Strategies for Extending Geminal-Based Wavefunctions:

Open Shells and Beyond

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We discuss some strategies for extending recent geminal-based methods to open-shells by replacing the geminal-creation operators with more general composite boson creation operators, and even creation operators that mix fermionic and bosonic components. We also discuss the utility of symmetry-breaking and restoration, but using a projective (not a variational) approach. Both strategies—either together or separately—give a pathway for extending geminals-based methods to open shells, while retaining the computational efficiency and conceptual simplicity of existing geminal product wavefunctions.

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I.   Introduction

In the past few decades, molecular electronic structure theory has evolved from a specialized research field, accessible only to the cognoscenti, to a mainstream research tool used by not only theoretical chemists and physicists, but experimentalists as well. Electronic structure theory is, therefore, often assumed to be a mature research field, and this is largely true for the large class of systems that are well-described by a single electron configuration. For such systems, a Slater determinant wavefunction is a good starting point for further improvements, and standard electronic structure theory software packages are available. Using these tools, a wealth of insight into the thermodynamic and electromagnetic properties of organic and main-group inorganic molecules and materials has been attained.[1-6]

Traditional electronic structure theory methods are unreliable, however, for systems that have many important electron configurations. These systems are labeled strongly-correlated, because the usual conceptual and computational methods for treating electron correlation—all of which are based on the assumption that a single Slater determinant provides an adequate representation of the electronic wavefunction—are inapplicable here. As a general rule, a system is strongly correlated if the values of the electron-electron repulsion integrals between electrons in the valence orbitals are comparable to the band gap. In these cases there are usually many important electron-electron configurations, each with its own trade-off between the aufbau principle (filling in the lowest-energy orbitals with two electrons apiece) and Hund's rules (spreading electrons around (quasi)degenerate orbitals to reduce the electron-electron repulsion energy). Prototypical cases include spin-glasses, stretched bonds, and compounds including one or more open-shell transition metal or rare-earth elements.[7-9]

Multireference methods—where the single-Slater-determinant reference is replaced by a linear combination of (possibly many) Slater determinants—are the most conventional and straightforward way to treat strongly-correlated systems. In a multiconfiguration self-consistent field approach (MCSCF), one takes a linear combination of the most important electron configurations and optimizes the linear coefficients and the underlying orbitals. It is sometimes challenging to converge MCSCF calculations, so often one considers all possible ways of filling the nearly-degenerate orbital space (complete-active-space self-consistent-field, CASSCF) or imposes other restrictions on the types of electron configurations that are included (restricted-active-space self-consistent-field, RASSCF).[10, 11] Multiconfiguration methods are notoriously difficult to use--it can be very challenging to pick the most important configurations and to make a suitable initial guess for the orbital optimization--and their cost grows with the number of electron configurations that must be included. Unfortunately, the number of important electron configurations grows exponentially as the number of "active" orbitals increases. Multiconfigurational methods are restricted, therefore, to relatively small systems. Moreover, multiconfigurational approaches merely define an improved reference state for further computation: just as in single-reference methods, corrections for dynamic (weak) correlation must be made. Unfortunately, compared to single-reference approaches for dynamic correlation, multireference dynamic correlation methods are comparatively immature.

Our goal is to develop methods for describing strong electron correlation in large systems. In such cases, traditional multireference approaches are unsuitable, primarily because of their exponentially increasing computational cost, though the difficulty of selecting a good active space and constructing a suitable initial guess for the orbitals is also problematic. Our ambition is to develop methods for strong electron correlation that resemble mean-field methods like Hartree-

Fock and Kohn-Sham density functional theory in terms of both computational cost and ease of use. Our strategy is to develop mean-field methods that can model strong electron correlation.

Most generally, a mean-field wavefunction is a simple product form. In second quantization, we can express the wavefunction as:

$$\left| \Psi_{\text{mean-field}} \right\rangle = \prod_{q=1}^{Q} c_q^\dagger \left| \theta \right\rangle , \tag{1}$$

where $\left| \theta \right\rangle$ denotes the vacuum state (typically chosen as the state with no electrons), $c_q^\dagger$ creates a particle in the state q, and Q is the total number of particles created. If the particle is an electron, then Eq. (1) is a Slater determinant. If the particle is a composite particle, often called a quasiparticle, then the wavefunction in Eq. (1) explicitly describes the correlations between the electrons that compose the particle, but not between electrons that compose different particles.[12-16] (Each composite particles moves in the mean-field due to the cloud of other composite particles, so correlations between the electrons in different composite particles are treated only in an average sense.) The words "composite particle" and "quasiparticle" are used more-or-less interchangeably in the literature, with quasiparticle terminology more prevalent when one views the particle as a collective excitation, and composite particle terminology more prevalent when one focuses on the explicit composition of the particles. Our approach in this paper is to construct composite particles that are suitable for modeling strong electron correlation. This strategy is motivated by our recent successes using geminals (electron-pair composite particles).[17-23]

There are numerous examples from the literature that demonstrate that, by making suitable choices for the composite particles, one can ensure computational feasibility.[12, 16, 24, 25] We will explore general principles that ensure computational affordability in subsequent sections of this paper. Similarly, one can always obtain the *exact* wavefunction by making a suitable choice

of composite particles. There are several different approaches to doing this, ranging from the trivial

(an N-electron system can be described as an N-electron composite particle) to the obscure. For

example, the exact N-electron wavefunction can be written as an N-electron unitary transformation

of a Slater determinant,

$$\left|\Psi_{\text{exact}}\right\rangle = U_N^\dagger \left(a_1^\dagger a_2^\dagger \cdots a_N^\dagger\right)|\theta\rangle, \tag{2}$$

where $a_k^\dagger$ is the electron-creation operator that generates an electron in the kth spin-orbital. This

can clearly be rewritten as a product of composite fermions (compare Eq. (1))

$$\left|\Psi_{\text{exact}}\right\rangle = \prod_{n=1}^{N}\left(U_N^\dagger a_n^\dagger U_N\right)|\theta\rangle. \tag{3}$$

where it is understood that the unitary transformation maps the vacuum to itself. If one expresses

an N-electron unitary transformation as the exponential of an N-electron antiHermitian operator,

and uses the Baker-Campbell-Hausdorff formula to simplify Eq. (3), it becomes clear that the

composite particles in Eq. (3) are composed of electrons and holes. Clearly the composite

particles in Eq. (3) are computationally intractable, however.

Recently, we have been pursuing approaches based on composite particles built from

electron pairs, called geminals,

$$G_q^\dagger = \sum_{i=1}^{2B}\sum_{j=1}^{2B} c_{q;ij}^{(\text{APG})} a_i^\dagger a_j^\dagger. \tag{4}$$

B denotes the number of spatial orbital basis functions; $2B$ is the dimensionality of the single-

particle basis which is, in our context, equal to the number of spin-orbitals. The mean-field

wavefunction constructed as a product of geminals is called an antisymmetric product of geminals

(APG),[26-49]

$$\left|\Psi_{\text{APG}}\right\rangle = \prod_{q=1}^{N/2} G_q^\dagger |\theta\rangle. \tag{5}$$

Optimizing the general APG wavefunction is computationally intractable,[27] but by imposing suitable restrictions on the geminal expansion coefficients, $c_{q;ij}$, we were able to develop computationally efficient methods that retained useful accuracy. All of our geminal models were special cases of the antisymmetric product of interacting geminals (APIG),[50-52] which is the antisymmetric product of so-called natural geminals, which are constructed by directly building geminals from orbital-pairs,

$$P_q^\dagger = \sum_{i=1}^{B} c_{q;i}^{(\text{APIG})} a_i^\dagger a_{B+i}^\dagger \tag{6}$$

$$\left|\Psi_{\text{APIG}}\right\rangle = \prod_{q=1}^{N/2} P_q^\dagger \left|\theta\right\rangle \tag{7}$$

Equation (6) corresponds to the assumption that every geminal has the same natural orbitals.

In our research, we have focused on cases where the paired orbitals have the same spatial part and differ only in spin, i.e.,

$$P_q^\dagger = \sum_{i=1}^{B} c_{q;i}^{(\text{APIG})} a_{i\alpha}^\dagger a_{i\beta}^\dagger \tag{8}$$

With this additional restriction, the APIG wavefunction is a seniority-zero wavefunction, and can be viewed as a mean-field parameterization of the doubly-occupied configuration interaction (DOCI) wavefunction.[53-69] In DOCI, every wavefunction is written as a linear combination of Slater determinants in which every orbital is either doubly-occupied or empty.

$$\left|\Psi_{\text{DOCI}}\right\rangle = \sum_{\left\{m_i \in \{0,1\} \middle| \frac{N}{2} = \sum_{i=1}^{B} m_i \right\}} c_{m_1 m_2 \dots m_B}^{\text{DOCI}} \left(a_{1\alpha}^\dagger a_{1\beta}^\dagger\right)^{m_1} \left(a_{2\alpha}^\dagger a_{2\beta}^\dagger\right)^{m_2} \cdots \left(a_{B\alpha}^\dagger a_{B\beta}^\dagger\right)^{m_B} \left|\theta\right\rangle \tag{9}$$

In APIG, the coefficients of the DOCI wavefunction are parameterized by the geminal expansion coefficients in (6). Specifically, the coefficient of a Slater determinant is a permanent of the geminal coefficients of the occupied orbitals,[17, 18]

$$c^{\text{DOCI}}_{m_1 m_2 \ldots m_B} = \left. \left| c^{(\text{APIG})}_{q;i} \right|^+ \right|_{\substack{q=1,2,\ldots N/2 \\ m_i = 1}} \tag{10}$$

Because evaluating the permanent of a matrix is #P-complete, one must impose restrictions on the geminal coefficients to attain computational feasibility. For example, because the permanent of a Cauchy matrix (the Hadamard inverse of a rank-two matrix) is easily evaluated by Borchardt's theorem,[70, 71] it is sensible to parameterize the geminal coefficient matrix as:[17, 18]

$$c_{q;i} = \frac{\zeta_i \eta_q}{\varepsilon_i - \lambda_q} \tag{11}$$

With this choice, it is computationally feasible to compute the coefficient of any desired Slater determinant in the expansion (9). It is feasible, then, to determine the geminal coefficients which solve the Schrodinger equation by projecting the Schrödinger equation onto Slater determinants,

$$\left\langle \theta \left| a_{k_1} a_{k_2} \cdots a_{k_N} \hat{H} \right| \Psi_{\text{APIG}} \right\rangle = E \left\langle \theta \left| a_{k_1} a_{k_2} \cdots a_{k_N} \right| \Psi_{\text{APIG}} \right\rangle \tag{12}$$

If the number of Slater determinants that one projects against is greater than the number of free parameters in the APIG-like wavefunction, then one solves the nonlinear equations (12) in the least-squares sense. The particular approach based on the projected Schrödinger equation, (12), where the APIG coefficients are parameterized by an inverse-rank-two matrix, (11), is called the antisymmetric product of rank-two geminals (APr2G).[17]

The applicability of this approach is clearly limited to systems that can be reliably described by seniority-zero wavefunctions. For example, one can treat closed-shell singlets with this approach. One can also treat some special types of open-shell systems (e.g., some singlet diradicals) with seniority-zero wavefunction forms. In general, however, seniority-zero approaches are inadequate for systems whose important electron configurations include singly-occupied orbitals. We view "seniority-zero" as the appropriate extension of the concept of "closed-

shell singlet" to multireference quantum chemistry, where the distinction between occupied and unoccupied orbitals no longer exists. Consistent with this interpretation, in this paper we will use the terms "closed shell" and "seniority zero" interchangeably. Similarly, we use "open-shell" to mean "beyond seniority zero."

In the subsequent sections of this paper, we will consider general strategies for extending composite particle methods and, in particular, geminals-based methods, to open-shells. In section III, we will explore techniques based on symmetry-breaking. For example, by allowing the orbital-pairs in Eq. (6) to be unrestricted orbitals (different spatial orbitals for different spins), or even allowing "generalized" orbitals that are not spin-eigenfunctions, the expansion in Eq. (9) (in a restricted spin-orbital basis) is versatile enough to include every Slater determinant, not just the seniority-zero determinants. In section IV, we will consider an alternative approach, where the geminal creation operators (e.g., (6)) are generalized to explicitly accommodate open shells. In section IV we will also discuss how products of geminals can be used to treat odd numbers of electrons. Section V offers some perspectives for the future.

II.   Composite Particles

While our primary focus is on geminals-related approaches, many of the features that determine whether a given type of geminals is computationally tractable are, in fact, generic to all types of composite particles. In particular, it is usually only feasible to consider composite particles where the (anti)commutation relation between two creation (or two annihilation) operators for the composite particles has a simple expression like

$$c_i^\dagger c_j^\dagger = e^{i\eta} c_j^\dagger c_i^\dagger \qquad (13)$$

If $\eta = 2n\pi$ (n is an integer), then the composite particles are symmetric with respect to interchange and they are referred to as cobosons. Cobosons are composite particles built from even numbers of fermion creation/annihilation operators; the prototypical example is a geminal. If $\eta = (2n+1)\pi$, then the composite particles are antisymmetric with respect to exchange and they are referred to as cofermions. Cofermions are composite particles built from odd numbers of fermion creation/annihilation operators. Other cases of Eq. (13) would be called co-anyons.[72, 73] Even co-anyons are very special composite particles: a generic composite particle of the form

$$c_q^\dagger = a_q^{(0)} + \sum_{j=1}^{2B}\left(c_{q;j}^{(p)}a_j^\dagger + c_{q;j}^{(h)}a_j\right) + \sum_{j=1}^{2B}\sum_{k=1}^{2B}\left(c_{q;jk}^{(pp)}a_j^\dagger a_k^\dagger + c_{q;jk}^{(ph)}a_j^\dagger a_k + c_{q;j}^{(hh)}a_j a_k\right) + \cdots \tag{14}$$

has no simple (anti)commutation expression comparable to Eq. (13). Composite particles that do not have a simple expression analogous to Eq. (13) tend to be intractable.[12, 18]

Computationally tractable methods built on composite particles also tend to have simple expressions for the (generalized) commutation relation between creation and annihilation operators. Typically, one has an expression like

$$c_i c_j^\dagger = \begin{cases} e^{i\eta}c_j^\dagger c_i & i \neq j \\ \hat{M}_i - c_i^\dagger c_i & i = j \end{cases} \tag{15}$$

which generalizes the normal expression for "elementary" anyons. Ideally $\hat{M}_i$ is a simple operator (even just a constant). Choosing composite particles with simple expressions for the reordering of creation and annihilation operators is extremely nontrivial. The approach we have taken in our research is to define creation/annihilation operators that are raising/lowering operators from an algebra.[18][74] This ensures convenient expressions for all the (anti)commutation relations we need. For example, our approach to APIG is based on the realization that the creation/annihilation of an electron pair in a spatial orbital defines a quasi-spin algebra, su(2).[18, 75-77] The results

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we present in this paper, especially in section IV, will also be heavily influenced by this algebraic perspective.

III. Symmetry-breaking (and restoration)

A. Breaking and Restoring Symmetry

Relaxing constraints on an approximate wavefunction—even if those constraints are exactly satisfied by the exact wavefunction—often leads to a lower energy. While this energy-lowering is an artifact of the imperfections in the approximate wavefunction form being considered, it is practically convenient (because the symmetry-broken energy is closer to the true energy) and conceptually insightful (because symmetry-breaking is a sentinel for the presence of nearly-degenerate states with different symmetry labels, and therefore of strong correlation). Moreover, if one can *restore* the symmetry, then it is often possible to obtain even better results.[78-89]

To understand this, expand a symmetry-broken wavefunction, $|\Psi\rangle$, as a linear combination of symmetry-labeled pieces $|\Psi_{\mathcal{S}}\rangle$. We now consider the projected Schrödinger equation, and we will choose to project only on configuration state functions, $\left|\Phi_{\mathcal{S}_0,j}\right\rangle$, that have the same symmetry label as the target state,

$$\left\langle \Phi_{\mathcal{S}_0,j}\left|\hat{H}\right|\sum_{\mathcal{S}}c_{\mathcal{S}}\Psi_{\mathcal{S}}\right\rangle = E\left\langle \Phi_{\mathcal{S}_0,j}\left|\sum_{\mathcal{S}}c_{\mathcal{S}}\Psi_{\mathcal{S}}\right.\right\rangle \tag{16}$$

Because the Hamiltonian does not link sectors with different symmetry,

$$0 = \left\langle \Phi_{\mathcal{S},j}\left|\hat{H}\right|\Psi_{\mathcal{S}'}\right\rangle = \left\langle \Phi_{\mathcal{S},j}\middle|\Psi_{\mathcal{S}'}\right\rangle \qquad\qquad \mathcal{S} \neq \mathcal{S}', \tag{17}$$

the projected Schrödinger equation in (16) effectively targets the state with the symmetry-label of interest,

$$\left\langle \Phi_{\mathcal{S}_0,j} \middle| \hat{H} \middle| \Psi_{\mathcal{S}_0} \right\rangle = E_{\mathcal{S}_0} \left\langle \Phi_{\mathcal{S}_0,j} \middle| \Psi_{\mathcal{S}_0} \right\rangle \tag{18}$$

and is therefore equivalent to first projecting the wavefunction onto the symmetry sector of interest, and then solving the projected Schrödinger equation for the symmetry-projected wavefunction. This is helpful because the wavefunction-form of $\left| \Psi_{\mathcal{S}_0} \right\rangle$ might be very complicated, so much so that expression (18) may be computationally inaccessible even though it is easy to evaluate the (entirely equivalent) expression (16). Notice that the energy value corresponding to the symmetry-restored state can be much lower than the expectation value for the energy of the symmetry-broken state because the non-symmetry-projected wavefunction will generally include contributions from symmetry-states with higher energy than the targeted state:

$$\min_{\mathcal{S}} \left\langle \Psi_{\mathcal{S}} \middle| \hat{H} \middle| \Psi_{\mathcal{S}} \right\rangle \leq \left\langle \sum_{\mathcal{S}} c_{\mathcal{S}} \Psi_{\mathcal{S}} \middle| \hat{H} \middle| \sum_{\mathcal{S}'} c_{\mathcal{S}'} \Psi_{\mathcal{S}'} \right\rangle \tag{19}$$

B. Spin

Although the general form of the antisymmetric product of interacting geminals (APIG) in Eq. (7) makes no restriction on the form of spin-orbitals that are paired, pairing the α- and β-spin components of the same spatial orbitals is consistent with the chemical intuition provided by the Lewis picture, and ensures that the APIG wavefunction is a singlet-spin eigenfunction, with $S = M_S = 0$. Allowing the α- and β-spin orbitals to have different spatial parts (unrestricted orbitals) can, in some cases, lead to a lower energy due to spin-symmetry breaking.[17-19, 44, 81, 90] (For example, in the stretched Nitrogen molecule, a product of geminals with restricted orbitals can actually have a higher energy than unrestricted Hartree-Fock.[91]) The drawback of this approach

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is that the APIG wavefunction no longer corresponds to a pure singlet-spin state, though it is still true that $M_S = 0$. In order to describe systems with $M_S > 0$ like triplet biradicals or a high-spin transition metal complexes, we need to allow even more flexibility, so that spin-orbitals with the same spin can pair. Rather than (semi-arbitrarily) picking a spin-orbital pairing scheme, it seems better to optimize the spin-orbitals without any constraints, allowing "generalized" spin-orbitals that are not eigenfunctions of $\hat{s}_z$. The resulting APIG wavefunction is generally not a spin-eigenfunction.

To make this discussion more specific, suppose that we are given an initial set of restricted spin-orbitals; this could be the output, for example, of a restricted Hartree-Fock (RHF) calculation. By convention, we will choose the first B orbitals to be α-spin orbitals and the second B orbitals to be β-spin orbitals, with the spatial parts of orbitals j and $B+j$ defined to be the same. Optimization of spin-orbitals is essential to most geminals-based methods, and is typically performed by optimizing the antiHermitian matrix that we use to parameterize a unitary transformation of the orbitals, $\mathbf{U} = \exp(\boldsymbol{\kappa})$. Writing $\boldsymbol{\kappa}$ in terms of its $B \times B$ spin-blocks,[18]

$$\boldsymbol{\kappa} = \begin{bmatrix} \boldsymbol{\kappa}_{\alpha\alpha} & \boldsymbol{\kappa}_{\alpha\beta} \\ -\boldsymbol{\kappa}_{\alpha\beta}^{*} & \boldsymbol{\kappa}_{\beta\beta} \end{bmatrix} \qquad \boldsymbol{\kappa}_{\sigma\sigma'} = -\boldsymbol{\kappa}_{\sigma'\sigma}^{\dagger} \qquad (20)$$

the choice of restricted ($\boldsymbol{\kappa}_{\alpha\alpha} = \boldsymbol{\kappa}_{\beta\beta}$; $\boldsymbol{\kappa}_{\alpha\beta} = 0$) and unrestricted ($\boldsymbol{\kappa}_{\alpha\alpha} \neq \boldsymbol{\kappa}_{\beta\beta}$; $\boldsymbol{\kappa}_{\alpha\beta} = 0$) spin-orbitals correspond to additional restrictions on $\boldsymbol{\kappa}$.

Unrestricted and generalized spin-orbitals break the spin-symmetry of the APIG wavefunction, but it is feasible to (at least partially) restore symmetry. In the most general case, this requires building configuration state functions (or at least approximate eigenfunctions of $\hat{S}^2$, $\hat{S}_z$, and any other symmetries of interest) that are linear combinations of only a few Slater determinants, so that the terms that enter the projected Schrödinger equation are easy to evaluate.

For unrestricted or generalized orbitals, it is generally only possible to form approximate eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$, since exact eigenfunctions usually have contributions from a combinatorial number of Slater determinants.

Consider the orbital transformation generated by $\mathbf{T} = \exp(\boldsymbol{\tau})$ with

$$\boldsymbol{\tau} = \begin{bmatrix} \boldsymbol{\tau}_{\alpha\alpha} & \mathbf{0} \\ \boldsymbol{\tau}_{\beta\alpha} & \boldsymbol{\tau}_{\beta\beta} \end{bmatrix} \qquad \boldsymbol{\tau}_{\alpha\alpha} = -\boldsymbol{\tau}_{\alpha\alpha}^{\dagger} \tag{21}$$

This includes unrestricted orbitals (when $\boldsymbol{\tau}_{\beta\alpha} = 0$ and $\boldsymbol{\tau}_{\beta\beta} = -\boldsymbol{\tau}_{\beta\beta}^{\dagger}$), but in general the "β-spin" orbitals are not spin-eigenfunctions and are nonorthogonal. We use only the spatial orbitals from the α-spin set for projection. That is, we project on Slater determinants where the first B (α-spin) orbitals are constructed according to Eq. (21), but the next B "β-spin" orbitals are constructed by spin-flipping the α-spin orbitals. I.e.,

$$\tilde{a}_{B+i}^{\dagger} = |\beta\rangle\langle\alpha| a_i^{\dagger} \qquad 1 \leq i \leq B \tag{22}$$

Slater determinants of the form

$$\prod_{k=1}^{N/2} a_{i_k}^{\dagger} \tilde{a}_{B+i_k}^{\dagger} |\theta\rangle \tag{23}$$

are singlet-state spin-eigenfunctions. We also write the Hamiltonian using the spin-flipped basis, Eq. (22).

The overlap of the wavefunction form in Eq. (23) with an APIG wavefunction built using the transformed β-spin orbitals from (21) is

$$\left\langle \theta \left| \prod_{k=1}^{N/2} \tilde{a}_{B+i_k} a_{i_k} \right| \Psi_{\text{APIG}} \right\rangle = \left| c_{q;i_k}^{(\text{APIG})} \right|^{+}_{\substack{q=1,2,\dots N/2 \\ k=1,2,\dots N/2}} \left\langle \theta \left| \prod_{k=1}^{N/2} \tilde{a}_{B+i_k} a_{B+i_k}^{\dagger} \right| \theta \right\rangle \tag{24}$$

The second factor on the right-hand-side of Eq. (24) does not depend on $\boldsymbol{\tau}_{\beta\alpha}$ (which can therefore be set to zero without loss of generality) and is just the overlap between the spatial parts of the α-

spin orbitals and the (possibly nonorthogonal) β-spin orbitals. Therefore, one can break spin-symmetry in any APIG family wavefunction by using an orbital transformation of the form (21), and then restoring spin-symmetry by projecting the Schrödinger equation onto singlet-state determinants composed from spatial orbitals taken from the α-spin set, Eq. (23). This provides a practical approach to spin-symmetry-breaking-and-restoration in projected APIG methods.

C. Particle Number

Because products of geminals do not include electron correlation between electrons assigned to different geminals, these wavefunctions do not fully describe dynamic correlation. Inter-geminal correlations can be included by a linear combination of geminal products but, in analogy to the configuration interaction method for Slater determinants, any practical realization of such approach requires truncation of the expansion, and is therefore not size consistent. An alternative approach, analogous to coupled-cluster methods, would be to consider a coupled-cluster method for composite particles,

$$\left| \Psi_{\text{composite-CC}} \right\rangle = \exp\left(\sum_{b} \sum_{j\in\text{occ}}^{Q} t_j^b c_b^\dagger c_j + \sum_{b,c} \sum_{j,k\in\text{occ}}^{Q} t_{jk}^{bc} c_b^\dagger c_c^\dagger c_k c_j + \cdots \right)\left(\prod_{q=1}^{Q} c_q^\dagger \right)\left| \theta \right\rangle \qquad (25)$$

This approach is significantly more complicated than the analogous approach for spin-orbitals because of the more complicated (anti)commutation relations between the composite particles. (The linearized version of this coupled-cluster method is still practical, however.[92, 93]) Except for cofermions, it is important to allow excitations to all states (not just the "unoccupied" states of composite particles) because it is possible to have multiple composite particles in the same state. However, it is important to restrict the composite-particle states from which excitation can occur, because if all possible initial states are allowed in this approach one will sometimes recover a traditional coupled-cluster approach, and the treatment of strong correlation that was the *raison*

d'être of the composite fermion approach is lost. (This is the case, for example, if one allows all possible initial states for the antisymmetric product of 1-reference orbital geminals, AP1roG.[94, 95])

Methods motivated by Eq. (25) may be accurate, but they incur considerable additional computational expense. One can also construct linear combinations of products of composite particles by breaking particle-number symmetry; this is done by adding a constant term to the creation operator for the composite particle. For example, the expression for the APIG geminal (cf. Eq. (6)) becomes

$$\tilde{P}_q^\dagger = c_{q;0}^{(\mathrm{APIG})} + \sum_{i=1}^{B} c_{q;i}^{(\mathrm{APIG})} a_i^\dagger a_{B+i}^\dagger \tag{26}$$

$$\left| \Psi_{\mathrm{APIG}} \right\rangle = \prod_{q=1}^{Q} \tilde{P}_q^\dagger \left| \theta \right\rangle \tag{27}$$

The resulting product wavefunction is a specific linear combination of geminals. It is size consistent since if you do calculations on two separated systems, *A* and *B*, using this ansatz, the product of their wavefunctions, $\left| \Psi_{\mathrm{APIG;A}} \Psi_{\mathrm{APIG;B}} \right\rangle$, has the form of Eq. (27) and will solve the projected Schrödinger equation for $\hat{H}_{\mathrm{A\cdots B}} = \hat{H}_{\mathrm{A}} + \hat{H}_{\mathrm{B}}$.

The projection of the APIG wavefunction in Eq. (27) onto an *N*-electron seniority-zero Slater determinant becomes

$$\left\langle \theta \left| a_{k_1} a_{k_1+B} a_{k_2} a_{k_2+B} \cdots a_{k_{N/2}} a_{k_{N/2}+B} \prod_{q=1}^{Q} \tilde{P}_q^\dagger \right| \theta \right\rangle$$

$$= \frac{1}{\left(Q - \frac{1}{2}N\right)!} \left| \begin{array}{ccccc} c_{1;0}^{(\mathrm{APIG})} & c_{1;0}^{(\mathrm{APIG})} & c_{1;k_1}^{(\mathrm{APIG})} & \cdots & c_{1;k_{N/2}}^{(\mathrm{APIG})} \\ c_{2;0}^{(\mathrm{APIG})} & c_{2;0}^{(\mathrm{APIG})} & c_{2;k_1}^{(\mathrm{APIG})} & \cdots & c_{2;k_{N/2}}^{(\mathrm{APIG})} \\ & & & & \\ \underbrace{c_{Q;0}^{(\mathrm{APIG})} \qquad c_{Q;0}^{(\mathrm{APIG})}}_{(Q-N/2 \text{ times})} & & c_{Q;k_1}^{(\mathrm{APIG})} & \cdots & c_{Q;k_{N/2}}^{(\mathrm{APIG})} \end{array} \right|^{+} \tag{28}$$

Specifically, using the Laplace expansion for the permanent one recognizes that Eq. (28) can be rewritten as a sum over all possible ways of selecting $N/2$ geminals from the Q available geminals, with a coefficient that is the permanent of the constants associated with the unselected geminals. Then, exploiting the freedom to normalize geminals as we see fit, all the constant terms can be chosen to be the same for each geminal (*e.g.*, $c_{q;0}^{(\mathrm{APIG})} = 1$). Every term in the Laplace expansion now has the same coefficient, so the projection is the permanent of a rectangular matrix,

$$\left\langle \theta \left| a_{k_1} a_{k_1+B} a_{k_2} a_{k_2+B} \cdots a_{k_{N/2}} a_{k_{N/2}+B} \prod_{q=1}^{Q} \tilde{P}_q^\dagger \right| \theta \right\rangle$$

$$= \frac{1}{\left(Q - \frac{1}{2}N\right)!} \left| \begin{array}{ccc} c_{1;k_1}^{(\mathrm{APIG})} & \cdots & c_{1;k_{N/2}}^{(\mathrm{APIG})} \\ c_{2;k_1}^{(\mathrm{APIG})} & \cdots & c_{2;k_{N/2}}^{(\mathrm{APIG})} \\ & & \\ c_{Q;k_1}^{(\mathrm{APIG})} & \cdots & c_{Q;k_{N/2}}^{(\mathrm{APIG})} \end{array} \right|^{+} \tag{29}$$

This rectangular permanent can be simply evaluated for geminal coefficients of the inverse-rank-two form (cf. Eq. (11)) using a generalization of Borchardt's theorem.[96] A different strategy for evaluating number-symmetry-broken geminals will be presented in section IV.E.

D. Particle Type

One way to motivate breaking spin- and particle-number symmetry is to notice that the composite particles may differ in spin and cardinality from the elementary particles that compose them. Similarly, composite particles may have different statistics: one can build composite bosons (like geminals) from elementary fermions (like electrons). This motivated us to explore breaking the fundamental fermionic symmetries of the spin-orbitals.

The first approach we considered was based on anyons.[72, 73, 97-99] Suppose we impose the anyonic particle symmetries on the spin orbitals, *i.e.*,

$$
\begin{aligned}
\tilde{a}_i^\dagger \tilde{a}_j^\dagger &= e^{i\eta} \tilde{a}_j^\dagger \tilde{a}_i^\dagger & i < j \\
\tilde{a}_i \tilde{a}_j &= e^{i\eta} \tilde{a}_j \tilde{a}_i & i < j \\
\tilde{a}_i \tilde{a}_j^\dagger &= \begin{cases} e^{-i\eta} \tilde{a}_j^\dagger \tilde{a}_i & i \neq j \\ 1 - \tilde{a}_i^\dagger \tilde{a}_i & i = j \end{cases}
\end{aligned}
\tag{30}
$$

We can then build composite particle (e.g., geminals) out of these anyons. However, the essential difficulty will be clear even if we consider only a simple product of anyons. For simplicity, consider the analogue of a Slater determinant of two anyons,

$$
\left\langle 1,2 \left| \tilde{a}_k^\dagger \tilde{a}_l^\dagger \right| \theta \right\rangle = \phi_k(1)\phi_l(2) + e^{i\eta}\phi_k(2)\phi_l(1) = \frac{1}{2} \begin{vmatrix} \phi_k(1) & \phi_l(1) \\ \phi_k(2) & \phi_l(2) \end{vmatrix}^\eta
\tag{31}
$$

where we have denoted the anyonic analogue of the determinant as $\left| \phi_{k_1} \phi_{k_2} \cdots \phi_{k_N} \right|^\eta$. We can expand a 2-anyon wavefunction as a linear combination of a determinant and a permanent,

$$
\begin{vmatrix} \phi_k(1) & \phi_l(1) \\ \phi_k(2) & \phi_l(2) \end{vmatrix}^\eta = e^{\frac{1}{2}i\eta} \left(\cos\left(\tfrac{1}{2}\eta\right) \begin{vmatrix} \phi_k(1) & \phi_l(1) \\ \phi_k(2) & \phi_l(2) \end{vmatrix}^+ - i\sin\left(\tfrac{1}{2}\eta\right) \begin{vmatrix} \phi_k(1) & \phi_l(1) \\ \phi_k(2) & \phi_l(2) \end{vmatrix}^- \right)
\tag{32}
$$

and if we project this wavefunction against a determinant built from the same spatial orbitals, only the determinant contribution survives. For a many-anyon wavefunction, one can expand

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$\left| \phi_{k_1} \phi_{k_2} \cdots \phi_{k_N} \right|^{\eta}$ in terms of the irreducible representations of the symmetric group S_N, one of which

is the determinant. The coefficient of this determinant in the expansion is singled-out when

$\left| \phi_{k_1} \phi_{k_2} \cdots \phi_{k_N} \right|^{\eta}$ is projected against $\left| \phi_{k_1} \phi_{k_2} \cdots \phi_{k_N} \right|$. Since the coefficient of all the determinants is

determined by the characters of S_N, using anyonic creation operators instead of fermionic creation

operators in composite-particle methods merely scales the wavefunction by a constant unless the

(anti)commutation parameter η is different for different orbital pairs. Using different η for different

orbital pairs, however, leads to a seemingly intractable problem.

An alternative to using anyons is to replace the physical electron-creation operators, $a_k^\dagger$,

with composite fermions. One choice of cofermion with especially interesting properties are the

Majorana fermions,[100-104] which are self-adjoint,

$$\gamma_k^\dagger = \gamma_k \tag{33}$$

and satisfy the anticommutation relation

$$\gamma_k \gamma_l + \gamma_l \gamma_k = \gamma_k^\dagger \gamma_l^\dagger + \gamma_l^\dagger \gamma_k^\dagger = 2\delta_{kl} \tag{34}$$

Notice that you can "create" two Majorana fermions in the same state because the anticommutation

relation implies that

$$\left(\gamma_k \right)^2 = \left(\gamma_k^\dagger \right)^2 = \gamma_k^\dagger \gamma_k = \gamma_k \gamma_k^\dagger = 1 \tag{35}$$

There are many ways to construct cofermions that are Majorana fermions. It seems impractical to

consider all these possibilities, so we restrict ourselves to a specific representation that is motivated

by the pairing structure inherent in the APIG wavefunction. Specifically, for $k = 1,2,\ldots,B$, we

define

$$
\begin{aligned}
\gamma_{2k-1} &= a_k^\dagger + a_k & \gamma_{2B+2k-1} &= a_{k+B}^\dagger + a_{k+B} \\
\gamma_{2k} &= i\left(a_k^\dagger - a_k \right) & \gamma_{2B+2k} &= i\left(a_{k+B}^\dagger - a_{k+B} \right)
\end{aligned}
\tag{36}
$$

Consider forming interacting geminals from Majorana fermions,

$$
\begin{aligned}
P_q^\dagger &= \sum_{k=1}^{2B} c_{q;k}^{(\text{Majorana})} \gamma_k^\dagger \gamma_{2B+k}^\dagger \\
&= \sum_{k=1}^{B} c_{q;2k-1}^{(\text{Majorana})} \left(a_k^\dagger a_{k+B}^\dagger + a_k^\dagger a_{k+B} + a_k a_{k+B}^\dagger + a_k a_{k+B} \right) \\
&+ \sum_{k=1}^{B} c_{q;2k}^{(\text{Majorana})} \left(-a_k^\dagger a_{k+B}^\dagger + a_k^\dagger a_{k+B} + a_k a_{k+B}^\dagger - a_k a_{k+B} \right)
\end{aligned}
\tag{37}
$$

and project against an N-electron seniority-zero determinant

$$
\left\langle \theta \left| a_{k_1} a_{k_1+B} a_{k_2} a_{k_2+B} \cdots a_{k_{N/2}} a_{k_{N/2}+B} \prod_{q=1}^{Q} P_q^\dagger \right| \theta \right\rangle
\tag{38}
$$

If the physical vacuum is used, the particle-number-conserving terms in Eq. (37) never contribute. If we also choose the number of physical and Majorana fermions to be the same, $Q = N/2$, the particle-removing term in Eq. (37) also vanishes and the wavefunction is equivalent to an APIG wavefunction, with $c_{q,k}^{(\text{APIG})} = c_{q,2k-1}^{(\text{Majorana})} - c_{q,2k}^{(\text{Majorana})}$. If we choose the number of Majorana fermions to surpass the number of electrons by an even number of pairs, $Q = N/2 + 2M$, the number of permanents that need to be evaluated to determine the overlap in Eq. (38) proliferates at a combinatorial rate.

Finally, we consider a noncanonical quasiparticle, which we define as

$$
\tilde{a}_k^\dagger = \exp\left(\hat{T}\right) a_k^\dagger \exp\left(-\hat{T}\right)
\tag{39}
$$

This is a canonical quasiparticle if $\hat{T}$ is antiHermitian, but we are interested in more general operators, specifically, the form

$$
\hat{T} = \hat{T}_1 + \hat{G}_1 = \sum_{p,q=1}^{2B} \tau_{pq} a_p^\dagger a_q + \gamma_{pq} a_p a_q
\tag{40}
$$

A product of these noncanonical quasiparticles can be rewritten,

$$\tilde{a}_{k_1}^\dagger \tilde{a}_{k_1}^\dagger \cdots \tilde{a}_{k_Q}^\dagger |\theta\rangle = \exp\left(\hat{T}\right) a_{k_1}^\dagger a_{k_1}^\dagger \cdots a_{k_Q}^\dagger |\theta\rangle, \tag{41}$$

where we have assumed that $|\theta\rangle$ is the physical vacuum.

Let us first consider the special cases where one of the two terms in Eq. (40) vanishes. If $\gamma_{pq} = 0$, then the Schrödinger equation has the form

$$\hat{H} \exp\left(\hat{T}_1\right) a_{k_1}^\dagger a_{k_2}^\dagger \cdots a_{k_Q}^\dagger |\theta\rangle = E \exp\left(\hat{T}_1\right) a_{k_1}^\dagger a_{k_2}^\dagger \cdots a_{k_Q}^\dagger |\theta\rangle \tag{42}$$

If we project this Schrödinger equation onto a set of Q-electron Slater determinants, $\langle\theta| a_{j_Q} a_{j_{Q-1}} \cdots a_{j_1} \exp\left(-\hat{T}_1\right)$, then Eq. (42) is seen to be equivalent to coupled-cluster with single excitations.

If $\tau_{pq} = 0$, then the Schrödinger equation has the form

$$\hat{H} \exp\left(\hat{G}_1\right) a_{k_1}^\dagger a_{k_2}^\dagger \cdots a_{k_Q}^\dagger |\theta\rangle = E \exp\left(\hat{G}_1\right) a_{k_1}^\dagger a_{k_2}^\dagger \cdots a_{k_Q}^\dagger |\theta\rangle \tag{43}$$

Projecting onto an N-electron state where $Q - N$ is a nonnegative even integer

$$\langle\theta| a_{j_N} a_{j_{N-1}} \cdots a_{j_1} \hat{H} \exp\left(\hat{G}_1\right) a_{k_1}^\dagger a_{k_2}^\dagger \cdots a_{k_Q}^\dagger |\theta\rangle = E \langle\theta| a_{j_N} a_{j_{N-1}} \cdots a_{j_1} \exp\left(\hat{G}_1\right) a_{k_1}^\dagger a_{k_2}^\dagger \cdots a_{k_Q}^\dagger |\theta\rangle \tag{44}$$

inserting the Taylor series for $\exp\left(\hat{G}_1\right)$, and substituting zero for overlaps between wavefunctions with different electron number, one obtains,

$$\langle\theta| a_{j_N} a_{j_{N-1}} \cdots a_{j_1} \hat{H} \hat{G}_1^{\frac{1}{2}(Q-N)} a_{k_1}^\dagger a_{k_2}^\dagger \cdots a_{k_Q}^\dagger |\theta\rangle = E \langle\theta| a_{j_N} a_{j_{N-1}} \cdots a_{j_1} \hat{G}_1^{\frac{1}{2}(Q-N)} a_{k_1}^\dagger a_{k_2}^\dagger \cdots a_{k_Q}^\dagger |\theta\rangle \tag{45}$$

The key to evaluating this expression is evaluating overlaps like those which appear on the right-hand-side. This is just the overlap between an antisymmetrized geminal power wavefunction built on an N-electron pseudovacuum,

$$\langle\theta| a_{j_N} a_{j_{N-1}} \cdots a_{j_1} \left|\left(\tilde{G}_1\right)^{\frac{1}{2}(Q-N)} \tag{46}\right.$$

and the "untransformed" Q-electron Slater determinant

$$a_{k_1}^\dagger a_{k_1}^\dagger \cdots a_{k_Q}^\dagger |\theta\rangle \tag{47}$$

The geminal operator in Eq. (46) can be simplified by eliminating terms that do not contribute because of the choice of pseudovacuum, i.e.,

$$\tilde{G}_1 = \sum_{\substack{p,q=1 \\ p,q\neq\{j_1,j_2,\ldots,j_N\}}}^{2B} \gamma_{pq} a_p a_q . \tag{48}$$

This special case is tractable since it only requires evaluating terms that appear in the equations for the projected form of the antisymmetrized geminal power (AGP) method. Unfortunately, this approach inherits the non-size-consistency of AGP.

To evaluate Eq. (40) in the general case, it is helpful to recall that $\left[\hat{G}_1,\hat{G}_1\right]=0$. More generally, any multiple commutator where $\hat{G}_1$ appears multiple times will vanish. (E.g.,

$\left[\left[\hat{T}_1,\hat{G}_1\right],\hat{G}_1\right]=\left[\left[\left[\hat{T}_1,\hat{G}_1\right],\hat{T}_1\right],\hat{G}_1\right]=0$.) Furthermore, note that

$$
\begin{aligned}
\left[\hat{T}_1,\hat{G}_1\right] &= \sum_{pqrs}\tau_{pq}\gamma_{rs}\left[a_p^\dagger a_q, a_r a_s\right] \\
&= \sum_{pqs}\tau_{pq}\gamma_{ps}\left(a_s a_q\right)-\sum_{pqr}\tau_{pq}\gamma_{rp}a_r a_q \\
&= \sum_{p,q}\left[\boldsymbol{\tau}^T\left(\boldsymbol{\gamma}-\boldsymbol{\gamma}^T\right)\right]_{pq} a_q a_p
\end{aligned} \tag{49}
$$

where $\boldsymbol{\tau}$ and $\boldsymbol{\gamma}$ are the matrices with elements τ_{pq} and γ_{pq}, respectively. That is, the commutator $\left[\hat{T}_1,\hat{G}_1\right]$ is another geminal. In this manner, we can define an infinite sequence of geminals,

$$\hat{G}_2 = -\tfrac{1}{2}\left[\hat{T}_1, \hat{G}_1\right]$$

$$\hat{G}_3 = -\tfrac{1}{3}\left[\hat{T}_1, \hat{G}_2\right] = \tfrac{1}{3!}\left[\hat{T}_1, \left[\hat{T}_1, \hat{G}_1\right]\right]$$

$$\vdots$$

$$\hat{G}_n = -\tfrac{1}{n}\left[\hat{T}_1, \hat{G}_{n-1}\right]$$

(50)

with coefficients,

$$\hat{G}_n = \sum_{p,q=1}^{2B} \gamma_{pq}^{(n)} a_p a_q .$$

(51)

These geminals appear in the Zassenhaus formula,[105] which in this case reduces to

$$\exp\left(\hat{T}_1 + \hat{G}_1\right) = \exp\left(\hat{T}_1\right)\exp\left(\hat{G}_1\right)\exp\left(-\tfrac{1}{2}\left[\hat{T}_1,\hat{G}_1\right]\right)\exp\left(\tfrac{1}{3!}\left[\hat{T}_1,\left[\hat{T}_1,G_1\right]\right]\right)\cdots$$

$$= \exp\left(\hat{T}_1\right)\prod_{n=1}^{\infty}\exp\left(\hat{G}_n\right)$$

$$= \exp\left(\hat{T}_1\right)\exp\left(\sum_{n=1}^{\infty}\hat{G}_n\right)$$

(52)

In the last line we have again used the fact that geminals commute.

Inserting Eq. (52) into the Schrödinger equation, and projecting on a set of *N*-electron Slater determinants, $\left\langle\theta\middle| a_{j_N} a_{j_{N-1}} \cdots a_{j_1} \exp\left(-\hat{T}_1\right)\right.$, where $Q - N$ is a nonnegative even integer, we obtain the equation,

$$\left\langle\theta\middle| a_{j_N} a_{j_{N-1}} \cdots a_{j_1} \exp\left(-\hat{T}_1\right)\hat{H}\exp\left(\hat{T}_1\right)\left(\sum_{n=1}^{\infty}\hat{G}_n\right)^{\frac{1}{2}(Q-N)} a_{k_1}^{\dagger} a_{k_2}^{\dagger} \cdots a_{k_Q}^{\dagger}\middle|\theta\right\rangle$$

$$= E\left\langle\theta\middle| a_{j_N} a_{j_{N-1}} \cdots a_{j_1}\left(\sum_{n=1}^{\infty}\hat{G}_n\right)^{\frac{1}{2}(Q-N)} a_{k_1}^{\dagger} a_{k_2}^{\dagger} \cdots a_{k_Q}^{\dagger}\middle|\theta\right\rangle$$

(53)

The key to solving this equation is evaluating overlaps like those that appear on the right-hand-side of Eq. (53). This equation, however, has the same structure as Eq. (45). As in Eqs. (45)-(47), one needs to evaluate the overlap between an antisymmetrized geminal power wavefunction built

on an *N*-electron pseudovacuum and a *Q*-electron Slater determinant. The only difference is that the geminal that appears in the geminal power expression has a more complicated expression,

$$\tilde{G} = \sum_{n=1}^{\infty} \tilde{G}_n = \sum_{\substack{p,q=1 \\ p,q \neq \{j_1, j_2, \ldots, j_N\}}}^{2B} \tilde{\gamma}_{pq} a_p a_q \,. \tag{54}$$

where

$$\tilde{\gamma}_{pq} = \sum_{n=1}^{\infty} \gamma_{pq}^{(n)} \tag{55}$$

The general-form of noncanonical quasiparticle defined in Eqs. (39)-(40) is therefore tractable computationally, presuming that the sum in Eq. (55) converges sufficiently rapidly. However, because this method is a just a special form of the antisymmetrized geminal power (AGP) method, this approach is not size consistent.

IV.   Open-Shell Geminal Forms

A.   APIG and its Generalization to Sequentially-Occupied Orbitals

The most straightforward way to treat unpaired electrons in a geminals-based theory is to allow more general pairing schemes than the simple one-to-one orbital pairing in APIG, Eq. (6). For example, the fully general antisymmetric product of geminals wavefunction, Eqs. (4)-(5), includes all possible singlet (both closed-shell and open-shell) and triplet pairings between the two electrons. Unfortunately, fully general APG is intractable.

In the same way that APIG is intractable unless one chooses a specific form for the coefficient matrix, it seems possible that a tractable form of the APG wavefunction might be constructed by imposing suitable restrictions on $c_{q:ij}^{(\text{APG})}$ in Eq. (4). This motivates the strategies we

pursue in the next section. In this section, we consider an alternative approach, where the restrictions on the APIG are relaxed to allow for multiple orbital-pairing schemes.

To motivate our generalization of the APIG, it is helpful to understand the derivation of the overlap formula in Eq. (10). Specifically, given a product of $N/2$ geminals, the coefficient of a doubly-occupied Slater determinant is obtained by recognizing that each orbital pair $a_{k_j}^\dagger a_{k_j+B}^\dagger |\theta\rangle$ can be generated by any of the $N/2$ geminals. The coefficient of the Slater determinant is therefore a sum over all permutations of the geminals, denoted $\pi(1,2,\ldots,N/2)$, which is equivalent to the matrix-permanent of the orbitals that are occupied in the Slater determinant,

$$
\left\langle \theta \left| a_{k_1} a_{k_1+B} a_{k_2} a_{k_2+B} \cdots a_{k_{N/2}} a_{k_{N/2}+B} \prod_{q=1}^{N/2} P_q^\dagger \right| \theta \right\rangle
$$

$$
= \sum_{\pi(1,2,\ldots N/2)} \prod_{q=1}^{N/2} c_{q;k_{\pi(q)}}^{(\text{APIG})} \tag{56}
$$

$$
= \begin{vmatrix}
c_{1;k_1}^{(\text{APIG})} & c_{1;k_1}^{(\text{APIG})} & \cdots & c_{1;k_{N/2}}^{(\text{APIG})} \\
c_{2;k_1}^{(\text{APIG})} & c_{2;k_2}^{(\text{APIG})} & \cdots & c_{2;k_{N/2}}^{(\text{APIG})} \\
\vdots & \vdots & & \vdots \\
c_{N/2;k_1}^{(\text{APIG})} & c_{N/2;k_2}^{(\text{APIG})} & \cdots & c_{N/2;k_{N/2}}^{(\text{APIG})}
\end{vmatrix}^+
$$

The key design principle is that a given Slater determinant can be constructed in only one way (up to a permutation of the geminals). (We have already observed that when one considers more general wavefunctions where a given Slater determinant can be constructed by several different pathways, combinatorial computational complexity results.)

The first generalization of APIG we consider allows *every* orbital to be paired with the following spin-orbital,

$$
R_q^\dagger = \sum_{i=1}^{2B-1} c_{q;i}^{(\text{APseq0G})} a_i^\dagger a_{i+1}^\dagger \tag{57}
$$

If one considers restricted spin-orbitals and orders them so that orbital *2k-1* and orbital *2k* have the same spatial part, then this antisymmetric product of sequential-orbital geminals includes APIG (if $c_{q;i}^{(\text{APseq0G})} = 0$ when *i* is even) but also allows open-shell pairing between orbitals that appear consecutively in the orbital-list. The result for the overlap with a Slater determinant in which all orbitals are paired sequentially is a trivial extension of Eq. (56) for APIG,

$$
\left\langle \theta \left| a_{k_1} a_{k_1+1} a_{k_2} a_{k_2+1} \cdots a_{k_{N/2}} a_{k_{N/2}+1} \prod_{q=1}^{N/2} R_q^\dagger \right| \theta \right\rangle
$$

$$
= \sum_{\pi(1,2,\ldots N/2)} \prod_{q=1}^{N/2} c_{q;k_{\pi(q)}}^{(\text{APseq0G})} = \left| c_{q;k_{\pi(q)}}^{(\text{APseq0G})} \right|^+_{\substack{k \text{ is the first in a} \\ \text{sequential pair} \\ \text{of orbitals}}}
$$

(58)

This result can be generalized to include orbitals that are not sequential. For example, if one wishes to include Slater determinants that include orbitals that are separated by a single orbital, one can consider a geminal like

$$
R_q'^\dagger = \sum_{i=1}^{2B-1} c_{q;i}^{(\text{APseq0G})} a_i^\dagger a_{i+1}^\dagger + \sum_{i=1}^{2B-2} c_{q;i}'^{(\text{APseq1G})} a_i^\dagger a_{i+2}^\dagger \left(1-\hat{n}_{i-1}\right)\left(1-\hat{n}_{i+1}\right)\left(1-\hat{n}_{i+3}\right)
$$

(59)

Here, $\hat{n}_i = a_i^\dagger a_i$ is the operator for the occupation number of the *i*[th] orbital. The terms containing the number operator are necessary to ensure that one cannot construct sequentially-occupied orbitals by sequentially generating orbitals with a gap between them. For example, if it were possible to generate a configuration like $a_i^\dagger a_{i+1}^\dagger a_{i+2}^\dagger a_{i+3}^\dagger |\theta\rangle$ by acting first with a geminal that creates $a_i^\dagger a_{i+2}^\dagger$ and subsequently with a geminal that creates $a_{i+1}^\dagger a_{i+3}^\dagger$, then there would be two qualitatively different ways to generate this configuration. Accumulating the sum of all the possible ways to generate the configurations then incurs combinatorial computational cost, which we wish to avoid.

Equation (59) can obviously be further generalized, both by including a constant term (number-symmetry breaking) and by including spin-orbitals separated by two orbitals, three orbitals, etc.. In general,

$$\tilde{R}_q'^\dagger = c_{q;0}^{(\text{APseqG})} + \sum_{i=1}^{2B-1} c_{q;i}^{(\text{APseq0G})} a_i^\dagger a_{i+1}^\dagger + \sum_{i=1}^{2B-2} c_{q;i}'^{(\text{APseq1G})} a_i^\dagger a_{i+2}^\dagger \left(1-\hat{n}_{i-1}\right)\left(1-\hat{n}_{i+1}\right)\left(1-\hat{n}_{i+3}\right)$$

$$+ \sum_{i=1}^{2B-3} c_{q;i}'^{(\text{APseq2G})} a_i^\dagger a_{i+3}^\dagger \left(1-\hat{n}_{i-2}\right)\left(1-\hat{n}_{i-1}\right)\left(1-\hat{n}_{i+1}\right)\left(1-\hat{n}_{i+2}\right)\left(1-\hat{n}_{i+3}\right)\left(1-\hat{n}_{i+4}\right) \qquad (60)$$

$$+\cdots$$

To evaluate the overlap of an antisymmetrized product of sequential-orbital geminals with a Slater determinant, one performs the procedure:

1. Starting from the lowest-indexed occupied orbital in the Slater determinant one is projecting against, identify all orbitals that occur consecutively. These orbitals contribute a column with the values $c_{q;i}^{(\text{APseq0G})}$ to the permanent. Remove these orbitals from the list of occupied orbitals.

2. Restarting from the lowest-indexed occupied orbital that remains after step 1, identify all orbitals where both the ith and the $i+2^{\text{nd}}$ orbitals are occupied. These orbitals contribute a column with the values $c_{q;i}^{(\text{APseq1G})}$ to the permanent. Remove these orbitals from the list of occupied orbitals in the Slater determinant one is projecting against.

3. Proceeding in like manner, for $n = 2, 3, \ldots$, restart from the lowest-indexed occupied orbital that remains, and identify all orbitals where both the ith and the $i+n^{\text{th}}$ orbitals are occupied. These orbitals contribute a column with the values $c_{q;i}^{(\text{APseq}n\text{G})}$ to the permanent. Remove these orbitals from the list of occupied orbitals, increment n, and repeat step 3 until every occupied orbital has been assigned to a column in the matrix.

4. The overlap between the Slater determinant and the APseq$n$G wavefunction is then

$$\left\langle \theta \middle| a_{k_1} a_{k_1+1} \cdots a_{l_1} a_{l_1+2} \cdots a_{m_1} a_{m_1+3} \cdots a_{n_1} a_{n_1+4} \cdots \prod_{q=1}^{Q} \tilde{P}_q^\dagger \middle| \theta \right\rangle$$

$$= \frac{1}{\left(Q - \frac{1}{2}N\right)!} \begin{vmatrix} c_{1;0}^{(\mathrm{APseqG})} & \cdots & c_{1;0}^{(\mathrm{APseqG})} & c_{1;k_1}^{(\mathrm{APseq0G})} & \cdots & c_{1;l_1}^{(\mathrm{APseq1G})} & \cdots & c_{1;m_1}^{(\mathrm{APseq2G})} & \cdots & \cdots \\ c_{2;0}^{(\mathrm{APseqG})} & \cdots & c_{2;0}^{(\mathrm{APseqG})} & c_{2;k_1}^{(\mathrm{APseq0G})} & \cdots & c_{2;l_1}^{(\mathrm{APseq1G})} & \cdots & c_{2;m_1}^{(\mathrm{APseq2G})} & \cdots & \cdots \\ \vdots & & \vdots & \vdots & & \vdots & & \vdots & & \\ c_{Q;0}^{(\mathrm{APseqG})} & \cdots & c_{Q;0}^{(\mathrm{APseqG})} & c_{Q;k_1}^{(\mathrm{APseq0G})} & \cdots & c_{Q;l_1}^{(\mathrm{APseq1G})} & \cdots & c_{Q;m_1}^{(\mathrm{APseq2G})} & \cdots & \cdots \end{vmatrix}^+ \tag{61}$$

$\underbrace{}_{(Q-N/2)\text{ times constant term}}$ $\underbrace{}_{\text{sequential orbitals }\{k,k+1\}}$ $\underbrace{}_{\text{sequential orbitals }\{l,l+2\}}$ $\underbrace{}_{\text{sequential orbitals }\{m,m+3\}}$

This permanent is only readily evaluated if the geminal coefficients are selected with the inverse-rank-2 form, Eq. (11).

There are other ways of defining "sequential" geminals, in addition to this. In general, any unique procedure that defines a mapping from an ordered list of occupied orbitals to a list of ordered pairs of orbitals can be used. Notice that in general the APseqG wavefunction is not a spin eigenfunction. One can, however, restore spin-symmetry by projecting onto spin eigenfunctions.

B. APG and its Restriction to Disjoint Orbital Sets

Insofar as APIG was motivated by the su(2) algebra, more general forms of antisymmetrized product of geminals can be motivated by algebras with additional elements. Motivated by the structure of the sp(N) algebra, we propose to divide the orbitals into two disjoint sets (e.g., α- and β- spin-orbitals). Then we can generalize APIG (and restrict APG) to include all pairings between orbitals in different sets,

$$S_q^\dagger = \sum_{i=1}^{B} \sum_{j=B+1}^{2B} c_{q;ij}^{(\mathrm{APsetG})} a_i^\dagger a_j^\dagger \tag{62}$$

In the antisymmetric product of set-divided geminals,

$$\left| \Psi_{\text{APsetG}} \right\rangle = \prod_{q=1}^{N/2} S_q^\dagger \left| \theta \right\rangle, \tag{63}$$

only Slater determinants that have equal numbers of occupied orbitals from each of the two orbital-sets have nonzero coefficient.

The geminals created by (62) are generally not spin eigenfunctions, but (a) if the two orbital sets have the same spatial orbitals and differ only in spin and (b) the coefficients are defined with the appropriate symmetry (e.g., $c_{q;i,B+j}^{(\text{APsetG})} = \mp c_{q;j,B+i}^{(\text{APsetG})}$), then the form includes as special cases the most general possible type of singlet geminal and the most general form of $M_S = 0$ triplet geminal. More general divisions into orbital sets allow for contributions from high-spin triplet-pairing.

The overlap of the APsetG wavefunction with a Slater determinant involves a double sum over the symmetric group because a given occupied spin-orbital from the first set can be (a) generated by any of the geminals and (b) can be paired to any of the occupied spin-orbitals in the second set. Remembering that geminals are co-bosons and that spin-orbitals are fermions, the overlap is then,

$$\left\langle \theta \left| a_{i_1} a_{i_2} \cdots a_{i_{N/2}} a_{j_1} a_{j_2} \cdots a_{j_{N/2}} \prod_{q=1}^{N/2} S_q^\dagger \right| \theta \right\rangle$$
$$= \sum_{\pi(1,2,\ldots N/2)} \sum_{\sigma(1,2,\ldots N/2)} (-1)^{\text{sgn}(\sigma)} \prod_{q=1}^{N/2} c_{\pi(q);i_q j_{\sigma(q)}}^{(\text{APsetG})} \tag{64}$$

The mathematical object in Eq. (64) is the mixed discriminant of the tensor c_{qij}.

The mixed discriminant includes the permanent as a special case, and is therefore intractable computationally. One special tractable form is to assume that the coefficients can be factored,

$$c_{q;ij} = b_{q;i} d_{ij} \tag{65}$$

Then

$$\left\langle \theta \left| a_{i_1} a_{i_2} \cdots a_{i_{N/2}} a_{j_1} a_{j_2} \cdots a_{j_{N/2}} \prod_{q=1}^{N/2} S_q^\dagger \right| \theta \right\rangle$$

$$= \sum_{\pi(1,2,\ldots N/2)} \prod_{q=1}^{N/2} b_{\pi(q);i_q} \sum_{\sigma(1,2,\ldots N/2)} (-1)^{\mathrm{sgn}(\sigma)} \prod_{q=1}^{N/2} d_{i_q j_{\sigma(q)}} \tag{66}$$

$$= \left| b_{q;i_q} \right|_{i_q \in \mathrm{occ}}^+ \left| d_{i_q j_q} \right|_{i_q, j_q \in \mathrm{occ}}$$

The elements d_{ij} can be chosen arbitrarily, but to ensure evaluating the permanent is computationally tractable the $b_{q;i}$ should have a special form, e.g. (11). Forms analogous to the antisymmetric product of 1-reference orbital geminals (AP1roG) are also available.

Unfortunately, Eq. (65) is an extremely strong assumption, equivalent to the symmetry-broken APIG constructed using the orbital transformation in Eq. (21). To see this, insert $c_{p;ij}^{(\mathrm{APsetG})} = b_{p;i} d_{ij}$ into Eq. (62), and then rewrite it as:

$$S_q^\dagger = \sum_{i=1}^{B} b_{q;i} a_i^\dagger \tilde{a}_{B+i}^\dagger \tag{67}$$

where

$$\tilde{a}_{B+i}^\dagger = \sum_{j=B+1}^{2B} d_{ij} a_j^\dagger . \tag{68}$$

C. Combined forms for Open Shells

To retain the power of the seniority-zero form while still allowing the flexible treatment of open shells, one can combine the approaches in section §§IV.B with either the orbital-pairing form (APIG) or the consecutive-orbital form (§§IV.A). To do this, one first orders the spin-orbitals (orbitals will be paired with the orbitals adjacent to them in the orbital list) and then divides the spin-orbitals into two sets, $\mathcal{S}_1$ and $\mathcal{S}_2$. Then one constructs geminals like

$$T_q^\dagger = c_{q;0} + \sum_{i=1}^{B} c_{q;i}^{(\mathrm{cs})} a_{2i-1}^\dagger a_{2i}^\dagger$$
$$+ \sum_{j \in \mathcal{S}_1} \sum_{k \in \mathcal{S}_2} a_{q;j}^{(\mathrm{os})} b_{jk}^{(\mathrm{os})} a_j^\dagger a_k^\dagger \left(1 - \hat{n}_{j'}\right)\left(1 - \hat{n}_{k'}\right)$$

$$(69)$$

or

$$U_q^\dagger = c_{q;0} + \sum_{i=1}^{2B-1} c_{q;i}^{(\mathrm{cs})} a_i^\dagger a_{i+1}^\dagger$$
$$+ \sum_{j \in \mathcal{S}_1} \sum_{k \in \mathcal{S}_2} a_{q;j}^{(\mathrm{os})} b_{jk}^{(\mathrm{os})} a_j^\dagger a_k^\dagger \left(1 - \hat{n}_{j-1}\right)\left(1 - \hat{n}_{j+1}\right)\left(1 - \hat{n}_{k-1}\right)\left(1 - \hat{n}_{k+1}\right)$$

$$(70)$$

In Eqs. (69) and (70), it is important to ensure that the open-shell portions of two or more geminals do not combine to form orbital-pairs, which should be constructed using only the first, closed-shell part of the geminal. The use of number operators ensures that this does not happen. The notation in Eq. (69) uses j' to denote the orbital paired to j. Explicitly, we can write

$$j' = \begin{cases} j - 1 & j \text{ is even} \\ j + 1 & j \text{ is odd} \end{cases}$$

$$(71)$$

Using the floor function, one can write this explicitly as

$$j' = j - (-1)^j$$

$$(72)$$

A constant term (cf. Eqs. (26) and (60)) can be added to the geminal creation operators in Eq. (69)-(70) to obtain a number-projected solution. One can also combine the open-shell form from §§IV.B with the "higher-order" consecutive orbital forms like Eqs. (59) and (60).

The overlap of a product of T- or U-type geminals with a Slater determinant is computed as the product of a permanent (involving both the open-shell and closed-shell pieces) and a determinant involving only the open-shell orbitals. Specifically, we have

$$\left\langle \theta \left| a_{i_1} a_{i_2} \cdots a_{i_N} \prod_{q=1}^{Q} T_q^{\dagger} \right| \theta \right\rangle$$

$$= \underbrace{\begin{vmatrix} c_{1;i_1}^{(cs)} & c_{1;i_2}^{(cs)} & \cdots & c_{1;i_{N_{cs}}}^{(cs)} \\ c_{2;i_1}^{(cs)} & c_{2;i_2}^{(cs)} & \cdots & c_{2;i_{N_{cs}}}^{(cs)} \\ \vdots & \vdots & & \vdots \\ c_{Q;i_1}^{(cs)} & c_{Q;i_2}^{(cs)} & \cdots & c_{Q;i_{N_{cs}}}^{(cs)} \end{vmatrix}}_{\text{when orbitals } i_k \text{ and } i_k' \text{ are occupied}} \underbrace{\begin{vmatrix} a_{1;j_1}^{(os)} & a_{1;j_2}^{(os)} & \cdots & a_{1;j_{N_{os}}}^{(os)} \\ a_{2;j_1}^{(os)} & a_{2;j_2}^{(os)} & \cdots & a_{2;j_{N_{os}}}^{(os)} \\ \vdots & \vdots & & \vdots \\ a_{Q;j_1}^{(os)} & a_{Q;j_2}^{(os)} & \cdots & a_{Q;j_{N_{os}}}^{(os)} \end{vmatrix}^{+}}_{\text{when orbital } i_k \text{ is occupied but } i_k' \text{ is not}} \times \begin{vmatrix} b_{j_1 k_1}^{(os)} & b_{j_1 k_2}^{(os)} & \cdots & b_{j_1 k_{N_{os}}}^{(os)} \\ b_{j_2 k_1}^{(os)} & b_{j_2 k_2}^{(os)} & \cdots & b_{j_2 k_{N_{os}}}^{(os)} \\ \vdots & \vdots & & \vdots \\ b_{j_{N_{os}} k_1}^{(os)} & b_{j_{N_{os}} k_2}^{(os)} & \cdots & b_{j_{N_{os}} k_{N_{os}}}^{(os)} \end{vmatrix} \tag{73}$$

$$\left\langle \theta \left| a_{i_1} a_{i_2} \cdots a_{i_N} \prod_{q=1}^{Q} U_q^{\dagger} \right| \theta \right\rangle$$

$$= \begin{vmatrix} c_{1;i_1}^{(cs)} & c_{1;i_2}^{(cs)} & \cdots & c_{1;i_{N_{cs}}}^{(cs)} & a_{1;j_1}^{(os)} & a_{1;j_2}^{(os)} & \cdots & a_{1;j_{N_{os}}}^{(os)} \\ c_{2;i_1}^{(cs)} & c_{2;i_2}^{(cs)} & \cdots & c_{2;i_{N_{cs}}}^{(cs)} & a_{2;j_1}^{(os)} & a_{2;j_2}^{(os)} & \cdots & a_{2;j_{N_{os}}}^{(os)} \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ c_{Q;i_1}^{(cs)} & c_{Q;i_2}^{(cs)} & \cdots & c_{Q;i_{N_{cs}}}^{(cs)} & a_{Q;j_1}^{(os)} & a_{Q;j_2}^{(os)} & \cdots & a_{Q;j_{N_{os}}}^{(os)} \end{vmatrix}^{+} \underbrace{}_{\substack{\text{when orbital } i_k \text{ is consecutively} \\ \text{occupied orbital}}} \underbrace{}_{\substack{\text{when orbitals } i_k \text{ is not a consecutively} \\ \text{occupied orbital}}} \begin{vmatrix} b_{j_1 k_1}^{(os)} & b_{j_1 k_2}^{(os)} & \cdots & b_{j_1 k_{N_{os}}}^{(os)} \\ b_{j_2 k_1}^{(os)} & b_{j_2 k_2}^{(os)} & \cdots & b_{j_2 k_{N_{os}}}^{(os)} \\ \vdots & \vdots & & \vdots \\ b_{j_{N_{os}} k_1}^{(os)} & b_{j_{N_{os}} k_2}^{(os)} & \cdots & b_{j_{N_{os}} k_{N_{os}}}^{(os)} \end{vmatrix} \tag{74}$$

D. Combined Orbital-Geminal Forms

To explicitly treat systems with unpaired electrons, one needs to consider composite particles that contain not only electron pairs, but also single electrons. Motivated by the operators that created composite particles in the gl(2|2) algebra, we can propose,[18]

$$V_q^{\dagger} = c_{q;0} + \sum_{i=1}^{B} c_{q;i}^{(\alpha)} a_{2i-1}^{\dagger} \left(1 - \hat{n}_{2i}\right) + \sum_{i=1}^{B} c_{q;i}^{(\beta)} a_{2i}^{\dagger} \left(1 - \hat{n}_{2i-1}\right) + \sum_{i=1}^{B} c_{q;i}^{(\alpha\beta)} a_{2i-1}^{\dagger} a_{2i}^{\dagger} \tag{75}$$

The operators here preserve the vacuum, create singly occupied (e.g., α-spin and β-spin), and create doubly-occupied orbitals in empty orbitals; this construction is designed to prevent the addition of an electron to a singly-occupied orbital, so that all doubly-occupied orbitals arise from action of the last term in Eq. (75). As mentioned before, this is important because approaches that

allow an individual electron configuration to be attained in multiple ways (with different weights) seem to be computationally intractable. Notice that the middle two terms in the *V*-type composite particle are fermionic, while the other terms are bosonic. *V*-type composite particles are neither bosons nor fermions, so the overlap between a product of *V*-type composite particles and a Slater determinant is neither a permanent nor a determinant, but a generalized matrix function which we denote as:

$$
\left\langle \theta \left| a_{2j_1-1} a_{2j_1} \cdots a_{2j_{N_{\alpha\beta}}-1} a_{2j_{N_{\alpha\beta}}} a_{2k_1-1} \cdots a_{2k_{N_\alpha}-1} a_{2l_1} \cdots a_{2l_{N_\beta}} \prod_{q=1}^{N/2} V_q^\dagger \right| \theta \right\rangle
$$

$$
= \frac{1}{\left(Q - N_\alpha - N_\beta - N_{\alpha\beta}\right)!} \times \begin{vmatrix} c_{1;k_1}^{(\alpha)} & \cdots & c_{1;k_{N_\alpha}}^{(\alpha)} & c_{1;l_1}^{(\beta)} & \cdots & c_{1;l_{N_\beta}}^{(\beta)} & c_{1;j_1}^{(\alpha\beta)} & \cdots & c_{1;j_{N_{\alpha\beta}}}^{(\alpha\beta)} & c_{1;0} & \cdots & c_{1;0} \\ \vdots & & \vdots & \vdots & & \vdots & \vdots & & \vdots & \vdots & & \vdots \\ c_{Q;k_1}^{(\alpha)} & \cdots & c_{Q;k_{N_\alpha}}^{(\alpha)} & c_{Q;l_1}^{(\beta)} & \cdots & c_{Q;l_{N_\beta}}^{(\beta)} & c_{Q;j_1}^{(\alpha\beta)} & \cdots & c_{Q;j_{N_{\alpha\beta}}}^{(\alpha\beta)} & c_{Q;0} & \cdots & c_{Q;0} \end{vmatrix}^{\mp}
$$

(76)

Interchanging columns in the first portion of this matrix changes the sign by -1; interchanging columns in the second part of the matrix or between the two parts of the matrix does not change the sign of the generalized matrix function. Unfortunately, no result analogous to Borchardt's theorem seems to be known for these generalized matrix functions, so the computational tractability of this direct approach to treating open shells is unclear.

E.   Introducing Bath Orbitals

As the combined orbital-geminal form from the previous section is seemingly intractable, it is still desirable to be able to address a system where the total number of electrons is odd. There are at least two ways to do this. First of all, one can add an electron to the system (so that it now has an even number of electrons), treat the *N+1*-electron system with a geminal ansatz, and then

use the extended Koopmans' theorem (EKT) to compute the ionization potential, thereby attaining the energy of the odd-electron system.[106-108]

Recall that the EKT is equivalent to removing an electron from the asymptotic tail of the $N+1$-electron system.[109, 110] That is, one could add a diffuse spatial orbital far away from the system, and then by projecting only on Slater determinants in which that orbital is singly-occupied,

$$\langle \theta | a_{\substack{\text{far} \\ \text{away}}} \, a_{k_N} a_{k_{N-1}} \cdots a_{k_1} \tag{77}$$

one can define a suitable system. This is effectively a (number) symmetry-breaking and restoration approach.[111, 112] It is equivalent to the extended Koopmans' theorem for a full-CI wavefunction, but has advantages for a product of geminals because the geminal coefficients are chosen optimally for the target N-electron system, instead of the $N+1$-electron auxiliary system.

This approach can be generalized to allow for number-symmetry-breaking and restoration. Suppose one adds M fictitious spatial orbitals, which can be imagined to be infinitely diffuse and infinitely far from the system. To make the notation clear, we will label the creation operators for these orbitals with negative numbers, $\{a_{-1}^\dagger, a_{-2}^\dagger, \ldots a_{-2M}^\dagger\}$. These orbitals provide a noninteracting reservoir of electrons that is decoupled from the physical system, so all one- and two-electron integrals involving a fictitious orbital are defined as zero. One now forms a wavefunction that is a product of Q geminals involving both the physical and fictitious orbitals,

$$|\Psi\rangle = \prod_{q=1}^{Q} G_q^\dagger |\theta\rangle \tag{78}$$

$$G_q^\dagger = \sum_{k,l=-2M}^{2B} c_{q;k} a_k^\dagger a_l^\dagger . \tag{79}$$

If one wishes to target a state with N_α α-spin orbitals and N_β β-spin orbitals, then one projects on states with the form

$$\langle \theta | a_{k_{2Q}} a_{k_{2Q-1}} \cdots a_{k_1} \tag{80}$$

where

$$
\begin{aligned}
1 \le k_1 < k_2 < \cdots < k_{N_\alpha} \le B \\
B+1 \le k_{N_\alpha+1} < k_{N_\alpha+2} < \cdots k_{N_\alpha+N_\beta} \le 2B \\
-2M \le k_{N_\alpha+N_\beta+1} < k_{N_\alpha+N_\beta+2} < \cdots < k_{2Q} \le -1
\end{aligned} \tag{81}
$$

and we have chosen, as in section IV.B, to order the spin-orbitals so that the α-spin orbitals appear before the β-spin spatial orbitals. This approach to number-symmetry-breaking and restoration has more flexibility than the rectangular permanent approach, though it is perhaps less mathematically elegant.

F.   Strategies for Assigning Orbitals to Sets

The various geminal flavors considered here are not invariant to rotation or permutation of the orbitals. While rotation of the orbitals can be addressed by orbital optimization or other techniques, most of those strategies only find a local minimum.[22, 23, 53, 95, 113-116] A sensible permutation of orbitals therefore needs to be selected from the beginning.

Our strategy for selecting an appropriate assignment of orbitals to geminals uses results from graph theory. We start by assigning each spin-orbital as a vertex, and associating with each pair of vertices, j and k, an edge with a weight $a_{jk} = a_{kj}$. This defines an undirected weighted graph. The edge-weights should capture the "linkedness" between the spin-orbitals: when two spin-orbtials are very tightly coupled, a_{jk} should be large; spin-orbital-pairs that are nearly independent

should be connected by edges with negligible weights. There are various sensible ways to define a_{jk}. Most simply, we could assess whether the orbitals are located in similar regions of space, e.g.,

$$a_{jk} = \int \left| \phi_j^*(\mathbf{r}) \phi_k(\mathbf{r}) \right| d\mathbf{r} \tag{82}$$

It has also been suggested to use the exchange integral ($a_{jk} = K_{jk}$, which assigns zero to opposite-spin pairs),[117] the cumulant distribution function for the orbital occupations,[118, 119]

$$a_{jk} = \left\langle \Psi \left| a_k^\dagger a_k a_j^\dagger a_j \right| \Psi \right\rangle - \left\langle \Psi \left| a_k^\dagger a_k \right| \Psi \right\rangle \left\langle \Psi \left| a_j^\dagger a_j \right| \Psi \right\rangle \tag{83}$$

or the entanglement between the spin-orbitals.[120]

Given the graph-theory representation of the links between orbitals, we can decide how to select the best permutations of orbitals. For example, in APIG we wish to find the maximum matching: a way to assign each spin-orbital, j, to one and only one partner spin-orbital, $k(j)$, such that the sum of the included edges is maximized. The APIG geminals are then assigned to the form

$$G_{q;j}^\dagger = \sum_j c_{q;jk(j)} a_j^\dagger a_{k(j)}^\dagger \tag{84}$$

The maximum matching can be found by the blossom algorithm, with cost $O(B^4)$.[121]

The sequence geminals in Eq. IV.A bear a strong similarity to the orbital-ordering problem in the density matrix renormalization group, for which numerous heuristics have been developed. (See, e.g., [117, 122].) However, in the special case of APseq0G, Eq. (58), one wishes to find a path through the graph such that the sum of the weights of the edges on the path is maximized. This longest path problem is equivalent to the travelling salesman "maximum" problem, and is NP hard. However, good heuristics exist, and those heuristics are likely to suffice for our purposes.

In section IV.B and IV.C, we need to divide the graph into two parts. The APsetG (Eq. (62)) and the open-shell T- and U-type geminals (Eqs. (69)-(70)) account for correlation between

the sets, but not within the sets, and so this is the maximum-cut problem, where one divides a graph into two pieces such that the edges which are cut have maximal weight. The maximum-cut problem is NP-hard, but the algorithm of Goemans and Willliamson provides a reasonable approximate solution. (If one wishes for the two sets of spin-orbitals to have equal size, that is also possible.[123])

V. Outlook

The purpose of this work is to explore extensions of geminals-based approaches. To do this, we started by putting geminals into the general framework of composite particles, which gives some insights into what sorts of extensions are likely to be computationally tractable. We then considered several different approaches, including symmetry-breaking (both spin-and number-symmetry breaking seem tractable; breaking symmetries associated with the *type* of particles seems intractable) and more general types of composite bosons. Some of the more general geminal flavors are computationally tractable, and allow us to move beyond the antisymmetric product of interacting geminals (APIG) form towards fully general antisymmetric products of nonorthogonal geminals, without severely increasing the computational cost. In particular, the open-shell geminals approach in section IV.C allows geminals approaches to be applied to states of any spin-multiplicity and with any number of electrons. (The method in section IV.D. also achieves this, but requires one to evaluate a type of mixed permanent-determinant that seems to be unknown in the mathematics literature and, based on our own investigations, very difficult to evaluate.)

With these techniques, it is now possible to treat open-shell systems using geminals-based approaches. We will present our numerical results separately, but clearly all of these methods still require corrections for dynamic correlation. That is a difficult problem, and one for which we do

not have a definitive solution. The only strategy we know that fits cleanly into the composite particle framework is the coupled-cluster expression for composite particles in Eq. (25). Note, however, that adding correlations between the geminals will generally require terms like $t_{jk}^{bc} G_b^\dagger G_c^\dagger G_k G_j$. These "double-excitations of geminals" are four-electron excitations, and therefore computationally expensive.

It is also possible to extend these methods to excited states. Recall that the composite particle methods we are considering amount to solving the projected Schrödinger equation,

$$\left\langle \Phi_k \left| \hat{H} \right| \Psi(\mathbf{p}) \right\rangle = E \left\langle \Phi_k \middle| \Psi(\mathbf{p}) \right\rangle \tag{85}$$

Here $\left| \Phi_k \right\rangle$ are test states (typically Slater determinants, but eigenfunctions of the Richardson Hamiltonian could also be used in some cases) that are chosen so that it is computationally facile to evaluate the overlaps of $\left\langle \Phi_k \right|$ and $\left\langle \hat{H} \Phi_k \right|$ with the wavefunction formed as a product of composite particles,

$$\left| \Psi(\mathbf{p}) \right\rangle = \prod_{q=1}^{Q} c_q^\dagger(\mathbf{p}) \left| \theta \right\rangle. \tag{86}$$

Here $\mathbf{p}$ denotes the parameters on which the composite particles depend.

Equation (85) is a system of nonlinear equations for the unknowns $\{\mathbf{p}, E\}$, and can be solved as a nonlinear least-squares procedure. By choosing different initial guesses for the parameters, one will converge to different eigenstates of the Schrödinger equation. However, one can also converge to several eigenstates simultaneously by minimizing the objective function,[124]

$$\min_{\{\mathbf{p}_\ell, E_\ell\}} \sum_{\ell=1}^{L} \left| \frac{\left\langle \Phi_k \left| \hat{H} \right| \Psi(\mathbf{p}_\ell) \right\rangle - E_\ell \left\langle \Phi_k \middle| \Psi(\mathbf{p}_\ell) \right\rangle}{\left\langle \Phi_{\mathrm{ref},\ell} \middle| \Psi(\mathbf{p}_\ell) \right\rangle} \right|^2 \tag{87}$$

The denominator is selected as an "intermediate normalization" because otherwise the method can find solutions where the norm of the wavefunction becomes zero. One advantage of using Eq. (87) is that one uses a single set of orbitals for describing both ground and excited states, which can lead to a more balanced description of excitation energies (in the spirit of state-averaged CASSCF).

This manuscript has focussed on one specific type of cobosons, namely geminals. Certainly there are other choices, for example, cofermions of three, five, etc. electrons, or cobosons of four, six, etc. electrons. These have interesting combinatoric structures of their own, though of course the associated theories are more computationally demanding than geminals-based approaches. Due to the ubiquity of electron-pairs in chemistry we feel that for applications to the electronic structure of molecules and materials, geminals-based approaches will provide a more favorable trade-off between cost and accuracy than either orbital-based approaches (the one-electron picture) or approaches based on composite particles with three or more electrons.

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