



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

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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,

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

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