Construction of linearly independent non-orthogonal AGP states

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We show how to construct a linearly independent set of antisymmetrized geminal power (AGP) states, which allows us to rewrite our recently introduced geminal replacement (GR) models as linear combinations of non-orthogonal AGPs. This greatly simplifies the evaluation of matrix elements and permits us to introduce an AGP-based selective configuration interaction (SCI) method, which can reach arbitrary excitation levels relative to a reference AGP, balancing accuracy and cost as we see fit.

I. INTRODUCTION

Most wave function methods require expanding the wave function in a many-body basis. The basis of a many-electron wave function is typically chosen as a set of orthonormal Slater determinants, constructed as particle-hole excitations out of a reference determinant. This approach has the advantage that the Hamiltonian matrix is sparse, matrix elements are easy to compute, and for weakly-correlated systems, the expansion coefficients can be factorized using, e.g., some variant of coupled cluster theory. For strongly-correlated systems, however, Slater determinants and, in turn, molecular orbitals are probably not the most efficient basis and building blocks, respectively. While we can, in principle, use any basis we wish, we often resort to Slater determinants even when they may not be optimal, largely because there are not many alternatives that facilitate easy computation.

In a series of papers, our group has explored abandoning Slater determinants as the many-electron basis and proposed instead working with wave functions where the basic building blocks are two-electron functions called geminals instead of one-electron spin-orbitals. Specifically, the exact wave function can be written in the basis of identical geminal product states known as the antisymmetrized geminal power (AGP) which can be obtained as the number-projected Bardeen-Cooper-Schrieffer (PBCS) wave function. AGP is related to the symmetric tensor decomposition of the exact wave function and non-orthogonal construction of AGP bases is natural due to the close connection between AGPs and elementary symmetric polynomials (ESPs).

Given a set of AGPs, optimizing the expansion coefficients in LC-AGP is easily done as a non-orthogonal configuration interaction. On the other hand, optimizing the geminals of the AGPs is quite difficult; the problem becomes somewhat akin to that of a non-orthogonal multi-configurational self-consistent field. Numerical issues with full variational optimization of LC-AGP, which would require optimizing both configuration and geminal coefficients of individual states, have been observed in the literature.

For this reason, we pursue a different goal in this paper. Rather than optimizing AGP states in an LC-AGP, we wish to construct a linearly independent set of non-orthogonal AGP states such that the LC-AGP identically reproduces the geminal replacement (GR) theories we have considered in previous work. This would allow us to develop a selective configuration interaction (SCI) algorithm designed for a non-orthogonal manifold to energetically approximate different GR methods using as few AGPs as possible. To the best of our knowledge, all of the SCI schemes in the literature are concerned with orthonormal Slater determinants, except one in which orthonormal cluster states were employed as the many-electron basis.

This paper is organized as follows. In section II, we present the LC-AGP wave function. Section III discusses construction of the aforementioned linearly independent non-orthogonal set of AGPs. In section IV, we show how to remove energetically less important states before concluding in section V.
II. LC-AGP

An AGP state with \(n\) electron pairs is defined as
\[
|n; \mu\rangle = \frac{1}{n!} (\Gamma^\dagger_\mu)^n |\rangle,
\]
where \(\mu\) labels this AGP amongst a manifold of AGPs, |\rangle represents the physical vacuum state, and \(\Gamma^\dagger_\mu\) is a geminal creation operator, which in its canonical basis can be expanded as
\[
\Gamma^\dagger_\mu = \sum_{p=1}^{m} \eta^p_\mu P^\dagger_p,
\]
where \(m\) is the number of spatial orbitals, \(\eta^p_\mu\) is the \(p\)-th geminal coefficient of this AGP, and the pair creation operator is
\[
P^\dagger_p = c^\dagger_p c^\dagger_p.
\]
Here, \(c^\dagger_p\) is a fermion creation operator and \(p\) and \(p\) are paired, i.e., they are defined by conjugate pairs in the canonical unitary congruent transformation of an antisymmetric matrix. For notational simplicity, we will use \(|n; \mu\rangle\) and \(|\mu\rangle\) interchangeably to denote an AGP. The state \(|n\rangle\) without additional indices should be understood as the reference AGP state.

The LC-AGP wave function is
\[
|\Psi\rangle = \sum_{\mu}^{R} C_\mu |\mu\rangle,
\]
where \(R\) is the number of AGPs and an \(n\)-pair AGP \(|\mu\rangle\) is created by the geminal creation operator defined in eq. (2). Given a set of AGPs, the LC-AGP coefficients \(C_\mu\) can be solved as a generalized eigenvalue problem
\[
\mathbf{H C} = \mathbf{M C E},
\]
where
\[
\begin{align}
H_{\mu \nu} &= \langle \mu | H | \nu \rangle, \\
M_{\mu \nu} &= \langle \mu | \nu \rangle,
\end{align}
\]
and \(\mathbf{E}\) is a diagonal matrix containing the ground and excited state energies, and the columns of \(\mathbf{C}\) are the corresponding LC-AGP coefficients.

In this work, we limit ourselves to the pairing or reduced BCS Hamiltonian
\[
H = \sum_p \epsilon_p N_p - G \sum_{pq} P^\dagger_p P_q,
\]
where the pair annihilation operator \(P_q\) is the adjoint of the pair creation operator \(P^\dagger_q\), and the number operator \(N_p\) is defined as
\[
N_p = c^\dagger_p c_p + c^\dagger_p c_p.
\]

The pair and number operators form a representation of generators of the \(su(2)\) algebra
\[
\begin{align}
[P^\dagger_p, P_q] &= \delta_p q (N_p - 1), \\
[N_p, P^\dagger_q] &= 2 \delta_{pq} P^\dagger_q.
\end{align}
\]
In eq. (7), the indices \(p\) and \(q\) label spatial orbitals or levels, the one-body interaction is assumed to be \(\epsilon_p = p\), and the two-body interaction strength \(G\) may be repulsive \((G < 0)\) or attractive \((G > 0)\). For strongly correlated systems, a useful way to rank the different sectors of the Hilbert space is seniority, where zero-seniority means that all electrons are paired. The reduced BCS Hamiltonian discussed in this work conserves seniority. Since this Hamiltonian describes electron pairs, its eigenfunctions can be solved as a doubly-occupied configuration interaction (DOC) problem, which is the most general seniority-zero wave function. However, the reduced BCS Hamiltonian is exactly solvable through a set of nonlinear Richardson-Gaudin equations. Exact ground states of the reduced BCS Hamiltonian have recently been applied to the molecular Hamiltonian. Although simplistic, this Hamiltonian shows non-trivial physics in the attractive regime which traditional quantum chemistry methods fail to describe. In contrast, AGP and AGP-based methods are able to capture most of the correlation energies systematically.

We need to compute overlaps between AGPs to build the LC-AGP metric and need the following transition reduced density matrix (RDM) elements
\[
\begin{align}
Z^{1,1}_{\mu \nu, pq} &= \langle \mu | N_p | \nu \rangle, \\
Z^{0,2}_{\mu \nu, pq} &= \langle \mu | P^\dagger_p P_q | \nu \rangle,
\end{align}
\]
and then build the Hamiltonian matrix of the reduced BCS Hamiltonian defined in eq. (7)
\[
\langle \mu | H | \nu \rangle = \sum_p \epsilon_p Z^{1,1}_{\mu \nu, p} - G \sum_{pq} Z^{0,2}_{\mu \nu, pq}.
\]

The AGP overlaps and transition RDMs can be computed as ESPs. The computational complexity for \(\mathbf{M}\) and \(\mathbf{H}\) are \(O(m R^2)\) and \(O(m^3 R^2)\), respectively. In the regime where all \(\eta^\mu\) coefficients are different, the latter can be reduced to \(O(m^3 R^2)\) via the reconstruction formulae, in which higher-order RDMs are expressed as linear combinations of lower-order ones. Relevant expressions are presented in Appendix A. Alternatively, we may express the AGPs as PBSC states and evaluate the AGP transition RDMs as BCS transition RDMs integrated over a gauge angle; see Appendix A.2. The costs of computing \(\mathbf{M}\) and \(\mathbf{H}\) scale as \(O(ln R^2)\) and \(O(ln^2 R^2)\), respectively, where \(l\) denotes the size of the numerical quadrature for the gauge integration. In fact, we can evaluate \(Z^{11}\) in \(O(ln R^2)\) and then \(\mathbf{H}\) in \(O(m^2 R^2)\) by combining the ideas discussed above.

The most general seniority-zero geminal product wave function, the antisymmetrized product of interacting
is a promising wave function for strong correlation. In general, APIGs are computationally complex to work with since the APIG RDMs are permanents. However, an arbitrary APIG for \( n \) pairs can be expressed as a sum of \( 2^{n-1} \) non-orthogonal AGPs, as shown in the Appendix of Ref. 4. Incidentally, the exact ground states of the reduced BCS Hamiltonian are a special form of APIG, which means \( 2^{n-1} \) non-orthogonal AGPs are in principle enough to find the exact ground state of the reduced BCS Hamiltonian. In general, these AGPs have complex-valued geminal coefficients, and their optimization is exceptionally cumbersome. We prefer to avoid these difficulties by working with a fixed basis of AGPs, the construction of which we will now describe.

### III. GENERATING AGP STATES

Here we show how to construct a linearly independent non-orthogonal set of AGPs from any reference AGP. We will first discuss the constructions and then discuss how to reproduce different GR models with LC-AGP.

#### A. Cosenior transformation of AGP

As shown in Ref. 6, one AGP can be transformed to another with modified geminal coefficients via

\[
|n; \mu\rangle = e^{J^\mu} |n\rangle, \tag{13}
\]

where

\[
J^\mu = \sum_p s^\mu_p N_p, \tag{14}
\]

with the corresponding geminal coefficient transformed as

\[
\eta_p^\mu = e^{2s_p^\mu} \eta_p = \alpha_p^\mu \eta_p. \tag{15}
\]

Conversely, any AGP \(|n; \mu\rangle\) can be generated from a reference AGP \(|n\rangle\) through eq. (13), provided that \(s^\mu_p\) is complex-valued and \(|n; \mu\rangle\) and \(|n\rangle\) are cosenior, i.e., they share the same canonical orbitals. Eq. (13) for cosenior AGPs can be considered as an analogue of the Thouless theorem for Slater determinants.

By expanding the exponential of \(J^\mu_1\) in eq. (13), it is straightforward to show that the new AGP can be generated by acting a product of shifted number operators on the reference AGP

\[
|n; \mu\rangle = \xi \prod_p \left( N_p + \beta_p^\mu \right) |n\rangle, \tag{16}
\]

where

\[
\beta_p^\mu = \frac{2}{\alpha_p^\mu - 1}, \tag{17a}
\]

\[
\xi = \prod_p \frac{1}{\beta_p^\mu}. \tag{17b}
\]

We have used the fact that different number operators commute and

\[
N_p^2 = 2N_p \tag{18}
\]

for seniority-zero states. When \(s_p^\mu = 0\) for a given \( p \), \(\alpha_p^\mu = 1\) and \(\beta_p^\mu\) is not well defined, but eq. (16) still holds after removing the \( p \)-th factor from the product sequence. We refer to the remaining \(\alpha_p^\mu\) and \(\beta_p^\mu\) as pivots and shifts, respectively.

Here we provide an alternative perspective on the same transformation. An \( n \)-level, \( n \)-pair AGP can be represented as an \( n \)-variable, \( n \)-degree ESP of \(\eta_p P_p^\dagger\) acting on the vacuum

\[
|n\rangle = \sum_{1\leq p_1 < \cdots < p_n \leq m} \eta_{p_1} \cdots \eta_{p_n} P_{p_1}^\dagger \cdots P_{p_n}^\dagger |−⟩ \tag{19a}
\]

\[
= S^n_m \left( \{\eta_p P_p^\dagger \mid 1 \leq i \leq n\} \right) |−⟩ \tag{19b}
\]

since all the pairing creation operators commute with each other. Using the recursion formula of an ESP we can partition any AGP as

\[
|n\rangle = \eta_p P_p^\dagger |n-1\rangle_{-p} + |n\rangle_{-p}, \quad \forall p. \tag{20}
\]

Here the subscript \(-p\) means that the level \( p \) is excluded from the AGP expansion in eq. (19a). Eq. (20) and the commutation relation of eq. (9b) imply that

\[
(N_p + \beta_p^\mu) |n\rangle
= (2 + \beta_p^\mu) \eta_p P_p^\dagger |n-1\rangle_{-p} + \beta_p^\mu |n\rangle_{-p} \tag{21a}
\]

\[
= \beta_p^\mu \left[ (1 + \frac{2}{\beta_p^\mu}) \eta_p P_p^\dagger |n-1\rangle_{-p} + |n\rangle_{-p} \right]. \tag{21b}
\]

Hence shifting \(N_p\) by \(\beta_p^\mu\) pivots the corresponding geminal coefficient \(\eta_p\) by

\[
\alpha_p^\mu = 1 + \frac{2}{\beta_p^\mu}, \tag{22}
\]

corroborating eqs. (13)-(17).

To systematically generate manifolds spanning the DOCI space, we consider AGPs generated by \( k \) shifted number operators

\[
|n; p_1 \cdots p_k\rangle = \prod_{i=1}^{k} (N_{p_i} + \beta_{p_i}^\mu) |n\rangle, \tag{23}
\]

where the index \(\mu\) should be understood as a composite index of \( p_1, \cdots, p_k \). Note that we have neglected the normalization factor here.
A few remarks are in order. First, when all the shifts are zero, eq. 23 reduces to a basis state of a $J_k$-CI wave function

$$|J_k\text{-CI}\rangle = \sum_{p_1<\cdots<p_k} S_{p_1\cdots p_k} N_{p_1} \cdots N_{p_k} |n\rangle, \quad (24)$$

or equivalently, a $k$-th order geminal replacement ($k$-GR) model

$$|k\text{-GR}\rangle = \sum_{\mu} \lambda_\mu (\Gamma_\mu^k)^k |n-k\rangle, \quad (25)$$

where the coefficients $S_{p_1\cdots p_k}$ and $\lambda_\mu$ are related by a symmetric tensor decomposition. Second, regardless of the choice of the shifts, the number of states generated by eq. 23 is $\binom{m}{k}$, which equals the dimensionality of the $J_k$-CI manifold. Third, using the theorem in the Appendix of Ref. 6 it can be readily shown that $|n; p_1\cdots p_k\rangle$ is contained in the $J_k$-CI manifold. Consequently, the $\binom{m}{k}$ states generated by eq. 23 span the $J_k$-CI manifold as long as they are linearly independent. We have indeed observed that a wave function of the form

$$|\Psi_1\rangle = \sum_{p_1<\cdots<p_k} C_{p_1\cdots p_k} |n; p_1\cdots p_k\rangle \quad (26)$$

reproduces $J_k$-CI energies when the set of AGPs are linearly independent. However, linear independence is not always guaranteed, as discussed in Appendix B. Thus, our next task is to modify the construction in such a way as to assure linear independence.

### B. The freeze-and-pivot construction

We have observed that one way to get a linearly independent set of AGPs is to freeze an arbitrary level, excluding it from being pivoted. This is understandable since all the cases of accidental linear dependence examined in Appendix B are consequences of AGP being an eigenfunction of the total number operator

$$N = \sum_{p=1}^{m} N_p, \quad (27a)$$

$$N |n\rangle = 2n |n\rangle. \quad (27b)$$

Freezing one level prevents the total number operator from appearing in a linear combination of AGPs of the form given in eq. 23. For simplicity, we freeze the first level from now on, and define the elementary manifolds using

- reference AGP (i): $|n\rangle$,
- elementary singles (s): $\{|n; p| 1 < p \leq m\}$,
- elementary doubles (d): $\{|n; pq| 1 < p < q \leq m\}$,

and so on. Figure 1 presents an illustration of different elementary manifolds.

Numerical tests also suggest that for any choice of pivots $\alpha_p^\mu$ (or equivalently, shifts $\beta_p^\mu$), the AGPs in a given elementary manifold are linearly independent of those in

| Table I: Percentage of off-diagonal metric elements with absolute values $> 10^{-3}$, for the zero-pivot composite manifolds. The system is the half-filled 20-level reduced BCS Hamiltonian ($G_C \sim 0.2674$). |
|---------------------|---------------------|---------------------|---------------------|---------------------|
| $G$    | $S$    | $D$    | $T$    | $Q$    |
| -0.60  | 100.00 | 79.52  | 45.40  | 19.82  |
| -0.30  | 88.95  | 55.03  | 27.40  | 13.69  |
| 0.30   | 100.00 | 81.42  | 52.35  | 27.64  |
| 0.60   | 100.00 | 99.83  | 92.31  | 69.52  |
FIG. 3: Metric matrix heat-maps covering AGP to elementary quadruples manifolds (i+s+d+t+q) for the half-filled 16-level reduced BCS Hamiltonian with $G = 0.30$ ($G_C \sim 0.2866$). The left and right panels correspond to sing-flip and zero-pivot manifolds, respectively. Only absolute values of the matrix elements are plotted for the sign-flip manifolds. Note that for the sign-flip case, only neighboring elementary manifolds may combine to generate linearly independent AGPs whereas combination of any two elementary manifolds generate linearly independent AGPs for the zero-pivot construction. Combinations of more than two elementary manifolds would introduce linear dependence unless some states are removed.

a neighboring manifold. We thus define composite manifolds using

- composite singles (S): reference + elementary singles (i + s),
- composite doubles (D): elementary singles + elementary doubles (s + d),
- composite triples (T): elementary doubles + elementary triples (d + t),

and so on. In general, a state in the $k$-th order composite manifold can be written as

$$|\Psi_2\rangle = \sum_{1<p_1<\cdots<p_{k-1}\leq m} C_{p_1\cdots p_{k-1}} |n; p_1\cdots p_{k-1}\rangle + \sum_{1<p_1<\cdots<p_k\leq m} C_{p_1\cdots p_k} |n; p_1\cdots p_k\rangle,$$

(28)

(29)

The dimensionality of this manifold is

$$\binom{m-1}{k-1} + \binom{m-1}{k} = \binom{m}{k},$$

(30)

identical to that of $J_k$-CI. We have numerically verified the equivalence between the $k$-th order composite manifold and $J_k$-CI by comparing ground state energies after variation. We show examples of such equivalences in figure [2]. Note that LC-AGP with the composite singles manifold coincides with the reference AGP, because $J_1$-CI does not improve the variationally optimized AGP (although this is not necessarily true when the reference AGP is not optimized). It should also be noted that the highest-order composite manifold ($k = n$) reproduces DOCI or exact energies for the reduced BCS Hamiltonian, even when the reference AGP is not optimized.

Let us discuss some special pivots. When all the pivots are $-1$ (shifts are $-1$), we get the sign-flip manifolds, and the AGP vectors, in this case, resemble the power sum decomposition columns of an ESP [38,39]. When all the pivots are zero (shifts are $-2$), the AGPs of zero-pivot manifolds amounts to a reduction of levels from the AGP expansion defined in eq. (19a). An interesting scenario arises when all the shifts are zero; the pivots, and in turn the corresponding geminal coefficients become infinity (eq. [22]).

FIG. 4: Hamiltonian matrix heat-map for the zero-pivot manifolds, covering AGP to elementary quadruples manifolds (i+s+d+t+q). The system is half-filled 16-level reduced BCS Hamiltonian with $G = 0.30$ ($G_C \sim 0.2866$). Only absolute values of the matrix elements are plotted.
The resulting states are still well-defined since the unshifted number operators acting on an \( n \)-pair AGP state do not create another \( n \)-pair AGP state
\[
N_{p_1} \cdots N_{p_k} |n \rangle = \frac{2^k}{(n-k)!} \left( \prod_{i=1}^{k} \eta_{p_i} P_{p_i}^{\dagger} \right) (\Gamma^\dagger)^{n-k} |\rangle
\]
but an antisymmetrized product of \( k \) doubly-occupied orbitals and geminal power of \( (n-k) \) pairs. The shift –2 and shift 0 manifolds represent two limiting cases of eq. (21b) since only one term is present in either case. These two shifts are also unique because, in their case, combined states from any two elementary manifolds are observed to form a linearly independent set, not just the neighboring ones. More discussions on the shift 0 manifolds are beyond the scope of this paper since we are concerned with only AGP states here.

The construction described in this section is one of the two main results of this paper. For any set of shift or pivot parameters, the procedure outlined above permits us to construct a linearly independent non-orthogonal set of AGPs. By choosing the appropriate set (e.g., composite doubles) we can exactly reproduce the corresponding geminal replacement models. The simplicity of evaluating the required matrix elements would permit us to consider fairly complicated theories which replace a large number of geminals, but such theories yield large Hamiltonian and metric matrices. Thus we now turn our attention to pruning the LC-AGP basis in a SCI approach, mentioned in Section II. We discuss this in the next section.

IV. SCI WITH AGP STATES

Although LC-AGP wave functions with different pivots are variationally equivalent, the constructed spaces may have different properties. For example, in figure 5, we compare the metric matrices resulting from sign-flip and zero-pivot manifolds, and clearly, they have different metric densities. In addition to the unique relations between the elementary manifolds discussed in Section II.B the zero-pivot metric is moderately sparse for systems that are not too strongly interacting, and the sparsity increases for higher-order elementary manifolds, as shown in table 4. The Hamiltonian matrices follow similar patterns to the corresponding metrics, and one example is shown in figure 3 for the zero-pivot case.

We use these to our advantage by selecting only energetically important states for a given composite manifold, using a selective SCI algorithm outlined below

- partition the AGPs into model and candidate spaces,
- do LC-AGP with the model space states,
- decide if a state from the candidate state should be chosen,
- update model space if a new state is chosen,
- do LC-AGP with the new model space states,
- continue until all the candidate states are tested.

The SCI method discussed here is different from others in certain important ways. First, the AGPs from higher elementary manifolds are related to the AGPs from the lower manifolds, a consequence of the AGP partition introduced in eq. (20). We have observed that a combination of more than two elementary manifolds generates a linearly independent set of AGPs only when some states are excluded. Hence the SCI procedure must make sure that the states which can cause linear dependence are never selected. Second, the AGPs discussed here are non-orthogonal. We have introduced selection criteria for SCI with non-orthogonal states in Appendix C based on a metric and a Hamiltonian test, to check linear independence and energy contribution, respectively. Both tests depend on a real-valued threshold, and for tighter thresholds, the SCI procedure selects more states but guarantees better accuracy.

We have chosen the initial model space to be composite singles so that the SCI energies remain at least as accurate as the reference AGP energies. Depending on the candidate space, as illustrated in figure 3 we compare the metric matrices resulting from sign-flip and zero-pivot manifolds, and clearly, they have different metric densities. In addition to the unique relations between the elementary manifolds discussed in Section II.B the zero-pivot metric is moderately sparse for systems that are not too strongly interacting, and the sparsity increases for higher-order elementary manifolds, as shown in table 4. The Hamiltonian matrices follow similar patterns to the corresponding metrics, and one example is shown in figure 3 for the zero-pivot case.

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We use these to our advantage by selecting only energetically important states for a given composite manifold, using a selective SCI algorithm outlined below

- partition the AGPs into model and candidate spaces,
- do LC-AGP with the model space states,
- decide if a state from the candidate state should be chosen,
- update model space if a new state is chosen,
- do LC-AGP with the new model space states,
FIG. 6: SCI results for the half-filled 16-level reduced BCS Hamiltonian with $G = 0.60$ ($G_C \sim 0.2866$). The metric threshold is constant at $10^{-4}$ for all the methods. The $x$-axis for both the panels are Hamiltonian thresholds, $h_0$. In the $y$-axis of the left panel, we plot total energy errors ($E_{\text{method}} - E_{\text{exact}}$) for different SCI methods. In the $y$-axis of the right panel, we plot the fractions of AGPs selected from different elementary manifolds. For example, the label ‘d’ represents fraction of AGPs selected from the elementary doubles, which is same for all the SCI methods for a given $h_0$. Note that there are total 105, 455, and 1365 states in elementary singles, doubles, and triples, respectively.

FIG. 7: SCI results for the half-filled 16-level reduced BCS Hamiltonian with $G = 0.60$ ($G_C \sim 0.2866$). Here the Hamiltonian thresholds for different candidate elementary manifolds are chosen different. The metric threshold and the Hamiltonian threshold for elementary doubles manifold are constant for all the methods; they are $10^{-4}$ and $10^{-12}$, respectively. The labels ‘a’, ‘b’, and ‘c’ of the SCI-Q methods indicate different Hamiltonian thresholds chosen for the elementary triples: $10^{-6}$, $5 \times 10^{-7}$, and $10^{-7}$, respectively. The $x$-axis for both the panels are Hamiltonian thresholds for elementary quadruples, $h_0$. In the $y$-axis of the left panel, we plot total energy errors ($E_{\text{method}} - E_{\text{exact}}$) for different SCI-Q methods. In the $y$-axis of the right panel, we plot total number of AGPs selected by the SCI-Q methods divided by the total number of states (= 560) in composite triples manifold, or equivalently, in $J_3$-CI.

from the lower-order elementary manifolds, SCI-T contains SCI-D, SCI-Q contains both SCI-D and SCI-T, and so on. If the Hamiltonian threshold $h_0$ is identical for all the elementary manifolds, then for a specific $h_0$, the number of AGPs selected from the elementary doubles would be the same for SCI-D, SCI-T, and SCI-Q methods. Similarly, the number of AGPs selected from the elementary triples would be identical for SCI-T and SCI-Q methods.

Figure 6 presents how different SCI methods perform in the attractive strong correlation regime of the reduced BCS Hamiltonian due to different Hamiltonian thresholds, fixed for all the elementary manifolds. It is clear from the right panel of figure 6 that lower-order elementary manifolds are energetically more important. Thus, it is more appropriate to choose different Hamiltonian thresholds for different candidate elementary manifolds.
In figure 7, we choose different Hamiltonian thresholds for elementary doubles, triples, and quadruples for doing SCI-Q. We choose a minimal Hamiltonian threshold for elementary doubles so that the SCI energies are at least as accurate as $J_2$-CI. The different SCI-Q methods in figure 7 are defined based on their different Hamiltonian thresholds for elementary triples. In the right panel of figure 7, we plot the fractions of the states contained in $J_3$-CI, selected by different SCI-Q methods. It is clear from figure 7 that lower energies than $J_3$-CI can be achieved with close to or less than half of the total basis states needed for $J_3$-CI upon choosing suitable Hamiltonian thresholds.

V. CONCLUSION

We have explored expanding the many-electron wave function in a basis of non-orthogonal AGPs. We have chosen to avoid, as a first step, the task of optimizing each AGP state by generating linearly independent non-orthogonal AGP states from a given reference AGP, making LC-AGP optimization a linear problem. We have shown how different GR models (eq. (25)) are variationally equivalent to a linear combination of AGPs that differ by one or more geminal coefficients and can also be constructed using shifted number operators acting on an AGP.

LC-AGP provides more freedom to tune the Hilbert space than the GR models, as shown by the variational invariances of LC-AGP due to different pivots (or shifts). Indeed, the basis states of the $J_k$-CI expansion of eq. (24), equivalent to the $k$-GR model, are a limiting case of AGPs, which we have discussed in Section III B. Clearly, one way to go beyond the composite manifolds is to change the geminal coefficients that do not take part in pivots while maintaining linear independence.

We have shown how to remove energetically less important AGPs while maintaining linear independence by introducing an SCI method for non-orthogonal states, thus solving a lower-dimensional generalized eigenvalue problem while retaining a respectable portion of correlation energy. An important question is if better AGP constructions for SCI than the zero-pivot exist so that the LC-AGP wave function can be represented as compactly as possible. Along with our past work, the benchmark results here show that the geminal-based methods capture major portion of the correlation energies for the reduced BCS Hamiltonian, even with a moderate number of states. Extension of the present framework to include Hamiltonians that do not preserve seniority is under development and will be presented in due time.

The use of non-orthogonal Slater determinants is well known in quantum chemistry; they are often more representative of the electronic structure and are related to symmetry broken and restored states. However, non-orthogonal determinants have the corresponding disadvantage that it is not easy to provide a mechanism by which they can systematically span the relevant Hilbert space, a task for which orthogonal Slater determinants constructed by particle-hole excitations are well suited. The same ideas hold in the world of AGP. One can write very general and complicated geminal product models as linear combinations of non-orthogonal AGPs, but it is difficult to optimize them. If, instead, one chooses to write a basis of non-orthogonal AGPs, it is not easy to do so in a way that spans Hilbert space.

In this work, we have shown how we can approach various highly accurate and conceptually appealing geminal product-based CI methods via LC-AGP. The composite manifolds introduced here for doing LC-AGP with pivots systematically allow us to construct a linearly independent albeit non-orthogonal basis, and thereby provide a rigorous alternative to the particle-hole framework.

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Appendix A: AGP transition RDMs

In this section, we will discuss how to compute the matrix elements of eq. (6).

\[ N_p = 2 \sum_{p} P_{1p} \]  

for any seniority-zero state, the transition RDMs of eq. (10) are related:

\[ Z_{|\mu\nu,p\rangle} = 2 Z_{|\mu\nu,pp\rangle} \]  

There are different ways to compute the AGP overlaps and transition RDMs. For simplicity, we assume the geminal coefficients to be real-valued.

1. ESPs and reconstruction formulae

The overlap between AGPs $|\mu\rangle$ and $|\nu\rangle$ is an $m$-variable, $n$-degree ESP of $X_{p\mu} = \eta_{p\mu}^{\nu} \eta_{p\nu}^{\mu}$

\[ M_{\mu\nu} = \sum_{1\leq p_1 < \cdots < p_n \leq m} X_{p_1}^{\mu\nu} \cdots X_{p_n}^{\mu\nu} \]  

where $S^n_m = S^n_m (\{|X_{p_i}^{\mu\nu}| \mid 1 \leq i \leq n\})$.

The elements of $Z_{\mu\nu,pp}^{0,2}$ are related to $(m-2)$-variable, $(n-1)$-degree ESPs of $X_{p\mu
u}$

\[ Z_{\mu\nu,pp}^{0,2} = \eta_{p\mu}^{\nu} \eta_{p\nu}^{\mu} \sum_{1\leq p_1 < \cdots < p_{n-1}} X_{p_1}^{\mu\nu} \cdots X_{p_{n-1}}^{\mu\nu} \]  

where $S^{m-2}_n = S^{m-2}_n (\{|X_{p_i}^{\mu\nu}| \mid 1 \leq i \leq n-1\})$. 

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where \( p_i \neq p, q \). Eq. [A3] and [A4] can be computed by the sumESP algorithm, as discussed in Ref. 13. Alternatively, we first compute \( Z_{\mu,\nu}^{1,1} \) via eq. [A4], using eq. [A2]. Then the \( Z_{\mu,\nu}^{0,2} \) elements can be computed using \( Z_{\mu,\nu}^{1,1} \). This is due to a modified version of the reconstruction formulae for AGP RDMs, which allow expressing higher-order RDM elements in terms of lower-order ones. We discuss it briefly below.

We assume that all the indices of a transition RDM element are different, and other cases can be transformed to this irreducible form easily. Any transition RDM element with a string of number operators can be written as

\[
\langle \mu | N_{p_1} \cdots N_{p_n} | \nu \rangle = 2^{k-1} \sum_{i=1}^n \left( \prod_{j \neq i=1}^k A^\mu_{\nu, p_i} \right) Z_{\mu,\nu}^{1,1},
\]

where

\[
A^\mu_{\nu, pq} = \frac{\eta^\mu_p \eta^\nu_q}{X^\mu_p - X^\nu_q}.
\]

The operator

\[
K_{\mu, pq} = (\eta^\mu_p)^2 P^\mu_p P_q + (\eta^\nu_q)^2 P^\nu_q P_p + \frac{1}{2} \eta^\mu_p \eta^\nu_q (N_p N_q - N_p - N_q),
\]

 annihilates the AGP \( |\mu\rangle \).

If \( K^\dagger_{\mu, pq} \) is the adjoint of the operator defined in eq. [A7], then by solving the coupled equations below

\[
\langle \mu | K_{\nu, pq} | \nu \rangle = 0,
\]

\[
\langle \mu | K^\dagger_{\mu, pq} | \nu \rangle = 0,
\]

we arrive at

\[
\langle \mu | \cdots P^\mu_p P_q \cdots | \nu \rangle = \frac{1}{2} \frac{\eta^\mu_p \eta^\nu_q}{X^\mu_p + X^\nu_q} \times \langle \mu | \cdots (N_p + N_q - N_p N_q) \cdots | \nu \rangle.
\]

Here, we have used the facts that all the other operators in the string of eq. [A10] have different indices and number operators are Hermitian.

Applying eqs. [A5] and [A10] to \( \langle \mu | P^\mu_p P_q | \nu \rangle \), we get

\[
Z_{\mu,\nu}^{0,2} = \frac{1}{2} \frac{\eta^\mu_p \eta^\nu_q}{X^\mu_p + X^\nu_q} \times (Z_{\mu,\nu}^{1,1} + Z_{\mu,\nu}^{2,2} - Z_{\mu,\nu}^{1,1}),
\]

\[
Z_{\mu,\nu}^{2,2} = 2 \left( A^\mu_{\nu, pq} Z_{\mu,\nu}^{1,1} + A^\nu_{\mu, pq} Z_{\mu,\nu}^{1,1} \right),
\]

where \( Z_{\mu,\nu}^{2,2} = \langle \mu | N_p N_q | \nu \rangle \). Other AGP transition RDMs can be similarly derived using eqs. [A5] and [A10].

We can thus skip computing the full transition RDM \( Z_{\mu,\nu}^{0,2} \) and only need \( Z_{\mu,\nu}^{1,1} \) and \( A^\mu_{\nu, pq} \) with the geminal coefficients to compute the \( H \) elements. Note that the reconstruction formulae are only applicable when \( X^\mu_p \neq X^\nu_q \).

2. Transition RDMs from PBCS

AGP transition RDMs may be evaluated using transition RDMs of BCS states since an \( n \)-pair AGP \( |\mu\rangle \) can be represented as a PBCS:

\[
|\mu\rangle = P_{2n} |\Phi^\mu\rangle,
\]

where

\[
P_{2n} = \frac{1}{2\pi} \int_0^{2\pi} d\phi \ e^{i\phi(N-2n)}
\]

is the number-projection operator to the Hilbert space of \( 2n \) electrons, and

\[
|\Phi^\mu\rangle = \prod_p \left( \nu^\mu_p + v^\mu_p c^\dagger_p c_p^\dagger |-\rangle \right)
\]

is a BCS state with broken number symmetry. Here, \( \nu^\mu_p, v^\mu_p \in \mathbb{R} \) satisfy

\[
(\nu^\mu_p)^2 + (v^\mu_p)^2 = 1,
\]

and are related to \( \eta^\mu_p \) by

\[
\eta^\mu_p = \frac{\nu^\mu_p}{\nu^\mu_p}.
\]

A BCS state rotated by a gauge angle of \( \phi \) is

\[
|\Phi^\mu(\phi)\rangle = e^{i\phi N} |\Phi^\mu\rangle.
\]

Using the idempotency of \( P_{2n} \), it is readily shown that

\[
\langle \mu | |\nu\rangle = \frac{1}{2\pi} \int_0^{2\pi} d\phi \ e^{-i\phi(2n)} \langle \Phi^\mu | \Phi^\nu(\phi) \rangle,
\]

and

\[
Z_{\mu,\nu}^{0,2} = \frac{1}{2\pi} \int_0^{2\pi} d\phi \ e^{-i\phi(2n)} \langle \Phi^\mu | \Phi^\nu(\phi) \rangle Z_{\mu,\nu}^{0,2}(\phi),
\]

where

\[
Z_{\mu,\nu}^{0,2}(\phi) = \frac{\langle \Phi^\mu | c_p^\dagger c_p^\dagger c_q c_q | \Phi^\nu(\phi) \rangle}{\langle \Phi^\mu | \Phi^\nu(\phi) \rangle}.
\]

Namely, the AGP overlap \( \langle \mu | \nu \rangle \) and transition RDM \( Z_{\mu,\nu}^{0,2} \) are expressed in terms of the BCS overlap \( \langle \Phi^\mu | \Phi^\nu(\phi) \rangle \) and transition RDM \( Z_{\mu,\nu}^{0,2}(\phi) \), respectively.

The BCS overlap is a pfaffian, which in this case can be further simplified into

\[
\langle \Phi^\mu | \Phi^\nu(\phi) \rangle = \prod_p e^{i\phi} \sigma^\mu_{\nu, p}(\phi),
\]

where

\[
\sigma^\mu_{\nu, p}(\phi) = e^{-i\phi} (\nu^\mu_p)^2 + e^{i\phi} (v^\mu_p)^2.
\]
The BCS transition RDM $Z^{0.2}_{\nu\mu; pq}(\phi)$ may be decomposed by generalized Wick’s theorem. This leads to

$$Z^{0.2}_{\nu\mu; pq}(\phi) = \delta_{pq} \left( \rho^{\nu\mu}_p(\phi) \right)^2 + \tilde{\rho}^{\nu\mu}_p(\phi) \kappa^{\nu\mu}_q(\phi),$$  \hspace{1cm} (A23)

where

$$\rho^{\nu\mu}_p(\phi) = \frac{\langle \Phi\mu | c^\dagger_p c_p | \Phi\nu(\phi) \rangle}{\langle \Phi\nu | \Phi\nu(\phi) \rangle}$$  \hspace{1cm} (A24a)$$
\rho^{\nu\mu}_p(\phi) = e^{i\phi} v^\nu_p \sigma^\mu_p(\phi)^{-1} v^\mu_p, \hspace{1cm} (A24b)$$

$$\kappa^{\nu\mu}_p(\phi) = \frac{\langle \Phi\mu | c^\dagger_p c_p | \Phi\nu(\phi) \rangle}{\langle \Phi\nu | \Phi\nu(\phi) \rangle}$$  \hspace{1cm} (A24c)$$
\kappa^{\nu\mu}_p(\phi) = e^{i\phi} v^\nu_p \sigma^\mu_p(\phi)^{-1} u^\mu_p, \hspace{1cm} (A24d)$$

$$\tilde{\rho}^{\nu\mu}_p(\phi) = \frac{\langle \Phi\mu | c^\dagger_p c_p | \Phi\nu(\phi) \rangle}{\langle \Phi\nu | \Phi\nu(\phi) \rangle}$$  \hspace{1cm} (A24e)$$
\tilde{\rho}^{\nu\mu}_p(\phi) = e^{-i\phi} u^\nu_p \sigma^\mu_p(\phi)^{-1} v^\mu_p. \hspace{1cm} (A24f)$$

are one-body BCS transition RDMs, which have been represented as diagonal matrices. These quantities are of $m \times l$ dimension, where $l$ denotes the size of the numerical quadrature for the gauge integration. Therefore, eqs. (A19) and (A23) provide a decomposed expression of $Z^{0.2}_{\nu\mu; pq}$ that facilitates robust and efficient computation. Expressions of other AGP transition RDMs can be derived similarly. In practice, we do not need to construct full AGP transition RDMs; instead, $\rho^{\nu\mu}_p$, $\kappa^{\nu\mu}_p$, and $\tilde{\rho}^{\nu\mu}_p$ can be directly contracted with other tensors.

**Appendix B: Special cases of linear dependence**

Without freezing an level, linear dependence of states in form of eq. (23) may arise. Two special cases of such linear dependence are shown here, which are by no means exhaustive. Here we restrict ourselves to identical shifts $\beta^\mu_p = \beta$, and define

$$\bar{N}_p = N_p + \beta.$$  \hspace{1cm} (B1)

Eq. (23) then becomes

$$|n; p_1 \cdots p_k \rangle = \prod_{i=1}^k \bar{N}_{p_i} |n\rangle.$$  \hspace{1cm} (B2)

1. **Totally symmetric states**

The totally symmetric linear combination of the states defined in eq. (B2) is special because it may be generated by acting polynomials of the total number operator $N$ (eq. (27a)) on the reference AGP $|n\rangle$. Since $|n\rangle$ is an eigenfunction of $N$ (eq. (27b)), it follows that this totally symmetric state is a multiple of $|n\rangle$. Linear dependence arises when the coefficient is zero.

Let us define the $k$-degree ESP of the shifted number operator

$$S^m_k = \sum_{1 \leq p_1 < \cdots < p_k \leq m} \bar{N}_{p_1} \cdots \bar{N}_{p_k},$$  \hspace{1cm} (B3)

where $S^m_k$ is short for $S^m_k (N_{p_i} | 1 \leq i \leq k)$. The totally symmetric state is then written as

$$\bar{S}^m_k |n\rangle = \sum_{1 \leq p_1 < \cdots < p_k \leq m} |n; p_1 \cdots p_k \rangle,$$  \hspace{1cm} (B4)

using eqs. (B2) and (B3). We may readily verify that

$$\bar{S}^m_0 |n\rangle = |n\rangle,$$

$$\bar{S}^m_1 |n\rangle = (2n + m\beta) |n\rangle,$$

$$\bar{S}^m_2 |n\rangle = \frac{1}{2} \left[ m(m-1) \beta^2 + 4n(m-1) \beta + 4n(m-n) \right] |n\rangle.$$  \hspace{1cm} (B4a)

From eq. (B5b), the states in $\{|n; p\rangle | 1 \leq p \leq m\}$ are linearly dependent when

$$\beta = -2n \frac{m}{m-1}.$$  \hspace{1cm} (B6)

Similarly, using eq. (B5c), linear dependence arises for the states in $\{|n;m\rangle | 1 \leq p < q \leq m\}$ when

$$\beta = -2 \left[ n(m-1) + \sqrt{n(m-1)(m-n)} \right] \frac{m(m-1)}{m(m-1)}.$$  \hspace{1cm} (B7)

Generally, the following recursive relation is true

$$(k + 1) S^m_{k+1} |n\rangle$$

$$+ \left[ (2k - m) \beta + 2k - 2n \right] S^m_k |n\rangle$$

$$+ (k - m - 1) (\beta^2 + 2\beta) S^m_{k-1} |n\rangle = 0,$$  \hspace{1cm} (B8)

which can be used to write out the expression of $S^m_k |n\rangle$ for any $k \geq 2$. We have used eq. (A8), or

$$\bar{N}^2_p = 2 (\beta + 1) \bar{N}_p + \beta^2 + 2\beta,$$  \hspace{1cm} (B9)

true for seniority-zero states, in the derivation of eq. (B8).

2. **A special case for sign-flip**

For the sign-flip manifolds ($\beta = -1$), we also observe linear dependence at $2k = m$ as

$$\prod_{i=1}^k \bar{N}_{p_i} |n\rangle = e^{+n} \prod_{i=k+1}^m \bar{N}_{p_i} |n\rangle.$$  \hspace{1cm} (B10)

This relation can be shown by observing

$$(-1)^k \prod_{i=1}^k \bar{N}_{p_i} |n\rangle = e^{\pm i \frac{\pi}{2} \sum_{i=1}^k \bar{N}_{p_i}} |n\rangle,$$  \hspace{1cm} (B11)

which is a special case of eq. (A3).
Appendix C: Non-orthogonal SCI criteria

Suppose we have a collection of non-orthogonal states \{|p\rangle, |q\rangle, \cdots\}, which we call the model space. We want to decide if a non-orthogonal state \(|\mu\rangle\) should be added to the model space. We assume all the states are normalized, although it is not necessary.

First, we want to know if \(|\mu\rangle\) is linearly independent of the model space. This can be accomplished by using the projector

\[
Q = I - \sum_{pq} |p\rangle X_{pq} \langle q|,
\]

where \(X\) is inverse of the model space metric

\[
X = S^{-1}.
\]

The metric of the expanded space, with the projection of \(|\mu\rangle\) off the model space included is

\[
M = \left( \begin{array}{cc} S & 0 \\ 0 & \langle \mu | Q | \mu \rangle \end{array} \right). \tag{C3}
\]

We have our first criterion that the state must pass:

\[
\langle \mu | Q | \mu \rangle > m_0 \langle \mu | \mu \rangle = m_0, \tag{C4}
\]

where \(m_0\) is a small threshold. This guarantees that \(Q|\mu\rangle\) is normalizable with good precision, and hence \(|\mu\rangle\) is numerically linearly independent.

If \(|\mu\rangle\) passes the metric test (eq. (C4)), that means it could be added to the model space. However, we need to decide if we should add it, based on a Hamiltonian test that we discuss now. Let us assume that the Hamiltonian in the model space has normalized eigenvector

\[
|\psi\rangle = \sum_{p} C_p |p\rangle, \tag{C5}
\]

with eigenvalue \(E\). Then in the basis of \{\(|\psi\rangle, Q|\mu\rangle\}\}, the metric and Hamiltonian matrices are

\[
M = \begin{pmatrix} 1 & 0 \\ 0 & \langle \mu | Q | \mu \rangle \end{pmatrix}, \tag{C6a}
\]

\[
H = \begin{pmatrix} E & \langle \psi | H Q | \mu \rangle \\ \langle \mu | Q H | \psi \rangle & \langle \mu | Q H Q | \mu \rangle \end{pmatrix}. \tag{C6b}
\]

For brevity let us define

\[
\bar{M} = \langle \mu | Q | \mu \rangle, \tag{C7a}
\]

\[
\bar{T} = \langle \psi | H Q | \mu \rangle, \tag{C7b}
\]

\[
\bar{H} = \langle \mu | Q H Q | \mu \rangle. \tag{C7c}
\]

Then the smallest generalized eigenvalue of \{\(H, M\)\} is

\[
\varepsilon = \frac{1}{2} \frac{1}{\bar{M}} (\bar{H} + E \bar{M} - \bar{R}), \tag{C8a}
\]

\[
\bar{R} = \sqrt{(\bar{H} - E \bar{M})^2 + 4 \bar{M} \bar{T}^2}. \tag{C8b}
\]

The new state should be added to the model space if the energy correction is sufficiently large. Hence to pass the Hamiltonian test, the following must be true

\[
\left| \frac{\varepsilon - E}{E} \right| > h_0, \tag{C9}
\]

where \(h_0\) is a small threshold.

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