yet every wavefunction approximates the FCI wavefunction, and through this common goal, they are intrinsically connected to one another. There are known mathematical connections between certain ansätze and these are occasionally exploited to derive new flavours of these methods. For example, many geminal methods can be rewritten as special CC wavefunctions. However, these insights are seldom transferred between ansätze and the development of new ansätze seems even rarer. If the goal within electronic structure theory is to find the ansatz that strikes the best balance between the cost and accuracy for a given system,
then do we not limit ourselves by committing to a particular ansatz and its assumptions? In this article, we present a general wavefunction structure in which new ansätze can be easily developed and relations between existing ansätze can be elucidated. We express popular existing multideterminant ansätze (CI, CC, TPS, and APG wavefunctions) within this framework and develop new structures by combining their features. We hope to demonstrate that wavefunction design can be reduced to unique combinations of modular structures, indicating that an incredible number of “new” ansätze can be trivially developed.

2. Flexible Ansatz for N-particle Configuration Interaction (FANCI)

The proposed wavefunction structure is quite simple and resembles the CI wavefunction (Equation 3):

$$|\Psi_{\text{FANCI}}\rangle = \sum_{m \in S_m} f(m, \vec{P}) |m\rangle$$ (9)

where $S_m$ is a set of allowed Slater determinants and $f$ is a function that controls the weight of each Slater determinant, $m$, using the parameters, $\vec{P}$. Since Slater determinants can be uniquely represented with an excitation operator and a reference, Equation 9 can be rewritten with respect to excitation operators, $\hat{E}$.

$$|\Psi_{\text{FANCI}}\rangle = \sum_{\hat{E} \in S_{\hat{E}}} f(\hat{E}, \vec{P}) \hat{E} |\Phi_{\text{ref}}\rangle$$ (10)

where $S_{\hat{E}}$ is a set of allowed excitation operators and $f$ is a function that maps the weight of the excitation operator from $\hat{E}$ and $\vec{P}$. The $S_m$ and $S_{\hat{E}}$ are equivalent representations of a set of Slater determinants and can be used interchangeably.

In this paper, we aim to demonstrate the generality, utility, and flexibility of this framework. In the next section, we show that the framework is general by expressing popular ansätze as FANCI wavefunctions. Then, in Section 4, we discuss how the choices of $S$, $\vec{P}$, and $f$ affect the accuracy, cost, and size-consistency of the wavefunction. Finally, we demonstrate the flexibility of this framework by constructing novel wavefunction structures.

3. Examples

3.1. Hartree-Fock

The ground-state Hartree-Fock (HF) wavefunction is the Slater determinant of orthonormal orbitals that provides the lowest energy\textsuperscript{105, 106}. Starting from an arbitrary set of orthonormal
orbitals, created by \{a^\dagger_j\}, the HF wavefunction can be obtained by optimizing the unitary transformation that provides the lowest energy.

\[
|\Psi_{HF}\rangle = \prod_{i=1}^{N} \left( \sum_{j=1}^{2K} a^\dagger_j U_{ji} \right) |0\rangle 
\]

\[
= \sum_m |U(m)|^- |m\rangle 
\]

where \(U\) is a unitary matrix, and \(U(m)\) is a submatrix of \(U\) obtained by selecting the rows that correspond to the spin-orbitals in \(m\). The derivation is given in the Appendix 8.1. If only \(N\) orthonormal orbitals are rotated, or alternatively, if there is no mixing of the occupied and virtual orbitals, then the HF wavefunction is obtained trivially:

\[
|\Psi_{HF}\rangle = \prod_{i=1}^{N} \left( \sum_{j=1}^{N} a^\dagger_j U_{ji} \right) |0\rangle 
\]

\[
= |U(m)|^- |m\rangle 
\]

where \(m\) is the set of the occupied orbitals. With normalization, \(|U(m)|^-\) becomes 1. In other words, the HF wavefunction is invariant to rotation of the occupied orbitals if there is no mixing between occupied and virtual orbitals [107].

### 3.2. Truncated Configuration Interaction

The truncated CI wavefunction (Equation 3) is a linear combination of selected Slater determinants [108]. Such wavefunctions can be trivially described in the proposed framework: the set of allowed Slater determinants, \(S\), is the same; the parameters, \(\tilde{P}\), are the coefficients of the Slater determinants, \(\tilde{C}\); and the parameterizing function, \(f\), simply selects the appropriate coefficient, \(C_m\), given the Slater determinant, \(m\).

\[
f(m, \tilde{C}) = \tilde{e}_m \cdot \tilde{C}
\]

where \(\tilde{e}_m\) is a vector that gives 1 in the position of \(m\) and 0 elsewhere. Altogether, the CI wavefunction is

\[
|\Psi_{CI}\rangle = \sum_{m \in S_m} \left( \tilde{e}_m \cdot \tilde{C} \right) |m\rangle 
\]

If the CI wavefunction is expressed with respect to excitations on a reference, we get

\[
|\Psi_{CI}\rangle = \sum_{E_i \in S_E} \left( \tilde{e}_{E_i} \cdot \tilde{C} \right) \tilde{E}_i |\Phi_{ref}\rangle 
\]
3.3. Coupled-Cluster

The CC wavefunction (Equation 13) uses the exponential operator to approximate high-order excitations as a product of lower-order excitations [109].

\[ |\Psi_{CC}\rangle = \exp(\hat{T})|\Phi_{HF}\rangle \]

\[ = \sum_{n=0}^{\infty} \frac{1}{n!}\hat{T}^n|\Phi_{HF}\rangle \]

where

\[ \hat{T} = \sum_{\hat{E}^a_t \in \tilde{S}_E} t^a \hat{E}^a_t \]

and \( \tilde{S}_E \) is a set of excitation operators. The Maclaurin series in Equation 15 lets one express the CI coefficients in terms of CC cluster amplitudes \( t^a_i \). Specifically, the cluster amplitudes are cumulants of the CI coefficients [110, 111, 112, 113, 114]. The powers of \( \hat{T} \) (cluster operator) give the wavefunction access to excitations beyond those allowed (\( \tilde{S}_E \)) by generating all (product-wise) combinations of the allowed excitation operators. However, an excitation can be described with different combinations of excitation operators, and the cumulant can be simplified by grouping together terms that correspond to the same excitation (or Slater determinant). Each combination corresponds to a subset of \( \tilde{S}_E \), such that the set of all Slater determinants in the CC wavefunction can be described in terms of all possible subsets of \( \tilde{S}_E \):

\[ S_E = \left\{ \prod_{\hat{E}_k \in T} \hat{E}_k \bigg| T \subseteq \tilde{S}_E \right\} \]

Then, the wavefunction can be written as a sum over all possible Slater determinants and a sum over all possible combinations of excitation operators that produce the given Slater determinant.

\[ f(\hat{E}_1^a, t) = \sum_{\{ \hat{E}_1^{a_1}...\hat{E}_n^{a_n} \} \subseteq \tilde{S}_E} \text{sgn}(\sigma_{\hat{E}_1^{a_1}...\hat{E}_n^{a_n}}) \frac{1}{n!} \begin{pmatrix} t_{1 i_1}^{a_1} & \cdots & t_{1 i_n}^{a_n} \\ \vdots & \ddots & \vdots \\ t_{n i_1}^{a_1} & \cdots & t_{n i_n}^{a_n} \end{pmatrix} \]

\[ = \sum_{\{ \hat{E}_1^{a_1}...\hat{E}_n^{a_n} \} \subseteq \tilde{S}_E} \text{sgn}(\sigma_{\hat{E}_1^{a_1}...\hat{E}_n^{a_n}}) \prod_{k=1}^{n} t_{k i_k}^{a_k} \]

\[ \text{sgn}(\sigma_{\hat{E}_1^{a_1}...\hat{E}_n^{a_n}}) = \left\{ \begin{array}{cl} 1 & \text{if } \sigma_{\hat{E}_1^{a_1}...\hat{E}_n^{a_n}} \text{ is even} \\ -1 & \text{if } \sigma_{\hat{E}_1^{a_1}...\hat{E}_n^{a_n}} \text{ is odd} \end{array} \right. \]
where \( n \) is the dimension of the subset \( \{ \hat{E}_a \} \). The sum can be interpreted as a sum over all possible partitions of a given excitation operator, \( \hat{E}_a \), into excitations from the given set. The signature of the permutation, \( \text{sgn}(\sigma_\hat{E}_a) \), results from reordering the creation and annihilation operators of the lower-order excitations to the same order as the given excitation operator:

\[
\hat{E}_a = \text{sgn}(\sigma_\hat{E}_a) \hat{E}_a \hat{E}_a \cdot \cdot \cdot \hat{E}_a
\]

(19)

The permanent, \( |A| \), accounts for all possible orderings within a given set of excitation operators. Altogether, the CC wavefunction can be reformulated as

\[
|\Psi_{CC}\rangle = \sum_{\hat{E}_a \in \mathcal{S}} \left( \sum_{\substack{\{\hat{E}_a\}_{i=1}^n \subseteq \mathcal{S} \\ \text{sgn}(\prod_{k=1}^n \hat{E}_a_{i_k}) = \hat{E}_a_{i_1} \hat{E}_a_{i_2} \cdot \cdot \cdot \hat{E}_a_{i_n}}} \right) \hat{E}_a |\Phi_{HF}\rangle
\]

(20)

More details are provided in the Appendix 8.4.

### 3.4. Tensor Product State

The TPS (and MPS) wavefunction (Equation 5) determines the weight of a Slater determinant by tensor (and matrix) contractions, where each shared index corresponds to a correlation between orbitals:

\[
|\Psi_{TPS}\rangle = \sum_{n_1, \ldots, n_K} \sum_{i_1, \ldots, i_K} (M_1)_{i_1}^{n_1} (M_2)_{i_2}^{n_2} \cdots (M_K)_{i_K}^{n_K} |n_1 \cdots n_K\rangle
\]

Each spatial orbital, \( k \), is associated with a tensor, \( M_k \), and each tensor is associated with the occupation of its spatial orbital (i.e., its state), \( n_k \), and with other tensors using its auxiliary indices, \( \{i_k \cdots i_{k-1} \} \). Then, the coefficient associated with the Slater determinant, represented by \( \{n_1 \cdots n_K\} \), is approximated by tensor-contraction. Many variants of TPS, including MPS, impose some structure on the tensor product so that the evaluation and optimization of the wavefunction are computationally tractable.

Since \( \{n_1 \cdots n_K\} \) is yet another representation of the Slater determinant, we can describe the wavefunction with respect to \( n \):

\[
n = \{n_1 \cdots n_K\}
\]
Therefore, the TPS wavefunction can be rewritten as

\[ |\Psi_{TPS}\rangle = \sum_{n \in S_{FCI}} K \bigodot (M_k)^{n_k} |n\rangle \]  \hspace{1cm} (21)

where \( K \) is the number of spatial orbitals, and \( \bigodot \) describes the specific tensor-contraction used in the wavefunction. While it is not common to do so, the TPS wavefunctions can be equivalently expressed with respect to spin-orbitals. If each state of the TPS wavefunction corresponds to the occupation of a spin-orbital, \( m_k \), then the same notation can be used as in Equation 9

\[ |\Psi_{TPS}\rangle = \sum_{m \in S_{FCI}} 2^K \bigodot (M_k)^{m_k} |m\rangle \]  \hspace{1cm} (22)

where \( M_k \) is the tensor associated with spin-orbital \( k \).

### 3.5. Antisymmetrized Product of Geminals

Just as the HF wavefunction is constructed as an antisymmetrized product of one-electron wavefunctions (orbitals), the APG wavefunction is constructed as an antisymmetrized product of two-electron wavefunctions (geminals) \[66, 68, 69, 74\]:

\[ |\Psi_{APG}\rangle = \prod_{p=1}^{N/2} G_p^\dagger |0\rangle = \prod_{p=1}^{N/2} \sum_{ij}^ {2K} C_{p,ij} a_i^\dagger a_j^\dagger |0\rangle = \prod_{p=1}^{N/2} \sum_{m_k} C_{p,m_k} A_{m_k}^\dagger |0\rangle \]

where the \( m_k \) denotes a set of a pair of indices and \( A_{m_k}^\dagger \) denotes the creation operator that corresponds to \( m_k \). Similar to the CC wavefunction, the product of sums can be expanded out as a sum over each Slater determinant and a sum over the different combinations of electron pairs that create the Slater determinant. In the HF wavefunction, the product of sums results in a determinant due to the antisymmetry with respect to the interchange of electrons. In the APG wavefunction, however, the interchange of electron pairs is symmetric, and the product of sums results in a permanent. Given the set of all possible two-electron creation operators, \( \tilde{S} \), a subset of exactly \( N^2 \) two-electron creators, \( \{A_{m_1}^\dagger \ldots A_{m_{N/2}}^\dagger\} \), is needed to construct a given Slater determinant, \( m \), where the number of electrons, \( N \), is even. Since an orbital cannot be occupied more than once
and all the orbitals are necessary to construct a given Slater determinant, any selection of orbital pairs, \( \{m_1 \ldots m_{N/2}\} \), must be disjoint and exhaustive.

\[
\begin{align*}
  f(m, C) &= \sum_{\{m_1 \ldots m_{N/2}\} \subseteq \hat{S}} \sgn(\sigma_{m_1 \ldots m_{N/2}})|C(m_1, \ldots, m_{N/2})|^+ \\
  &= \sum_{\{m_1 \ldots m_{N/2}\} \subseteq \hat{S}} \sgn(\sigma_{m_1 \ldots m_{N/2}})|C(m_1, \ldots, m_{N/2})|^+ \\
  &= \prod_{i \in m} a_i^\dagger = \sgn(\sigma_{m_1 \ldots m_{N/2}}) \prod_{p=1}^{N/2} A_{m_p}^\dagger
\end{align*}
\]  

(23)

where the orbital pairs, \( \{m_1 \ldots m_{N/2}\} \), are selected such that they result in the given Slater determinant, \( m \), without duplicate orbitals. Similar to the CC wavefunction (Equation 18), the sum can be interpreted as a sum over all allowed partitions of the given Slater determinant into the electron pairs. The signature of the permutation, \( \sgn(\sigma_{m_1 \ldots m_{N/2}}) \), results from reordering the creation operators in the electron pairs to the same order as in the given Slater determinant:

\[
\prod_{i \in m} a_i^\dagger = \sgn(\sigma_{m_1 \ldots m_{N/2}}) \prod_{p=1}^{N/2} A_{m_p}^\dagger
\]  

(24)

 Altogether, the APG wavefunction is reformulated as

\[
|\Psi_{\text{APG}}\rangle = \sum_{m \in S_{\text{FCI}}^m} \left( \sum_{\{m_1 \ldots m_{N/2}\} \subseteq \hat{S}} \sgn(\sigma_{m_1 \ldots m_{N/2}})|C(m_1, \ldots, m_{N/2})|^+ \right) |m\rangle
\]  

(25)

where \( S_{\text{FCI}}^m \) is a set of all possible Slater determinants (i.e. Slater determinants of a FCI wavefunction). The derivation is given in the Appendix 8.2.

The Antisymmetrized Product of Interacting Geminals (APIG) is a special case of the APG wavefunction such that only the electron pairs within the same spatial orbital, i.e. doubly occupied spatial orbitals, are used to build the wavefunction. The sum over the partitions reduces to a single element because there is only one way to construct a given (seniority-zero) Slater determinant from electron pairs of doubly occupied orbitals.

\[
|\Psi_{\text{APG}}\rangle = \sum_{m \in S_{\text{DOCI}}^m} |C(m)|^+ |m\rangle
\]  

(26)
where $S^{\text{DOSi}}_m$ is the set of all seniority-zero (no unpaired electrons) Slater determinants, and $|C(m)|^+$ is a permanent of the parameters that correspond to the spatial orbitals used to construct $m$. The APIG wavefunction can be further simplified by imposing structures onto the permanent: the Antisymmetrized Product of 1-reference Orbitals Geminals (AP1roG) wavefunction assumes that a large portion of the coefficient matrix is an identity matrix \[103\]; and the Antisymmetrized Product of rank-2 Geminals (APr2G) wavefunction assumes that the coefficient matrix is a Cauchy matrix \[104\]. APr2G reduces the cost of evaluating a permanent ($O(n^3)$) to that of a determinant ($O(n!)$). AP1roG has the cost of $O(m!)$ where $m$ is the order of excitation with respect to the reference Slater determinant. It is cheap to evaluate the overlap of the AP1roG wavefunction with low-order excitations of the reference determinant.

3.6. Universality of FANCI

The CI, CC, TPS, and APG wavefunctions and their variants can be expressed within the FANCI framework using different $S$, $\vec{P}$, and $f$. We can define a multideterminant wavefunction as a function that has a well-defined overlap with a set of orthonormal Slater determinants. Provided that the wavefunction exists within the space spanned by the Slater determinants, the wavefunction can be re-expressed as a linear combination of Slater determinants via a projection:

$$|\Psi(\vec{P})\rangle = \sum_{m \in S_m} |m\rangle \langle m| \Psi(\vec{P})\rangle = \sum_{m \in S_m} f(m, \vec{P}) |m\rangle$$

(27)

where

$$f(m, \vec{P}) = \langle m | \Psi(\vec{P}) \rangle$$

(28)

Therefore, all multideterminant wavefunctions, as defined above, can be expressed within the framework of Equation 9: $S$ is the minimal set of Slater determinants required to fully describe the wavefunction; $\vec{P}$ is the parameters of the wavefunction; and $f$ is the overlap of the wavefunction with the Slater determinant, $m$.

4. Characteristics

In the formulation of Equation 9, a multideterminant wavefunction is defined using only a specified (sub)set of Slater determinants, $S$, wavefunction parameters, $\vec{P}$, and function $f$. Since the
characteristics of a wavefunction ansatz depend on its structure, all characteristics of a multideterminant wavefunction can be deduced from the specified $S$, $\vec{P}$, and $f$. Designing a wavefunction with desirable characteristics, therefore, merely requires selecting $S$, $\vec{P}$, and $f$. We propose to approach method development in electronic structure theory as a search for $S$, $\vec{P}$, and $f$ that induce the desired wavefunction features. While many features can be considered, and we shall consider additional features in future work, here we shall address just three important characteristics: accuracy, cost, and size-consistency.

4.1. Accuracy

Ultimately, the FANCI wavefunction models the FCI wavefunction by parameterizing the weights of each Slater determinant. If there are Slater determinants absent from the FANCI wavefunction, i.e. $S \subset S_{\text{FCI}}$, then the omitted Slater determinants are assumed to have no contributions to the FCI wavefunction. The effects of $S$ can be viewed as a modification of the parameterizing function.

$$|\Psi_{\text{FANCI}}\rangle = \sum_{m \in S_{\text{FCI}}} g(m, \vec{P}) |m\rangle$$

where

$$g(m, \vec{P}) = \begin{cases} f(m, \vec{P}) & ; m \in S \\ 0 & ; m \notin S \end{cases}$$

Alternatively, the FANCI wavefunction can be viewed as a model for the CI wavefunction built using the same restricted set of Slater determinants. In either case, preventing Slater determinants from contributing to the wavefunction will cause deviations from the FCI wavefunction.

As with any parameterization (or fitting) problem, it becomes easier to find a function that accurately describes each weight as the number of parameters increase. FANCI wavefunctions cannot be exact, in general, unless the number of parameters is greater than or equal to the number of parameters in the Hamiltonian which, in the case of electronic structure theory, means there should be at least as many parameters as there are two-electron integrals\textsuperscript{[115, 116]}. Methods with many fewer parameters are, typically, static correlation methods. On the other hand, appropriately constructed FANCI ansätze should approach the FCI limit as the number of parameters approaches the number of Slater determinants. However, the cost associated with optimizing the wavefunction typically increases superlinearly as the number of parameters increases.
4.2. Cost

The cost associated with a wavefunction can be divided into the cost of its storage, evaluation, and optimization, all of which are intricately linked. The cost of storage is associated with the number of parameters needed to describe the wavefunction. The cost of evaluating the wavefunction depends on the cost of evaluating $f$ and on the number of times $f$ needs to be evaluated. For example, in order to evaluate the norm of a wavefunction, $f$ must be evaluated for every Slater determinant in $S$.

$$
\langle \Psi | \Psi \rangle = \sum_{m \in S} \sum_{n \in S} f^*(m) \langle m | n \rangle f(n) = \sum_{m \in S} f^*(m)f(m)
$$

Upon optimization, a new set of parameters are found such that the wavefunction satisfies the Schrödinger equation.

$$
\hat{H} | \Psi \rangle = E | \Psi \rangle
$$

Equation 29 is often rewritten in its variational form or its projected form to make it easier to solve numerically. The optimization procedure and the associated costs depend on the equations that are being solved.

The variational Schrödinger equation involves integrating both sides of Equation 29 with the wavefunction $\Psi$.

$$
\langle \Psi | \hat{H} | \Psi \rangle = E \langle \Psi | \Psi \rangle
$$

$$
\sum_{m, n \in S} f^*(m, \vec{P}) \langle m | \hat{H} | n \rangle f(n, \vec{P}) = E \sum_{m \in S} f^*(m, \vec{P}) f(m, \vec{P})
$$

If the number of Slater determinants in $S$ is comparable to those in the FCI wavefunction, even setting up Equation 30 will require far too many evaluations of $f$ to be computationally tractable. During the optimization, all terms need to be evaluated at each step, where the number of steps needed for convergence varies depending on the system and the optimization algorithm.

The projected Schrödinger equation can be obtained from Equation 29 using the resolution of
identity:

\[ \hat{H} |\Psi\rangle = E |\Psi\rangle \]

\[ \left( \sum_{m \in S_{\text{FCI}}} |m\rangle \langle m| \right) \hat{H} |\Psi\rangle = E \left( \sum_{m \in S_{\text{FCI}}} |m\rangle \langle m| \right) |\Psi\rangle \]

\[ \sum_{m \in S_{\text{FCI}}} |m\rangle \left( \langle m|\hat{H}|\Psi\rangle - E \langle m|\Psi\rangle \right) = 0 \]

Since the Slater determinants are linearly independent, this equation will hold only if \( \langle m|\hat{H}|\Psi\rangle = E \langle m|\Psi\rangle \) for every Slater determinant \( m \). These equations are expressed as a system of equations:

\[ \langle m_1|\hat{H}|\Psi\rangle - E \langle m_1|\Psi\rangle = 0 \]

\[ \vdots \]

\[ \langle m_M|\hat{H}|\Psi\rangle - E \langle m_M|\Psi\rangle = 0 \]

Essentially, the Schrödinger equation (Equation 29) is broken apart into separate equations for each contributing Slater determinant. If the projection operator is not complete (i.e. contributions from certain Slater determinants are discarded) then the equation (or system of equations) will be an approximation of the original Equation 29.

In general, the Schrödinger equation can be expressed with respect to arbitrary function, \( \Phi \).

\[ \langle \Phi|\hat{H}|\Psi\rangle = E \langle \Phi|\Psi\rangle \]

If \( \Phi \) is not \( \Psi \), then certain components of \( \Psi \) may be projected out, imposing additional structure on the wavefunction through the optimization process. We can express this projection explicitly with a projection operator onto a set of basis functions. When this basis set is complete, the projected Schrödinger equation is equivalent to the variational formulation.

Therefore, we can interpret the projected Schrödinger equation as an approximation to the variational formulation that reduces it to a set of functions that capture the important characteristics of the wavefunction. The cost of evaluating Equation 32 and 33 depends on the functions onto which the Schrödinger equation is projected. Some wavefunction structures have special functions such that Equation 32 or 33 can be evaluated cheaply. For example, the CC wavefunctions are often projected against \( \langle \Phi_{\text{HF}}|\exp(-\hat{T}) \) because \( \langle \Phi_{\text{HF}}|\exp(-\hat{T}) \hat{H} \exp(\hat{T}) |\Phi_{\text{HF}}\rangle \), can be simplified using the Baker-Campbell-Hausdorff expansion. For a general FANCI wavefunction, however,
it is convenient to project onto a set of Slater determinants, \( \{ \mathbf{m}_1 \ldots \mathbf{m}_M \} \), obtaining a system of (generally nonlinear) equations to solve:

\[
\begin{align*}
\sum_{\mathbf{m} \in S} f(\mathbf{m}, \vec{P}) \langle \mathbf{m}_1 | \hat{H} | \mathbf{m} \rangle &= E_f(\mathbf{m}_1, \vec{P}) \\
\vdots \\
\sum_{\mathbf{m} \in S} f(\mathbf{m}, \vec{P}) \langle \mathbf{m}_M | \hat{H} | \mathbf{m} \rangle &= E_f(\mathbf{m}_M, \vec{P}) 
\end{align*}
\]  

(34)

In order to find a solution, the number of equations in the system of equations must be greater than the number of unknowns. Since the number of possible Slater determinants grows exponentially, there will not be a shortage of equations (Slater determinants), and the number of equations will almost always be greater than the number of unknowns. If the least-squares solution of the nonlinear equations is found, then the residual can be used to measure the error associated with the optimized wavefunction (and energy).

Unless there is a special algorithm that limits the number of evaluated terms in the variational Schrödinger equation (Equation 30) or a function \( \Phi \) that allows cheap integration of the Schrödinger equation (Equation 33), a wavefunction should be evaluated using the projected Schrödinger equation (Equation 32) to control the optimization process. Both the cost and accuracy of the wavefunction can be controlled; as the number of projections increases, both accuracy and cost increases.

In addition, we can impose symmetry on the wavefunction by projecting the Schrödinger equation onto a space that satisfies a particular symmetry [99, 8, 118, 119, 120]. For example, we can reintroduce particle number symmetry onto a number-symmetry broken wavefunction by projecting it onto Slater determinants with the selected particle number.

4.3. Size-Consistency

Let there be a system, \( \text{AB} \), composed of two non-interacting subsystems, \( A \) and \( B \). Then, a wavefunction is size-consistent if the energy of the wavefunction for \( \text{AB} \) is the sum of the energies of the wavefunctions for \( A \) and \( B \), i.e.

\[
H_{\text{AB}} |\Psi_{\text{AB}}\rangle = E_{\text{AB}} |\Psi_{\text{AB}}\rangle = (E_A + E_B) |\Psi_{\text{AB}}\rangle
\]

(35)
where

$$H_A |\Psi_A\rangle = E_A |\Psi_A\rangle$$

$$H_B |\Psi_B\rangle = E_B |\Psi_B\rangle$$

(36)

Since subsystems $A$ and $B$ are non-interacting, there are no nonzero terms in the Hamiltonian that couple $A$ and $B$, i.e. $H_{AB} = H_A + H_B$. Then, the (partially symmetry broken) wavefunction $\Psi_{AB}$ can be written as a product of the (orthogonal) subsystem wavefunctions, $\Psi_A$ and $\Psi_B$.

$$|\Psi_{AB}\rangle = |\Psi_A\rangle |\Psi_B\rangle$$

Similarly, a FANCI wavefunction is size-consistent if the weight function is multiplicatively separable:

$$|\Psi_{AB}\rangle = \sum_{m \in S_{AB}} f_{AB}(m, \vec{P}) |m\rangle$$

$$= \sum_{m_A \in S_A} \sum_{m_B \in S_B} f_A(m_A, \vec{P}_A) f_B(m_B, \vec{P}_B) |m_A\rangle |m_B\rangle$$

$$= \sum_{m_A \in S_A} f_A(m_A, \vec{P}_A) |m_A\rangle \sum_{m_B \in S_B} f_B(m_B, \vec{P}_B) |m_B\rangle$$

(37)

$$= |\Psi_A\rangle |\Psi_B\rangle$$

where subscripts $A$ and $B$ designate that the quantity belongs only to subsystem $A$ and $B$, respectively. This not only requires that $f$ be multiplicatively separable, i.e. $f_{AB} = f_A f_B$, but also that the Slater determinants, $m$, and the parameters, $\vec{P}$, must be divisible into two disjoint parts, $\{m_A, m_B\}$ and $\{\vec{P}_A, \vec{P}_B\}$ respectively. To separate each Slater determinant into the subsystems, $m$ must be expressed using orbitals localized to each subsystem. Since each $m$ can have varying contribution from the subsystems $A$ and $B$, $S_A$ and $S_B$ contain Slater determinants with different numbers of electrons. However, we can impose the particle number symmetry during the optimization process. Similarly, the parameters must represent quantities that are specific to each subsystem. Notice that $f_{AB} = f_A f_B$ is true when $f$ is a determinant (Hartree-Fock), exponential (Coupled-Cluster), or permanent (geminals). Note that this is a simplified approach to size-consistency and a more rigorous approach requires ensuring that the systems have the correct symmetries upon dissociation.
5. Ansätze

In the formulation of Equation 9, a multideterminant wavefunction can be entirely expressed with a set of Slater determinants, \( S \), parameters, \( \vec{P} \), and a weight function, \( f \). Altering the \( S \), \( \vec{P} \), or \( f \) of a given ansatz will effectively result in a new ansatz. Additionally, the optimization method can be modified to produce an “ansatz” with a different accuracy and cost. For example, DMRG is an algorithm for optimizing MPS\(^{121}\). Here, we modify the FANCI forms of the CC (Equation 20), TPS (Equation 21), and APG (Equation 25) wavefunctions to construct several new wavefunction structures.

5.1. CC with Creators

Just as the TPS and APG wavefunctions are expressed with respect to creation operators, we can replace the excitation operators in the CC wavefunction with creation operators.

\[
|\Psi_{CC}\rangle = \exp \left( \sum_{b_i} C_{b_i} \hat{A}_{b_i}^\dagger + \sum_{f_i} C_{f_i} \hat{A}_{f_i}^\dagger \right) |0\rangle
\]

(38)

where \( \hat{A}_{b_i}^\dagger \) is a creation operator of even number of electrons (denoted as even-electron), \( \hat{A}_{f_i}^\dagger \) is a creation operator of odd number of electrons (denoted as odd-electron), \( b_i \) is the set of orbitals created by \( \hat{A}_{b_i}^\dagger \), and \( f_i \) is the set of orbitals created by \( \hat{A}_{f_i}^\dagger \). For a consistent notation, we define \( \tilde{S}_b \) and \( \tilde{S}_f \) as the set of allowed creation operators. Since each creation operator can create a different number of electrons, the total number of operators needed for \( m \) can vary depending on the selection of creation operators. For a given Slater determinant, let \( n_b \) be the number of even-electron creators and \( n_f \) be the number of odd-electron creators. Similar to the APG wavefunction, there can be multiple combinations of creation operators that give the same Slater determinant. We represent these combinations as a sum over \( \{b_1 \ldots b_{n_b} f_1 \ldots f_{n_f}\} \) such that the product of the associated creators results in the given Slater determinant:

\[
\prod_{i \in m} a_i^\dagger = \text{sgn} \left( \sigma(\hat{A}_{b_1}^\dagger \ldots \hat{A}_{b_{n_b}}^\dagger \hat{A}_{f_1}^\dagger \ldots \hat{A}_{f_{n_f}}^\dagger) \right) \hat{A}_{b_1}^\dagger \ldots \hat{A}_{b_{n_b}}^\dagger \hat{A}_{f_1}^\dagger \ldots \hat{A}_{f_{n_f}}^\dagger
\]

(39)

Similar to the signature in the CC wavefunction, \( \text{sgn} \left( \sigma(\hat{A}_{b_1}^\dagger \ldots \hat{A}_{b_{n_b}}^\dagger \hat{A}_{f_1}^\dagger \ldots \hat{A}_{f_{n_f}}^\dagger) \right) \) is the signature resulting from reordering the one-electron creators into the same order as the given Slater determinant.
In the CC wavefunction, all of the excitation operators commute with one another. Accounting for all possible orderings of the operators results in a permanent of the parameters with identical rows, i.e.

\[
| \begin{array}{cccc}
  a_1^i & \cdots & a_N^i \\
  \vdots & & \vdots \\
  a_1^i & \cdots & a_N^i \\
\end{array} \right|^{+}
\]

Similarly, if all of the creation operators commute with one another, i.e. they are all even-electron creators, then

\[
|\Psi\rangle = \sum_{m \in S_m} \left( \sum_{\{b_1, \ldots, b_{n_b}\} \subseteq \tilde{S}_b} \operatorname{sgn}(\hat{A}_{b_1}^\dagger \cdots \hat{A}_{b_{n_b}}^\dagger) \prod_{i=1}^{n_b} C_{b_i} \right) |m\rangle
\]

where

\[
S_m = \left\{ \prod_{\hat{A}_k \in T} \hat{A}_k |0\rangle \Big| T \subseteq \tilde{S}_b \right\}
\]

For systems with an odd number of electrons, there must be at least one odd-electron creator. The anticommutation between these creators results in a determinant. Unlike the permanent, the determinant of a matrix with identical rows is zero. Therefore, there must be one odd-electron creator within a set of creation operators that construct \( m \).

\[
|\Psi\rangle = \sum_{m \in S_m} \left( \sum_{\{b_1, \ldots, b_{n_b}\} \subseteq \tilde{S}_b} \operatorname{sgn}(\hat{A}_{b_1}^\dagger \cdots \hat{A}_{b_{n_b}}^\dagger \hat{A}_f^\dagger) \left( \prod_{i=1}^{n_b} C_{b_i} \right) C_f \right) |m\rangle
\]

The derivation is provided in the Appendix 8.5.

In the case where only two-electron creation operators are used, this wavefunction reduces to the Antisymmetrized Geminal Power (AGP)\cite{91}, HF-Bogoliubov\cite{122}, or the BCS superconducting\cite{123}.
wavefunction (Equation 42).

\[ |\Psi\rangle = \exp \left( \sum_{ij} c_{ij} a_i^\dagger a_j^\dagger \right) |0\rangle \]

\[ = \sum_{m \in S_m} \left( \sum_{\{m_1 \ldots m_{N/2}\} \subseteq \tilde{S}} \sum_{\text{sgn} A_{m_1}^\dagger \ldots A_{m_{N/2}}^\dagger |0\rangle = |m\rangle} \text{sgn}(\sigma_{m_1 \ldots m_{N/2}}) \prod_{k=1}^{N/2} C_{m_k} \right) |m\rangle \]

Notice that this type of coupled-cluster wavefunction is not size consistent and that it breaks particle number symmetry (unless it is restored with a projection onto correct particle number).

5.2. TPS Variants

5.2.1. TPS with Quasiparticles

In the TPS wavefunction (Equation 22), each parameter in \((M_k)^n\) describes the correlation between a spatial orbital, \(k\), and all of the other orbitals. In the APG wavefunction (Equation 7) and CC-motivated quasiparticle wavefunction (Equation 41), each parameter is associated with a cluster of spatial orbitals (quasiparticle). Then, we should be able to build a TPS-like wavefunction using creation operators of an arbitrary number of electrons, rather than the one-electron creation operators.

\[ |\Psi\rangle = \sum_{m \in S_m} \left( \sum_{\{m_1 \ldots m_n\} \subseteq \tilde{S}} \sum_{\text{sgn} A_{m_1}^\dagger \ldots A_{m_n}^\dagger |0\rangle = |m\rangle} \text{sgn}(\sigma_{m_1 \ldots m_n}) \bigodot (M_k)^{\delta(k,\{m_1 \ldots m_n\})} \right) |m\rangle \]

where

\[ S_m = \left\{ \prod_{\hat{A}_k \in T} \hat{A}_k^\dagger |0\rangle \mid T \subseteq \tilde{S} \right\} \]

\(M_k\) is a tensor that corresponds to the creation operator \(\hat{A}_k^\dagger\), and \(\delta\) is a function that checks if the creator \(\hat{A}_k^\dagger\) is in a set of creators, \(\{m_1 \ldots m_n\}\).

\[ \delta(k,\{m_1 \ldots m_n\}) = \begin{cases} 1 & \text{if } k \in \{m_1 \ldots m_n\} \\ 0 & \text{if } k \notin \{m_1 \ldots m_n\} \end{cases} \]
Then, \((M_k)^0\) and \((M_k)^1\) are tensors that correspond to the absence and presence of the creator \(\hat{A}_k\), respectively.

### 5.2.2. TPS with Excitation Operators

Just as the CC wavefunction can be rebuilt with creation operators, we can rebuild the TPS wavefunction with excitation operators. Each tensor, \(t_{\hat{E}_a}\), can be associated with \(\hat{E}_a\), and has auxiliary indices that describe the correlation between operators.

\[
|\Psi\rangle = \sum_{\hat{E}_a \in S_E} \left( \sum_{\{\hat{E}_{i_1}^{a_1}, \ldots, \hat{E}_{i_n}^{a_n}\} \subseteq \tilde{S}_E} \operatorname{sgn}(\sigma_{\hat{E}_{i_1}^{a_1}, \ldots, \hat{E}_{i_n}^{a_n}}) \bigotimes_{\hat{E}_k \in \tilde{S}_E} (t_{\hat{E}_k})^{\delta(\hat{E}_k, \{\hat{E}_{i_1}^{a_1}, \ldots, \hat{E}_{i_n}^{a_n}\})} \right) \hat{E}_a |\Phi_{HF}\rangle \tag{44}
\]

where

\[
S_E = \left\{ \prod_{\hat{E}_k \in T} \hat{E}_k \left| T \subseteq \tilde{S}_E \right. \right\}
\]

and \(\delta\) describes the presence of an excitation operator, \(\hat{E}_k\), in the given set, \(\{\hat{E}_{i_1}^{a_1}, \ldots, \hat{E}_{i_n}^{a_n}\}\)

\[
\delta(\hat{E}_k, \{\hat{E}_{i_1}^{a_1}, \ldots, \hat{E}_{i_n}^{a_n}\}) = \begin{cases} 1 & \text{if } \hat{E}_k \in \{\hat{E}_{i_1}^{a_1}, \ldots, \hat{E}_{i_n}^{a_n}\} \\ 0 & \text{if } \hat{E}_k \notin \{\hat{E}_{i_1}^{a_1}, \ldots, \hat{E}_{i_n}^{a_n}\} \end{cases} \tag{45}
\]

Comparing Equation 44 with Equation 20, the CC wavefunction can be considered a special case of this wavefunction, where the tensor \((t_{\hat{E}_k})^{\delta_k}\) is 1 if \(\delta_k = 0\) and a variable scalar value if \(\delta_k = 1\).

### 5.3. APG Generalized to Excitation Operators

Just as the TPS wavefunction can be built with excitation operators (Equation 44), we can rewrite the APG wavefunction with excitation operators.

\[
|\Psi\rangle = \prod_{p=1}^n \left( \sum_{\hat{E}_k \in \tilde{S}_E} t_{p,\hat{E}_k} \hat{E}_k \right) |\Phi_{HF}\rangle \tag{46}
\]

where \(n\) is the number of excitation operators that will be multiplied together. Unlike the CC wavefunction, which can generate all possible combinations of the excitation operators, this wavefunction can only account for the combinations of \(n\) excitation operators. The corresponding weight
function in the FANCI notation is

$$|\Psi\rangle = \sum_{E_1^a \in \tilde{S}_E} \left( \sum_{\{E_1^a, \ldots, E_n^a\} \subseteq \tilde{S}_E} \text{sgn} \left( \prod_{k=1}^{n} E_k = \hat{E}_1^a \right) \left| \Phi_{HF} \right\rangle \right)^+ \hat{E}_1^a \left| \Phi_{HF} \right\rangle$$ (47)

where

$$\tilde{S}_E = \left\{ \prod_{E_k \in T} \hat{E}_k \mid T \subseteq \tilde{S}_E \right\}$$

and \(\text{sgn}(\sigma_{E_1^a, \ldots, E_n^a})\) is the signature of the permutation of the one-electron creation and annihilation operators from the product of excitation operators, \(\hat{E}_1^a \ldots \hat{E}_n^a\), to the given excitation operator, i.e.

$$\hat{E}_1^a = \text{sgn}(\sigma_{E_1^a, \ldots, E_n^a}) \hat{E}_1^a \ldots \hat{E}_n^a$$ (48)

Other combinations of excitation operators can be included into Equation 47 via the summation.

$$|\Psi\rangle = \sum_{n \in P} \frac{1}{n!} \prod_{p=1}^{n} \left( \sum_{E_k \in \tilde{S}_E} t_{p,E_k} \hat{E}_k \right) \left| \Phi_{HF} \right\rangle$$ (49)

where \(P\) is the allowed number of excitation operators that can be combined. Recall that removing an index (so that all the geminals are identical) in the traditional APG wavefunction form leads to the AGP wavefunction. Similarly, when one removes the index, \(p\), from the excitation-based APG wavefunction form and allows all possible combinations of excitation operators, one obtains the CC wavefunction:

$$|\Psi_{CC}\rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \prod_{p=1}^{n} \left( \sum_{E_k \in \tilde{S}_E} t_{E_k} \hat{E}_k \right) \left| \Phi_{HF} \right\rangle$$

$$= \sum_{n=0}^{\infty} \frac{1}{n!} \left( \sum_{E_k \in \tilde{S}_E} t_{E_k} \hat{E}_k \right)^n \left| \Phi_{HF} \right\rangle$$ (50)

$$= \exp \left( \sum_{E_k \in \tilde{S}_E} t_{E_k} \hat{E}_k \right) \left| \Phi_{HF} \right\rangle$$

5.4. General Quasiparticle Wavefunctions

In the Equation 50 any creation operator can be used (within the sets \(\tilde{S}_b\) and \(\tilde{S}_f\)) to construct a Slater determinant. Similarly, we can generalize the APG wavefunction to include all even-electron
creation operators.

\[ |\Psi\rangle = \prod_{p=1}^{n} \left( \sum_{\hat{A}_i \in \tilde{S}_b} C_{p, \nu} \hat{A}_i^\dagger \right) |0\rangle \]  

(51)

where \( n \) is the number of quasiparticles in the wavefunction (i.e. number of operators used to construct a Slater determinant), and \( \tilde{S}_b \) is a set of even-electron creation operators. In the FANCI formulation,

\[
|\Psi\rangle = \sum_{m \in S_m} \left( \sum_{\{m_1 \ldots m_n\} \subseteq \tilde{S}_b} \text{sgn}(\sigma_{m_1 \ldots m_n}) \begin{vmatrix} C_{1; m_1} & \cdots & C_{1; m_n} \\ \vdots & \ddots & \vdots \\ C_{n; m_1} & \cdots & C_{n; m_n} \end{vmatrix} \right) |m\rangle 
\]  

(52)

where \( \tilde{S}_b \) is a set of allowed even-electron creation operators, \( S_m = \left\{ \prod_{\hat{A}_i \in T} \hat{A}_i^\dagger |0\rangle \right| T \subseteq \tilde{S}_b \} \)

and \( \text{sgn}(\sigma_{m_1 \ldots m_n}) \) is the signature of the permutation needed to reorder the one-electron creation operators from the product of quasiparticle creation operators to the given Slater determinant.

\[
\prod_{i \in m} a_i^\dagger = \text{sgn}(\sigma_{m_1 \ldots m_n}) \prod_{k=1}^{n} \prod_{i \in m_k} a_i^\dagger 
\]  

(53)

Note that the zero-electron creation operator can be considered as an even-electron creation operator.

Similarly, the wavefunction constructed using only odd-electron creation operator can be expressed using a determinant.

\[
|\Psi\rangle = \sum_{m \in S_m} \left( \sum_{\{m_1 \ldots m_n\} \subseteq \tilde{S}_f} \text{sgn}(\sigma_{m_1 \ldots m_n}) \begin{vmatrix} C_{1; m_1} & \cdots & C_{1; m_n} \\ \vdots & \ddots & \vdots \\ C_{n; m_1} & \cdots & C_{n; m_n} \end{vmatrix} \right) |m\rangle 
\]  

(54)

where \( S_m = \left\{ \prod_{\hat{A}_i \in T} \hat{A}_i^\dagger |0\rangle \right| T \subseteq \tilde{S}_f \} \)

and \( \tilde{S}_f \) is a set of selected odd-electron creation operators.
When both even and odd-electron creation operators are present in $\tilde{S}$, the interchange of creators commutes or anticommutes depending on the pair of creators, and additional structure is necessary to account for this behaviour. First, we distinguish between the set of even and odd orbitals with $b_i$ and $f_j$, respectively. A given Slater determinant $m$ is constructed with $n = n_b + n_f$ creation operators, where $n_b$ is the number of even-electron creators and $n_f$ is the number of odd-electron creators. A permanent is needed to account for all possible ordering of the even-electron creators and the resulting commutations. A determinant is needed to account for all possible ordering of the odd-electron creators and the resulting anticommutations. Finally, the commutation between an even-electron and an odd-electron creator can be accounted for by a sum over all possible selections of the $n_b$ even-electron creators from $n$ positions, i.e. $\{i_1^b \ldots i_{n_b}^b \}$ $\subseteq \{b_1 \ldots b_{n_b} f_1 \ldots f_{n_f} \}$. The positions of the odd-electron creators are the remaining $n_f$ positions, i.e. $\{i_1^f \ldots i_{n_f}^f \} = b_1 \ldots b_{n_b} f_1 \ldots f_{n_f} \setminus \{i_1^b \ldots i_{n_b}^b \}$. Then, we can construct the generalized quasiparticle wavefunction (Equation 55) in which any set of creators can be used.

$$|\Psi\rangle = \sum_m \left( \sum_{\{b_1 \ldots b_{n_b} \} \subseteq \tilde{S}_b, \{f_1 \ldots f_{n_f} \} \subseteq \tilde{S}_f} \left| \text{sgn}(\sigma_{A_{b_1}^\dagger \ldots A_{b_{n_b}}^\dagger A_{i_1}^\dagger \ldots A_{i_{n_f}}^\dagger}) \right| \sum_{\{i_1^b \ldots i_{n_b}^b \} \subseteq \{b_1 \ldots b_{n_b} f_1 \ldots f_{n_f} \}} \left| \text{sgn}(\sigma_{A_{i_1}^\dagger \ldots A_{i_{n_f}}^\dagger}) \right| C_{1i_1^b}^\dagger \ldots C_{1i_{n_b}^b}^\dagger \right) \right)$$

where

$$S_m = \left\{ \prod_{A_i^\dagger \in T} A_i^\dagger |0\rangle \bigg| T \subseteq \tilde{S}_b \cup \tilde{S}_f \right\}$$

$$\prod_{i \in m} a_i^\dagger = \text{sgn}(\sigma_{A_{b_1}^\dagger \ldots A_{b_{n_b}}^\dagger A_{i_1}^\dagger \ldots A_{i_{n_f}}^\dagger}) \prod_{k=1}^{n_b} A_{b_k}^\dagger \prod_{l=1}^{n_f} A_{f_l}^\dagger$$

and $C$ is a $n \times \dim(\tilde{S}_b \cup \tilde{S}_f)$ matrix. Note that the set of orbitals, $b_i$ and $f_j$, correspond to a column in $C$ and thus are used as a column index. Here, the column indices are made explicit using the index $i$.

The derivation and more details are in the Appendix 8.6

5.5. Changing Solvers

Often times, the algorithm for optimizing the parameters is synonymous with the wavefunction ansatz. For example, DMRG is often associated with MPS wavefunctions, and Quantum Monte-
Carlo (QMC) is often associated with FCI wavefunctions. Using different algorithms to optimize the parameters will change the cost and the reliability of the wavefunction. Certain algorithms can be applied to a wide range of wavefunction structures and systems; whereas specialized algorithms are cheaper, but are often limited to specific wavefunction structures and systems.

For example, the DMRG algorithm with the MPS wavefunction provides variational results and is effective in describing linear systems. The algorithm is specific to the MPS wavefunction, wherein the orbitals are ordered such that adjacent orbitals are more correlated than the rest. As a result, DMRG must be extended beyond MPS to more general TPS forms, but these algorithms do not seem to be as elegant or as computationally efficient. Solving the TPS wavefunction as a projected Schrödinger equation mitigates certain complications that are present in DMRG, such as ordering of the orbitals and generalizing a one-dimensional algorithm to multiple dimensions. It is true, however, that the tensor structures that are most efficiently optimized in a variational ansatz are, at least in all cases we have considered, the same as those that are most efficiently optimized using the projected Schrödinger equation.

5.6. Generalization

Above, we constructed new wavefunction structures by constructing the CC wavefunction with creation operators and the TPS and APG wavefunctions using excitation operators. Effectively, the parameters are changed from the contributions of creation operators to those of excitation operators, and vice versa. Since both operators originate from orbitals, the wavefunctions are size-consistent if \( f \) is selected appropriately, provided the orbitals are localized. In Equations 41, 52, 54, and 55, particle number symmetry is not conserved, which is not a problem since the wavefunction can be optimized and projected onto the appropriate particle number. Then, just as excitation operators change the state of a reference Slater determinant, products of an arbitrary number of creation and annihilation operators can be used to explore different particle numbers with respect to the reference. For example, the product of creators and annihilators, where the number of creators exceeds the number of annihilators, will ionize a Slater determinant. Expressing the wavefunction with respect to different operators will result in different sets of parameters, even if these operators make no reference to the Slater determinants or creation operators. For example, grid-based wavefunctions will have parameters for each point in space.

So far, we have seen weight functions, \( f \), in various forms: the CC wavefunction (Equation 20)
uses a cumulant; the TPS wavefunction (Equation 21) uses a tensor product; the even-electron quasiparticle wavefunction (Equation 54) uses a permanent; the odd-electron quasiparticle wavefunction (Equation 52) uses a determinant; and the generalized quasiparticle wavefunction (Equation 55) uses some mix of a permanent and determinant (an immanent). In Equations 25, 41, and 55, creators of arbitrary number of electrons are combined in fairly complicated manner. Since creators have distinct commutative (and anticommutative) relations with one another, the corresponding $f$ must be symmetric (and antisymmetric) with respect to interchange of different creation operators (or parameters). Grouping together all the terms that correspond to the same set of creation operators results in a sum over all combinations of products of parameters. These combinatorial variants of product functions seem to be useful for size-consistency since they are multiplicatively separable by construction. Therefore, we can construct novel wavefunctions with quasiparticle origins using different symmetric (or antisymmetric) polynomial functions, including but not limited to determinant, permanent, immanent [124], pfaffian [125], hafnian [126, 127], hyperdeterminant [128], multidimensional permanent [129], hyperpfaffian [130], hyperhafnian [131], and mixed discriminant [132]. Unfortunately, among all the aforementioned size-consistent combinatoric forms, only the determinant can be evaluated in polynomial time. If we disregard size-consistency and do not require any quasiparticle structure, then any function can be chosen. One alternative, however, is to use a ratio of a product of determinants as the overlap; this form retains size-consistency and computational feasibility, and generalizes a single Slater determinant (one determinant in the numerator, none in the denominator) and the APr2G wavefunction (a special case with one structure determinant in the denominator and the determinant of its element-wise square in the numerator). If the total number of determinants is odd, this wavefunction describes a normal fermionic wavefunction, while if the number of determinants is even, this wavefunction represents a bosonic seniority-zero structure.

A great deal of flexibility is available within the proposed wavefunction framework: the set of Slater determinants, $S$, can be any set of orthonormal (for convenience) Slater determinants; the parameters, $\vec{P}$, can be any set of numbers that describe the wavefunction or the operators with which it is built; the parameterizing function, $f$, can be any function that maps the parameters to a coefficient for a given Slater determinant. We hope to find the combination that effectively models the optimized coefficients of the FCI wavefunction (for accuracy) using the minimal number of parameters (for cost) for as many systems as possible (for generality).
6. Conclusion

In the proposed framework, any multideterminant wavefunction can be expressed with respect to the components $S$, $\vec{P}$, and $f$. A wavefunction can be characterized using only these components and different combinations will result in different wavefunction characteristics. Then, we can systematically develop new structures by simply finding novel combinations. While the proposed wavefunctions are not necessarily cheap to compute, the general ansatz does not need to be cheap to be effective. For example, the CC wavefunction with all orders of excitations, the TPS wavefunction with infinitely large tensors, and the quasiparticle wavefunctions with $N$ electron quasiparticles are no less expensive than the FCI wavefunction. However, different wavefunction structures inspire different approximations and new algorithms that reduce the computational cost to a tractable level. The greatest advantage to this perspective is that it is pragmatic: approximations and algorithms that were restricted to one wavefunction can be generalized to others using the FANCI framework; and many different methods can be implemented computationally using a common framework. Though we will defer detailed discussions on dynamical correlation corrections and orbital optimization to future papers, these elaborations to FANCI are clearly possible and are performed using similar techniques to what one would use in traditional selected CI and CC methods. Many of the proposed methods have been implemented in an open-source library called Fanpy, which will be presented elsewhere.

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8. Appendix

8.1. HF

$$|\Psi_{HF}\rangle = \prod_{i=1}^{N} \left( \sum_{j=1}^{2K} a_{j,i}^\dagger U_{j,i} \right) |0\rangle$$

$$= \left( \sum_{j_1=1}^{2K} a_{j_1,1}^\dagger U_{j_1,1} \right) \left( \sum_{j_2=1}^{2K} a_{j_2,2}^\dagger U_{j_2,2} \right) \cdots \left( \sum_{j_N=1}^{2K} a_{j_N,N}^\dagger U_{j_N,N} \right) |0\rangle$$

$$= \sum_{j_1=1}^{2K} \sum_{j_2=1}^{2K} \cdots \sum_{j_N=1}^{2K} a_{j_1}^\dagger a_{j_2}^\dagger \cdots a_{j_N}^\dagger U_{j_1,1} U_{j_2,2} \cdots U_{j_N,N} |0\rangle$$

(56)

We can group together the terms that result in the same Slater determinant, defined here by the set of creation operators, \{a_{j_1}^\dagger a_{j_2}^\dagger \cdots a_{j_N}^\dagger\}. Since the order of operators only affects the sign of the Slater determinant, we can split the sum over all indices into a sum over the set of creation operators and a sum over the different orderings of the given set of creation operators.

$$|\Psi_{HF}\rangle = \sum_{j_1 < j_2 \cdots < j_N} \sum_{\sigma \in S_N} U_{j_{\sigma(1)},1} U_{j_{\sigma(2)},2} \cdots U_{j_{\sigma(N)},N} a_{j_{\sigma(1)},1}^\dagger a_{j_{\sigma(2)},2}^\dagger \cdots a_{j_{\sigma(N)},N}^\dagger |0\rangle$$

(57)

where \(\text{sgn}(\sigma)\) is the signature of the permutation \(\sigma\).

\[
\text{sgn}(\sigma) = \begin{cases} 
1 & \text{if } \sigma \text{ is even} \\
-1 & \text{if } \sigma \text{ is odd}
\end{cases}
\]  

(58)

Using the definition of the determinant,

$$|A|^\ast = \sum_{\sigma \in S_N} \text{sgn}(\sigma) \prod_{i=1}^{N} A_{i\sigma(i)}$$

$$= \sum_{\sigma \in S_N} \text{sgn}(\sigma) \prod_{i=1}^{N} A_{\sigma(i)i}$$

(59)
we find

$$|\Psi_{\text{HF}}\rangle = \sum_{j_1 < j_2 \cdots j_N}^K \begin{vmatrix} U_{j_11} & U_{j_12} & \ldots & U_{j_1N} \\ U_{j_21} & U_{j_22} & \ldots & U_{j_2N} \\ \vdots & \vdots & \ddots & \vdots \\ U_{j_N1} & U_{j_N2} & \ldots & U_{j_NN} \end{vmatrix} a_{j_1}^\dagger a_{j_2}^\dagger \ldots a_{j_N}^\dagger |0\rangle$$

$$= \sum_m |U(m)|^{-1} |m\rangle$$

where $$m = \{j_1, j_2, \ldots, j_N\}$$, $$|m\rangle = a_{j_1}^\dagger a_{j_2}^\dagger \ldots a_{j_N}^\dagger |0\rangle$$ where $$j_1 < j_2 < \cdots < j_N$$, and $$U(m)$$ is a submatrix of $$U$$ composed of rows that correspond to $$m$$.

8.2. APG

For convenience, let $$P = \frac{N}{2}$$.

$$|\Psi_{\text{APG}}\rangle = \prod_{p=1}^P \sum_{ij} C_{p;ij} a_i^\dagger a_j^\dagger |0\rangle$$

$$= \left( \sum_{i_1j_1}^{2K} a_{i_1}^\dagger a_{j_1}^\dagger C_{1;i_1j_1} \right) \left( \sum_{i_2j_2}^{2K} a_{i_2}^\dagger a_{j_2}^\dagger C_{2;i_2j_2} \right) \cdots \left( \sum_{i_Pj_P}^{2K} a_{i_P}^\dagger a_{j_P}^\dagger C_{P;i_Pj_P} \right) |0\rangle$$

$$= \sum_{i_1j_1}^{2K} \ldots \sum_{i_Pj_P}^{2K} a_{i_1}^\dagger a_{j_1}^\dagger a_{i_2}^\dagger a_{j_2}^\dagger \ldots a_{i_P}^\dagger a_{j_P}^\dagger C_{1;i_1j_1} C_{2;i_2j_2} \cdots C_{P;i_Pj_P} |0\rangle$$

Just as in the HF derivation, we can group together the creation operators, $$\{a_{i_1}^\dagger, a_{j_1}^\dagger, \ldots, a_{i_P}^\dagger, a_{j_P}^\dagger\}$$, that corresponds to the same Slater determinant. However, there are multiple ways to construct a Slater determinant from a set of pairs of creators, $$\{a_{i_1}^\dagger a_{j_1}^\dagger, a_{i_2}^\dagger a_{j_2}^\dagger, \ldots, a_{i_P}^\dagger a_{j_P}^\dagger\}$$ (Note the placement of commas). Since the Slater determinant is expressed with respect to a specific ordering of the one-electron creation operators, the sign resulting from ordering the product of creator pairs to this specific ordering must be taken into account. Then, the sum over all indices can be split into a sum over each Slater determinant, a sum over different orbital pairs that construct the given Slater determinant, and a sum over the permutation of the orbital pair creation operators.

$$|\Psi_{\text{APG}}\rangle = \sum_{m \in \mathcal{S}} \sum_{\{i_1j_1, \ldots, i_Pj_P\} = m} \sum_{\tau \in \mathcal{S}_P} C_{1;\tau(1)\tau(1)} \cdots C_{P;\tau(P)\tau(P)} a_{\tau(1)}^\dagger a_{\tau(1)}^\dagger \cdots a_{\tau(P)}^\dagger a_{\tau(P)}^\dagger |0\rangle$$

$$= \sum_{m \in \mathcal{S}} \sum_{\{i_1j_1, \ldots, i_Pj_P\} = m} \text{sgn}(\sigma(i_1j_1, \ldots, i_Pj_P)) \sum_{\tau \in \mathcal{S}_P} C_{1;\tau(1)\tau(1)} \cdots C_{P;\tau(P)\tau(P)} a_{\tau(1)}^\dagger a_{\tau(1)}^\dagger \cdots a_{\tau(P)}^\dagger a_{\tau(P)}^\dagger |0\rangle$$

$$= \sum_{m \in \mathcal{S}} \sum_{\{i_1j_1, \ldots, i_Pj_P\} = m} \text{sgn}(\sigma(i_1j_1, \ldots, i_Pj_P)) \sum_{\tau \in \mathcal{S}_P} C_{1;\tau(1)\tau(1)} \cdots C_{P;\tau(P)\tau(P)} a_{\tau(1)}^\dagger a_{\tau(1)}^\dagger \cdots a_{\tau(P)}^\dagger a_{\tau(P)}^\dagger |0\rangle$$

(61)
where $\sigma$ is the permutation for ordering the creation operators to that of the Slater determinant and $\tau$ is the permutation of the given pairs of creation operators. Note that the pair of creation operators commute with one another. From the definition of a permanent,

$$|A|^+ = \sum_{\tau \in S_N} \prod_{i=1}^N A_{i\tau(i)}$$

we find

$$|\Psi_{\text{APG}}\rangle = \sum_{m \in S} \sum_{\{i_1, j_1, \ldots, i_P, j_P\} = m} \text{sgn}(\sigma(i_1, j_1, \ldots, i_P, j_P)) \begin{bmatrix} C_{1; i_1 j_1} & \cdots & C_{1; i_P j_P} \end{bmatrix}^+ \begin{bmatrix} a_{i_1}^\dagger a_{j_1}^\dagger \cdots a_{i_P}^\dagger a_{j_P}^\dagger |0\rangle \\ \vdots & \ddots & \vdots \\ C_{P; i_1 j_1} & \cdots & C_{P; i_P j_P} \end{bmatrix}$$

$$= \sum_{m \in S} \sum_{\{m_1, \ldots, m_P\} \in S} \text{sgn}(\sigma(m_1, \ldots, m_P)) |C(m_1, \ldots, m_P)|^+ |m\rangle$$

(63)

where $m_p = \{i_p, j_p\}$, $A_{m_p}^\dagger = a_{i_p}^\dagger a_{j_p}^\dagger$, $|m\rangle = a_{i_1}^\dagger a_{j_1}^\dagger \cdots a_{i_P}^\dagger a_{j_P}^\dagger |0\rangle$, and $C(m_1, \ldots, m_P)$ is a submatrix of $C$ composed of columns that correspond to the orbital pairs, $\{m_1, \ldots, m_P\}$.  

8.3. Product of Linear Combinations of Operators

Using the two examples above, we can generalize the approach to reformulating wavefunctions of the form

$$|\Psi\rangle = \prod_{i=1}^n \sum_j C_{ij} \hat{Q}_j |\theta\rangle$$

(64)
where $\hat{Q}_j$ is an operator, $C_{ij}$ is a coefficient that corresponds to the index $i$ and operator $\hat{Q}_j$, and $\theta$ is some vacuum/reference. Taking the same approach as above,

$$|\Psi\rangle = \prod_{i=1}^{n} \sum_{j} C_{ij} \hat{Q}_j |\theta\rangle$$
$$= \left( \sum_{j_1} C_{1j_1} \hat{Q}_{j_1} \right) \cdots \left( \sum_{j_n} C_{nj_n} \hat{Q}_{j_n} \right) |\theta\rangle$$
$$= \sum \sum_{\{\hat{Q}_{j_1}, \ldots, \hat{Q}_{j_n}\}} \text{sgn}(\sigma(\hat{Q}_{j_1}, \ldots, \hat{Q}_{j_n})) \sum_{\tau \in S_n} \text{sgn}(\tau) C_{1j_{\tau(1)}} \cdots C_{nj_{\tau(n)}} |\mathbf{m}\rangle$$

(65)

Depending on the commutation/anticommutation relationships between the elements of $\{\hat{Q}_{j_1}, \ldots, \hat{Q}_{j_n}\}$, the $\text{sgn}(\tau)$ is different.

If all operators are expressed with an even number of one-electron operators (which we will denote as even-electron operators), then

$$\text{sgn}(\tau) = 1$$

and

$$\sum_{\tau \in S_n} \text{sgn}(\tau) C_{1j_{\tau(1)}} \cdots C_{nj_{\tau(n)}} = \begin{bmatrix} C_{1j_1} & \cdots & C_{1j_n} \\ \vdots & \ddots & \vdots \\ C_{nj_1} & \cdots & C_{nj_n} \end{bmatrix}^+$$

(66)

If all operators are expressed with an odd number of one-electron operators (which we will denote as odd-electron operators), then

$$\text{sgn}(\tau) = \begin{cases} 1 & \text{if even} \\ -1 & \text{if odd} \end{cases}$$
and

\[
\sum_{\tau \in S_n} \text{sgn}(\tau) C_{1_{\tau(1)}} \cdots C_{n_{\tau(n)}} = \begin{vmatrix}
C_{1j_1} & \cdots & C_{1j_n} \\
\vdots & \ddots & \vdots \\
C_{nj_1} & \cdots & C_{nj_n}
\end{vmatrix}
\]  

(67)

If the operators are a mix of even and odd-electron operators, then \(\tau\) must be split into three components: \(\tau_b\) for permutation of the positions of even-electron operators, \(\tau_f\) for permutation of the positions of odd-electron operators, and \(\tau_{bf}\) for remaining permutations that mix the positions of even-electron operators with the odd-electron operators.

\[
\tau = \tau_b \tau_f \tau_{bf}
\]

\[
\text{sgn}(\tau) = \text{sgn}(\tau_b) \text{sgn}(\tau_f) \text{sgn}(\tau_{bf})
\]

\[
\text{sgn}(\tau_b) = 1
\]

\[
\text{sgn}(\tau_f) = \begin{cases} 
1 & \text{if even} \\
-1 & \text{if odd}
\end{cases}
\]

\[
\text{sgn}(\tau_{bf}) = 1
\]

(68)

Let there be \(n_b\) even-electron operators and \(n_f\) odd-electron operators.

\[
n = n_b + n_f
\]

We will assume (with no loss of generality) that the first \(n_b\) columns of the coefficients correspond to the even-electron and the rest to the odd-electron operators. Then \(\tau_{bf}\) would correspond to swapping the first \(n_b\) columns with the rest of the columns. After the swapped columns are obtained, the \(\tau_b\)
will permute the first \( n_b \) columns and \( \tau_f \) will permute the others.

\[
\sum_{\tau \in S_n} \text{sgn}(\tau)C_{1_{\tau(1)}} \cdots C_{n_{\tau(n)}}
= \sum_{\tau_f \in S_{n_f}} \sum_{\tau_b \in S_{n_b}} \sum_{\tau \in S_{n_b} \setminus S_{n_f}} \text{sgn}(\tau_b)\text{sgn}(\tau_f)\text{sgn}(\tau_f)C_{1_{\tau_{b,\tau_f}(1)}} \cdots C_{n_{\tau_{b,\tau_f}(n)}} C_{(n_b+1)_{\tau_f(1)}} \cdots C_{n_{\tau_f(n)}}
= \sum_{\tau_b \in S_{n_b} \setminus S_{n_f}} \text{sgn}(\tau_b) \sum_{\tau \in S_{n_b}} \text{sgn}(\tau)C_{1_{\tau_{b,\tau}(1)}} \cdots C_{n_{\tau_{b,\tau}(n)}} \sum_{\tau_f \in S_{n_f}} \text{sgn}(\tau_f)C_{(n_b+1)_{\tau_f(1)}} \cdots C_{n_{\tau_f(n)}}
\]

where \( S_n, S_{n_b}, \text{and} S_{n_f} \) are sets of permutations of all indices, first \( n_b \) indices, and the remaining \( n_f \) indices, respectively. Then \( S_{n_b} \setminus S_{n_f} \) is the set of permutations of the first \( n_b \) columns with the rest.

In other words, \( \tau_{b,f} \) accounts for the different ways in which the columns of the coefficient matrix can be split into two, one for \( \tau_b \) and other for \( \tau_f \). Since only the first \( n_b \) rows are needed for the sum over \( \tau_b \) and the remaining rows for the sum over \( \tau_f \), we will denote \( C^b \) as the submatrix composed of the first \( n_b \) rows of \( C \), and \( C^f \) as the submatrix composed of the remaining rows. Note that \( C^b \) has dimensions \( n_b \times n \) and \( C^f \) has dimensions \( n_f \times n \). Then, we can rewrite the sum over \( \tau_{b,f} \) to be somewhat more transparent:

\[
\sum_{\tau \in S_n} \text{sgn}(\tau)C_{1_{\tau(1)}} \cdots C_{n_{\tau(n)}} = \sum_{\{i_1^{b}, \ldots, i_{n_f}^{b}\} \subseteq \{j_1, \ldots, j_{n_f}\}} \sum_{\{i_1^{f}, \ldots, i_{n_f}^{f}\} = \{j_1, \ldots, j_{n_f}\} \setminus \{i_1^{b}, \ldots, i_{n_f}^{b}\}} \begin{vmatrix} C_{1_{i_1^{b}}}^{b} \cdots C_{1_{i_{n_f}^{b}}}^{b} \\ \vdots \cdots \vdots \\ C_{n_{i_1^{b}}}^{b} \cdots C_{n_{i_{n_f}^{b}}}^{b} \end{vmatrix}^+ \begin{vmatrix} C_{1_{i_1^{f}}}^{f} \cdots C_{1_{i_{n_f}^{f}}}^{f} \\ \vdots \cdots \vdots \\ C_{n_{i_1^{f}}}^{f} \cdots C_{n_{i_{n_f}^{f}}}^{f} \end{vmatrix}^-
\]

If the given operators do not commute or anticommute with one another, then an explicit sum through every permutation might be necessary, along with the signature of each permutation, unless there is a specialized structure that simplifies this sum.
\[ |\Psi_{CC}\rangle = \exp \left( \sum_{ia} t_i^a \hat{E}_i^a \right) |\Phi_{HF}\rangle \]
\[ = \sum_{n=0}^{\infty} \frac{1}{n!} \left( \sum_{ia} t_i^a \hat{E}_i^a \right)^n |\Phi_{HF}\rangle \]
\[ = \sum_{n=0}^{\infty} \frac{1}{n!} \prod_{k=1}^{n} \sum_{ia} t_i^a \hat{E}_i^a |\Phi_{HF}\rangle \]
\[ (71) \]

For each \( n \), we can treat \( \prod_{k=1}^{n} \sum_{ia} t_i^a \hat{E}_i^a \) with the approach from Equation 65. Then, the operators, \( \{ \hat{Q}_{j_1} \ldots \hat{Q}_{j_n} \} \), are excitation operators, \( \{ \hat{E}_i^{a_1} \ldots \hat{E}_i^{a_n} \} \), and \( n \) controls the number of operators used in the second summation of Equation 65. Since they all commute with one another, \( \text{sgn}(\tau) = 1 \) which means that the final sum of Equation 65 will be a permanent (Equation 18).

\[ \prod_{k=1}^{n} \sum_{ia} t_i^a \hat{E}_i^a = \sum_{m} \sum_{\{ \hat{E}_i^{a_1} \ldots \hat{E}_i^{a_n} \} \subseteq \hat{S}_E} \prod_{k=1}^{n} t_i^a \hat{E}_i^a |\Phi_{HF}\rangle = |m\rangle \]
\[ = \sum_{m} \sum_{n=0}^{\infty} \text{sgn}(\sigma(\hat{E}_i^{a_1} \ldots \hat{E}_i^{a_n})) n! \prod_{k=1}^{n} t_i^a \hat{E}_i^a |m\rangle \]
\[ (72) \]

where \( \hat{S}_E \) is the set of all excitation operators used in the wavefunction. Substituting into the Equation 71 we get

\[ |\Psi_{CC}\rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{m} \sum_{\{ \hat{E}_i^{a_1} \ldots \hat{E}_i^{a_n} \} \subseteq \hat{S}_E} \prod_{k=1}^{n} t_i^a \hat{E}_i^a |m\rangle \]
\[ = \sum_{m} \sum_{n=0}^{\infty} \sum_{\{ \hat{E}_i^{a_1} \ldots \hat{E}_i^{a_n} \} \subseteq \hat{S}_E} \text{sgn}(\sigma(\hat{E}_i^{a_1} \ldots \hat{E}_i^{a_n})) \prod_{k=1}^{n} t_i^a \hat{E}_i^a |m\rangle \]
\[ (73) \]

where the second sum is the sum over all possible combinations of excitations that would produce the given Slater determinant from the reference. Though it is unnecessary, \( n \in \mathbb{N} \) was included to
specify that the subset is no longer constrained to be of a certain size by an external variable, \( n \).

In the rest of the article, this notation will be dropped.

### 8.5. CC with Creation Operators

Let \( \mathbf{b}_i \) be a set of an even number of orbitals, \( \mathbf{f}_i \) be a set of an odd number of orbitals, \( \hat{A}_{\mathbf{b}_i} \) and \( \hat{A}_{\mathbf{f}_i} \) be the creation operators that create these orbitals, and \( C_{\mathbf{b}_i} \) and \( C_{\mathbf{f}_i} \) are the coefficient for the associated creation operators. Then, the CC wavefunction using creation operators will be

\[
|\Psi_{\text{CC}}\rangle = \exp \left( \sum_{\mathbf{b}_i} C_{\mathbf{b}_i} \hat{A}_{\mathbf{b}_i} + \sum_{\mathbf{f}_i} C_{\mathbf{f}_i} \hat{A}_{\mathbf{f}_i} \right) |0\rangle
\]

(74)

Taking the same approach as Equation 65, we have operators, \( \{ \hat{Q}_{j_1} \ldots \hat{Q}_{j_n} \} \), that are creation operators, \( \{ \hat{A}_{\mathbf{b}_1} \ldots \hat{A}_{\mathbf{b}_{n_b}} \hat{A}_{\mathbf{f}_1} \ldots \hat{A}_{\mathbf{f}_{n_f}} \} \), and the sum over the permutation is given by Equation 70.

Following Equation 65 and 70,

\[
|\Psi\rangle = \sum_{\mathbf{b}_i} \sum_{\mathbf{f}_i} \frac{1}{n!} \sum_{\sigma} \text{sgn} \left( \sigma\left( \hat{A}_{\mathbf{b}_1} \ldots \hat{A}_{\mathbf{b}_{n_b}} \hat{A}_{\mathbf{f}_1} \ldots \hat{A}_{\mathbf{f}_{n_f}} \right) \right) \sum_{\sigma} \left| C_{\mathbf{b}_1} \ldots C_{\mathbf{b}_{n_b}} \right|^+ \left| C_{\mathbf{f}_1} \ldots C_{\mathbf{f}_{n_f}} \right|^{-} \\
= \sum_{\mathbf{b}_i} \sum_{\mathbf{f}_i} \frac{1}{n!} \sum_{\sigma} \text{sgn} \left( \sigma\left( \hat{A}_{\mathbf{b}_1} \ldots \hat{A}_{\mathbf{b}_{n_b}} \hat{A}_{\mathbf{f}_1} \ldots \hat{A}_{\mathbf{f}_{n_f}} \right) \right) \left| C_{\mathbf{b}_1} \ldots C_{\mathbf{b}_{n_b}} \right|^+ \left| C_{\mathbf{f}_1} \ldots C_{\mathbf{f}_{n_f}} \right|^{-} \\
= \sum_{\mathbf{b}_i} \sum_{\mathbf{f}_i} \frac{1}{n_b!n_f!} \sum_{\sigma} \text{sgn} \left( \sigma\left( \hat{A}_{\mathbf{b}_1} \ldots \hat{A}_{\mathbf{b}_{n_b}} \hat{A}_{\mathbf{f}_1} \ldots \hat{A}_{\mathbf{f}_{n_f}} \right) \right) \left| C_{\mathbf{b}_1} \ldots C_{\mathbf{b}_{n_b}} \right|^+ \left| C_{\mathbf{f}_1} \ldots C_{\mathbf{f}_{n_f}} \right|^{-}
\]

(75)

Note that the \( n \in \mathbb{N} \) was omitted and it is implied that the size of the subset is not constrained by an external variable.

Since the determinant is zero when any two rows are equivalent, \( n_f \leq 1 \). In contrast, we can
take the permanent of a matrix with repeating rows:
\[
\begin{vmatrix}
  a_1 & \ldots & a_n \\
  \vdots & \ddots & \vdots \\
  a_1 & \ldots & a_n \\
\end{vmatrix}^+ = \sum_{\sigma \in S_n} \prod_{i=1}^{n} a_i \\
= n! \prod_{i=1}^{n} a_i
\]

Therefore, we get
\[
\sum_{\{b_1 \ldots b_{n_b}\} \subseteq \tilde{S}_b, f \in \tilde{S}_f \atop \text{sgn} \tilde{A}_{b_1}^\dagger \ldots \tilde{A}_{b_{n_b}}^\dagger \tilde{A}_f^\dagger \langle 0 \rangle = |m\rangle} \prod_{i=1}^{n_b} C_{b_i} |C_f \rangle \\
\left( \prod_{i=1}^{n_b} C_{b_i} \right) |m\rangle
\]

Since the sum over \( \{b_1 \ldots b_{n_b}\} \) only occurs when \( m \) has an odd number of electrons and the sum over \( \{b_1 \ldots b_{n_b}\} \) only occurs when \( m \) has an even number of electrons, we can separate these two cases if the desired number of electrons in the system, \( N \), is either even or odd.

\[
\Psi = \begin{cases} 
\sum_{m} \sum_{\{b_1 \ldots b_{n_b}\} \subseteq \tilde{S}_b, f \in \tilde{S}_f \atop \text{sgn} \tilde{A}_{b_1}^\dagger \ldots \tilde{A}_{b_{n_b}}^\dagger \tilde{A}_f^\dagger \langle 0 \rangle = |m\rangle} \prod_{i=1}^{n_b} C_{b_i} |C_f \rangle |m\rangle \quad \text{if } N \text{ is odd} \\
\sum_{m} \sum_{\{b_1 \ldots b_{n_b}\} \subseteq \tilde{S}_b \atop \text{sgn} \tilde{A}_{b_1}^\dagger \ldots \tilde{A}_{b_{n_b}}^\dagger \langle 0 \rangle = |m\rangle} \prod_{i=1}^{n_b} C_{b_i} |m\rangle \quad \text{if } N \text{ is even}
\end{cases}
\]

8.6. Generalized Quasiparticle

Just as in Section 8.5, let \( b_i \) be a set of an even number of orbitals, \( f_i \) be a set of an odd number of orbitals, \( \tilde{A}_{b_i}^\dagger \) and \( \tilde{A}_{f_i}^\dagger \) be the creation operators that create the associated orbitals. We can construct a quasiparticle as a linear combination of these creation operators. The desired wavefunction is a product of these quasiparticles

\[
|\Psi\rangle = \prod_{i=1}^{n} \left( \sum_{b_i} C_{p:b_i} \tilde{A}_{b_i}^\dagger + \sum_{f_i} C_{p:f_i} \tilde{A}_{f_i}^\dagger \right) |0\rangle
\]

where \( C_{p:b_i} \) and \( C_{p:f_i} \) are coefficients of the creation operators \( \tilde{A}_{b_i}^\dagger \) and \( \tilde{A}_{f_i}^\dagger \) in the construction of the \( p^{th} \) quasiparticle.
Taking the same approach as Equation \[65\] we have operators, \(\{\hat{Q}_{j1}, \ldots, \hat{Q}_{jn}\}\), that are creation operators, \(\{\hat{A}_{b1}, \ldots, \hat{A}_{bn}\}\), \(\hat{A}_{f1}, \ldots, \hat{A}_{fn}\)\), and the sum over the permutation is given by Equation \[70\]

\[
|\Psi\rangle = \sum_{m} \sum_{\{b_{1}, \ldots, b_{nb}\} \subseteq \tilde{S}_{b}, \{f_{1}, \ldots, f_{nf}\} \subseteq \tilde{S}_{f}} \text{sgn} \left( \sigma(\hat{A}_{b1}^{\dagger}, \ldots, \hat{A}_{bn}^{\dagger}, \hat{A}_{f1}^{\dagger}, \ldots, \hat{A}_{fn}^{\dagger}) \right) \sum_{\{i_{1}^{b}, \ldots, i_{nb}^{b}\} \subseteq \{b_{1}, \ldots, b_{nb}\}, \{i_{1}^{f}, \ldots, i_{nf}^{f}\} = \{b_{1}, \ldots, b_{nb}\} \setminus \{i_{1}^{b}, \ldots, i_{nb}^{b}\}} C_{1i_{1}^{b}}^{b} \cdots C_{1i_{nb}^{b}}^{b} C_{1i_{1}^{f}}^{f} \cdots C_{1i_{nf}^{f}}^{f} |m\rangle
\]

where \(C_{b}^{b}\) is the submatrix of \(C\) composed of the first \(n_{b}\) rows and \(C_{f}^{f}\) is composed of the remaining rows. It was assumed that the first \(n_{b}\) columns belong to the even-electron operators and the remaining columns to the odd-electron operators.