



A size-consistent approach to strongly correlated systems using a generalized antisymmetrized product of nonorthogonal geminals

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ARTICLE INFO

Article history:

Received 17 August 2012

Received in revised form 27 September 2012

Accepted 27 September 2012

Available online 6 October 2012

Keywords:

Antisymmetrized product of geminals wavefunctions

Strong electron correlation

Richardson Hamiltonian

Lie Algebraic Hamiltonians

Bethe Ansatz

Off-shell Bethe vectors

ABSTRACT

Inspired by the wavefunction forms of exactly solvable algebraic Hamiltonians, we present several wavefunction ansätze. These wavefunction forms are exact for two-electron systems; they are size consistent; they include the (generalized) antisymmetrized geminal power, the antisymmetrized product of strongly orthogonal geminals, and a Slater determinant wavefunctions as special cases. The number of parameters in these wavefunctions grows only linearly with the size of the system. The parameters in the wavefunctions can be determined by projecting the Schrödinger equation against a test-set of Slater determinants; the resulting set of nonlinear equations is reminiscent of coupled-cluster theory, and can be solved with no greater than $O(N^5)$ scaling if all electrons are assumed to be paired, and with $O(N^6)$ scaling otherwise. Based on the analogy to coupled-cluster theory, methods for computing spectroscopic properties, molecular forces, and response properties are proposed.

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1. Motivation

Modern quantum chemistry, at both the conceptual and computational levels, is dominated by the orbital paradigm [1,2]. For example, most of our understanding of chemical processes is based on molecular orbital theory, in which electrons are assigned to occupied orbitals, while virtual (unoccupied) orbitals are accessible by electronic excitation. The wavefunction that corresponds to this conceptual framework is a single Slater determinant.

Slater determinants are the foundation for all of the most popular methods in computational quantum chemistry [2,3]. In some methods (Hartree–Fock, Kohn–Sham density functional theory), the wavefunction is a single Slater determinant. Other methods attempt to add corrections to the Slater determinant picture, typically by including excited-state electron configurations (configuration interaction, coupled-cluster). These approaches tend to fail for systems where the Slater determinant is a bad starting point for approximating the true wavefunction unless an exponential number of excited-state configurations are included. Such systems are said to be strongly correlated [4].

When electrons are strongly correlated, the orbital picture breaks down: it is no longer useful, either conceptually or computationally, to classify orbitals as occupied or unoccupied. However, practical and simple forms for the wavefunction may still exist. A classic example of a strongly-correlated system is a superconductor, and while a simple wavefunction built from orbitals is not appropriate, a simple wavefunction built from Cooper pairs (geminals) is [5].

The purpose of this paper is to present families of wavefunctions that are appropriate for both strongly-correlated and weakly-correlated electronic materials. The forms we propose are still mean-field models in the sense that the number of parameters in the wavefunction grows linearly with the size of the system. However, the wavefunction forms are based on antisymmetrized products of nonorthogonal geminals. *In these models, it is the pairs of electrons that are weakly correlated to each other, not electrons themselves.*

Unfortunately, the equations for determining wavefunctions built from antisymmetrized products of nonorthogonal geminals are computationally intractable. To circumvent this problem, many authors have imposed orthogonality restrictions on the geminals [6,7]. Our approach is different: in Section 2. A we will present a special mathematical structure; when the nonorthogonal geminals have this structure the wavefunction is said to be an antisymmetrized product of rank-two geminals (APr2Gs), and the equations for determining the wavefunction are computationally tractable (Sec-

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tion 2.3). The Apr2G form was inspired by the eigenfunctions of the Richardson Hamiltonian, which can be determined by a Bethe ansatz (Section 3.1) [8,9].

The Apr2G wavefunction requires each electron to be paired (albeit not necessarily to an electron with the opposite spin); it is associated with $gl(2, \mathbb{C})$: the general linear algebra of degree 2 on the field of complex numbers, the set of complex 2×2 matrices. In Sections 3.2, 3.3, 3.4, wavefunctions that are appropriate for systems with unpaired electrons are derived by considering algebras of higher degree, $gl(n|k)$. $gl(n|k)$ is the general linear algebra acting on n bosonic states (integer spin) and k fermionic (half-integer spin) states.

Methods for computing properties from these wavefunctions are proposed in Section 4; these methods are similar to those in coupled cluster theory. Section 5 provides a summary of the main results in the paper. Readers who are primarily interested in the key results may safely skip Section 3, which is focused on the mathematical tools needed to derive the results in Section 2 and extend them to systems with unpaired electrons.

2. Pairing Models for the Wavefunction; $gl(2, \mathbb{C})$

2.1. Pairing models

The Slater determinant is an antisymmetrized product of one-electron wavefunctions, called spin-orbitals. When this model is not appropriate, the next simplest model is an antisymmetrized product of two-electron wavefunctions, called geminals. In second quantization, the operator for creating an electron pair is

$$\hat{G}_p^\dagger = \sum_{ij=1}^{2K} c_{ij,p} a_j^\dagger a_i^\dagger \quad (1)$$

with $c_{ij} = -c_{ji}$. Throughout this paper, K denotes the number of spatial basis functions. By a suitable unitary transformation of the spin-orbital basis [6,10], the pair-creation operator may be rewritten as a sum over pairs of spin-orbitals,

$$\hat{G}_p^\dagger = \sum_{i=1}^K c_{i,p} a_{2i}^\dagger a_{2i-1}^\dagger = \sum_{i=1}^K c_{i,p} a_i^\dagger a_i^\dagger \quad (2)$$

This is typically called the “diagonal” or “natural” form for the geminal. Typically the spin-orbitals indexed with i and \bar{i} are the α - and β -spin forms of the same spatial orbital; when this is not true, one is using broken-symmetry geminals [11,12]. (Obviously this is not true if the geminal is not a singlet. However, we will not even require that the geminal is a spin eigenfunction.) Hereafter, we will use the word “orbital” to refer to a spin-orbital.

The wavefunction ansatz we choose is an antisymmetric product of P geminals,

$$|\Psi\rangle = \prod_{q=1}^P G_q^\dagger |\theta\rangle = \left(\sum_{i_1=1}^K c_{i_1,1} a_{i_1}^\dagger a_{i_1}^\dagger \right) \left(\sum_{i_2=1}^K c_{i_2,2} a_{i_2}^\dagger a_{i_2}^\dagger \right) \cdots \left(\sum_{i_p=1}^K c_{i_p,p} a_{i_p}^\dagger a_{i_p}^\dagger \right) |\theta\rangle \quad (3)$$

where P is the number of electron pairs and where $|\theta\rangle$ denotes the vacuum state. The vacuum state does not need to be the physical vacuum, only a vacuum with respect to the creation of geminals. For example, one can use a model wavefunction like this only in a small active space by choosing a many-electron vacuum state. States with an odd number of electrons can be treated quite simply by using a one-electron state as the vacuum.

In the 1970s, an alternative form of antisymmetrized product of geminals, based on the antisymmetrized product of $N(N-1)/2$ pair functions, was proposed by Silver and explored by Náray-Szabó [13–15]. This “all pairs” wavefunction does not seem to lend itself to the type of analysis performed here. For example, in the all-pair wavefunction, the pair functions are defined in the Banach space $\mathbb{L}^{2(N-1)}$, which means that a second-quantized description is probably extremely difficult. (Banach spaces are not self-dual, so the creation operators would act on $\mathbb{L}^{2(N-1)}$, while the annihilation operators would act on $\mathbb{L}^{(2N-2)/(2N-3)}$.)

Eq. (3) is an antisymmetrized product of nonorthogonal geminals. It is not the most general possible form, however, because all the geminals share the same pairing scheme for the orbitals (i.e., the same unitary transformation converts the mathematical form in Eq. (1) to the form in Eq. (2) for all the geminals, $p = 1, 2, \dots, P$). Without this assumption, geminal product theories are very complicated mathematically and very expensive computationally [16,17].

The wavefunction in Eq. (3) can be expanded in terms of Slater determinants,

$$|\Psi\rangle = \sum_{\{P_i\}_p} \phi_{\{P_i\}_p} (\hat{g}_1^\dagger)^{P_1} (\hat{g}_2^\dagger)^{P_2} \cdots (\hat{g}_K^\dagger)^{P_K} |\theta\rangle \quad (4)$$

where

$$\hat{g}_i^\dagger = a_i^\dagger a_i^\dagger \quad (5)$$

generates an electron in the i th set of paired orbitals and the notation $\{P_i\}_p$ indicates that the sum runs over all possible ways of partitioning P pairs of electrons into the K pairs of orbitals,

$$\sum_{i=1}^K P_i = P \quad 0 \leq P_i. \quad (6)$$

The expansion coefficient is

$$\phi_{\{P_i\}_p} = \frac{1}{P_1! P_2! \cdots P_K!} |\mathbf{C}_{\{P_i\}_p}|^+ \quad (7)$$

where $|\mathbf{C}|^+$ denotes the permanent of \mathbf{C} . The \mathbf{C} matrix has the coefficients of each G_q^\dagger listed in the rows and the columns lists the coefficients of \hat{g}_i^\dagger , each of which appears P_i times,

$$\mathbf{C}_{\{P_i\}_p} \equiv \begin{array}{ccccccc} & \overbrace{\quad\quad\quad}^{P_1 \text{ times}} & & \overbrace{\quad\quad\quad}^{P_2 \text{ times}} & & & \overbrace{\quad\quad\quad}^{P_K \text{ times}} \\ & c_{1,1} & \cdots & c_{1,1} & c_{2,1} & \cdots & c_{2,1} & \cdots & c_{K,1} & \cdots & c_{K,1} \\ \mathbf{C}_{\{P_i\}_p} & c_{1,2} & \cdots & c_{1,2} & c_{2,2} & \cdots & c_{2,2} & \cdots & c_{K,2} & \cdots & c_{K,2} \\ & & \vdots & & & \vdots & & & & \vdots & \\ & c_{1,P} & \cdots & c_{1,P} & c_{2,P} & \cdots & c_{2,P} & \cdots & c_{K,P} & \cdots & c_{K,P} \end{array} \quad (8)$$

Eq. (7) is valid for the general boson case, where it is possible to put multiple bosons into a single state. We will not derive Eq. (7) in the general case: because electron pairs are hard-core bosons, repeated operations are zero in our method ($(\hat{g}_i^\dagger)^n = 0$ for $n > 1$). The permanent arises because it is the coefficient of $\hat{o}_{k_1} \hat{o}_{k_2} \cdots \hat{o}_{k_p}$ in the polynomial

$$\prod_{l=1}^L \left(\sum_{k=1}^K c_{k,l} \hat{o}_{k_l} \right) \quad (9)$$

when the operators in the sum commute, $\hat{o}_k \hat{o}_l = \hat{o}_l \hat{o}_k$. This establishes the validity of Eq. (7) for all terms with $P_i \in \{0, 1\}$, which suffices for electron pairs. If the operators anticommuted, $\hat{o}_k \hat{o}_l = -\hat{o}_l \hat{o}_k$, then the coefficient of $\hat{o}_{k_1} \hat{o}_{k_2} \cdots \hat{o}_{k_L}$ would be the determinant, $|\mathbf{C}|^-$. (This will be useful in Section 3, where the open-shell case is treated.)

Eq. (7) is of limited computational utility because the permanent of a general matrix cannot be computed in polynomial time. We need to choose a special structure for the coefficients of the geminals so that the permanent can be computed. A key result is given by Borchart's theorem [18], which implies that if the geminal coefficients have the form,

$$c_{i,p} = \frac{1}{\varepsilon_i - \lambda_p}, \quad (10)$$

then the permanent is just a ratio of determinants,

$$|[\mathbf{C}_{i,p}]^+| = \frac{|\mathbf{C}_{\{(P_i\}p}]^+ \circ \mathbf{C}_{\{(P_i\}p}]^-|}{|\mathbf{C}_{\{(P_i\}p}]^-|} \quad (11)$$

where $\mathbf{C}_{\{(P_i\}p}]^+ \circ \mathbf{C}_{\{(P_i\}p}]^-$ denotes the Hadamard product of $\mathbf{C}_{\{(P_i\}p}]^+$ with itself; this is the matrix whose elements are the squares of the entries of the original matrix, $\mathbf{C}_{\{(P_i\}p}]^+ \circ \mathbf{C}_{\{(P_i\}p}]^- \equiv [\mathbf{C}_{i,p}^2]$ [19,20]. (N.B. There is an analog of Borchart's theorem that allows Hafnians to be converted to Pfaffians [21], which may be useful, given the recent interest in Pfaffian wavefunctions in the quantum Monte Carlo community [12,22,23]).

Borchart's result was generalized to generic rank-two matrices by Carlitz and Levine [24] given complex numbers $\{a_p\}_{p=1}^P$, $\{\varepsilon_i\}_{i=1}^K$, $\{b_i\}_{i=1}^K$, $\{\lambda_p\}_{p=1}^P$, if the geminal coefficients in Eq. (2) are the reciprocal of the elements in a rank-two matrix,

$$c_{i,p} = \frac{1}{a_p \varepsilon_i + b_i \lambda_p}, \quad (12)$$

then Eq. (11) still holds. This is the type of coefficients we will use. Our wavefunction ansatz is then,

$$|\Psi(\mathbf{a}, \boldsymbol{\varepsilon}, \mathbf{b}, \boldsymbol{\lambda})\rangle = \prod_{p=1}^P \left(\sum_{i=1}^K \frac{a_i^\dagger a_i^\dagger}{a_p \varepsilon_i + b_i \lambda_p} \right) |\theta\rangle. \quad (13)$$

We call this the antisymmetric product of rank-two geminals, APr2G. It can be expanded in terms of Slater determinants, (4), where the coefficients in the expansion have the form of a ratio of determinants,

$$\phi_{\{(P_i\}p]} = \frac{\left| \left[\frac{1}{(a_p \varepsilon_i + b_i \lambda_p)^2} \right]^- \right|}{\left| \left[\frac{1}{a_p \varepsilon_i + b_i \lambda_p} \right]^- \right|} \quad (14)$$

where only the columns corresponding to the occupied orbitals appear in the matrix (cf. Eq. (8)).

2.2. Links to other models

In order to elucidate the relationship between the APr2G wavefunction and previous models, it is helpful to rewrite Eq. (13) in the form

$$|\Psi(\mathbf{v}, \boldsymbol{\zeta}, \tilde{\boldsymbol{\varepsilon}}, \tilde{\boldsymbol{\lambda}})\rangle = \prod_{p=1}^P v_p \left(\sum_{i=1}^K \frac{\zeta_i a_i^\dagger a_i^\dagger}{\tilde{\varepsilon}_i + \tilde{\lambda}_p} \right) |\theta\rangle \quad (15)$$

with

$$\begin{aligned} \tilde{\varepsilon}_i &= \varepsilon_i / b_i \\ \zeta_i &= 1 / b_i \\ \tilde{\lambda}_p &= \lambda_p / a_p \\ v_p &= 1 / a_p \end{aligned} \quad (16)$$

The constant prefactors, v_p , can be chosen to normalize the geminals, but because they merely change the normalization of the wavefunction, they are not optimizable parameters. To make this clear, we rewrite the wavefunction form one final time,

$$|\Psi_v(\boldsymbol{\zeta}, \tilde{\boldsymbol{\varepsilon}}, \tilde{\boldsymbol{\lambda}})\rangle = \left(\prod_{p=1}^P v_p \right) \prod_{p=1}^P \left(\sum_{i=1}^K \frac{\zeta_i}{\tilde{\varepsilon}_i + \tilde{\lambda}_p} a_i^\dagger a_i^\dagger \right) |\theta\rangle \quad (17)$$

When we expand this wavefunction in terms of Slater determinants, we have

$$|\Psi_v(\boldsymbol{\zeta}, \tilde{\boldsymbol{\varepsilon}}, \tilde{\boldsymbol{\lambda}})\rangle = \left(\prod_{p=1}^P v_p \right) \sum_{\{m_i=(0,1)\}_{\sum_{i=1}^K m_i=p}} \left| \frac{\zeta_i}{\tilde{\varepsilon}_i + \tilde{\lambda}_p} \right|^+ (a_1^\dagger a_1^\dagger)^{m_1} (a_2^\dagger a_2^\dagger)^{m_2} \cdots (a_K^\dagger a_K^\dagger)^{m_K} |\theta\rangle \quad (18)$$

where $\left| \frac{\zeta_i}{\tilde{\varepsilon}_i + \tilde{\lambda}_p} \right|^+$ is a permanent of a matrix that includes only the contributions from the orbitals with $m_i = 1$ (cf. Eq. (8)). The wavefunction in Eq. (15) is a generalization of the wavefunction form one obtains from a completely factorizable interaction [25], i.e. an interaction that may be decomposed

$$\hat{V} = \sum_{ij} \left(C_i a_i^\dagger a_i^\dagger \right) (C_j a_j a_j) \quad (19)$$

Examples of such models include $p + ip$ wave [26–28] and $d + id$ wave superconductors [29], along with related models for heavy nuclei [30]. In these models, the $\tilde{\varepsilon}_i$ are interpreted as orbital energies and the $\tilde{\lambda}_p$ are the energies of electron pairs, or quasimomenta (because we imagine them to be the energy of the noninteracting electron pairs) [31].

Eq. (17) clarifies that the APr2G wavefunction is an antisymmetrized product of nonorthogonal geminals. It has close links to other wavefunction forms that are based on pairing electrons in geminals [7]. For example, the antisymmetrized geminal power wavefunction (AGP, [32–36]) is the special case where $\tilde{\boldsymbol{\varepsilon}} = \mathbf{0}$, $\tilde{\boldsymbol{\lambda}} = \mathbf{1}$. AGP is an antisymmetrized product of rank-one geminals: APr1G = AGP. A special case of AGP is the Slater determinant wavefunction, which arises when $\tilde{\boldsymbol{\varepsilon}} = \tilde{\boldsymbol{\lambda}} = \mathbf{1}$, with $\zeta_i = 1$ for the occupied orbitals and $\zeta_i = 0$ for the unoccupied orbitals.

There are also links to conventional quantum chemistry methods. An antisymmetrized product of strongly orthogonal geminals (APSGs) form was proposed [6,37,38] and explored [35,39–54] as a wavefunction form in the 1950s and 1960s, and use of the APSG wavefunction form continues to the present day [7,55–67]. (The generalized-valence bond (GVB) wavefunction, “perfect pairing” wavefunction, and Piris natural orbital functional version 5 (PNOF5) are special cases of APSG [6,7,68–75].) The APSG is a limiting case of the present form: choose $\boldsymbol{\zeta} = \mathbf{1}$, then choose $\tilde{\lambda}_p = p\Delta$. $\tilde{\lambda}_p$ can be interpreted as the characteristic energy of the p th electron pair and if one examines the form of the geminal creation operator, Eq. (13), it is clear that only the orbitals whose energy, $\tilde{\varepsilon}_i$, is close to $\tilde{\lambda}_p$ make significant contributions to the p th geminal. As the spacing between the pairing energies goes to infinity ($\Delta \rightarrow \infty$), each geminal is built from a distinct orbital subspace, which is the characteristic feature of strongly orthogonal geminal product wavefunctions [76,77]. The APSG wavefunction is also a special case of the Richardson wavefunction, which arises from APr2G when

$\zeta = \mathbf{1}$, with $\tilde{\lambda}$ and $\tilde{\mathbf{e}}$ related to each other by Richardson's equations [8,9].

There is also a link to the variation-after-projection Hartree–Fock Bogoliubov (PHFB) method [78–85] that Scuseria et al. [11,86–88] are developing for the electronic structure problem. Their wavefunction has a very similar form to AGP (cf. Eq. (5) in Ref. [11]), and for a system with an even number of electrons, after projecting onto a state with the correct number of electrons, PHFB gives the $\tilde{\mathbf{e}} = \tilde{\lambda} = \mathbf{1}$ case of Eq. (15). Just as in PHFB, we can consider cases where the orbital-pairing scheme is increasingly flexible. If we write our geminals in the form

$$\hat{G}_p^\dagger = \sum_{i=1}^K c_{ip} a_i^\dagger a_{K+i}^\dagger \quad (20)$$

and build the orbital basis for Eq. (20) as a unitary transformation of the orthonormal spin-orbitals,

$$a_i^\dagger|\theta\rangle = \sum_{\kappa=1}^{2K} u_{i;\kappa} \tilde{a}_\kappa^\dagger|\theta\rangle \quad (21)$$

where the orbitals created by \tilde{a}_κ^\dagger and $\tilde{a}_{K+\kappa}^\dagger$ have the same spatial part, but differ because ϕ_κ is an α -spin orbital for $\kappa = 1, 2, \dots, K$ and ϕ_κ is a β -spin orbital for $\kappa = K+1, K+2, \dots, 2K$. The unitary transformation can be written as a block matrix,

$$\mathbf{U} = \begin{bmatrix} \mathbf{U}_{\alpha\alpha} & \mathbf{U}_{\alpha\beta} \\ \mathbf{U}_{\beta\alpha} & \mathbf{U}_{\beta\beta} \end{bmatrix}. \quad (22)$$

More typically, one would restrict oneself to real coefficients, so one would have an orthogonal (as opposed to a unitary) basis set transformation,

$$\mathbf{Q} = \begin{bmatrix} \mathbf{Q}_{\alpha\alpha} & \mathbf{Q}_{\alpha\beta} \\ \mathbf{Q}_{\beta\alpha}^T & \mathbf{Q}_{\beta\beta} \end{bmatrix} \quad (23)$$

The link between our approach and the PHFB approach is clarified by considering a hierarchy of increasingly general pairing schemes and relating these to the corresponding PHFB labels. Specifically, we can consider pairing orbitals which (1) have the same spatial part and differ only in spin (“R”; $\mathbf{Q}_{\alpha\beta} = 0$; $\mathbf{Q}_{\alpha\alpha} = \mathbf{Q}_{\beta\beta}$), (2) have different spatial parts but differ in spin (“U”; $\mathbf{Q}_{\alpha\beta} = 0$, $\mathbf{Q}_{\alpha\alpha} \neq \mathbf{Q}_{\beta\beta}$), and (3) are arbitrary orbital pairs and not necessarily eigenfunctions of $\hat{s}_z(1)$ (“G”; $\mathbf{Q}_{\alpha\beta} \neq 0$; $\mathbf{Q}_{\alpha\alpha} \neq \mathbf{Q}_{\beta\beta}$). Projecting the RHF, UHF, and GHF functions onto the N -electron space (NRHF, NUHF, NGHFB) gives antisymmetrized geminal power wavefunctions with unbroken (NRHF = AGP) or broken (NUHF = UAGP; NGHFB = GAGP) symmetry geminals [12,22,23,89]. NGHFB is the most general APr1G wavefunction, and is thus a special case of the APr2G wavefunction. The NUHF and NGHFB wavefunctions are generally not spin eigenfunctions, but spin symmetry can be restored by projection (i.e., SNGHFB). Projecting the wavefunction cannot decrease the energy because the wavefunction after a projection must still be in the Hilbert space of number-projected HFB wavefunctions. Except for the complex number symmetry restoration, denoted K, for which the wavefunction form is not obvious, the entire PHFB hierarchy is contained inside APr1G, and therefore is a special case of APr2G.

One implication of our results is that the PHFB approach can be extended to wavefunctions with the more general form,

$$|\tilde{\Psi}_v(\zeta, \tilde{\mathbf{e}}, \tilde{\lambda})\rangle = \left(\prod_{p=1}^K v_p \right) \prod_{p=1}^K \left(\sum_{i=1}^K \left(1 + \frac{\zeta_i}{\tilde{e}_i + \tilde{\lambda}_p} a_i^\dagger a_i^\dagger \right) \right) |\theta\rangle \quad (24)$$

without a debilitating increase in computational expense. The link between APr2G and other popular wavefunction forms is summarized in Fig. 1.

The APr2G wavefunction is a special case of the most general antisymmetrized product of geminals wavefunction, where the

geminals are allowed to be nonorthogonal and have no special structure [48]. This most general form of geminals is computationally daunting and mathematically intimidating [17], so we restricted the form of the geminal product so that all of the geminals have the same orbital-pairing scheme. This restriction was originally proposed by Silver [90,91], who calls the wavefunction in Eq. (3) an antisymmetric product of interacting geminals (APIGs). Even the APIG form is not computationally facile [92], however; the appearance of the permanent in the expansion coefficients (cf. Eq. (7)) indicates that directly employing the APIG wavefunction is likely to be challenging. The restricted form of APIG in Eq. (13) is computationally facile, however.

Finally, the APr2G wavefunction is a special case of the doubly-occupied configuration interaction (DOCI) calculation method that was first proposed in the context of reduced density matrix theory by Weinhold and Wilson [93]. When the orbitals are optimized (i.e., configuration interaction is extended to multi-configuration self-consistent field (MCSCF)), this method is referred to as complete MCSCF [94,95], doubly-occupied MCSCF [96], pair-excited MCSCF [96–103], even-replacement MCSCF [101], closed-shell-MCSCF [104], and seniority-zero MCSCF [97]. These methods are CI (or MCSCF, where the spin-orbitals are optimized) calculations including all the Slater determinants in which every orbital pair is either unoccupied or doubly occupied. The unpaired electron configurations contribute most of the correlation energy in larger molecules, and the APr2G wavefunction ansatz, like DOCI and its APSG wavefunction special case, is not expected to recover dynamical correlation effects [97]. The APr2G wavefunction includes the electron correlation between paired electrons (intra-geminal correlation) but the correlation between electron pairs (inter-geminal correlation) is neglected, just like it is in any antisymmetric geminal project form. We anticipate, however, that it is a suitable starting point for dynamical correlation theories, and that the techniques that have been used to address dynamical correlation with the APSG wavefunction [7,61–63,105] will be even more effective if the APr2G wavefunction is used as a starting point.

In agreement with Bytautas et al.'s results [97], our preliminary calculations suggest that optimizing the orbitals is important, and can significantly increase the fraction of the correlation energy that is obtained with DOCI. Our preliminary calculations also suggest that the APIG wavefunction gives results that are almost numerically indistinguishable from orbital-optimized DOCI [106]. While APIG is not computationally tractable, these results encouraged us to develop computational procedures for determining the parameters in the APr2G wavefunction.

2.3. The projected-Schrödinger equations for the APr2G wavefunction

To optimize the parameters in the wavefunction (17), we use the projected Schrödinger equation,

$$\langle \Phi_{\text{test}} | \hat{H} | \Psi_v(\zeta, \tilde{\mathbf{e}}, \tilde{\lambda}) \rangle = E \langle \Phi_{\text{test}} | \Psi_v(\zeta, \tilde{\mathbf{e}}, \tilde{\lambda}) \rangle \quad (25)$$

or, equivalently,

$$\langle \hat{H} \Phi_{\text{test}} | \Psi_v(\zeta, \tilde{\mathbf{e}}, \tilde{\lambda}) \rangle = E \langle \Phi_{\text{test}} | \Psi_v(\zeta, \tilde{\mathbf{e}}, \tilde{\lambda}) \rangle. \quad (26)$$

Here Φ_{test} is any N -electron wavefunction, but the conventional choice is a Slater determinant. The idea of using the projected Schrödinger equation, instead of the variational method, is standard in coupled cluster theory [107]. In the context of geminal product wavefunctions, the idea of using the projected Schrödinger equation was proposed by Cullen [108] and developed further by the Head-Gordon group [74,109,110].

Because the overlaps between $\Psi_v(\zeta, \tilde{\mathbf{e}}, \tilde{\lambda})$ and Slater determinants can be computed efficiently, we choose Φ_{test} in Eq. (25) to be Slater determinants. It seems logical to choose the determinant

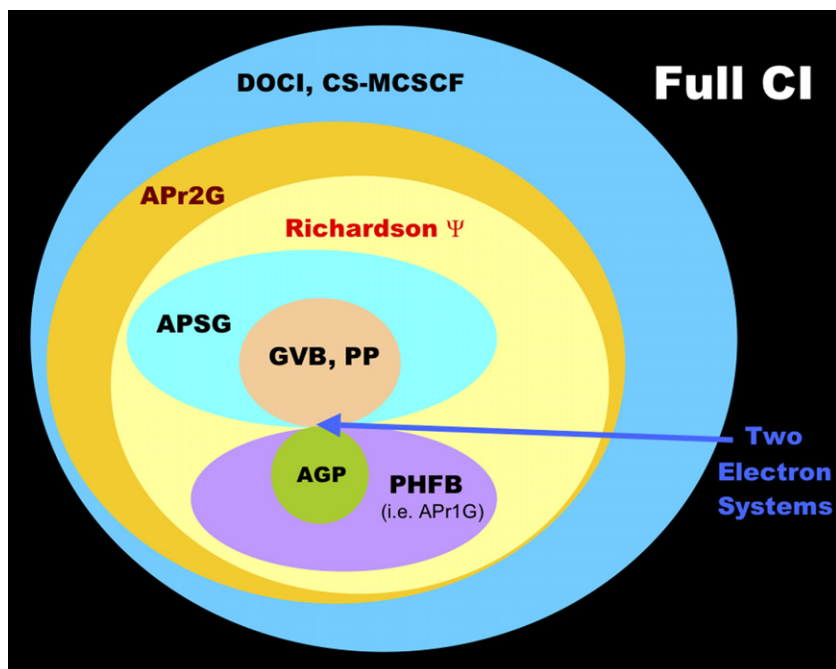


Fig. 1. The antisymmetrized product of rank-2 geminals wavefunction (APr2G; cf. Eq. (15)) and its relationship to other, more common, wavefunction forms in quantum chemistry. See Section 2.2 for details. The coefficients in the Richardson wavefunction have the form of Eq. (10). APSG is the antisymmetric product of strongly orthogonal geminals, which includes the generalized valence bond (GVB) wavefunction (also known as perfect-pairing, PP) as a special case. AGP is the antisymmetrized geminal power, and PHFB is the projected Hartree–Fock–Bogoliubov wavefunction; unlike the other wavefunctions on this diagram, they are not size-extensive. All of these wavefunctions are exact for two-electron systems.

defined by occupying the lowest-energy pairs (Hartree–Fock) and a subset of its pair-excited determinants,

$$|\Phi_{ii}^{aa}\rangle = a_a^\dagger a_a^\dagger a_i a_i |\Phi_{\text{HF}}\rangle, \quad (27)$$

as test functions, but other choices are possible. Note that because there are only $2K + 2P$ unknown parameters, only a small number of Slater determinant test functions suffice to determine all the unknown parameters. Adding more test functions than needed converts the problem from a system of nonlinear equations to a nonlinear least-squares problem. Determining the best choice for the number and type of Slater determinant test functions will require computational testing.

The computational cost of evaluating these nonlinear equations is the cost of evaluating overlaps like $\langle \Phi_{ijj}^{aa} \Phi_{kk\dots}^{bb} | \Psi_V(\zeta, \tilde{\epsilon}, \tilde{\lambda}) \rangle$, times the number of overlaps that need to be determined. (Overlaps that are not of this form are always zero.) Notice that because the Hamiltonian is a 2-electron operator, all the determinants that appear are related by a single pair-excitation to a test determinant. If the test functions are also related by pair excitation, then the coefficient matrices for which we need to take the determinant typically differ by just one column. If we compute the determinants in Eq. (14) for one of the Slater determinants of interest, and we also compute the inverse of the corresponding coefficient matrix, then we can compute the determinant of a related matrix using the identity for a rank-one update of the determinant. Denoting \mathbf{e}_k as the vector that is zero except for a 1 in position k , replacing orbital-pair i with orbital pair a in the changes the determinants by,

$$|\mathbf{c}_{ii}^{aa}\rangle^- = |\mathbf{C} + (\mathbf{c}_{aa} - \mathbf{c}_{ii})\mathbf{e}_k^T|^- = \left(1 + \mathbf{e}_k^T \mathbf{C}^{-1} (\mathbf{c}_{aa} - \mathbf{c}_{ii})\right) |\mathbf{C}|^-. \quad (28)$$

This means that, for a given electron configuration, the cost of Eq. (14) is just $O(P^2)$, instead of the naively expected $O(P^3)$.

The number of determinants that appear depends on the choice of test functions. If $O(K)$ pair-excited determinants are used as test functions, then the determinants that appear are (1) all $P(P - K)$ pair-excited determinants and (2) a subset of $O((K - P)PK)$ of the two-pair excited determinants, $\Phi_{ij}^{aa} \Phi_{jj}^{bb}$. The overall computational cost per iteration will then be $O(P^3(K - P)K)$, which grows as the fifth power of the system's size.

Alternatively, one could use $O(K)$ single-excited Slater determinants, denoted Φ_i^a or Φ_i^a , as test functions. Applying the Hamiltonian to these test functions does not generate any two-pair excitations, so only the coefficients of the $P(K - P)$ pair-excited determinants need to be determined. The overall computational cost per iteration will then be $O(P^3(K - P))$, which grows as the fourth power of system size. The caveat is that the equations may not converge to the desired solution if only single-excitations are used. Brillouin's theorem indicates that $\langle \Phi_i^a | \hat{H} | \Phi_{\text{HF}} \rangle = \langle \Phi_i^a | \Phi_{\text{HF}} \rangle = 0$, so the Hartree–Fock wavefunction is a solution to the projected-Schrödinger equation if only single excitations are used. (It may or may not be the only solution.) One needs to have a suitable *non*-Hartree–Fock initial guess for the parameters in the wavefunction in order to use only single excitations. Alternatively, one could include a few pair excitations (enough to avoid the Hartree–Fock solution, but not enough to ruin the scaling). It seems safe to claim, however, that the nonlinear equations for the parameters in the wavefunction can *potentially* be solved with the quartic scaling that is characteristic of a mean-field method like Hartree–Fock.

In order to solve the nonlinear equations, we anticipate using a quasi-Newton method. However, Newton's method (or a partial quasi-Newton method where some elements of the inverse Jacobian are computed exactly) is feasible because the Jacobian can be evaluated analytically without great difficulty. The key is the

formula for the derivative of a determinant with respect to one of the parameters, q , that enter into the coefficients is

$$\frac{\partial |\mathbf{C}|^-}{\partial q} = |\mathbf{C}|^- \left(\text{Tr} \left[\mathbf{C}^{-1} \frac{\partial \mathbf{C}}{\partial q} \right] \right) \quad (29)$$

Using the Sherman–Morrison formula for the rank-one update of a matrix inverse,

$$\left(\mathbf{C}_{ii}^{aa} \right)^{-1} = \mathbf{C}^{-1} + \frac{\mathbf{C}^{-1} (\mathbf{c}_{aa} - \mathbf{c}_{ii}) \mathbf{e}_k^T \mathbf{C}^{-1}}{1 + \mathbf{e}_k^T \mathbf{C}^{-1} (\mathbf{c}_{aa} - \mathbf{c}_{ii})}, \quad (30)$$

the derivative can be efficiently evaluated,

$$\begin{aligned} \frac{\partial |\mathbf{C}_{ii}^{aa}|^-}{\partial q} &= |\mathbf{C}_{ii}^{aa}|^- \left(\text{Tr} \left[\mathbf{C}^{-1} \frac{\partial \mathbf{C}}{\partial q} \right] - 1 + \left(1 + \frac{\mathbf{e}_k^T \mathbf{C}^{-1} (\mathbf{c}_{aa} - \mathbf{c}_{ii})}{1 + \mathbf{e}_k^T \mathbf{C}^{-1} (\mathbf{c}_{aa} - \mathbf{c}_{ii})} \right) \right. \\ &\quad \left. \times \left(1 + \mathbf{e}_k^T \mathbf{C}^{-1} \left(\frac{\partial (\mathbf{c}_{aa} - \mathbf{c}_{ii})}{\partial q} \right) \right) \right). \end{aligned} \quad (31)$$

3. Generalization to open shells; $\mathfrak{gl}(n|k)$

3.1. Bethe ansatz wavefunctions

The wavefunction in Eq. (13) is limited to systems with an even number of electrons. Systems with an odd number of electrons can be treated by using a 1-electron vacuum state, but the electron in the 1-electron state will not be correlated to the other electrons in the system. This is undesirable: a good description of the electron correlation in a free radical requires, above all, describing the correlation between the unpaired electron and the other electrons in the system.

To propose wavefunction forms that do not possess this limitation, it is useful to explain how we “discovered” the wavefunction in Eq. (13) (which is different from the motivation we gave for it in Section 2). We have been studying exactly solvable Hamiltonians. Given a Lie algebra, there are well-studied ways for constructing a Hamiltonian which has an exact solution. Eigenvectors of these models are expressed in terms of a nested Bethe ansatz, or generalized Bethe hypothesis [111,112]. The Richardson wavefunction, which is commonly written in the form of Eq. (15) with $\zeta = \mathbf{1}$, can be derived by considering the algebra $\mathfrak{gl}(2, \mathbb{C})$ or, more conventionally, $\mathfrak{su}(2)$. ($\mathfrak{gl}(2, \mathbb{C})$ is the general linear algebra based on complex 2×2 matrices.)

The fundamental operators in the $\mathfrak{gl}(2, \mathbb{C})$ algebra can be chosen to create a pair of electrons, to remove a pair of electrons, to count the number of electron pairs, and to count the number of spatial orbitals. This last operation yields a constant, and hence can be disregarded. If one considers an algebra that has different, or even better, more types of operators, then different types of electron configurations can be generated. We have followed this path of research, which involves (1) studying various algebras, (2) finding an interesting “physical” representation of the operators in the algebras in terms of fermion creation and annihilation operators, (3) constructing a Hamiltonian from the set of (classical) Yang–Baxter equations for the algebra, and then (4) formulating a (nested) Bethe ansatz for the Hamiltonian. A detailed description of this work will be presented elsewhere; for the purposes of this paper it is only important to note that the wavefunction forms we will propose are motivated by our desire to be able to write the *exact* solution to increasingly realistic model Hamiltonians. (We believe that using wavefunction forms that are inspired by the eigenfunctions of interesting Hamiltonians is important because this ensures that our wavefunctions are not entirely devoid of physical relevance.)

Our procedure for deriving new wavefunction forms can be made slightly more concrete by summarizing the derivation of

the Richardson wavefunction using $\mathfrak{gl}(2, \mathbb{C})$. We define the state “2” as the physical vacuum, $|\theta\rangle$, and the state “1” as a two-electron state with the k th orbital pair occupied, $|k\bar{k}\rangle$. We denote this ladder of states as a vector,

$$\begin{bmatrix} |k\bar{k}\rangle \\ |\theta\rangle \end{bmatrix} \quad (32)$$

The operator that creates a pair of electrons in the k th orbital pair is denoted $\hat{E}_{12}(k)$ and its adjoint, $\hat{E}_{21}(k) = \hat{E}_{12}^\dagger(k)$ removes a pair. These operators can be represented with 2×2 matrices; $\hat{E}_{fi}(k)$ is a matrix of zeros except for a one in the fi position. I.e., the m th element of the matrix is,

$$[\hat{E}_{fi}(j)]_{mn} = \delta_{mf} \delta_{ni} \quad (33)$$

Making K copies of the algebra, where K is the number of spatial basis functions, we construct a Hamiltonian that resembles the Casimir operator for the algebra,

$$\begin{aligned} \hat{H}_{\text{Richardson}} &= \sum_{k=1}^K \varepsilon_k \left(a_k^\dagger a_k + a_k^\dagger a_k \right) + g \sum_{k,k'}^K \hat{E}_{12}(k) \hat{E}_{21}(k') \\ &= \sum_{k=1}^K \varepsilon_k \left(a_k^\dagger a_k + a_k^\dagger a_k \right) + g \sum_{i,i'}^K a_k^\dagger a_k^\dagger a_{i'} a_{i'} \end{aligned} \quad (34)$$

The manner in which this Hamiltonian can be systematically constructed is presented by Cambiaggio et al. [113] building on previous work of Gaudin [114]. A Lie algebra with continuous complex coefficients is constructed. The conditions which ensure that the Casimir-like operators of this algebra commute take the form of classical Yang–Baxter equations. One solution, called the “rational model,” has the form

$$|\Psi_{\mathfrak{gl}(2,\mathbb{C})}\rangle = \prod_{p=1}^P \left(\sum_{k=1}^K \frac{\hat{E}_{12}(k)}{\lambda_p - \varepsilon_k} \right) |\theta\rangle = \prod_{p=1}^P \left(\sum_{k=1}^K \frac{a_k^\dagger a_k^\dagger}{\lambda_p - \varepsilon_k} \right) |\theta\rangle. \quad (35)$$

(This equation differs by a constant factor from the conventional form of the Richardson wavefunction, but it is more convenient for the following analysis.)

Once we have found an algebraically motivated wavefunction form, we then try to generalize the coefficients of expansion (just as Eq. (12) generalizes Eq. (10)) as much as we can without sacrificing computational practicality (i.e., instead of actually using the wavefunctions we obtain by solving an exactly solvable model using the Bethe ansatz, we use off-shell Bethe vectors). This generalization is not without drawbacks. There are approaches for deriving expressions for the expectation values (including the energy and its derivatives) of the wavefunction, but those approaches work only for the eigenfunctions of the model Hamiltonian (e.g., Eq. (34)). So while one can use a *variational* approach (like configuration interaction) when the wavefunction is an eigenfunction of the model Hamiltonian, one can usually only use a projection algorithm (like coupled cluster, cf. Eq. (26)) after one generalizes the wavefunction form. (Our initial *variational* calculations using the eigenfunctions of the Richardson Hamiltonian (Eq. (34)) have given promising results; these will be presented separately [115].) The focus of this paper is on the more general wavefunction forms. In the remainder of this section, the wavefunctions we propose are classified by the algebra that inspired them.

Basing our approach on model Hamiltonians seems to ensure that our wavefunctions are essentially size consistent. That is, suppose that our system consists of M distinct fragments, with $\{P_m\}_{m=1}^M$ pairs and $\{K_m\}_{m=1}^M$ orbitals. Assume furthermore that the orbitals from different fragments are orthogonal. Define the number of pairs and number of orbitals in the first m fragments as, $Q_m = \sum_{i=1}^m P_m$ and $L_m = \sum_{i=1}^m K_m$, respectively. The optimal wavefunctions for the individual fragments can be written as

$$|\Psi_{\text{gl}(2,C)}^{(m)}\rangle = \prod_{p=Q_{m-1}+1}^{Q_m} \left(\sum_{k=L_{m-1}+1}^{L_m} \frac{a_k^\dagger a_k^\dagger}{\lambda_p - \varepsilon_k} \right) |\theta\rangle. \quad (36)$$

However, the optimal wavefunction of the supersystem contain all M fragments is also of this form,

$$|\Psi_{\text{gl}(2,C)}\rangle = \lim_{\Delta \rightarrow \infty} \prod_{p=1}^P \left(\sum_{k=1}^K \frac{a_k^\dagger a_k^\dagger}{(\lambda_p + m_p \Delta) - (\varepsilon_k + n_k \Delta)} \right) |\theta\rangle \quad (37)$$

where m_p and n_k indicate which fragment the pair p and orbital k belong to. I.e., $Q_{m_p-1} < p \leq Q_{m_p}$ and $L_{n_k-1} < k \leq L_{n_k}$. (In chemical systems, where the fragments are never entirely noninteracting, one never needs to go all the way to the $\Delta \rightarrow \infty$ limit.) By similar, but slightly more complicated arguments, the wavefunctions we construct from more complicated algebras can also be shown to be essentially size consistent.

We say that these wavefunctions are “essentially size consistent” because of the limit in Eq. (37). The fact that we can write the wavefunction as an antisymmetrized product of fragment wavefunctions, however, is enough to show that if the parameters in the APr2G wavefunction were determined by minimizing the energy, then the energy of system composed of non-overlapping, noninteracting fragments will equal the sum of the fragment energies and the wavefunction will be the antisymmetrized product of the fragment wavefunctions. Establishing the analogous result for the projected Schrödinger equation is more involved, but does not seem to be impossible [116].

3.2. All unpaired electrons have the same spin; $\text{gl}(2|1)$

To describe a system with both paired and unpaired electrons, we need an algebra that is built from at least three states. We define the states 1, 2, and 3 as the unpaired, paired, and vacuum states respectively,

$$\begin{bmatrix} |k\rangle \\ |k\bar{k}\rangle \\ |\theta\rangle \end{bmatrix} \quad (38)$$

In this case the algebra is the general linear algebra of complex 3×3 matrices acting on two bosonic states ($|\theta\rangle, |k\bar{k}\rangle$) and one fermionic state ($|k\rangle$). As before, we define operators that shift the system from an initial state $i = 1, 2, 3$ to a final state $f = 1, 2, 3$, and evaluate to zero otherwise; in matrix notation, these operators are $\hat{E}_{fi}(k) = \hat{E}_{if}^\dagger(k) = \delta_{mf} \delta_{ni}$. Notice that the $\hat{E}_{fi}(k)$ operators have a different meaning in this algebra. (Now, for example, $\hat{E}_{12}(k)|k\bar{k}\rangle = |k\rangle$. We have resisted the temptation to add another index to the operators to specify which algebra they belong to, and will rely on the operators' context to make this clear.) In conventional second-quantized form, we have

$$\begin{aligned} \hat{E}_{23}(k) &= a_k^\dagger a_k^\dagger \\ \hat{E}_{13}(k) &= a_k^\dagger \\ \hat{E}_{12}(k) &= a_k \end{aligned} \quad (39)$$

The Hamiltonian is of the form

$$\begin{aligned} \hat{H}_{\text{gl}(2|1)} &= \sum_{i=1}^K \varepsilon_i (a_i^\dagger a_i + a_i^\dagger a_i) + g \sum_{i,i'}^K (\hat{E}_{12}(i) \hat{E}_{21}(i') \\ &\quad + \hat{E}_{13}(i) \hat{E}_{31}(i') + \hat{E}_{23}(i) \hat{E}_{32}(i')) \end{aligned} \quad (40)$$

and the nested Bethe ansatz for the eigenvectors of this Hamiltonian is,

$$|\Psi_{\text{gl}(2|1)}\rangle = \prod_{p=1}^P \left(\sum_{i=1}^K \frac{\hat{E}_{23}(i)}{\lambda_p - \varepsilon_i} \right) \prod_{q=1}^Q \left(\sum_{p'=1}^P \frac{\hat{I}(p')}{\mu_q - \lambda_{p'}} \right) |\theta\rangle \quad (41)$$

$\hat{I}(p')$ is a notational convenience introduced by Dukelsky et al. [117]. These operators anticommute among themselves but commute with everything else except the p' th pair in the preceding product, where it converts that $\hat{E}_{23}(i)$ to $\hat{E}_{13}(i)$ for that pair. $(\hat{I}(P))^k$ is zero for $k > 1$. For example,

$$\begin{aligned} \prod_{p=1}^P \left(\sum_{i=1}^K \frac{\hat{E}_{23}(i)}{\lambda_p - \varepsilon_i} \right) \frac{\hat{I}(p')}{\mu_q - \lambda_{p'}} |\theta\rangle &= \frac{1}{\mu_q - \lambda_{p'}} \left(\sum_{i=1}^K \frac{\hat{E}_{23}(i)}{\lambda_1 - \varepsilon_i} \right) \cdots \left(\sum_{i=1}^K \frac{\hat{E}_{23}(i)}{\lambda_{p-1} - \varepsilon_i} \right) \\ &\quad \times \left(\sum_{i=1}^K \frac{\hat{E}_{13}(i)}{\lambda_{p'} - \varepsilon_i} \right) \left(\sum_{i=1}^K \frac{\hat{E}_{23}(i)}{\lambda_{p'+1} - \varepsilon_i} \right) \cdots \left(\sum_{i=1}^K \frac{\hat{E}_{23}(i)}{\lambda_P - \varepsilon_i} \right) |\theta\rangle \end{aligned} \quad (42)$$

Eq. (41) is just a compact way of writing the sum of all possible replacements of a geminal-creation operator with the creator of an unpaired electron. Let N be the total number of electrons and n and \bar{n} denote the number of unpaired electrons of type one (created by operators like a_i^\dagger and typically α -spin) and type two (created by operators like a_i^\dagger and typically β -spin), respectively. Ensuring that there are the correct number of electrons of each type in the wavefunction (41) requires choosing Q to be the number of unpaired type-one electrons ($Q = n$) and $P = \frac{1}{2}(N + n)$. There are no unpaired type-two electrons in this model ($\bar{n} = 0$). Choosing the correct value for n requires the insight from the user, but if the user wishes to choose n objectively, the value of n that gives the lowest total energy should be selected.

An approach based on the wavefunction form in (41) is superior to the conventional approach of choosing the vacuum state in the APr2G wavefunction (Eq. (17)) as a wavefunction for the unpaired electrons. In the conventional approach, the unpaired electrons are not correlated with the electron pairs. In Eq. (41), the unpaired electrons and the electron pairs are coupled together.

To use the projection algorithm from Section 2.3, we need to write $\Psi_{\text{gl}(2|1)}$ as a linear combination of Slater determinants. Using the relationship between a product of a sum and permanents/determinants (cf. Eq. (9) and the surrounding discussion), we can rewrite Eq. (41) as:

$$\begin{aligned} |\Psi_{\text{gl}(2|1)}\rangle &= \left(\prod_{p=1}^P \sum_{i=1}^K \frac{\hat{E}_{23}(i)}{\lambda_p - \varepsilon_i} \right) \\ &\quad \times \left(\sum_{\left\{ m_p \in \{0,1\} \mid \sum_{p=1}^P m_p = Q \right\}} \left| \frac{1}{\mu_q - \lambda_p} \right| \hat{I}^{m_1}(1) \hat{I}^{m_2}(2) \cdots \hat{I}^{m_P}(P) \right) |\theta\rangle. \end{aligned} \quad (43)$$

The matrix determinant only includes the column $[1/|\mu_q - \lambda_p|]_{q=1}^Q$ if $m_p = 1$. Using the definition of the Dukelsky operator,

$$\sum_{i=1}^K \frac{\hat{E}_{23}(i) \hat{I}^{m_p}(P)}{\lambda_p - \varepsilon_i} = \begin{cases} \sum_{i=1}^K \frac{\hat{E}_{23}(i)}{\lambda_p - \varepsilon_i} & m_p = 0 \\ \sum_{i=1}^K \frac{\hat{E}_{13}(i)}{\lambda_p - \varepsilon_i} & m_p = 1 \\ 0 & m_p > 1 \end{cases} \quad (44)$$

the remaining product of pair creators is decomposed in two pieces, corresponding to the two cases in Eq. (44),

$$\begin{aligned} |\Psi_{\text{gl}(2|1)}\rangle &= \sum_{\left\{ m_p \in \{0,1\} \mid \sum_{p=1}^P m_p = Q \right\}} \left| \frac{1}{\mu_q - \lambda_p} \right| \left(\prod_{\{p=1,2,\dots,P \mid m_p=1\}} \sum_{i=1}^K \frac{\hat{E}_{13}(i)}{\lambda_p - \varepsilon_i} \right) \\ &\quad \times \left(\prod_{\{p=1,2,\dots,P \mid m_p=1\}} \sum_{i=1}^K \frac{\hat{E}_{23}(i)}{\lambda_p - \varepsilon_i} \right) |\theta\rangle \end{aligned} \quad (45)$$

$$|\Psi_{\text{gl}(2|1)}\rangle = \sum_{\left\{m_p \in \{0,1\} \mid \sum_{p=1}^P m_p = Q\right\}} \sum_{\left\{k_i \in \{0,1\} \mid \sum_{i=1}^K k_i = Q\right\}} \sum_{\left\{l_i \in \{0,1\} \mid \sum_{i=1}^K l_i = P-Q\right\}} \left(\begin{array}{c} p \text{ includes } p \text{ includes} \\ \text{indices with indices with} \\ m_q = 1 \quad m_q = 0 \\ \left| \frac{1}{\lambda_p - \varepsilon_i} \right| \quad \left| \frac{1}{\lambda_p - \varepsilon_i} \right| \\ \mu_q - \lambda_p \quad \lambda_p - \varepsilon_i \end{array} \right) \widehat{E}_{13}^{k_1}(1) \widehat{E}_{13}^{k_2}(2) \cdots \widehat{E}_{13}^{k_K}(K) \widehat{E}_{23}^{l_1}(1) \widehat{E}_{23}^{l_2}(2) \cdots \widehat{E}_{23}^{l_K}(K) |\theta\rangle \quad (46)$$

Using the result for the product of sums again (remember that the $\widehat{E}_{13}(i)$ operators anticommute),

Unfortunately this form is intractable for a large Q because the number of contributions to a given Slater determinant grows factorially with the number of unpaired electrons. (In particular, one must sum over all $\binom{P}{Q}$ ways of combining paired (generated by \widehat{E}_{23}) and unpaired (generated by \widehat{E}_{13}) states).

Eq. (46) is practical for one unpaired electron ($Q = 1$), and gives a promising method for systems with an odd number of electrons. For $Q = 1$, the wavefunction form is,

$$|\Psi_{\text{gl}(2|1)}\rangle = \sum_{q=1}^P \prod_{p=1}^P \left(\delta_{qp} \sum_{j=1}^K b_{j;q} a_j \right) \left(\sum_{i=1}^K c_{i;p} a_i^\dagger a_i \right) |\theta\rangle, \quad (47)$$

with $P = \frac{1}{2}(N + 1)$. The Slater determinant expansion of Eq. (47) is

$$|\Psi_{\text{gl}(2|1)}\rangle = \sum_{q=1}^P \sum_{\left\{k_i \in \{0,1\} \mid \sum_{i=1}^K k_i = 1\right\}} \sum_{\left\{l_i \in \{0,1\} \mid \sum_{i=1}^K l_i = P-1\right\}} (b_{i;q}) |c_{i;p \neq q}|^+ \times (a_i^\dagger)^{k_1} \cdots (a_k^\dagger)^{k_K} (a_1^\dagger a_1^\dagger)^{l_1} \cdots (a_k^\dagger a_k^\dagger)^{l_K} \quad (48)$$

As before, the permanent $|c_{i;p \neq q}|$ includes only the orbitals with $l_i = 1$ and only the pairs with $p \neq q$; $b_{i;q}$ is the coefficient of the orbital in which $k_i = 1$. The geminal coefficients $c_{i;p}$ have to be structured so that evaluating the permanent is feasible.

In analogy to the procedure for $\text{gl}(2, \mathbb{C})$, we would like to build a computationally practical wavefunction for large Q , inspired by the wavefunction forms associated with $\text{gl}(2|1)$. The wavefunction ansatz we choose is,

$$|\widetilde{\Psi}_{\text{gl}(2|1)}\rangle = \left(\prod_{p=1}^{P_{12}} \left(\sum_{i=1}^K c_{i,p}^{(12)} \widehat{E}_{12}(i) \right) \right) \left(\prod_{p=1}^{P_{13}} \left(\sum_{i=1}^K c_{i,p}^{(13)} \widehat{E}_{13}(i) \right) \right) \times \left(\prod_{p=1}^{P_{23}} \left(\sum_{i=1}^K c_{i,p}^{(23)} \widehat{E}_{23}(i) \right) \right) |\theta\rangle \quad (49)$$

The constants must be chosen so that the number of unpaired type-one electrons is $n = P_{12} + P_{13}$ and $N = 2P_{23} - P_{12} + P_{13}$. This wavefunction does have a compact expression as a sum of Slater determinants,

$$|\widetilde{\Psi}_{\text{gl}(2|1)}\rangle = \sum_{\left\{ \begin{array}{l} \sum_{i=1}^K m_i^{(12)} = P_{12} \\ m_i^{(12)}, m_i^{(13)}, m_i^{(23)} \in \{0,1\} \\ \sum_{i=1}^K m_i^{(13)} = P_{13} \\ \sum_{i=1}^K m_i^{(23)} = P_{23} \end{array} \right\}} |c_{i,p}^{(12)}|^- |c_{i,p}^{(13)}|^- |c_{i,p}^{(23)}|^+ \times \prod_{i=1}^K (a_i)^{m_i^{(12)}} (a_i^\dagger)^{m_i^{(13)}} (a_i^\dagger a_i^\dagger)^{m_i^{(23)}} |\theta\rangle \quad (50)$$

The coefficient matrices $\mathbf{C}^{(12)}$ and $\mathbf{C}^{(13)}$ can be entirely general. The factorial expense of evaluating the permanent is avoided by choosing

$$c_{i;p}^{(23)} = \frac{\zeta_i}{\tilde{\varepsilon}_i + \tilde{\lambda}_p}. \quad (51)$$

The projection method in Section 2.3 can be used to solve for the unknown coefficients, but because there are nonvanishing singly- and triply-excited determinants, the computational scaling increases by one order. The number of free parameters is still proportional to the size of the system, however, so Eq. (49) can still be viewed as a “mean-field” wavefunction ansatz, but one with two different types of quasiparticles.

$\widetilde{\Psi}_{\text{gl}(2|1)}$ (Eq. (49)) correlates the unpaired electrons with the paired electrons by allowing unpaired electrons to be generated by annihilation of an electron from a pair. The wavefunction of a 5-electron system could have the form

$$|\Psi\rangle = (g_1^\dagger g_2^\dagger (a_i g_3^\dagger) + g_1^\dagger (a_i g_2^\dagger) g_3^\dagger + (a_i g_1^\dagger) g_2^\dagger g_3^\dagger) |\theta\rangle \quad (52)$$

where g_k^\dagger is the operator for creating the k th electron pair. If there were only one term in Eq. (52), one would have the conventional “generalized” antisymmetrized product of geminals form $g_1^\dagger g_2^\dagger a_i^\dagger |\theta\rangle$, where the unpaired electron is not correlated with the pairs. Because Eq. (52) includes several such terms, the unpaired electron is correlated with the pairs. Because it is preferable to correlate the unpaired electrons with the pairs, it is reasonable (but not required) to choose $P_{13} = 0$ in Eq. (49).

The wavefunction form from the nested Bethe ansatz has additional correlation: in Eq. (47), the form of the single-particle state depends on which pair the electron is removed from, while in Eq. (49) the same single particle state is removed from all pairs, regardless of their structure.

3.3. Unpaired electrons of both spins; $\text{gl}(2|2)$

In singlet biradicals and in systems containing antiferromagnetically coupled metal atoms, it is convenient to be able to treat all possible occupations of an orbital pair. This requires the four-state algebra described by $\text{gl}(2|2)$ (the general linear algebra of 4×4

matrices with two boson states and two fermion states). With $gl(2|2)$ we can treat unpaired electrons of both types (typically these will be up- and down-spin unpaired electrons). We define states 1 and 2 as containing unpaired electrons of type one (there are n type-one unpaired electrons) and type two (there are \bar{n} type-two unpaired electrons); state three contains a pair of electrons and state four is the vacuum state:

$$\begin{bmatrix} |k\rangle \\ |\bar{k}\rangle \\ |k\bar{k}\rangle \\ |\theta\rangle \end{bmatrix} \quad (53)$$

and define the operators for moving between the states,

$$\begin{aligned} \widehat{E}_{34}(i) &= a_i^\dagger a_i \\ \widehat{E}_{24}(i) &= a_i^\dagger (1 - \hat{n}_i) \\ \widehat{E}_{14}(i) &= a_i^\dagger (1 - \hat{n}_i) \\ \widehat{E}_{23}(i) &= a_i \hat{n}_i \\ \widehat{E}_{13}(i) &= a_i \hat{n}_i \\ \widehat{E}_{12}(i) &= a_i^\dagger a_i. \end{aligned} \quad (54)$$

Here $\hat{n}_i = a_i^\dagger a_i$ is the number operator for state $|i\rangle$.

The Hamiltonian is of the form

$$\begin{aligned} \widehat{H}_{gl(2|2)} &= \sum_{i=1}^K \varepsilon_i (a_i^\dagger a_i + a_i^\dagger a_i) + g \sum_{i,i'}^K (\widehat{E}_{12}(i) \widehat{E}_{21}(i') + \widehat{E}_{13}(i) \widehat{E}_{31}(i') \\ &\quad + \widehat{E}_{14}(i) \widehat{E}_{41}(i') + \widehat{E}_{23}(i) \widehat{E}_{32}(i') + \widehat{E}_{24}(i) \widehat{E}_{42}(i') + \widehat{E}_{34}(i) \widehat{E}_{43}(i')) \end{aligned} \quad (55)$$

and the nested Bethe ansatz for the eigenvectors of this Hamiltonian is,

$$|\Psi_{gl(2|2)}\rangle = \prod_{p=1}^P \left(\sum_{i=1}^K \frac{\widehat{E}_{34}(i)}{\lambda_p - \varepsilon_i} \right) \prod_{q=1}^Q \left(\sum_{p=1}^P \frac{\widehat{I}(P)}{\mu_q - \lambda_p} \right) \prod_{r=1}^R \left(\sum_{q=1}^Q \frac{\widehat{J}(q)}{\nu_r - \mu_q} \right) |\theta\rangle \quad (56)$$

where the Dukelsky operators have the effect,

$$\sum_{i=1}^K \sum_{p=1}^P \widehat{E}_{34}(i) \widehat{I}^{m_p}(P) \widehat{J}^{n_q}(q) = \begin{cases} 0 & m_p > 1 \\ 0 & n_q > m_p \\ \sum_{i=1}^K \sum_{p=1}^P \frac{\widehat{E}_{34}(i)}{(\lambda_p - \varepsilon_i)(\mu_q - \lambda_p)} & m_p = n_q = 0 \\ \sum_{i=1}^K \sum_{p=1}^P \frac{\widehat{E}_{24}(i)}{(\lambda_p - \varepsilon_i)(\mu_q - \lambda_p)} & m_p = 1; n_q = 0 \\ \sum_{i=1}^K \sum_{p=1}^P \frac{\widehat{E}_{14}(i)}{(\lambda_p - \varepsilon_i)(\mu_q - \lambda_p)} & m_p = n_q = 1 \end{cases} \quad (57)$$

Ensuring that there are the correct number of unpaired electrons of type one and type two requires that,

$$\begin{aligned} R &= n \\ Q &= \bar{n} + n \\ P &= (N + n + \bar{n})/2 \end{aligned} \quad (58)$$

Similar to the nested Bethe ansatz wavefunction for $gl(2|1)$ (cf. Eq. (50)), in the expansion of $\Psi_{gl(2|2)}$, the number of terms that contributes to the coefficient of any given Slater determinant increases factorially with increasing n and \bar{n} . This wavefunction is only practical for systems with a few unpaired electrons (e.g., biradicals). For two unpaired electrons, $n = \bar{n} = 1$, a general wavefunction form is,

$$|\Psi_{gl(2|2)}\rangle = \sum_{r=1}^P \sum_{q=1}^P \prod_{p=1}^P \left(\delta_{rp} \sum_{k=1}^K b_{kr} a_k^\dagger \right) \left(\delta_{qp} \sum_{j=1}^K \bar{b}_{j,q} a_j \right) \left(\sum_{i=1}^K c_{i,p} a_i^\dagger a_i \right) |\theta\rangle \quad (59)$$

where $P = \frac{1}{2}(N + 2)$. The Slater determinant expansion has the form,

$$\begin{aligned} |\Psi_{gl(2|2)}\rangle &= \sum_{q,r=1}^P \sum_{\left\{ \begin{array}{l} \sum_{i=1}^K j_i = 1 \\ \sum_{i=1}^K k_i = 1 \\ \sum_{i=1}^K l_i = P - 2 \end{array} \right\}} (b_{i,r})(\bar{b}_{i,q}) |c_{i;p \neq q, p \neq r}|^+ \\ &\left((a_1^\dagger a_1^\dagger)^{j_1} \cdots (a_K^\dagger a_K^\dagger)^{j_K} (a_1^\dagger)^{k_1} \cdots (a_K^\dagger)^{k_K} (a_1^\dagger a_1^\dagger)^{l_1} \cdots (a_K^\dagger a_K^\dagger)^{l_K} \right) \end{aligned} \quad (60)$$

Notice that Eq. (60) assigns a coefficient to every Slater determinant with one broken pair (seniority two). A slightly different, and arguably more interesting, wavefunction assigns a coefficient to every Slater determinant with seniority either zero or two,

$$|\Psi_{gl(2|2)}\rangle = \sum_{r=1}^P \sum_{q=1}^P \prod_{p=1}^P \left(\delta_{rp} \sum_{k=1}^K b_{kr} a_k^\dagger \right) \left(\delta_{qp} \sum_{j=1}^K \bar{b}_{j,q} a_j \right) \left(\sum_{i=1}^K c_{i,p} a_i^\dagger a_i \right) |\theta\rangle \quad (61)$$

$$\begin{aligned} |\Psi_{gl(2|2)}\rangle &= \sum_{q,r=1}^P \sum_{\left\{ \begin{array}{l} \sum_{i=1}^K j_i = 1 \\ \sum_{i=1}^K k_i = 1 \\ \sum_{i=1}^K l_i = P - 2 \end{array} \right\}} (b_{i,r})(\bar{b}_{i,q}) |c_{i;p \neq q, p \neq r}|^+ \\ &\left((a_1^\dagger)^{j_1} \cdots (a_K^\dagger)^{j_K} (a_1^\dagger)^{k_1} \cdots (a_K^\dagger)^{k_K} (a_1^\dagger a_1^\dagger)^{l_1} \cdots (a_K^\dagger a_K^\dagger)^{l_K} \right) \end{aligned} \quad (62)$$

This is expected to be an extremely good model for static correlation in strongly correlated systems [97].

To use the projection algorithm from Section 2.3 for systems with many unpaired electrons, we need an alternative to $\Psi_{gl(2|2)}$ that has a compact expansion in terms of Slater determinants. The wavefunction ansatz we choose is,

$$\begin{aligned} |\widetilde{\Psi}_{gl(2|2)}\rangle &= \left[\left(\prod_{p=1}^{P_{12}} \left(\sum_{i=1}^K c_{i,p}^{(12)} \widehat{E}_{12}(i) \right) \right) \left(\prod_{p=1}^{P_{13}} \left(\sum_{i=1}^K c_{i,p}^{(13)} \widehat{E}_{13}(i) \right) \right) \right. \\ &\times \left(\prod_{p=1}^{P_{23}} \left(\sum_{i=1}^K c_{i,p}^{(23)} \widehat{E}_{23}(i) \right) \right) \times \left(\prod_{p=1}^{P_{14}} \left(\sum_{i=1}^K c_{i,p}^{(14)} \widehat{E}_{14}(i) \right) \right) \\ &\left. \times \left(\prod_{p=1}^{P_{24}} \left(\sum_{i=1}^K c_{i,p}^{(24)} \widehat{E}_{24}(i) \right) \right) \left(\prod_{p=1}^{P_{34}} \left(\sum_{i=1}^K c_{i,p}^{(34)} \widehat{E}_{34}(i) \right) \right) \right] |\theta\rangle \end{aligned} \quad (63)$$

The constants must be chosen so that:

$$\begin{aligned} n &= P_{12} + P_{13} + P_{14} \\ \bar{n} &= P_{23} + P_{24} - P_{12} \\ N &= 2P_{34} - P_{23} - P_{13} + P_{24} + P_{14} \end{aligned} \quad (64)$$

This wavefunction also has a reasonably compact expression in terms of Slater determinants,

$$\begin{aligned} |\widetilde{\Psi}_{gl(2|2)}\rangle &= \sum_{\left\{ m_k^{(i)} \in \{0,1\} \mid \sum_{k=1}^K m_k^{(i)} = P_i \right\}} \left[|c_{k,p}^{(12)}|^+ |c_{k,p}^{(13)}|^+ |c_{k,p}^{(23)}|^+ |c_{k,p}^{(14)}|^+ |c_{k,p}^{(24)}|^+ |c_{k,p}^{(34)}|^+ \right. \\ &\left. \times \prod_{i=1}^K (a_k^\dagger a_k)^{m_k^{(14)}} (a_k \hat{n}_k)^{m_k^{(13)}} (a_k \hat{n}_k)^{m_k^{(23)}} (a_k^\dagger)^{m_k^{(12)}} (a_k^\dagger)^{m_k^{(24)}} (a_k^\dagger a_k^\dagger)^{m_k^{(34)}} \right] |\theta\rangle \end{aligned} \quad (65)$$

The coefficients that enter as determinants can be chosen completely generally, but those that enter as permanents should be

assumed to take a restricted form. Evaluating the coefficient of a given Slater determinant in Eq. (65) requires considering all possible ways of generating a given electron configuration using the operators given. This process is dramatically simplified if one makes simplifying assumptions like $P_{12} = P_{14} = P_{24} = 0$, so that unpaired electrons can only be created by removing electrons from paired states.

One disadvantage of these wavefunction forms is that the number of broken pairs is a good quantum number. If we wish to design a wavefunction that includes both broken and unbroken pairs, this can be done by replacing the operators in Eq. (63) with forms that allow unpaired electrons to combine into pairs. This can be achieved by the following reassignment,

$$\begin{aligned}\widehat{E}_{24}(i) &= a_i^\dagger \\ \widehat{E}_{14}(i) &= a_i^\dagger \\ \widehat{E}_{23}(i) &= a_i \\ \widehat{E}_{13}(i) &= a_i\end{aligned}\quad (66)$$

3.4. Explicit coupling between pairs; $\mathfrak{gl}(8|8)$

It is clear from the preceding development that one can systematically extend this procedure to algebras of increasing dimensionality. For example, if one wishes to include coupling between pairs of fermions, one could consider $\mathfrak{gl}(8|8)$ based on the states,

$$\begin{aligned}|j\rangle & \quad |\bar{j}\rangle & |J\rangle & |\bar{J}\rangle \\ |\bar{J}\bar{J}\rangle & |\bar{j}\bar{J}\rangle & |j\bar{J}\rangle & |\bar{j}J\rangle & |jJ\rangle & |\bar{j}\bar{j}\rangle \\ |\bar{j}\bar{J}\bar{J}\rangle & |j\bar{J}\bar{J}\rangle & |\bar{j}\bar{j}\bar{J}\rangle & |\bar{j}\bar{j}J\rangle \\ |\bar{j}\bar{j}\bar{J}\bar{J}\rangle & |\theta\rangle\end{aligned}\quad (67)$$

namely,

$$|\widetilde{\Psi}_{\mathfrak{gl}(8|8)}\rangle = \prod_{f<i} \prod_{p=1}^{16} \left(\sum_{k=1}^{P_f} c_{k,p}^{(f)} \widehat{E}_{fi}(k) \right) |\theta\rangle \quad (68)$$

The coefficient matrices for operators that transfer between states separated by an even number of rows in Eq. (67) (zero or two, e.g., $\widehat{E}_{5,15}(k)$, $\widehat{E}_{6,10}(k)$) commute, so they enter the Slater determinant expansion as a permanent, and should be chosen as the element-inverse of a rank-two matrix. The coefficient matrices for operators that transfer between states separated by an odd number of rows (e.g., $\widehat{E}_{1,7}(k)$, $\widehat{E}_{5,13}(k)$) anticommute, so they enter the Slater determinant expansion as a determinant, and can be chosen arbitrarily. There are 120 operators in Eq. (68), but if one builds all 3-fermion states by removal from 4-fermion states, all 2-fermion states by removal from 3-fermion states, and all 1-fermion states by removal from 2-fermion states requires “only” 28 operators. This form could be useful in chemistry, as it allows for explicit coupling between bonding and antibonding orbitals. In nuclear physics, the states could represent the spin and isospin degrees of freedom.

3.5. Other generalizations

The wavefunction one obtains using these methods depends on how one chooses the order of the operators. For example, placing $\widehat{E}_{24}(i)$ before $\widehat{E}_{12}(i)$ in Eq. (63) will give a different wavefunction even if all the coefficient matrices are retained. Choosing the correct order of operators is potentially problematic; we have selected an order that seems reasonable to us.

It is also possible to use the adjoint operators in the expansion. For example, one could consider an operator like

$$\begin{aligned}|\widetilde{\Psi}_{\mathfrak{gl}(2|1)}\rangle &= \left[\left(\prod_{p=1}^{P_{32}} \left(\sum_{i=1}^K c_{i,p}^{(32)} \widehat{E}_{32}(i) \right) \right) \left(\prod_{p=1}^{P_{31}} \left(\sum_{i=1}^K c_{i,p}^{(31)} \widehat{E}_{31}(i) \right) \right) \right. \\ &\quad \times \left(\prod_{p=1}^{P_{21}} \left(\sum_{i=1}^K c_{i,p}^{(21)} \widehat{E}_{21}(i) \right) \right) \times \left(\prod_{p=1}^{P_{12}} \left(\sum_{i=1}^K c_{i,p}^{(12)} \widehat{E}_{12}(i) \right) \right) \\ &\quad \left. \times \left(\prod_{p=1}^{P_{13}} \left(\sum_{i=1}^K c_{i,p}^{(13)} \widehat{E}_{13}(i) \right) \right) \left(\prod_{p=1}^{P_{23}} \left(\sum_{i=1}^K c_{i,p}^{(23)} \widehat{E}_{23}(i) \right) \right) \right] |\theta\rangle \quad (69)\end{aligned}$$

where the operators on the first row decrease the number of electrons. This procedure adds to the variational freedom in the wavefunction and can be carried out indefinitely, with electrons repeatedly added to, rearranged within, and removed from the system as one ladders up and down the states. It is interesting to speculate whether it might be possible, in the limit where one considers arbitrarily long strings of the $2^{K-2}(2^{K-1} - 1)$ raising and operators in the most complicated possible algebra, $\mathfrak{gl}(2^{K-1}|2^{K-1})$, with completely general coefficients, whether one might converge to the exact result. That is, can we consider the methods we are presenting here as the first few elements of a hierarchy that converges to the exact solution of the Schrödinger equation, within a given basis?

The form of the coefficient matrix in Eq. (12) (equivalently, Eq. (15)) is motivated by the need to cheaply evaluate the permanent of the coefficient matrix. This led to the idea of considering matrices whose element-wise inverse had low rank, leading to the antisymmetrized product of rank- k geminal wavefunction ansatz (APr k G). It is easy to see that the antisymmetrized geminal power wavefunction is defined by APr1G; in this paper we focus on APr2G wavefunctions. We have tried to extend this model to higher-rank products of geminals, but methods based on geminals with $k > 2$ seem to have factorial cost [118].

The permanent of a matrix can be evaluated efficiently when almost all of the entries in the matrix are zero. We are also exploring that possibility, and it seems that very simple coefficient matrices (e.g., let each geminal depend on at most one occupied orbital) give excellent results [119].

4. Computing properties and optimizing orbitals

In this work, we have proposed optimizing the coefficients in the APr2G wavefunction and its open-shell extensions by using the projected Schrödinger equation, Eq. (25). This leads to a set of nonlinear equations for the wavefunction parameters that can, at least in principle, be solved at low ($O(K^4)$ or $O(K^2)$) computational cost. The equations we must solve are strongly reminiscent of coupled-cluster theory [2,120–125], and many coupled-cluster techniques can be used in this context also.

In DOCI, APSG, and GVB calculations, the quality of results strongly depends on the quality of the orbitals [97,126–128]. Likewise, it is important to optimize the orbitals in the APr2G ansätze. Fortunately, the orbitals can be optimized using the same techniques that are used for orbital-optimized coupled-cluster calculations [129]. The Lagrangian approach to constraints in coupled-cluster theory [2] is especially useful here: one rewrites the problem as the minimization of an energy expression,

$$\widetilde{E}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \equiv \frac{\langle \Phi | \widehat{H} | \widetilde{\Psi}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \rangle}{\langle \Phi | \widetilde{\Psi}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \rangle} \quad (70)$$

subject to the constraint that the projected Schrödinger equation holds. ($\boldsymbol{\eta}$ denotes the parameters on which the wavefunction depends.) This gives the Lagrangian,

$$\begin{aligned}A_{\mathfrak{gl}(2|k)}[\boldsymbol{\eta}; \boldsymbol{\lambda}] &= \widetilde{E}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) + \sum_i \lambda_i (\langle \Phi_i | \widehat{H} | \Psi(\boldsymbol{\eta}) \rangle - \widetilde{E}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta})) \\ &\quad \times \langle \Phi_i | \widetilde{\Psi}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \rangle\end{aligned}\quad (71)$$

After solving the nonlinear equations,

$$\begin{aligned}\nabla_{\eta} A_{\text{gl}(2|k)}[\boldsymbol{\eta}; \boldsymbol{\lambda}] &= 0 \\ \nabla_{\lambda} A_{\text{gl}(2|k)}[\boldsymbol{\eta}; \boldsymbol{\lambda}] &= 0\end{aligned}\quad (72)$$

the derivative of the energy with respect to any parameter can be evaluated,

$$\begin{aligned}\left. \frac{\partial \tilde{E}_{\text{gl}(2|k)}}{\partial \eta_k} \right|_{\boldsymbol{\eta}=\boldsymbol{\eta}_{\text{opt}}} &= \left. \frac{\partial \tilde{E}_{\text{gl}(2|k)}(\boldsymbol{\eta})}{\partial \eta_k} \right|_{\boldsymbol{\eta}=\boldsymbol{\eta}_{\text{opt}}} \\ &+ \lambda_{\text{opt}} \left. \frac{\partial [(\langle \Phi_i | \hat{H} | \Psi(\boldsymbol{\eta}) \rangle - \tilde{E}_{\text{gl}(2|k)}(\boldsymbol{\eta})) \langle \Phi_i | \tilde{\Psi}_{\text{gl}(2|k)}(\boldsymbol{\eta}) \rangle]}{\partial \eta_k} \right|_{\boldsymbol{\eta}=\boldsymbol{\eta}_{\text{opt}}}\end{aligned}\quad (73)$$

This procedure allows one to compute the first-order change in energy due to a change in the orbitals, and therefore allows one to optimize the orbitals in the APr2G (and related) wavefunctions. It also allows one to compute other molecular response properties, including derivatives with respect to the atomic positions (facilitating geometry optimization).

Other types of molecular response properties can be computed by an approach inspired by equation-of-motion coupled-cluster [124,130]. For example, ionization potentials and electron affinities can be computed using equations that are reminiscent of the extended Koopmans' theorem [131–135],

$$\langle \Phi_i | a_k^\dagger [\hat{H}, a_j] | \tilde{\Psi}_{\text{gl}(2|k)}(\boldsymbol{\eta}) \rangle \approx -I_\lambda \langle \Phi_i | a_k^\dagger a_j | \tilde{\Psi}_{\text{gl}(2|k)}(\boldsymbol{\eta}) \rangle \quad (74)$$

$$\langle \Phi_i | a_k [\hat{H}, a_j^\dagger] | \tilde{\Psi}_{\text{gl}(2|k)}(\boldsymbol{\eta}) \rangle \approx -A_\lambda \langle \Phi_i | a_k a_j^\dagger | \tilde{\Psi}_{\text{gl}(2|k)}(\boldsymbol{\eta}) \rangle \quad (75)$$

or its generalizations to higher-order operators like [136]

$$\begin{aligned}\langle \Phi_i | a_j^\dagger a_k^\dagger a_r [\hat{H}, a_l^\dagger a_k a_j] | \tilde{\Psi}_{\text{gl}(2|k)}(\boldsymbol{\eta}) \rangle \\ \approx -I_\lambda \langle \Phi_i | a_j^\dagger a_k^\dagger a_r a_l^\dagger a_k a_j | \tilde{\Psi}_{\text{gl}(2|k)}(\boldsymbol{\eta}) \rangle.\end{aligned}\quad (76)$$

Eq. (76) changes the computational scaling, but Eqs. (74) and (75) can be evaluated with negligible computational cost after the projected Schrödinger equation for $\tilde{\Psi}_{\text{gl}(2|k)}(\boldsymbol{\eta})$ has been solved. Excitation energies can be computed in several ways, including

$$\langle \Phi_i | a_j^\dagger a_l [\hat{H}, a_r^\dagger a_j] | \tilde{\Psi}_{\text{gl}(2|k)}(\boldsymbol{\eta}) \rangle \approx \omega_{0\lambda} \langle \Phi_i | a_j^\dagger a_l a_r^\dagger a_j | \tilde{\Psi}_{\text{gl}(2|k)}(\boldsymbol{\eta}) \rangle \quad (77)$$

In designing formulas like Eqs. (74)–(77), it is important to choose Hermitian operators: it is impractical to act directly on ket (the geminal product wavefunction) with the operator, so one needs to be able to apply operator to the bra (the Slater determinant test functions).

5. Summary

This paper presents a new wavefunction form, an antisymmetric product of nonorthogonal geminals (Section 2), and discusses its extensions to open shells (Section 3) and molecular property calculations (Section 4). The key insight is that the evaluation of a (generally computationally intractable) antisymmetric product of nonorthogonal geminals is greatly simplified if the geminal expansion coefficients take the form of an element-wise inverse of a rank-two matrix (cf. Eq. (12)). This reduces the number of unknown parameters to (a) a choice of unitary transformation that defines the orbitals and the orbital-pairing scheme and (b) $\frac{1}{2}N_{\text{electrons}} + N_{\text{basis}}$ complex numbers, where N_{basis} is the number of spin-orbitals. We call this the antisymmetric product of rank-two geminals wavefunction, APr2G. The unknown parameters in APr2G can be determined by solving the projected Schrödinger equation with computational scaling of $O(N_{\text{basis}}^5)$ and perhaps even $O(N_{\text{basis}}^4)$.

This paper is focused on the mathematical principles behind the theory; numerical tests are underway, and preliminary results are promising. However, it is apparent that the proposed method *must* give good results for problems like bond dissociation because it contains other methods like the antisymmetrized product of strongly orthogonal geminals, which are known to be useful for such problems. (See Section 2.2 and Fig. 1.)

We have elected to present this development here, recognizing the pioneering contributions of A. John Coleman to the antisymmetrized geminal power wavefunction (which is the special case APr1G). John was a friend and mentor to one of us (PWA), and he was entranced by the AGP wavefunction until the end, and persistently encouraged PWA to pursue it. He will be happy to know that PWA has finally embraced geminal-based wavefunctions.

Acknowledgements

PAJ and PWA wish to thank Andreas Savin for helpful discussions; he suggested the idea of using the projected Schrödinger equation. Helpful comments from Gus Scuseria and his team improved and clarified the presentation, especially in Section 2.2. Marcel Nooijen made helpful comments about size consistency. PAJ acknowledges funding from the Vanier Canada Graduate Scholarships. PAL is thankful to a fellowship for prospective researchers issued by the SNF (Swiss National Science Foundation). PWA was supported by NSERC and the Canada Research Chairs. We gratefully acknowledge FWO-Flanders and the research council of Ghent University for financial support.

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