Model Wavefunction Forms to Describe Strong Correlation in Quantum Chemistry

MODEL WAVEFUNCTION FORMS TO DESCRIBE STRONG CORRELATION IN QUANTUM CHEMISTRY

BY

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Chapter 1

Introduction

Before I refuse to take your questions, I have an opening statement.

– Ronald Reagan

At the physical level, chemistry is understood as clouds of negatively charged electron density surrounding positively charged nuclei. The system variable which contains all the information about the system, called the wavefunction, is what one needs to calculate to predict whether a chemical change is possible or not. The wavefunction is obtained by solving the Schrödinger equation which is unfortunately impossible to solve except for very simple systems. The task is then to develop approximate methods which are both sufficiently accurate to produce qualitatively correct behaviour and sufficiently efficient to be computationally tractable.

The next section will outline Dirac's bra and ket notation scheme, along with a minimal amount of quantum mechanics required: the Schrödinger equation. The three following sections will describe many-electron wavefunctions from different perspectives. The remaining sections will summarize what has come to be known as the standard approaches in quantum chemistry. The author has attempted to be as mathematically precise as possible without drowning the reader in details (which have been relegated to the appendices).

1.1 Bras and kets

We will begin with a brief description of the mathematical structure of the space of wavefunctions before describing the physics of the problem. The structure involved is a Hilbert space, which is roughly understood as a space where both linear algebra and analysis are possible.

Physical states are represented by *kets* $|a\rangle$, which form a linear space over the field of complex numbers.[1] A dual set of vectors $\langle a|$ called *bras* are defined as the adjoints of their corresponding kets:

$$\langle a| = |a\rangle^\dagger . \tag{1.1}$$

Evaluating a bra(c)ket produces a complex number, i.e. $\langle a|b\rangle = \langle b|a\rangle^*$ is a scalar product. The other way that bras and kets can be multiplied results in an operator, e.g. $|a\rangle \langle b|$ when acting on a state $|c\rangle$

$$(|a\rangle \langle b|) |c\rangle = \langle b|c\rangle |a\rangle \tag{1.2}$$

gives the state $|a\rangle$ scaled by the complex number $\langle b|c\rangle$. A physically observable quantity corresponds to a Hermitian operator, while its eigenvalues correspond to

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[1] The author's preferred reference is [Dir58]

the possible values of the observable, and the eigenvectors correspond to the possible states. Operators which commute can be diagonalized simultaneously. Hermitian operators have real eigenvalues, and can be expanded in terms of their eigenvalues and eigenvectors as

$$\hat{A} = \sum_i a_i \left| a_i \right\rangle \left\langle a_i \right| . \tag{1.3}$$

We generally assume that the operators we consider have discrete spectra, but they may or may not be finite. Similarly, given a complete set of states the identity operation is written:

$$\mathrm{id} = \sum_i \left| a_i \right\rangle \left\langle a_i \right| \tag{1.4}$$

Equation (1.4) is useful as the identity can be placed wherever desired. With a continuous spectrum, the completeness relation is written:

$$\mathrm{id} = \int d\mathbf{r} \left| \mathbf{r} \right\rangle \left\langle \mathbf{r} \right| . \tag{1.5}$$

Of particular importance to chemistry and physics is the *Hamiltonian* operator, $\hat{H}$, by including all contributions to the kinetic and potential energies. In the next section we will look at the relevant Hamiltonian for atoms and molecules. The time independent Schrödinger equation is the statement that the eigenvectors of the Hamiltonian are the physically allowed states with the eigenvalues being the corresponding energy of each state:

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \tag{1.6}$$

The state $|\Psi\rangle$ with the lowest energy is called the ground state, with others called excited states. The eigenvector $|\Psi\rangle$ is called the wavefunction or the state vector. Given the wavefunction, all the observable properties can be calculated: for an observable $\hat{Q}$, the expected value of that observable is

$$Q = \langle \Psi | \hat{Q} | \Psi \rangle . \tag{1.7}$$

1.2 The Schrödinger equation in Chemistry

Our picture of a molecule is that of negatively charged electrons surrounding positively charged nuclei. The Hamiltonian for a system of M nuclei $\{\mathbf{R}_I\}$ with masses $\{M_I\}$ and N electrons $\{\mathbf{r}_i\}$ is easily constructed by considering the contributions to the kinetic and potential energies

$$\begin{aligned}\hat{H} = &-\frac{\hbar^2}{2m_e}\sum_i^N \nabla_i^2 - \frac{\hbar^2}{2}\sum_I^M \frac{\nabla_I^2}{M_I} \\ &+ \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{2}\sum_{IJ}^M \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_I^M \sum_i^N \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{ij}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right).\end{aligned} \tag{1.8}$$

The Laplacian is a notational convenience:

$$\nabla_a^2 = \frac{\partial^2}{\partial x_a^2} + \frac{\partial^2}{\partial y_a^2} + \frac{\partial^2}{\partial z_a^2}. \tag{1.9}$$

To clean up the Hamiltonian (1.8), it is convenient to use atomic units where the elementary charge e, the reduced Planck constant $\hbar$, the electron mass m_e, and $4\pi\varepsilon_0$ are all set identically equal to one. Since nuclei are substantially heavier than electrons it is standard to treat the nuclei as a fixed arrangement of positive charges. This treatment, the *Born-Oppenheimer approximation*, is acceptable for most quantum chemistry calculations but is *not* acceptable for spectroscopic purposes. The nuclei thus have no kinetic energy, and the nuclear-nuclear repulsion

$$V_{NN} = \frac{1}{2}\sum_{IJ}^{M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \tag{1.10}$$

is an easily evaluated constant. The remaining contributions to the Hamiltonian are:

$$\hat{H} = -\frac{1}{2}\sum_{i}^{N} \nabla_i^2 - \sum_{I}^{M}\sum_{i}^{N} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{ij}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{1.11}$$

The goal of quantum chemistry is then to solve the time independent Schrödinger equation for the ground state electronic energy and the ground state wavefunction

$$\hat{H}\left|\Psi_{GS}\right\rangle = E_{GS}\left|\Psi_{GS}\right\rangle, \tag{1.12}$$

provided some arbitrary arrangement of nuclei.

The entire thesis concentrates on approximately solving (1.12), but before proceeding some discussion of the inherent assumptions and errors involved is merited. Nuclei are treated as classical point charges with no internal structure. On the energy scale of chemistry, the internal structure of nuclei is easily disregarded. Electrons and nuclei are assumed to only interact electromagnetically and this approximation is excellent. The structure of quantum mechanics is essentially incompatible with the concept of special relativity. Once again, near the bottom of the periodic table special relativity provides non-negligible effects. A proper treatment would then require quantum electrodynamics (QED). Attempts to use "effective Hamiltonians", i.e. rewriting the problem as an approximate version of quantum mechanics certainly exist. It is perhaps a little depressing that empirical pseudopotentials provide an entirely adequate treatment based on how accurate our electronic energies are anyway.

Most chemical processes occur in systems with a given temperature and pressure[2] for which the Gibbs' free energy is the appropriate thermodynamic potential. Given that we obtain a ground state electronic energy from Eq. (1.12) this is only the energy due to the "electronic degrees of freedom" at zero temperature. On this temperature scale there is typically little, if any, contribution from excited electronic states. This is however not true for structures with a large number of near-degenerate states close to the ground state. This tends to happen in metals. A molecule consisting of M nuclei has $3M-6$ vibrational degrees of freedom (or $3M-5$ if it is linear) along with its translations and rotations. Quantum chemistry codes usually add thermal corrections by treating systems as ideal gases for which the enthalpy and entropy contributions are easily obtained from the corresponding partition functions. Once again, compared with the accuracy of our ground state electronic energy, this type of thermal treatment is surprisingly adequate.

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[2] The usual choice is standard ambient temperature and pressure (SATP): 1 bar, 298.15K

1.3 Many-Electron States: First Quantization

The gist of first quantization is one of the postulates of quantum mechanics. Observable properties of a system are quantized: they are the eigenvalues of a corresponding operator, while the eigenvectors are the allowed states. Operators and eigenvectors are both described in real or momentum space. Physical laws are generally understood in terms of position and momentum making this description convenient.

Many-body wavefunctions are complicated objects. To understand and manipulate these objects, it is thus necessary to decompose them into ones that are comparatively simple. For 1-electron states there is no problem: a basis $\{\phi_\alpha = |\alpha\rangle\}$ of 1-electron states (orbitals) is introduced, and a physical state with quantum numbers $x = \{\mathbf{r}, m_s\}$ is the linear combination

$$\psi(x) = \sum_\alpha \langle x|\alpha\rangle = \sum_\alpha \psi_\alpha(x). \tag{1.13}$$

Following the notation of Dickhoff and Van Neck [DN08], two-electron basis states are obtained by taking direct products of the 1-electron basis elements

$$|\alpha_1\alpha_2) = |\alpha_1\rangle\,|\alpha_2\rangle\,. \tag{1.14}$$

Physically, we know that electrons are indistinguishable and obey the Pauli principle, the result being that

$$|\alpha_1\alpha_2) = -|\alpha_2\alpha_1). \tag{1.15}$$

Coupling the two states provides the more appropriate 2-body basis

$$|\alpha_1\alpha_2\rangle = \frac{1}{\sqrt{2}}\left(|\alpha_1\alpha_2) - |\alpha_2\alpha_1)\right). \tag{1.16}$$

States denoted with angular brackets like (1.16) signify antisymmetric linear combinations of direct product states (1.14). This may be extended to any number of electrons so that we obtain N-electron basis functions:

$$|\alpha_1\alpha_2\dots\alpha_N\rangle = \frac{1}{\sqrt{N!}}\sum_{\sigma} \mathrm{sgn}(\sigma)|\alpha_1\alpha_2\dots\alpha_N) \tag{1.17}$$

Here $\mathrm{sgn}(\sigma)$ is the *signature* or *sign* of the permutation σ: positive for even permutations and negative for odd permutations. A N-electron wavefunction is then expressed in this basis as:

$$\begin{aligned} \psi(x_1x_2\dots x_N) &= \sum_{\alpha_1\alpha_2\dots\alpha_N} (x_1x_2\dots x_N|\alpha_1\alpha_2\dots\alpha_N\rangle & (1.18)\\ &= \sum_{\alpha_1\alpha_2\dots\alpha_N} \psi_{\alpha_1\alpha_2\dots\alpha_N}(x_1x_2\dots x_N) & (1.19)\end{aligned}$$

The individual elements in the sum (1.19) are called Slater determinants since they may be represented as the determinants

$$\psi_{\alpha_1\alpha_2\dots\alpha_N}(x_1x_2\dots x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \langle x_1|\alpha_1\rangle & \dots & \langle x_N|\alpha_1\rangle \\ \langle x_1|\alpha_2\rangle & \dots & \langle x_N|\alpha_2\rangle \\ \vdots & \ddots & \vdots \\ \langle x_1|\alpha_N\rangle & \dots & \langle x_N|\alpha_N\rangle \end{vmatrix} \tag{1.20}$$

In a blatant abuse of notation one could also arrange (1.17) as a determinant if the product is understood as the direct product rather than just multiplication of complex numbers. For this reason, while a Slater determinant is strictly speaking (1.19), the N-body basis functions (1.17) are also generally referred to as Slater determinants. For the remainder of the text we will employ this nomenclature.

The manipulation of Slater determinants in the form of eq. (1.20) (and hence anything in that basis) is incredibly tedious, cumbersome, and generally inefficient. Evaluating scalar products in first quantization is not a productive area of discussion.[3]

1.4 Many-Electron States: Second Quantization

The *second* quantization is the quantization for the states themselves. I.e. we postulate that for any arbitrary $|\Psi\rangle$, there exists some operator which "creates" that state:

$$|\Psi\rangle = \Psi^\dagger |\theta\rangle \tag{1.21}$$

The state $|\theta\rangle$ is a "vacuum" state. In most cases it is a state with no particles. Similarly, the bra state:

$$\langle\Psi| = |\Psi\rangle^\dagger = \left(\Psi^\dagger |\theta\rangle\right)^\dagger = \langle\theta| \Psi \tag{1.22}$$

The operator $\Psi^\dagger$ is called a creator and creates a ket state. The operator Ψ is called an annihilator and creates a bra state. The remaining piece, the vacuum state, is trivial. The problem has been reassigned to the algebraic properties of creators and

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[3] Compare the difficulty of notation in [May03] and [DN08]

annihilators. We will now express many-electron states in this language.

1.4.1 Electron Creators and Annihilators

Electronic creators are defined:[4]

$$|\alpha\rangle = a^{\dagger}_{\alpha} |\theta\rangle \tag{1.23}$$

and correspondingly, the annihilators are

$$\langle\alpha| = |\alpha\rangle^{\dagger} = \left(a^{\dagger}_{\alpha}\right)^{\dagger} = \langle\theta| a^{\alpha}. \tag{1.24}$$

The upper and lower indices will be explained below. Since the problem has been transferred to the operators, they must themselves encode the physical constraints known for electrons. Without proof, we can state the "fundamental" anticommutation relations:

$$\{a^{\dagger}_{\alpha}, a^{\beta}\} = a^{\dagger}_{\alpha}a^{\beta} + a^{\beta}a^{\dagger}_{\alpha} = \delta_{\alpha\beta} \tag{1.25}$$

$$\{a^{\dagger}_{\alpha}, a^{\dagger}_{\beta}\} = \{a^{\alpha}, a^{\beta}\} = 0 \tag{1.26}$$

One can easily verify that:

$$a^{\dagger}_{\alpha}a^{\dagger}_{\alpha} = -a^{\dagger}_{\alpha}a^{\dagger}_{\alpha} = 0, \tag{1.27}$$

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[4] By α we mean a complete set of single-particle quantum numbers. We are not employing the quantum chemistry convention of labelling the spin quantum numbers as α and β.

and hence the Pauli principle is satisfied.

Now we can express the Slater determinant (1.17) in second quantization as:

$$|\alpha_1\alpha_2\dots\alpha_N\rangle = \prod_{i=1}^{N} a^{\dagger}_{\alpha_i} |\theta\rangle \tag{1.28}$$

1.4.2 Upper and Lower Indices

If we consider a unitary transformation of the single-particle state $|\alpha\rangle$ [RW10]

$$|\alpha\rangle \rightarrow \hat{U}|\alpha\rangle = \sum_{\lambda} \langle\lambda|\hat{U}|\alpha\rangle |\lambda\rangle = \sum_{\lambda} U^{\lambda}_{\alpha} |\lambda\rangle \tag{1.29}$$

then the corresponding creation operators transform covariantly, i.e. in the same manner as the states they create:

$$a^{\dagger}_{\alpha} \rightarrow \hat{U} a^{\dagger}_{\alpha} \hat{U}^{\dagger} = \sum_{\lambda} U^{\lambda}_{\alpha} a^{\dagger}_{\lambda} \tag{1.30}$$

Conversely, annihilation operators transform in the same manner as dual states, specifically for the same transformation acting to the left on the state $\langle\alpha|$:

$$\langle\alpha| \rightarrow \langle\alpha|\hat{U}^{\dagger} = \sum_{\lambda} \langle\alpha|\hat{U}^{\dagger}|\lambda\rangle \langle\lambda| = \sum_{\lambda} (U^{*})^{\alpha}_{\lambda} \langle\lambda| \tag{1.31}$$

the corresponding annihilator transforms as

$$a^{\alpha} \rightarrow \hat{U} a^{\alpha} \hat{U}^{\dagger} = \sum_{\lambda} (U^{*})^{\alpha}_{\lambda} a^{\lambda}. \tag{1.32}$$

Thus, creators are said to be *covariant* and labelled with lower indices, while annihilators are called *contravariant* and labelled by upper indices.

1.4.3 Operators

One body operators in Fock space are obtained by projecting a complete one body basis on both sides of the first quantized expression:

$$\hat{O} = \sum_{\alpha\beta} \langle\alpha|\, O(\mathbf{r})\, |\beta\rangle\, a^{\dagger}_{\alpha} a^{\beta} \tag{1.33}$$

The matrix element is explicitly (in a given one-particle basis $\{\phi\}$):

$$\langle\alpha|O(\mathbf{r})|\beta\rangle = \int d\mathbf{r}\ \phi^{*}_{\alpha}(\mathbf{r}) O(\mathbf{r}) \phi_{\beta}(\mathbf{r}) \tag{1.34}$$

Two-body operators are defined similarly, though care must be taken to avoid double-counting. In terms of direct matrix elements:

$$\hat{V} = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} (\alpha\beta|V(\mathbf{r}_1,\mathbf{r}_2)|\gamma\delta) a^{\dagger}_{\alpha} a^{\dagger}_{\beta} a^{\delta} a^{\gamma} \tag{1.35}$$

$$(\alpha\beta|V(\mathbf{r}_1,\mathbf{r}_2)|\gamma\delta) = \int d\mathbf{r}_1 d\mathbf{r}_2\ \phi^{*}_{\alpha}(\mathbf{r}_1)\phi^{*}_{\beta}(\mathbf{r}_2) V(\mathbf{r}_1,\mathbf{r}_2) \phi_{\gamma}(\mathbf{r}_1)\phi_{\delta}(\mathbf{r}_2) \tag{1.36}$$

An alternative is to use anti-symmetrized matrix elements, denoted with angular brackets:

$$\hat{V} = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle\alpha\beta|V(\mathbf{r}_1,\mathbf{r}_2)|\gamma\delta\rangle \tag{1.37}$$

$$\langle\alpha\beta|V(\mathbf{r}_1,\mathbf{r}_2)|\gamma\delta\rangle \equiv (\alpha\beta|V(\mathbf{r}_1,\mathbf{r}_2)|\gamma\delta) - (\alpha\beta|V(\mathbf{r}_1,\mathbf{r}_2)|\delta\gamma) \tag{1.38}$$

Provided that the basis is complete, i.e. that

$$\sum_{\alpha} |\alpha\rangle \langle\alpha| = 1 \tag{1.39}$$

then there is nothing lost in the translation to second quantization.

As a specific example, in first quantization the Hamiltonian is (1.11), while in second quantization it reads

$$\hat{H} = \sum_{\alpha\beta} h^{\alpha}_{\beta} a^{\dagger}_{\alpha} a^{\beta} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} V^{\alpha\beta}_{\gamma\delta} a^{\dagger}_{\alpha} a^{\dagger}_{\beta} a^{\delta} a^{\gamma}, \tag{1.40}$$

or in terms of angular brackets (in this case the two-body matrix element will be emphasized with a bar, $\bar{V}^{\alpha\beta}_{\gamma\delta} \equiv V^{\alpha\beta}_{\gamma\delta} - V^{\alpha\beta}_{\delta\gamma}$):

$$\hat{H} = \sum_{\alpha\beta} h^{\alpha}_{\beta} a^{\dagger}_{\alpha} a^{\beta} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \bar{V}^{\alpha\beta}_{\gamma\delta} a^{\dagger}_{\alpha} a^{\dagger}_{\beta} a^{\delta} a^{\gamma}. \tag{1.41}$$

The one and two body integrals are:

$$h^{\alpha}_{\beta} = \int d\mathbf{r}\ \phi^{*}_{\alpha}(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 - \sum_{I}^{M} \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \right) \phi_{\beta}(\mathbf{r}) \tag{1.42}$$

$$V^{\alpha\beta}_{\gamma\delta} = \int d\mathbf{r}_1 d\mathbf{r}_2\ \frac{\phi^{*}_{\alpha}(\mathbf{r}_1)\phi^{*}_{\beta}(\mathbf{r}_2)\phi_{\gamma}(\mathbf{r}_1)\phi_{\delta}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{1.43}$$

1.4.4 Scalar products and Wick's Theorem

In second quantization it is possible, though perhaps quite tedious, to evaluate scalar products between complicated states. The most efficient approach is based upon the relevant form of Wick's theorem, which we will now describe. First, we need to define a normal ordering. It is easiest to say that two second quantized operators are in normal order if all the creators are to the left of all the annihilators. (We will mention more interesting normal orderings below.) Next, an operator $\hat{N}$ is defined to arrange a set of second-quantized operators into normal order (with the appropriate sign based on the signature of the permutation required), e.g. for any $a^\dagger_i, a^j$,

$$\hat{N}[a^\dagger_i a^j] = a^\dagger_i a^j \tag{1.44}$$

$$\hat{N}[a^j a^\dagger_i] = -a^\dagger_i a^j. \tag{1.45}$$

With this choice, the normal ordering of two creators (or annihilators) is just the written ordering. A *contraction*[5] of any two second quantized operators $\hat{a}, \hat{b}$ is then defined as the difference of their written and normal orderings. It is thus denoted:

$$\hat{a}^\bullet \hat{b}^\bullet = \hat{a}\hat{b} - \hat{N}[\hat{a}\hat{b}] \tag{1.46}$$

The four possible contractions are then

$$a^{\dagger\bullet}_i a^{\dagger\bullet}_j = a^\dagger_i a^\dagger_j - \hat{N}[a^\dagger_i a^\dagger_j] = a^\dagger_i a^\dagger_j - a^\dagger_i a^\dagger_j = 0 \tag{1.47}$$

$$a^{\dagger\bullet}_i a^{j\bullet} = a^\dagger_i a^j - \hat{N}[a^\dagger_i a^j] = a^\dagger_i a^j - a^\dagger_i a^j = 0 \tag{1.48}$$

$$a^{i\bullet} a^{\dagger\bullet}_j = a^i a^\dagger_j - \hat{N}[a^i a^\dagger_j] = a^i a^\dagger_j + a^\dagger_j a^i \equiv \delta_{ij} \tag{1.49}$$

$$a^{i\bullet} a^{j\bullet} = a^i a^j - \hat{N}[a^i a^j] = a^i a^j - a^i a^j = 0 \tag{1.50}$$

The only non-trivial contraction is that for which the operators are not already in normal order. With these constructs, Wick's theorem (for second quantized fermions

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[5] The notation here is from [DN08]

at zero time) can be stated:

$$\begin{aligned}\hat{a}\hat{b}\hat{c}\ldots\hat{x}\hat{y}\hat{z} &= \hat{N}[\hat{a}\hat{b}\hat{c}\ldots\hat{x}\hat{y}\hat{z}] \\ &+ \sum_{singles} \hat{N}[\hat{a}^{\bullet}\hat{b}^{\bullet}\hat{c}\ldots\hat{x}\hat{y}\hat{z}] \\ &+ \sum_{doubles} \hat{N}[\hat{a}^{\bullet}\hat{b}^{\bullet}\hat{c}^{\bullet\bullet}\ldots\hat{x}^{\bullet\bullet}\hat{y}\hat{z}] \\ &+ \ldots \\ &+ \sum_{full} \hat{N}[\hat{a}^{\bullet}\hat{b}^{\bullet}\hat{c}^{\bullet\bullet}\ldots\hat{x}^{\bullet\bullet}\hat{y}^{\bullet\bullet\bullet}\hat{z}^{\bullet\bullet\bullet}] \end{aligned} \tag{1.51}$$

i.e. the string of operators on the left hand side is equivalent to its normal order, plus the normal order of all possible strings with a single contraction, plus the normal order of all strings with two contractions, and so on until all possible strings which are fully contracted. The notation in the last line of eq. (1.51) denotes that $\hat{a}$ is contracted with $\hat{b}$, $\hat{c}$ is contracted with $\hat{x}$, and $\hat{y}$ is contracted with $\hat{z}$. While perhaps elegant, this expression's utility is not apparent until we take the expectation of the vacuum. Because of our choice of normal order, all annihilators have been moved to the right, where they destroy the vacuum. Therefore only fully contracted terms contribute:

$$\langle\theta|\hat{a}\hat{b}\hat{c}\ldots\hat{x}\hat{y}\hat{z}|\theta\rangle = \sum_{full} \langle\theta|\hat{N}[\hat{a}^{\bullet}\hat{b}^{\bullet}\hat{c}^{\bullet\bullet}\ldots\hat{x}^{\bullet\bullet}\hat{y}^{\bullet\bullet\bullet}\hat{z}^{\bullet\bullet\bullet}]|\theta\rangle \tag{1.52}$$

This expression vanishes trivially unless there are an equal number n of creators and annihilators. The worst case is that all n annihilators are to the left of all n creators as this is the only non-vanishing contraction Eq. (1.49). A simple counting argument reveals that there are $n!$ terms: consider the creators fixed, each annihilator is contracted with a creator, and there are $n!$ such permutations of the annihilators among the creators. None of the objects in this counting can be equivalent, otherwise the Pauli principle would suggest that the result is trivially zero.

More interesting normal orderings may also be defined. Given a Slater determinant

$$|\Phi_{ref}\rangle = \prod_{i=1}^{N} a_i^{\dagger} |\theta\rangle \,, \tag{1.53}$$

the set of orbitals composing Eq. (1.53) are called *occupied* while the remainder are called *virtual*. A normal ordering can then be defined which moves all occupied creators and virtual annihilators to the right as their action on the state (1.53) is zero. Contractions are defined as before (as the difference between the written and normal ordered products), as is Wick's theorem with the state (1.53) as the "vacuum". This version is employed in Coupled-Cluster theory.

Time-dependence can also be included. Provided with second-quantized operators with a time dependence,[6] $a_i^{\dagger}(t), a^j(t')$ a *time* ordering is defined which arranges the operators such that their time arguments increase from right to left, with a sign appropriate for the required permutation. A contraction of two operators is then defined as the difference between their time and normal orderings. In the interaction picture case, the contraction ends up being the single-particle Green's function appropriate for time-dependent perturbation theory.[7]

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[6] The obvious choice is the interaction picture, though the Heisenberg picture should also be acceptable.

[7] In all of these cases, visually oriented individuals often choose to summarize terms with diagrams and rules for drawing them. Unfortunately, the author is not comfortable with this approach and must always expand expressions to verify that he has drawn a complete collection of diagrams, entirely defeating the purpose.

While first quantization is convenient to express physical laws, second quantization is far more convenient for practical implementations. Second quantization is a projection of the entire physical picture onto a fixed basis.

1.5 Many-Electron States: Hopf Algebra

We now consider the algebraic and co-algebraic structures of Fock space. The entire section is due to [CCP03] though the notation has adapted to accepted Hopf algebra notation. The pay-off of this viewpoint will be due to the duality between the algebraic and co-algebraic structures which make scalar products between complicated states simple to evaluate.

1.5.1 Fock Space: Algebra Structure

To exploit the deeper algebraic structure of Fock space a description in terms of the exterior, or Grassmann, algebra is advantageous. We start with a 1-fermion Hilbert space $\mathfrak{H}$, spanned by a set of spin orbitals $\{\varphi_i\}$. Define the exterior product, denoted $\wedge$, of any two spin orbitals

$$\varphi_i \wedge \varphi_j = -\varphi_j \wedge \varphi_i, \tag{1.54}$$

which immediately implies that $\varphi_i \wedge \varphi_i = 0$. The state $\varphi_i \wedge \varphi_j$ is an element of the two fermion Hilbert space induced by the exterior product of the 1-electron Hilbert space with itself $\mathfrak{H} \wedge \mathfrak{H} := \Lambda^2(\mathfrak{H})$. The exterior product extends to any number of spin orbitals so that a Slater determinant is written:

$$|\alpha_1\alpha_2\dots\alpha_N\rangle = \varphi_{\alpha_1}\wedge\varphi_{\alpha_2}\wedge\dots\wedge\varphi_{\alpha_N} \tag{1.55}$$

$$= \mathrm{sgn}(\sigma)\varphi_{\alpha_{\sigma(1)}}\wedge\varphi_{\alpha_{\sigma(2)}}\wedge\dots\wedge\varphi_{\alpha_{\sigma(N)}} \tag{1.56}$$

for any permutation of the indices σ. Slater determinants are to be considered as basis functions in the N-fermion Hilbert space $\Lambda^N(\mathfrak{H})$. The fermionic Fock space, $\mathfrak{F}$, is defined as the direct sum

$$\mathfrak{F} := \bigoplus_{i=0}^{N}\Lambda^i(\mathfrak{H}) \tag{1.57}$$

with $\Lambda^1(\mathfrak{H}) = \mathfrak{H}$, and $\Lambda^0(\mathfrak{H}) = \mathbb{C}$, the complex numbers. Fock space has the structure of an algebra $(\mathfrak{F},\mu,\eta)$ in the sense of Appendix A.5.1 with unit $\eta:\mathbb{C}\to\mathfrak{F}$ and a multiplication $\mu:\mathfrak{F}\otimes\mathfrak{F}\to\mathfrak{F}$. For any $\lambda\in\mathbb{C}$, the unit map has a purely formal effect:

$$\lambda\to\eta(\lambda)=\lambda\in\Lambda^0(\mathfrak{H}). \tag{1.58}$$

For any two $\Phi_a,\Phi_b\in\mathfrak{F}$, the multiplication is defined by the exterior product:

$$\Phi_a\otimes\Phi_b\to\mu(\Phi_a\otimes\Phi_b)=\Phi_a\wedge\Phi_b. \tag{1.59}$$

It is not necessarily required for Φ_a and Φ_b to have good numbers of particles, however if $\Phi_a\in\Lambda^p(\mathfrak{H})$ and $\Phi_b\in\Lambda^q(\mathfrak{H})$, then $\Phi_a\wedge\Phi_b\in\Lambda^{p+q}(\mathfrak{H})$. This should be no surprise: a p-fermion state coupled to a q-fermion state is a $(p+q)$-fermion state. With these structures, $(\mathfrak{F}, \mu, \eta)$ is a graded algebra since $\mathfrak{F}$ is the direct sum (1.57) and

$$\mu(\Lambda^p(\mathfrak{H}) \otimes \Lambda^q(\mathfrak{H})) \subseteq \Lambda^{p+q}(\mathfrak{H}). \tag{1.60}$$

For scalars $\lambda \in \mathbb{C}$, the multiplication is simply scalar multiplication

$$\lambda \wedge \Phi = \Phi \wedge \lambda = \lambda \Phi. \tag{1.61}$$

1.5.2 Fock Space: Coalgebra Structure

Fock space also has a coalgebra structure $(\mathfrak{F}, \Delta, \varepsilon)$ with counit $\varepsilon : \mathfrak{F} \to \mathbb{C}$ and comultiplication $\Delta : \mathfrak{F} \to \mathfrak{F} \otimes \mathfrak{F}$. The counit identifies scalars, and has zero action on any non-scalar element:

$$\varepsilon(\lambda) = \lambda, \quad \lambda \in \Lambda^0(\mathfrak{H}) \tag{1.62}$$

$$\varepsilon(\Phi) = 0, \quad \Phi \in \Lambda^n(\mathfrak{H}), n > 0. \tag{1.63}$$

The comultiplication takes N-fermion states and splits them into p-fermion states and $(N-p)$-fermion states for all $0 \leq p \leq N$. Since fermions obey the Pauli principle, there is a sign introduced any time that the indices are relabelled. For example, the coproduct of a two fermion state is:

$$\Delta(\varphi_i \wedge \varphi_j) = \varphi_i \wedge \varphi_j \otimes 1 + \varphi_i \otimes \varphi_j - \varphi_j \otimes \varphi_i + 1 \otimes \varphi_i \wedge \varphi_j. \tag{1.64}$$

For arbitrary N, the coproduct is:

$$\Delta(\varphi_1 \wedge \cdots \wedge \varphi_N) = \sum_{p=0}^{N} \sum_{\sigma} \frac{\mathrm{sgn}(\sigma)}{p!(N-p)!} \varphi_{\sigma(1)} \wedge \cdots \wedge \varphi_{\sigma(p)} \otimes \varphi_{\sigma(p+1)} \wedge \cdots \wedge \varphi_{\sigma(N)}. \tag{1.65}$$

The coproduct extends linearly. For example, for the state

$$\Phi = \sum_{ijkl} C_{ijkl} \varphi_i \wedge \varphi_j \wedge \varphi_k \wedge \varphi_l, \tag{1.66}$$

the coproduct is

$$\Delta(\Phi) = \sum_{ijkl} C_{ijkl} \Delta(\varphi_i \wedge \varphi_j \wedge \varphi_k \wedge \varphi_l). \tag{1.67}$$

1.5.3 Fock Space: Hopf Algebra Structure

Fock space thus has both an algebra and a coalgebra structure. It may be verified that the two structures are compatible, giving it a bialgebra structure provided that the twist operation τ is defined such that for $\Phi_p \in \Lambda^p(\mathfrak{H})$ and $\Phi_q \in \Lambda^q(\mathfrak{H})$,

$$\tau(\Phi_p \otimes \Phi_q) = (-1)^{pq} \Phi_q \otimes \Phi_p. \tag{1.68}$$

While not entirely useful, there is indeed an antipode mapping $S : \mathfrak{F} \to \mathfrak{F}$ which acts on individual terms as:

$$S(\varphi_1 \wedge \cdots \wedge \varphi_n) = (-1)^n \varphi_1 \wedge \cdots \wedge \varphi_n \tag{1.69}$$

and extends linearly to other elements in $\mathfrak{F}$.

We can now discuss the pay-off of employing this architecture: the evaluation of scalar products. There are three important ingredients in the recipe

- A Laplace pairing[8] expressing a duality between product and coproduct

$$\langle \Phi_p \wedge \Phi_q | \Phi_{p+q} \rangle \equiv \langle \mu(\Phi_p \otimes \Phi_q) | \Phi_{p+q} \rangle = \langle \Phi_p \otimes \Phi_q | \Delta(\Phi_{p+q}) \rangle \tag{1.70}$$

- Scalar products of tensor products factor into individual scalar products

$$\langle \phi_1 \otimes \phi_2 | \varphi_1 \otimes \varphi_2 \rangle = \langle \phi_1 | \varphi_1 \rangle \langle \phi_2 | \varphi_2 \rangle \tag{1.71}$$

- Compatibility of the product μ and the coproduct Δ

$$\Delta \circ \mu = (\mu \otimes \mu) \circ (\mathrm{id} \otimes \tau \otimes \mathrm{id}) \circ (\Delta \otimes \Delta) \tag{1.72}$$

Scalar products can then be performed recursively by expressing $\phi_1 \wedge \phi_2 \wedge \cdots \wedge \phi_n = \mu(\phi_1 \otimes (\phi_2 \wedge \cdots \wedge \phi_n))$ and progressively using the three above ingredients.

1.6 The Standard Approaches

Quantum chemistry is mature enough to have a core of understood "standard approaches". See ref. [HJO00] for a definitive reference. Their behaviour, successes, and most importantly their failures are widely known and accepted. With a couple

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[8] This does not in general exist for any Hopf algebra, but does exist in this case

of exceptions which we will not mention, all the known approaches fall into one of three categories.

Variational A wavefunction *ansatz* $|\tilde{\Psi}\rangle$ is assumed, which in turn defines an energy functional:

$$E[\tilde{\Psi}] = \frac{\langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle}{\langle\tilde{\Psi}|\tilde{\Psi}\rangle} \tag{1.73}$$

The parameters that define the wavefunction ansatz are then optimized such that the variation $\delta E = 0$. The variational theorem ensures that provided $|\tilde{\Psi}\rangle$ is a physical wavefunction, the energy obtained from Eq. (1.73) is always greater than the ground state energy of the system. Equality is achieved only when $|\tilde{\Psi}\rangle$ is the exact answer. Expanding the numerator of the objective function Eq. (1.73),

$$\langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle = \sum_{\alpha\beta} h^{\alpha}_{\beta} \langle\tilde{\Psi}|a^{\dagger}_{\alpha}a^{\beta}|\tilde{\Psi}\rangle + \frac{1}{2}\sum_{\alpha\beta\gamma\delta} V^{\alpha\beta}_{\gamma\delta} \langle\tilde{\Psi}|a^{\dagger}_{\alpha}a^{\dagger}_{\beta}a^{\delta}a^{\gamma}|\tilde{\Psi}\rangle \tag{1.74}$$

$$= \sum_{\alpha\beta} h^{\alpha}_{\beta}\gamma^{\beta}_{\alpha} + \frac{1}{2}\sum_{\alpha\beta\gamma\delta} V^{\alpha\beta}_{\gamma\delta}\Gamma^{\gamma\delta}_{\alpha\beta} \tag{1.75}$$

we see that the required data are the norm $\langle\tilde{\Psi}|\tilde{\Psi}\rangle$, the 1-body reduced density matrix γ^{β}_{α} (1-RDM) and the 2-body reduced density matrix $\Gamma^{\gamma\delta}_{\alpha\beta}$ (2-RDM).

Projected With a wavefunction ansatz $|\tilde{\Psi}\rangle$, we can project a set of known, simple states (almost always Slater determinants) against the Schrödinger equation to obtain a set of coupled non-linear equations for the energy and the parameters defining $|\tilde{\Psi}\rangle$. If,

$$\hat{H}\,|\tilde{\Psi}\rangle = \tilde{E}\,|\tilde{\Psi}\rangle\,, \tag{1.76}$$

then we can project a set of $\{\Phi_\alpha\}$ from the left and solve the resulting non-linear equations

$$\langle\Phi_\alpha|\hat{H}-\tilde{E}|\tilde{\Psi}\rangle = 0. \tag{1.77}$$

In a basis of Slater determinants the most expensive calculations are the scalar products $\langle\Phi_\alpha|\tilde{\Psi}\rangle$ rather than the 2-RDM. The variational theorem is no longer valid so it is certainly possible to find non-physical energies below the true ground state energy. Indeed even complex energies can be found, though the standard approach is to just ignore the imaginary component. [SB09]

Perturbative In Rayleigh-Schrödinger perturbation theory, one partitions the Hamiltonian as

$$\hat{H} = \hat{H}_0 + \lambda V \tag{1.78}$$

where $\hat{H}_0$ is a system for which the solution is available and ideally *close* to $\hat{H}$ such that the perturbation V is small. The parameter λ varies between 0 and 1, adiabatically connecting the reference system $\hat{H}_0$ to the physical $\hat{H}$. From the Schrödinger equations

$$(\hat{H}_0 + \lambda V)\,|\Psi_n\rangle = E_n\,|\Psi_n\rangle \tag{1.79}$$

one expands the energies and states as Maclaurin series in the parameter λ:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \tag{1.80}$$

$$|\Psi_n\rangle = |\Psi_n^{(0)}\rangle + \lambda |\Psi_n^{(1)}\rangle + \lambda^2 |\Psi_n^{(2)}\rangle + \dots \tag{1.81}$$

The individual terms are just the corresponding derivatives

$$E_n^{(k)} = \frac{1}{k!}\frac{d^k E_n}{d\lambda^k} \tag{1.82}$$

$$|\Psi_n^{(k)}\rangle = \frac{1}{k!}\frac{d^k |\Psi_n\rangle}{d\lambda^k}. \tag{1.83}$$

Expanding Eq. (1.79) and equating powers of λ yields:

$$E_n^{(1)} = \langle\Psi_n^{(0)}|V|\Psi_n^{(0)}\rangle \tag{1.84}$$

$$|\Psi_n^{(1)}\rangle = \sum_{k\neq n} \frac{\langle\Psi_k^{(0)}|V|\Psi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} |\Psi_k^{(0)}\rangle \tag{1.85}$$

To second order, the energy is:

$$E_n = E_n^{(0)} + \lambda \langle\Psi_n^{(0)}|V|\Psi_n^{(0)}\rangle + \lambda^2 \sum_{k\neq n} \frac{|\langle\Psi_k^{(0)}|V|\Psi_n^{(0)}\rangle|^2}{E_n^{(0)} - E_k^{(0)}} + \mathcal{O}(\lambda^3) \tag{1.86}$$

1.6.1 Hartree-Fock

Hartree-Fock (HF) theory is more important conceptually than as a numerical procedure. There are many ways of approaching this problem which yield the HF result. In any case, the description must be consistent: electrons interact only through an average potential produced by the other electrons. The wavefunction in this case is a single Slater determinant.

Starting with a Slater determinant $|\Phi\rangle$, we will perform an optimal unitary transformation to minimize the energy. So, we transform $|\Phi\rangle \rightarrow |\Phi'\rangle$ where

$$|\Phi'\rangle = \hat{U} |\Phi\rangle = e^{\hat{X}} |\Phi\rangle . \tag{1.87}$$

If $\hat{X}$ is skew-hermitian, i.e. $\hat{X}^\dagger = -\hat{X}$, then $e^{\hat{X}} \in U(N)$, the unitary group in N dimensions. The energy functional is then

$$\langle\Phi|e^{-\kappa\hat{X}}\hat{H}e^{\kappa\hat{X}}|\Phi\rangle = \langle\Phi|\hat{H}|\Phi\rangle + \kappa \langle\Phi|[\hat{H},\hat{X}]|\Phi\rangle + ..., \tag{1.88}$$

and is stationary provided that the first variation vanishes. Then we need to solve:

$$\langle\Phi|[\hat{H},\hat{X}]|\Phi\rangle = 0 \tag{1.89}$$

The requirement that $\hat{X}$ be skew-hermitian may be relaxed so that $\hat{X}$ may be any one body operator

$$\hat{X} = \sum_{\alpha\beta} X^{\alpha}_{\beta} a^\dagger_\alpha a^\beta, \tag{1.90}$$

and the variational condition then becomes

$$\langle\Phi|[\hat{H}, a^\dagger_\alpha a^\beta]|\Phi\rangle = 0, \quad \forall\alpha,\beta. \tag{1.91}$$

A straightforward yet tedious exercise yields

$$\langle\Phi|[\hat{H}, a^{\dagger}_{\alpha}a^{\beta}]|\Phi\rangle = \varepsilon^{\beta}_{\alpha}\sum_{i}(\delta_{\beta i} - \delta_{\alpha i}) \tag{1.92}$$

which vanishes provided that the matrix $\varepsilon^{\beta}_{\alpha}$ is diagonal. Its elements are:

$$\varepsilon^{\beta}_{\alpha} = h^{\beta}_{\alpha} + \sum_{i \in occ} \bar{V}^{\beta i}_{\alpha i} \tag{1.93}$$

The HF Slater determinant is then obtained as that which diagonalizes the Hamiltonian:

$$\hat{H}_0 = \sum_{\alpha\beta} \varepsilon^{\alpha}_{\beta} a^{\dagger}_{\alpha} a^{\beta}. \tag{1.94}$$

Since this effective Hamiltonian depends upon the occupied states, this operation must be performed iteratively. Provided such a determinant $|\Phi_{HF}\rangle$, the HF energy is then

$$\begin{aligned} E_{HF} &= \langle\Phi_{HF}|\hat{H}|\Phi_{HF}\rangle && (1.95)\\ &= \sum_{i}\left(h^{i}_{i} + \frac{1}{2}\sum_{j}\bar{V}^{ij}_{ij}\right) && (1.96)\\ &= \sum_{i}\left(\varepsilon^{i}_{i} - \frac{1}{2}\sum_{j}\bar{V}^{ij}_{ij}\right) && (1.97)\end{aligned}$$

The orbital energies ε_i may be interpreted as *approximate* ionization potentials and electron affinities. This fact is known as Koopmans' theorem. Specifically, the ionization potentials of the *occupied* orbitals are the negatives of their orbital energies,

$$\begin{aligned} I_i &= \langle \Phi_{HF} | a_i^\dagger \hat{H} a^i | \Phi_{HF} \rangle - \langle \Phi_{HF} | \hat{H} | \Phi_{HF} \rangle \\ &= -\varepsilon_i \end{aligned} \tag{1.98}$$

and similarly the electron affinities of the *virtual* orbitals are the negatives of their orbital energies

$$\begin{aligned} A_\alpha &= \langle \Phi_{HF} | \hat{H} | \Phi_{HF} \rangle - \langle \Phi_{HF} | a^\alpha \hat{H} a_\alpha^\dagger | \Phi_{HF} \rangle \\ &= -\varepsilon_\alpha. \end{aligned} \tag{1.99}$$

For chemical purposes, particularly near the top and the sides of the periodic table, a single Slater determinant provides an adequate description of reality. In these cases it is advantageous to first decompose the Coulomb Hamiltonian into an independent-particle portion $\hat{H}_0$, and a residual interaction $\hat{V}_{res}$,

$$\hat{H} = \hat{H}_0 + \hat{V}_{res}. \tag{1.100}$$

HF provides an exact answer for $\hat{H}_0$, and provided $\hat{V}_{res} \equiv \hat{H} - \hat{H}_0$ is small, the Slater determinant obtained provides a reasonable starting point for a perturbation expansion of some sort.

1.6.2 Møller-Plesset Perturbation Theory

Using HF as a reference, one considers Eq. (1.86) to second order to get MP2. HF is itself the first two terms in the energy series, so there is no "first-order correction".

Higher-order terms in the series have been used, but it does not necessarily converge, and gets progressively more expensive.

1.6.3 Coupled-Cluster

The coupled-cluster ansatz (see ref. [SB09]) is expressed as an exponential of a generalized excitation operator, the *cluster operator*, over a Hartree-Fock vacuum. The cluster operator is defined as a sum of smaller cluster operators: [9]

$$\hat{T}_{CC} = \sum_{i=1}^{N} T^{(i)}_{CC}. \tag{1.101}$$

The first few cluster operators are:

$$\hat{T}^{(1)}_{CC} = \sum_{\substack{i \in occ \\ \alpha \in virt}} t^{\alpha}_{i} a^{\dagger}_{\alpha} a^{i} \tag{1.102}$$

$$\hat{T}^{(2)}_{CC} = \frac{1}{(2!)^2} \sum_{\substack{ij \in occ \\ \alpha\beta \in virt}} t^{\alpha\beta}_{ij} a^{\dagger}_{\alpha} a^{\dagger}_{\beta} a^{j} a^{i} \tag{1.103}$$

$$\hat{T}^{(3)}_{CC} = \frac{1}{(3!)^2} \sum_{\substack{ijk \in occ \\ \alpha\beta\gamma \in virt}} t^{\alpha\beta\gamma}_{ijk} a^{\dagger}_{\alpha} a^{\dagger}_{\beta} a^{\dagger}_{\gamma} a^{k} a^{j} a^{i} \tag{1.104}$$

The coupled-cluster ansatz is thus defined:

$$|\Psi_{CC}\rangle = e^{\hat{T}_{CC}} |\Phi_{HF}\rangle \tag{1.105}$$

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[9] the subscript CC is added so that the cluster operator is clearly distinguished from the kinetic energy, though no confusion should arise in any case

While the chosen Slater determinant is typically the Hartree-Fock ground state any choice of Slater determinant is possible. The exponential of an operator is defined as the Taylor series, i.e. for the cluster operator:

$$e^{\hat{T}_{CC}} = \sum_{n=0}^{\infty} \frac{\left(\hat{T}_{CC}\right)^n}{n!}. \tag{1.106}$$

It is immediately apparent that minimizing the Rayleigh quotient Eq. (1.73) with the coupled-cluster ansatz is intractable. It is in effect equivalent to configuration interaction. The approach is to instead consider a set of projected Schrödinger equations. A set of Slater determinants are projected against the Schrödinger equation for the coupled-cluster ansatz, i.e. from

$$\hat{H} \left|\Psi_{CC}\right\rangle = E_{CC} \left|\Psi_{CC}\right\rangle, \tag{1.107}$$

we obtain a set of coupled non-linear equations

$$\left\langle\Phi_0\right| \hat{H} \left|\Psi_{CC}\right\rangle = E_{CC} \tag{1.108}$$

$$\left\langle\Phi_\alpha\right| \hat{H} \left|\Psi_{CC}\right\rangle = 0 \tag{1.109}$$

where the normalization has been conveniently chosen so that $\left\langle\Phi_0|\Psi_{CC}\right\rangle = 1$.

A more intellectually pleasant description entails a transformation of the Hamiltonian with the cluster operator, for which the Baker-Campbell-Hausdorff expansion may be employed. The "magic" of the result is that the seemingly difficult series terminates at fourth order if the reference is a single Slater determinant. I.e.

$$\hat{H}_{CC} = e^{-\hat{T}_{CC}}\hat{H}e^{\hat{T}_{CC}} = \hat{H} + [\hat{H},\hat{T}_{CC}] + \frac{1}{2!}[[\hat{H},\hat{T}_{CC}],\hat{T}_{CC}] + \frac{1}{3!}[[[\hat{H},\hat{T}_{CC}],\hat{T}_{CC}],\hat{T}_{CC}] \\ + \frac{1}{4!}[[[[\hat{H},\hat{T}_{CC}],\hat{T}_{CC}],\hat{T}_{CC}],\hat{T}_{CC}] + \hat{H}'_{CC}, \tag{1.110}$$

where $\hat{H}'_{CC}\left|\Phi_0\right\rangle = 0$. Projecting of a set of states then yields the coupled non-linear equations to be solved:

$$\left\langle\Phi_0\right| \hat{H}_{CC} \left|\Phi_0\right\rangle = E_{CC} \tag{1.111}$$

$$\left\langle\Phi_\alpha\right| \hat{H}_{CC} \left|\Phi_0\right\rangle = 0 \tag{1.112}$$

The majority of coupled-cluster calculations (and implementations) truncate the cluster operator to single and double excitations, and are thus labelled CCSD. The so-called "gold-standard" of quantum chemistry is CCSD(T), which is CCSD with the triple excitations added perturbatively. As will be discussed in section (1.9) CCSD and CCSD(T) are excellent in cases where *all the other standard approaches are already reasonable approximations.*

1.6.4 Configuration Interaction

In a given basis, the exact wavefunction can be expanded in a basis of N-electron Slater determinants

$$|\Psi\rangle = \sum_{(\omega)} |\Phi_\omega\rangle\langle\Phi_\omega|\Psi\rangle = \sum_{(\omega)} C_\omega|\Phi_\omega\rangle. \tag{1.113}$$

The method known as *configuration interation* (CI) proceeds by diagonalizing the Hamiltonian matrix in the basis of N-electron Slater determinants.

The CI expansion is typically truncated at single, or double excitations from a HF reference. This is fine for systems with a dominant configuration, but fails when the physical behaviour is collective in nature. A more rapidly converging partitioning of the expansion in terms of seniority (see subsection (1.11.1)) is more appropriate.

1.7 Density Functional Theory

Density Functional Theory (DFT) has become such a popular family of approaches that it deserves at least its own section. We will begin with the existence theorems that make DFT possible and describe some of its nice formal properties. Given its deceptive simplicity, a theory based on only the electron density is indeed seductive, and the Kohn-Sham trick is a clever pragmatic approach. However, DFT methods are often employed as black boxes for systems far outside their domain of validity. A standard and robust reference is [PY89]

1.7.1 Hohenberg-Kohn Theorems

Unlike the approaches in the previous section, DFT is most conveniently described in first quantization. As a physical observable the density, $\rho(\mathbf{r})$, is the expectation value of some operator:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \langle \Psi | \, \delta\left(\mathbf{r} - \mathbf{r}_i\right) | \Psi \rangle \tag{1.114}$$

which is precisely the quantization of the classical density of a distribution of point charges $\{q_i\}$

$$\rho_C(\mathbf{r}) = \sum_{i=1}^{N} q_i \delta\left(\mathbf{r} - \mathbf{r}_i\right). \tag{1.115}$$

The electronic Hamiltonian (1.11) is entirely determined by the number of electrons, and the positions of the nuclei (the external potential). By integrating the density over all space we recover the number of electrons:

$$N = \int d\mathbf{r} \rho\left(\mathbf{r}\right), \tag{1.116}$$

and provided that the density is *v-representable*, the external potential is determined by the density. Since both the number of electrons and the external potential are thus functionals (“functions of functions”) of the electron density, it follows that the Hamiltonian (1.11) is also a functional of the electron density. Further, the Hamiltonian determines the wave-function, which in turn describes all the properties of the system. Therefore, the electron density contains enough information to determine all the properties of the system. This is a statement of the first Hohenberg-Kohn theorem. Explicitly, this means that the energy may be written

$$E\left[\rho\right] = F\left[\rho\right] + \int d\mathbf{r}\, v\left(\mathbf{r}\right) \rho\left(\mathbf{r}\right), \tag{1.117}$$

where $F\left[\rho\right]$ is called the *Hohenberg-Kohn* (HK) functional. The HK functional is universal which is to say that it is the same for every system for which the Hamiltonian is of the same form. The only system-dependent ingredient is the external potential $v\left(\mathbf{r}\right)$, which for atoms and molecules is typically just the arrangement of nuclei (treated as point charges). The second Hohenberg-Kohn theorem is a variational principle, i.e. that the ground state density of a system is that which minimizes the energy functional (1.117).

The Hohenberg-Kohn theorems are *existence proofs*, i.e. permission to proceed. There is no mention of how to write the energy functional in terms of the density. How does one evaluate the kinetic energy of a density? This is an unsolved problem in general, and a few approximations exist. The HK functional is defined:[10]

$$F[\rho] \equiv T[\rho] + V_{ee}[\rho] \tag{1.118}$$

where the kinetic and electron-electron repulsions are defined

$$T[\rho] \equiv \langle \Psi[\rho] | T | \Psi[\rho] \rangle \tag{1.119}$$

$$V_{ee}[\rho] \equiv \langle \Psi[\rho] | V_{ee} | \Psi[\rho] \rangle \, . \tag{1.120}$$

These expressions are not practical since they require knowledge of the wavefunction, defeating the purpose of using the electron density. We can however rewrite the HK functional in terms of contributions that we know, or can approximate:

$$F[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho] \tag{1.121}$$

The first term, T_S is the non-interacting kinetic energy (which will be elaborated upon in the next section), J is the classical electrostatic interaction of charge densities (in

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[10] It is of course understood that the density is a function of position, and hence any functional of the density necessarily depends upon position. To clean up the notation, the dependence upon position will be suppressed.

atomic units)

$$J[\rho] \equiv \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{1.122}$$

and the last term is called the exchange-correlation energy functional,[11] which is tasked with making the expression exact. The HK theorems only ensure that E_{XC} *exists.*

The most naive attempt at DFT would be to write the HK functional:

$$F[\rho] = T_S^{TF}[\rho] + J[\rho] + E_X^D[\rho] + E_C^W[\rho] \tag{1.123}$$

in terms of the Thomas-Fermi kinetic energy

$$T_S^{TF}[\rho] = \frac{3(3\pi^2)^{2/3}}{10} \int d\mathbf{r} \rho^{5/3}(\mathbf{r}) \tag{1.124}$$

the Dirac exchange

$$E_X^D[\rho] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int d\mathbf{r} \rho^{4/3}(\mathbf{r}) \tag{1.125}$$

and the Wigner correlation

$$E_C^W[\rho] = -\int d\mathbf{r} \frac{\rho(\mathbf{r})}{17.7 + 2.27\rho^{-1/3}(\mathbf{r})}. \tag{1.126}$$

The numerical coefficients highlight the empirical nature of the functional. The expression (1.123) has the advantage of being conceptually and computationally simple.

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[11] the names "garbage," "cop-out," and "magic" are equally appropriate

Unfortunately, it is inadequate for densities that are far from the uniform electron gas reference that was used to derive Eq. (1.123).

It has the disadvantage of being entirely inadequate for densities which are not absolutely homogeneous.

1.7.2 Kohn-Sham Density Functional Theory

The kinetic energy does not have an obvious expression as an explicit functional of the electron density, but it does have a simple explicit expression for any model wavefunction. Thus we can avoid part of the difficulty of DFT if we can calculate the kinetic energy of a wavefunction which produces the same physical density as desired. This is the central idea of Kohn-Sham DFT. A non-interacting system (whose wavefunction is a Slater determinant) is used to calculate the kinetic energy.

$$F_{KS}[\rho] = \min_{\Phi \to \rho} \langle \Phi | T | \Phi \rangle + J[\rho] + E_{XC}[\rho] \tag{1.127}$$

It is important to emphasize: the fundamental variable is no longer the density, but an idempotent 1-RDM. No matter how advantageous it is to think in terms of the density, the theory is now built upon a set of auxiliary[12] orbitals which produce the physical density.

It is now the time to make a ladder of approximations to E_{XC}. Perdew's "Jacob's Ladder" of DFT models can be summarized:

Local Density Approximation (LDA) E_{XC} is a functional of only the density.

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[12] i.e. fake

Generalized Gradient Approximation (GGA) In addition to the density, (reduced) gradients and other derivatives of the density are included.

meta-GGA The kinetic energy density is included.

Hybrids Occupied Kohn-Sham orbitals are included.

Double hybrids Unoccupied orbitals are included.

All pretence is lost when one considers hybrids: if E_{XC} is an explicit functional of the auxiliary Kohn-Sham orbitals then the name "density" functional theory no longer seems appropriate. It is more correctly described as (some scaling of) Hartree-Fock plus correction. Double-hybrids are chimeras of methods from conventional quantum many-body theory and DFT. Technically, one could claim that DFT generalizes to full-CI. This is true, if the "functional" performs a full CI with the Kohn-Sham orbitals.

1.8 Reduced Density Matrix Approaches

The tantalizing feature of DFT is that the density itself contains all the information required about the system. The energy expression in terms of the density is however unknowable: there is an unknown functional. There are a variety of methods which attempt to use a fundamental variable which is simpler than the wavefunction yet has enough information to describe the system. In any of these "generalized DFTs" there are two possible issues concerning the system descriptors:

Unknown Functional Problem As discussed above for DFT: given a density, how does one write the energy functional? In general, provided a system descriptor, is it possible to write the energy expression?

N-Representability Problem Not an issue in DFT as any every positive function which integrates to the correct number of electrons is physically allowable. In general, provided a candidate system descriptor, is it physically allowed?

The next logical system descriptor after the density is the pair density $\rho_2(\mathbf{r}, \mathbf{r}')$ [Zie96, Zie94]. It is deceptively attractive since the electronic interaction is exactly written:

$$V_{ee} = \int d\mathbf{r}d\mathbf{r}' \frac{\rho_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{1.128}$$

One is quickly dispirited however once one realizes that the kinetic energy expression is not so simple. Worse there is also a N-representability problem for the pair density, i.e. given a "possible" pair density, how can we ensure that it is physically allowable? [Aye06] An unfortunately not very useful result is that a pair density is N-representable if and only if for *any* potential $V(\mathbf{r}, \mathbf{r}')$, the ground state energy is less than or equal to that provided with the pair density:

$$E_{GS}[V] \leq \int d\mathbf{r}d\mathbf{r}' \rho_2(\mathbf{r}, \mathbf{r}') V(\mathbf{r}, \mathbf{r}') \tag{1.129}$$

So, pair density functional theory is doomed due to both an unknown functional problem and a N-representability problem.

Provided a state $|\Psi\rangle$, its density operator is defined

$$\Gamma^{(N)} = |\Psi\rangle \langle\Psi| . \tag{1.130}$$

Density operators for ensemble states are defined:

$$\Gamma^{(N)} = \sum_{\alpha} w_\alpha \left|\Psi_\alpha\right\rangle \left\langle\Psi_\alpha\right|, \quad \sum_{\alpha} w_\alpha = 1. \tag{1.131}$$

We have already seen that the Coulomb Hamiltonian is a 2-body operator, and hence information relating to more than 2-body probabilities is essentially redundant. We can "trace out" the 2-body information of the N-body density operator, by projecting:

$$\begin{aligned}
\Gamma^{(2)} &= \sum_{\alpha} w_\alpha \left(\sum_{kl} \left|kl\right\rangle \left\langle kl\right| \right) \left|\Psi_\alpha\right\rangle \left\langle\Psi_\alpha\right| \left(\sum_{ij} \left|ij\right\rangle \left\langle ij\right| \right) \\
&= \sum_{ijkl} \left|kl\right\rangle \left\langle ij\right| \sum_{\alpha} w_\alpha \left\langle\Psi_\alpha\right| a^\dagger_i a^\dagger_j a^l a^k \left|\Psi_\alpha\right\rangle \\
&= \sum_{ijkl} \left|kl\right\rangle \left\langle ij\right| (\Gamma^{(2)})^{kl}_{ij} \qquad (1.132)
\end{aligned}$$

The object $\Gamma^{(2)}$ is the 2-body reduced density operator, whereas its matrix elements are referred to as the 2-body reduced density matrix (2-RDM). With this system descriptor, the energy is evaluated [Dav12]:

$$E[\Gamma^{(2)}] = \mathrm{Tr}[\Gamma^{(2)} H^{(2)}] = \frac{1}{4} \sum_{ijkl} (\Gamma^{(2)})^{kl}_{ij} (\hat{H}^{(2)})^{ij}_{kl} \tag{1.133}$$

The Hamiltonian is "reduced" to a 2-body form:

$$(\hat{H}^{(2)})^{ij}_{kl} = \frac{1}{N-1} (\delta_{ik} t^j_l - \delta_{il} t^j_k - \delta_{jk} t^i_l + \delta_{jl} t^i_k) + \bar{V}^{ij}_{kl} \tag{1.134}$$

There is thus *no unknown functional problem for the 2-RDM*, but alas an intractable N-representability problem [GP64]. Similar to the case for the pair density, a 2-RDM is N-representable provided that for *any* 2-body Hamiltonian,

$$\mathrm{Tr}[\hat{H}^{(2)}\Gamma^{(2)}] \geq E_{GS}[\hat{H}^{(2)}]. \tag{1.135}$$

Practical implementations are based upon redefining this problem as a semi-definite problem

$$\mathrm{Tr}[(\hat{H}^{(2)} - \mathbb{1} \cdot E_{GS}[\hat{H}^{(2)}])\Gamma^{(2)}] \geq 0, \tag{1.136}$$

and restricting “all possible Hamiltonians” to a select few. Unfortunately this approach is very difficult.

Similarly, we could use the 1-RDM [Gil75, Lev79, DP78]:

$$\begin{aligned}\gamma &= \sum_{ij} |j\rangle \langle i| \sum_{\alpha} w_\alpha \langle \Psi_\alpha | a_i^\dagger a^j | \Psi_\alpha \rangle \\ &= \sum_{ij} |j\rangle \langle i| \gamma_i^j \end{aligned} \tag{1.137}$$

The energy functional now contains an unknown term $E_C[\gamma]$:

$$E[\gamma] = \sum_{ij} t_j^i \gamma_i^j + \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} (\gamma_i^k \gamma_j^l - \gamma_i^l \gamma_j^k) + E_C[\gamma] \tag{1.138}$$

This unknown functional can at least be understood conceptually. The 2-body cumulant is defined as the 2-body information not expressible as 1-body information, specifically:

$$\Lambda_{ij}^{kl} = (\Gamma^{(2)})_{ij}^{kl} - (\gamma_i^k \gamma_j^l - \gamma_i^l \gamma_j^k) \tag{1.139}$$

The unknown term is thus:

$$E_C[\gamma] = \frac{1}{2} \sum_{ijkl} V^{ij}_{kl} \Lambda^{kl}_{ij} \tag{1.140}$$

This is unfortunately just a reshuffling of deck chairs. A practical form of the functional is unknowable [MSCY08, CMSY12]. On the other hand, there is no N-representability issue for the 1-RDM. It suffices for the eigenvalues to be between 0 and 1, and for the trace of the test matrix to be the number of electrons.

1.9 Weak and Strong Electron Correlation

The electron correlation energy is defined as the difference between the exact answer (full CI in a given basis) and the Hartree-Fock energy. The standard approaches described in the previous section are all built upon the idea that there is a single dominant electronic configuration with (perhaps) a few low lying excited states providing a much smaller contribution. As such they are *single reference* methods and only have a chance of accurately describing reality in cases where the inter-electronic repulsion is small compared to the band gap. Such systems are characteristic of *weak* or *dynamical* correlation. The weak correlation problem is essentially solved. There are standard *recipes* to account for it.

On the other hand, if the inter-electronic repulsion is of comparable magnitude with the orbital energies, a single reference is not an adequate ansatz for the physical wavefunction. As the strength of the interaction is increased many Slater determinants become near-degenerate and therefore provide non-negligible contributions.

Such systems are characteristic of *strong* or *static*[13] correlation. Static correlation is present whenever bonds are stretched or broken, i.e. whenever states approach one another in energy. In the limit of a completely dominant inter-electronic repulsion the motion of a single electron determines the motion of all the others through a long-range ordering. Forcing the movement of one electron forces the next electron to move which forces the next, etc..

Mainstream methods which attempt to include many Slater determinants are plentiful, e.g. complete active space self-consistent field (CASSCF), MCSCF, MC/MR-CCSD, etc.. So-called *multireference* methods are plagued with difficulties and are by no means black boxes, i.e. one does not simply press a button and obtain a correct answer.

1.10 Size-consistency and Extensivity

Consider a system with two fragments **A** and **B**. As the fragments are separated, the Coulomb interaction decays until they may be considered isolated from one another. The physical wavefunction for the isolated fragments becomes the (direct) product:

$$|\Psi_{\mathbf{AB}}\rangle = |\Psi_{\mathbf{A}}\rangle\,|\Psi_{\mathbf{B}}\rangle \tag{1.141}$$

The Hamiltonian is the sum of those for the individual fragments.

$$\hat{H}_{\mathbf{AB}} = \hat{H}_{\mathbf{A}} + \hat{H}_{\mathbf{B}} \tag{1.142}$$

---

[13] the asymmetry in nomenclature is emphasized

If we act with the Hamiltonian we find that

$$\hat{H}_{\mathbf{AB}} |\Psi_{\mathbf{AB}}\rangle = \left(\hat{H}_{\mathbf{A}} |\Psi_{\mathbf{A}}\rangle \right) |\Psi_{\mathbf{B}}\rangle + |\Psi_{\mathbf{A}}\rangle \left(\hat{H}_{\mathbf{B}} |\Psi_{\mathbf{B}}\rangle \right) \tag{1.143}$$

$$= (E_{\mathbf{A}} + E_{\mathbf{B}}) |\Psi_{\mathbf{A}}\rangle |\Psi_{\mathbf{B}}\rangle \tag{1.144}$$

the energy is thus the sum of those for the isolated fragments.

$$E_{\mathbf{AB}} = E_{\mathbf{A}} + E_{\mathbf{B}} \tag{1.145}$$

Computational models which satisfy the property (1.145) are said to be *size-consistent*. (Size-[14]) *Extensivity* is a related property. A model is extensive if the energy scales linearly with the size of the system. For example, if we consider n isolated copies of a system $\mathbf{A}$, the energy should be $nE_{\mathbf{A}}$. Recall the related concept from thermodynamics: extensive properties are those which scale with the size of the system.

Size-consistency and extensivity are crucial if one wants an accurate description of reality. Models which are not size-consistent degrade as the system size increases. Unfortunately few approaches are size-consistent, and the Hirata conjecture [HG14] asserts that no tractable variational theory is size-consistent.

If the model wavefunction can be expressed as the action of an exponential operator on some reference state, then the approach is usually size-consistent, since

$$e^{T_{\mathbf{A}}+T_{\mathbf{B}}} = e^{T_{\mathbf{A}}} e^{T_{\mathbf{B}}}. \tag{1.146}$$

---

[14] The name *size-extensive* is an unfortunate nomenclature that needs to disappear.

1.11 Geminals

Quantum chemistry is plagued by dogma of the occupied/virtual separation of single particle states. To have any chance of describing strong correlation correctly, we must move past this restrictive viewpoint. In many physical examples, it is known that electrons tend to pair.

1.11.1 Seniority

We define the seniority operator[15]

$$\hat{\Omega} = \sum_i \hat{\Omega}_i = \sum_i \left(a^\dagger_{i\frac{1}{2}} a^{i\frac{1}{2}} + a^\dagger_{i-\frac{1}{2}} a^{i-\frac{1}{2}} - 2 a^\dagger_{i\frac{1}{2}} a^\dagger_{i-\frac{1}{2}} a^{i-\frac{1}{2}} a^{i\frac{1}{2}} \right), \tag{1.147}$$

which counts broken pairs, and unpaired electrons. Slater determinants are eigenvectors of the seniority operator

$$\hat{\Omega} \left| \Phi \right\rangle = \Omega \left| \Phi \right\rangle . \tag{1.148}$$

Scuseria's group [BHJH$^+$11] have looked at prototypical strongly-correlated systems, hydrogen chains, with a CI scheme expanded based on seniority sectors. Their results are definitive: the dominant contribution is due to the $\Omega = 0$ sector with diminishing contributions from higher sectors. We should take this as a clear sign that the occupied/virtual picture is *not* appropriate for strongly-correlated systems. We should turn instead to collective, delocalized pairs of electrons: geminals.

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[15] The labels $\pm\frac{1}{2}$ are used to denote spins rather than the α, β convention used in quantum chemistry. The latter choice would certainly lead to confusion.

1.11.2 Geminal Flavours

Seniority-zero CI or doubly-occupied CI (DOCI) is a better starting point for strongly-correlated systems, but the complexity of the wavefunction makes any practical calculation impossible. In addition, the quality of DOCI is heavily dependent on the set of orbitals. The orbital optimization is in general a difficult problem. To write down the DOCI wavefunction, we'll first have to introduce a set of seniority zero pair operators.

$$S^+_i = a^\dagger_{i\frac{1}{2}} a^\dagger_{i-\frac{1}{2}} \tag{1.149}$$

$$S^-_i = a^{i-\frac{1}{2}} a^{i\frac{1}{2}} \tag{1.150}$$

The choice of notation will prove useful in the following chapters and thus the discussion will be deferred. For now, we merely note that these operators have the same algebraic structure raising and lowering spin operators. General pairing interactions may be written in the form

$$\hat{H}_P = \sum_i \varepsilon_i a^\dagger_i a^i - \sum_{ij} G^i_j S^+_i S^-_j , \tag{1.151}$$

and the DOCI wavefunction is:

$$|\mathrm{DOCI}\rangle = \sum_\omega C_\omega \prod_{a=1}^{N_P} S^+_{\omega_a} |\theta\rangle . \tag{1.152}$$

Each configuration ω has its own coefficient in the expansion, so if the basis has size N, there are $\binom{N}{N_P}$ parameters to be variationally determined. What if we approximate the DOCI coefficients as being composed of pairs? Consider the antisymmetric product of interacting geminals (APIG):

$$|\text{APIG}\rangle = \prod_{a=1}^{N_P} \sum_{i=1}^{N} g_a^i S_i^+ |\theta\rangle \tag{1.153}$$

The quantity $\sum_{i=1}^{N} g_a^i S_i^+$ is a geminal: it creates a pair of electrons delocalized over the single particle spectrum with coefficients g_a^i. The APIG state can be rewritten to emphasize the approximation to DOCI:

$$|\text{APIG}\rangle = \sum_{\omega} \left(\sum_{\sigma} \prod_{\alpha=1}^{N_P} g_\alpha^{\omega_{\sigma(\alpha)}} \right) \prod_{a=1}^{N_P} S_{\omega_a}^+ |\theta\rangle \tag{1.154}$$

Thus the approximation is that the DOCI coefficients can be written as the bracketed terms in Eq. (1.154). This term may be written as the permanent of a matrix:

$$\sum_{\sigma} \prod_{\alpha=1}^{N_P} g_\alpha^{\omega_{\sigma(\alpha)}} = \begin{vmatrix} g_1^{\omega_1} & & g_1^{\omega_{N_P}} \\ & \ddots & \\ g_{N_P}^{\omega_1} & & g_{N_P}^{\omega_{N_P}} \end{vmatrix}^+ \tag{1.155}$$

The permanent of a matrix is the same as a determinant except that all the signs in the expansion are positive. Determinants may be evaluated with a scaling of $\mathcal{O}(N^3)$ whereas permanents are of $\mathcal{O}(N!)$. This is because determinants are invariant to linear transformations and hence Gaussian elimination, pLU decompositions, etc. may be performed to evaluate determinants efficiently. Permanents are *not* invariant to linear transformations and hence must be expanded in a factorial manner.

It has been observed that APIG is an excellent approximation to DOCI, though given that both approaches are intractable this is little consolation. The goal is now to design geminal forms for which the expressions are tractable.

When all of the geminals are identical, the state is called the antisymmetric geminal power (AGP) [Col65, Col97]:

$$|\text{AGP}\rangle = \left(\sum_{i=1}^{N} G_i S_i^+ \right)^{N_P} |\theta\rangle \tag{1.156}$$

AGP can be viewed in a few different ways. First, as above it is a completely degenerate geminal state. It is also the projection of the Bardeen-Cooper-Schrieffer (BCS) ansatz onto a good particle number (in this case $2N_P$). The BCS state being [BCS57]:

$$|\text{BCS}\rangle = \prod_k (u_k + v_k S_k^+) |\theta\rangle \tag{1.157}$$

where the norm of the BCS state requires that

$$|u_k|^2 + |v_k|^2 = 1 \tag{1.158}$$

Or, if we define:

$$A^+ = \sum_k \frac{v_k}{u_k} S_k^+ \tag{1.159}$$

then the BCS state can be written as an exponential ansatz:

$$|\text{BCS}\rangle = \sum_{\nu}^{\infty} \frac{1}{\nu!} (A^+)^{\nu} |\theta\rangle = \exp(A^+) |\theta\rangle \tag{1.160}$$

The following chapters will describe several wavefunction forms. In the next chapter, we will look at Richardson's solution to the reduced BCS Hamiltonian. In terms of physical representations, it is built upon electron pairs but the integrability is built upon a $\mathfrak{su}(2)$ construction for any representation. Richardson's solution is at its heart a Bethe ansatz: the eigenvectors can be expressed as products of quasi-particles, parametrized by quasi-momenta. Consistency among the quasi-momenta is ensured by a set of non-linear equations which must solved numerically.

In chapter 3, we work with the same shape of wavefunction form as Richardson's solution, but we do not require it to be an eigenvector of a model Hamiltonian. Practical variational expressions are available provided that two equivalent descriptions are possible: one in terms of pairs, and the other in terms of pair holes. In general this is intractable so we outline how this may be done with a bivariational principle. A projected approach is certainly possible.

In chapter 4 we consider electron pairs split across several spatial orbitals. The pair creators for these states close the Lie algebras $\mathfrak{sp}(N)$ for singlets in N levels and $\mathfrak{so}(4N)$ for singlets and triplets in N levels.

In chapter 5 we look at generalizations involving unpaired electrons and different seniority sectors. The structure is that of a nested Bethe ansatz, though we do not necessarily desire eigenvectors. With even states and odd states, the representations are built upon a Lie superalgebra, and similar to the Lie algebra cases, it is always possible to define model Hamiltonians. For small numbers of unpaired electrons practical variational expressions are possible. Chapter 5 was originally published as [JAL^{+}13].

The general theme of the thesis is to employ model wavefunctions in quantum chemistry. They are products of quasi-particles which interact weakly among themselves. The desire is to capture strong correlation. Conventional approaches to add the remaining (qualitatively unimportant, but quantitatively essential) contributions of weak correlation can then be employed without too much effort.

Chapter 2

Bethe Ansatz Wavefunction Form: $\mathfrak{su}(2)$

In this chapter we employ the eigenvectors of Hamiltonians built from the Lie algebra $\mathfrak{su}(2)$. Their integrability will first be analyzed, followed by their solution. The eigenvectors will then be examined and employed to variationally minimize Coulomb Hamiltonians.

2.1 Quasi-spin representation of $\mathfrak{su}(2)$

Quasi-spins have roots in the shell model of nuclear structure where jj-coupling is dominant. An "orbital" with total angular momentum j_i has space for $\Omega_i = 2j_i + 1$ fermions. Given that $j_i = l_i + s_i$, where the orbital angular momentum $l_i \in \mathbb{Z}$ and the spin angular momentum for fermions $s_i = \pm\frac{1}{2}$, j_i will always be equal to half of an odd integer. The degeneracy Ω_i is thus an even integer. When there is a degeneracy in the single particle spectrum, it is convenient to treat the corresponding single particle states as a single state with higher degeneracy. In any real chemical system however, there is seldom any useful symmetry, and each single particle state can be occupied by a single pair $\Omega_i = 2$, $\forall i$.

In the shell model, one considers time-reversed pairs of fermions. For a state with total angular momentum j_i, the fermion creators are $a^\dagger_{j_i m_i}$ and $a^\dagger_{j_i \bar{m}_i} = (-1)^{j_i - m_i} a^\dagger_{j_i(-m_i)}$. Time reversed partners are denoted with an overbar. For each orbital, we can then define the set of operators (the j_i label will be suppressed):

$$S^+_i = \sum_{m_i>0} a^\dagger_{m_i} a^\dagger_{\bar{m}_i}, \quad S^-_i = \left(S^+_i\right)^\dagger = \sum_{\bar{m}_i>0} a^{\bar{m}_i} a^{m_i} \tag{2.1a}$$

$$S^z_i = \frac{1}{2}\left(\sum_{m_i>0} a^\dagger_{m_i} a^{m_i} + a^\dagger_{\bar{m}_i} a^{\bar{m}_i} - \frac{1}{2}\Omega_i\right) = \frac{1}{2}\hat{n}_i - \frac{1}{4}\Omega_i \tag{2.1b}$$

The operator $\hat{n}_i$ counts the number of fermions in state i, and has eigenvalues n_i. For each i, the three operators close the Lie algebra $\mathfrak{su}(2)$. Taken as a whole, the structure constants of $\bigoplus_{i=1}^N \mathfrak{su}(2)_i$, are easily verified:

$$[S^z_i, S^\pm_j] = \pm\delta_{ij} S^\pm_i \tag{2.2}$$

$$[S^+_i, S^-_j] = 2\delta_{ij} S^z_i. \tag{2.3}$$

Irreducible representations (irreps) of this algebra carry $SU(2) \supset U(1)$ labels

$$|d_i, \mu_i\rangle = \left|\frac{1}{4}\Omega_i - \frac{1}{2}v_i,\ \frac{1}{2}n_i - \frac{1}{4}\Omega_i\right\rangle \tag{2.4}$$

where v_i is the *seniority* of state i.

2.2 Integrability

2.2.1 Definitions

We consider a system to be integrable if there are as many linearly independent commuting quantities as there are degrees of freedom. This is to be contrasted with the classical case (see ref. [Arn89]). A classical system with a $2N$-dimensional phase space is integrable, in the Liouville sense, provided N independent functions H_i in involution (their Poisson brackets vanish),

$$\{H_i, H_j\} = \sum_{k=1}^{N} \left(\frac{\partial H_i}{\partial q_k}\frac{\partial H_j}{\partial p_k} - \frac{\partial H_i}{\partial p_k}\frac{\partial H_j}{\partial q_k} \right) = 0. \tag{2.5}$$

Liouville's theorem[1] then ensures that the system is then integrable by quadratures. A set of *action-angle* variables $(\mathbf{I}, \varphi)$ may be constructed in which the dynamics are trivial

$$\frac{d\mathbf{I}}{dt} = 0 \ , \quad \frac{d\varphi}{dt} = \omega, \tag{2.6}$$

and the system is essentially solved. There is unfortunately no "quantum analogue" of Liouville's theorem. Provided with a set of commuting quantities, there is no recipe to obtain their spectrum. The construction we will present is built upon a Lie algebra. For historical reasons, these types of models are referred to as Richardson-Gaudin (RG) Hamiltonians, or are said to be RG integrable. The RG version of integrability is now mature and well understood enough to be presented constructively rather than in a "this seems to work for some reason" manner.

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[1] There are too many *important* theorems that are referred to as "Liouville's theorem". It is always understood from context, but the author feels it would be helpful to distinguish them. Also, Liouville deserves a lot of credit both in complex analysis and mathematical physics.

2.2.2 Gaudin Algebra

We start with the Lie algebra $\mathfrak{su}(2)$, which has 3 elements $\{S^x, S^y, S^z\}$. The commutation relations are conveniently summarized

$$[S^a, S^b] = i\epsilon_{abc}S^c \tag{2.7}$$

with i the imaginary unit and the Levi-Civita symbol, ϵ_{abc}, is 1 if abc is an even permutation of xyz, -1 if abc is an odd permutation of xyz and zero otherwise. With these symbols, we can define a new Lie algebra where each generator depends on a complex number. The new generators are labelled $\{\mathbb{S}^x(u), \mathbb{S}^y(u), \mathbb{S}^z(u)\}$ with $u \in \mathbb{C}$. The defining relations of the (generalized) Gaudin algebra are [Gau76, OSDR05]:

$$[\mathbb{S}^x(u), \mathbb{S}^y(v)] = i(Y(u,v)\mathbb{S}^z(u) - X(u,v)\mathbb{S}^z(v)) \tag{2.8}$$

$$[\mathbb{S}^y(u), \mathbb{S}^z(v)] = i(Z(u,v)\mathbb{S}^x(u) - Y(u,v)\mathbb{S}^x(v)) \tag{2.9}$$

$$[\mathbb{S}^z(u), \mathbb{S}^x(v)] = i(X(u,v)\mathbb{S}^y(u) - Z(u,v)\mathbb{S}^y(v)) \tag{2.10}$$

$$[\mathbb{S}^a(u), \mathbb{S}^a(v)] = 0 \tag{2.11}$$

with X, Y, Z complex functions which are antisymmetric in their arguments, i.e. $X(u,v) = -X(v,u)$. Consistency of the algebra with the Jacobi identities requires that these amplitudes satisfy a set of classical Yang-Baxter equations:

$$X(u,v)Y(v,w) + Y(w,u)Z(u,v) + Z(v,w)X(w,u) = 0. \tag{2.12}$$

In general, the solutions are [Gau76]:

XXX: rational

$$X(u,v) = Y(u,v) = Z(u,v) = \frac{1}{u-v} \tag{2.13}$$

XXZ: trigonometric/hyperbolic

$$X(u,v) = Y(u,v) = \frac{1}{\sin(u-v)}, \quad Z(u,v) = \cot(u-v) \tag{2.14}$$

$$X(u,v) = Y(u,v) = \frac{1}{\sinh(u-v)}, \quad Z(u,v) = \coth(u-v) \tag{2.15}$$

XYZ: elliptic

$$X(u,v) = \mathrm{cs}(u-v), \quad Y(u,v) = \mathrm{ds}(u-v), \quad Z(u,v) = \mathrm{ns}(u-v) \tag{2.16}$$

In the XYZ case, the amplitudes are defined in terms of Jacobi elliptic functions.

If we were to construct the analogue of the Casimir operator for $\mathfrak{su}(2)$, i.e. S^2,

$$\mathbb{S}^2(u) = \mathbb{S}^x(u)\mathbb{S}^x(u) + \mathbb{S}^y(u)\mathbb{S}^y(u) + \mathbb{S}^z(u)\mathbb{S}^z(u), \tag{2.17}$$

it is easily verified that $[\mathbb{S}^2(u), \mathbb{S}^2(v)] = 0$ for arbitrary choices of the complex parameters. This means that we can construct an arbitrary number of commuting quantities by making specific choices of u. The most elegant approach consists of finding the eigenvectors of $\mathbb{S}^2(u)$ before making any choices. Integrable models are then constructed by choosing a set of values $u = \{\varepsilon_i\}$. $\mathbb{S}^2$ has simple poles whenever $u \to \varepsilon_i$, and conserved quantities result from the corresponding residues, along with their eigenvalues. Any "Hamiltonian" to be constructed can thus be solved by diagonalizing $\mathbb{S}^2(u)$. Unfortunately this approach is not as instructive, so we will make an arbitrary choice of u, then show that we obtain a Hamiltonian we want before diagonalizing it.

Before proceeding with the rational model a note on the Yang-Baxter equations are in order. In Gaudin's original paper[Gau76] an inspired choice of operators is presented. Gaudin considered the set of objects

$$H_j = \sum_{k \neq j} X(u_j, u_k) S^x_j S^x_k + Y(u_j, u_k) S^y_j S^y_k + Z(u_j, u_k) S^z_j S^z_k \tag{2.18}$$

and forcing $[H_i, H_j] = 0$ yields precisely the classical Yang-Baxter equations (2.12).

We'll restrict ourselves to the isotropic, XXX case, where it is more convenient to work in the basis

$$S^{\pm} = S^x \pm i S^y. \tag{2.19}$$

To express the Gaudin algebra explicitly, we employ a set of N discrete copies of an $\mathfrak{su}(2)$ algebra. Specifically, this means we are working with $\bigoplus_{i=1}^N \mathfrak{su}(2)_i$ with structure constants given by Eqs. (2.2, 2.3). Each copy carries a real number ε_i, and we make the specific choice:

$$\mathbb{S}^+(u) = \sum_{i=1}^N \frac{S^+_i}{u - \varepsilon_i}, \quad \mathbb{S}^-(u) = \sum_{i=1}^N \frac{S^-_i}{u - \varepsilon_i}, \quad \mathbb{S}^z(u) = \frac{1}{g} - \sum_{i=1}^N \frac{S^z_i}{u - \varepsilon_i} \tag{2.20}$$

where g is a constant real number. Explicitly $\mathbb{S}^2(u)$ becomes:

$$\mathbb{S}^2(u) = \frac{1}{g^2} - \frac{2}{g}\sum_{j=1}^{N} \frac{S^z_j}{u-\varepsilon_j} + \frac{1}{2}\sum_{jk} \frac{S^+_j S^-_k + S^-_j S^+_k + 2S^z_j S^z_k}{(u-\varepsilon_j)(u-\varepsilon_k)} \tag{2.21}$$

Now, $\mathbb{S}^2(u)$ has poles wherever u coincides with one of $\{\varepsilon_i\}$ with residue

$$\hat{R}_i = -\frac{2S^z_i}{g} + \sum_{j\neq i} \frac{1}{\varepsilon_i - \varepsilon_j}\left(S^+_i S^-_j + S^-_i S^+_j + 2S^z_i S^z_j\right) \tag{2.22}$$

and we can rescale the number g to obtain what are called "conserved charges" [CRS97]:

$$\hat{R}_i = S^z_i - g\sum_{j\neq i} \frac{1}{\varepsilon_i - \varepsilon_j}\left(S^+_i S^-_j + S^-_i S^+_j + 2S^z_i S^z_j\right). \tag{2.23}$$

Any linear combination of the conserved charges can be considered a "Hamiltonian" and is exactly solvable by construction. The choice

$$\sum_{i=1}^{N} \varepsilon_i \hat{R}_i = \sum_{i=1}^{N} \varepsilon_i S^z_i - g\sum_{ij} S^+_i S^-_j + cte = \hat{H}_{BCS} + cte \tag{2.24}$$

yields the reduced BCS Hamiltonian (plus some constant). To show that this is in fact the reduced BCS Hamiltonian, we need to use a specific representation of $\mathfrak{su}(2)$ introduced in the previous section. With the quasi-spin representation, we obtain

$$\hat{H}_{BCS} = \frac{1}{2}\sum_{i=1}^{N} \varepsilon_i \hat{n}_i - g\sum_{ij} S^+_i S^-_j \tag{2.25}$$

which is, up to a constant, the expression above. It is convenient to work with a Hamiltonian that is expressible in terms of the $\mathfrak{su}(2)$ generators, but it may be instructive to keep the explicit form in terms of electron pairs in mind.

2.3 Reduced BCS Hamiltonian: Bethe Ansatz

Eigenvectors of the reduced BCS Hamiltonian are constructed as products of $\mathfrak{su}(2)$ quasiparticles delocalized over the spectrum of single-particle states. We use the raising operators of the Gaudin algebra. Since $\mathbb{S}^2(u)$ commutes with S^z, eigenvectors have good particle number, and may be constructed as [Ric63, RS64, Gau76]:

$$|\{\lambda\}\rangle \equiv \prod_{a=1}^{N_P} \mathbb{S}^+(\lambda_a) \, |\theta\rangle \tag{2.26}$$

The numbers $\{\lambda\}$ are referred to by various names "rapidities" or "quasi-momenta" or "pair energies". We will henceforth use the name rapidities. The *pseudovacuum* $|\theta\rangle$ is chosen as a lowest weight state, i.e. so that

$$\mathbb{S}^-(u) \, |\theta\rangle = 0, \quad \forall u \in \mathbb{C}. \tag{2.27}$$

In terms of the quasi-spin representation, this is just the state

$$|\theta\rangle = \bigotimes_{i=1}^{N} |d_i, -d_i\rangle \tag{2.28}$$

which is either empty or has a single electron at every site. The easiest case is a physical vacuum, i.e. empty at every site.

It is to be emphasized that this construction relies *only on the structure* $\mathfrak{su}(2)$

and hence does not rely on a specific representation. We could also consider the spin representation:

$$S_i^+ = a^\dagger_{i\frac{1}{2}} a^{i-\frac{1}{2}}, \;\; S_i^- = a^\dagger_{i-\frac{1}{2}} a^{i\frac{1}{2}}, \;\; S_i^z = \frac{1}{2}(a^\dagger_{i\frac{1}{2}} a^{i\frac{1}{2}} - a^\dagger_{-i\frac{1}{2}} a^{i-\frac{1}{2}}) \tag{2.29}$$

with the only relevant distinctions that the Hamiltonian is no longer the reduced BCS Hamiltonian, and the pseudovacuum is the ferromagnetic vacuum, i.e. fully polarized spins in one direction.

We now describe the eigenvectors of the reduced BCS Hamilton with a brute force approach. Act with the Hamiltonian (2.25) on the state (2.26), moving the Hamiltonian to the right until it acts on the vacuum with result

$$\hat{H}_{BCS} \left|\theta\right\rangle = \frac{1}{2}\sum_{i=1}^{N} \varepsilon_i v_i. \tag{2.30}$$

Computing commutators of the Hamiltonian with the raising operators yields:

$$[\hat{H}_{BCS}, \mathbb{S}^+(\lambda_1)] = \lambda_1 \mathbb{S}^+(\lambda_1) - \sum_{i=1}^{N} S_i^+ \left(1 - 2g\sum_{j=1}^{N} \frac{S_j^z}{\lambda_1 - \varepsilon_j}\right) \tag{2.31}$$

$$[[\hat{H}_{BCS}, \mathbb{S}^+(\lambda_1)], \mathbb{S}^+(\lambda_2)] = \frac{2g}{\lambda_2 - \lambda_1}\sum_{i=1}^{N} S_i^+ \left(\mathbb{S}^+(\lambda_1) - \mathbb{S}^+(\lambda_2)\right) \tag{2.32}$$

with any higher commutators vanishing identically. We can thus write the result:

$$\begin{aligned}\hat{H}_{BCS}\left|\{\lambda\}\right\rangle &= \sum_{a=1}^{N_P}\sum_{b=a+1}^{N_P}\prod_{c\neq a,b}\mathbb{S}^+(\lambda_c)[[\hat{H}_{BCS},\mathbb{S}^+(\lambda_a)],\mathbb{S}^+(\lambda_b)]\left|\theta\right\rangle \\ &+\sum_{a=1}^{N_P}\prod_{c\neq a}\mathbb{S}^+(\lambda_c)[\hat{H}_{BCS},\mathbb{S}^+(\lambda_a)]\left|\theta\right\rangle \\ &+\prod_{c}\mathbb{S}^+(\lambda_c)\hat{H}_{BCS}\left|\theta\right\rangle \end{aligned} \tag{2.33}$$

and this can be rearranged to yield:

$$\hat{H}_{BCS}\left|\{\lambda\}\right\rangle = E\left|\{\lambda\}\right\rangle + \sum_{i=1}^{N} S_i^+ \sum_{a=1}^{N_P}\Lambda(\lambda_a)\prod_{b\neq a}\mathbb{S}^+(\lambda_b)\left|\theta\right\rangle. \tag{2.34}$$

The result is now easily understood: the state $\left|\{\lambda\}\right\rangle$ is an eigenvector of $\hat{H}_{BCS}$ with eigenvalue

$$E = \sum_{a=1}^{N_P}\lambda_a + \frac{1}{2}\sum_{i=1}^{N}\varepsilon_i v_i \tag{2.35}$$

provided that the *unwanted terms* in Eq. (2.34) vanish. Since the pseudovacuum is defined such that

$$S_j^z\left|\theta\right\rangle = -d_j\left|\theta\right\rangle, \tag{2.36}$$

we have a set of non-linear equations, originally obtained by Richardson and hence named Richardson's equations:

$$\Lambda(\lambda_a) = -\frac{1}{g} - 2\sum_{i=1}^{N}\frac{d_i}{\lambda_a-\varepsilon_i} + 2\sum_{b\neq a}\frac{1}{\lambda_a-\lambda_b} = 0. \tag{2.37}$$

Solving Richardson's equations numerically is the subject of the next section, but before proceeding some comments on the Bethe Ansatz are warranted. The theme of any method termed "Bethe Ansatz" is to assume that eigenvectors may be expressed in terms of quasi-particles parametrized in terms of some complex amplitudes (see [Gau14]). Consistency requirements of the amplitudes are expressed in terms of non-linear equations. The approach presented here is constructed upon a Lie algebra but more general constructions are possible. The Quantum Inverse Scattering Method (QISM) (see for example, [TF79] entirely developed by the Leningrad/St. Petersburg school of Faddeev is based upon the structure of a quantum group (which is essentially a Hopf algebra which is neither commutative or cocommutative). The integrability is ensured by a set of quantum Yang-Baxter equations. A "generating function" (called the transfer matrix) for any possible Hamiltonian is diagonalized by the Algebraic Bethe Ansatz (ABA). Hamiltonians diagonalized in this manner are generally one-dimensional nearest neighbour interactions such as Heisenberg models, the Hubbard model, the t-J model etc. There is an intimate connection with models of classical two-dimensional statistical mechanics (for which ref. [Bax07] is definitive) and the name *transfer matrix* is meant to emphasize this connection. For example, the XXX and XXZ Heisenberg models are related to the six vertex model of statistical mechanics [Lie67a, Lie67b, Lie67c], while the XYZ Heisenberg model is related to the eight vertex model [Bax72, Bax73a, Bax73b, Bax73c].

Taking the (unfortunately named) quasi-classical limit of the ABA recovers RG results. Specifically, the machinery behind the XXX and XXZ Heisenberg models yields the XXX and XXZ Richardson-Gaudin models in the quasi-classical limit.

2.4 Richardson's Equations

We need to have a reliable numerical algorithm to solve Richardson's equations as we will need to do so to evaluate the energy. Unfortunately, the most naive approach involves a finite difference gradient calculation, which will require one solution for every degree of freedom in the system at each iteration. There are many approaches in the literature, so for convenience we use that of De Baerdemacker [DB12], and we will summarize the main points in this section. The approach involves deforming the quasi-spin algebra until it breaks, resulting in genuine bosonic commutation relations. This limit is easily diagonalized, and the interaction may be turned on adiabatically until it is the physical value we desire. Other approaches in the literature involve a change of variables [RVND04], or exploiting the correspondence with orthogonal polynomials [EAGF12].

The present approach depends upon the ability to stretch the structure constants of the quasi-spin representation $\mathfrak{su}(2)$ where they represent pairs of fermions until we reach the harmonic oscillator Lie algebra, $hw(1)$, where the particles are genuine bosons. To accomplish this, we introduce a parameter ξ which varies between zero and one. The operators will in some way depend on this parameter, and the resulting structure constants are:

$$[S^z_i(\xi), S^{\pm}_j(\xi)] = \pm\delta_{ij} S^{\pm}_i(\xi), \quad [S^+_i(\xi), S^-_j(\xi)] = \delta_{ij}\left(2\xi S^z_i(\xi) + \frac{1}{2}(\xi - 1)\Omega_i\right) \tag{2.38}$$

When $\xi = 1$, this is clearly just $\mathfrak{su}(2)$ as above. When $\xi = 0$, label the objects as

$$b_i = \sqrt{\frac{2}{\Omega_i}} S^-_i(0), \quad b^{\dagger}_i = \sqrt{\frac{2}{\Omega_i}} S^+_i(0) \tag{2.39}$$

and the commutation relations become:

$$[b_i, b_j^\dagger] = \delta_{ij} \tag{2.40}$$

which corresponds to individual bosons. The Cartan element $S_i^z(\xi)$ is ξ-independent,

$$S_i^z(\xi) = \frac{1}{2}\hat{n}_i - \frac{1}{4}\Omega_i \tag{2.41}$$

while the other operators are ξ-dependent. For any $0 < \xi \leq 1$, the raising and lowering operators can be renormalized to:

$$A_i^\pm(\xi) = \frac{1}{\sqrt{\xi}} S_i^\pm(\xi). \tag{2.42}$$

Define $2A_i^z(\xi) = [A_i^+(\xi), A_i^-(\xi)]$; we can evaluate directly

$$\begin{aligned}
[A_i^+(\xi), A_j^-(\xi)] &= \frac{1}{\xi}[S_i^+(\xi), S_j^-(\xi)] \\
&= \delta_{ij}\left(2S_i^z(\xi) + \frac{1}{2}\left(1 - \frac{1}{\xi}\right)\Omega_i\right) \qquad (2.43)
\end{aligned}$$

giving

$$\begin{aligned}
A_i^z(\xi) &= S_i^z(\xi) + \frac{1}{4}\left(1 - \frac{1}{\xi}\right)\Omega_i \qquad (2.44)\\
&= \frac{1}{2}\hat{n}_i - \frac{1}{4\xi}\Omega_i. \qquad (2.45)
\end{aligned}$$

We can verify that in this renormalized basis, $\mathfrak{su}(2)$ structure constants are recovered.

$$[A^z_i(\xi), A^{\pm}_j(\xi)] = \pm\delta_{ij}A^{\pm}_i(\xi), \quad [A^+_i(\xi), A^-_j(\xi)] = 2\delta_{ij}A^z_i(\xi) \tag{2.46}$$

What does this accomplish? A rough physical interpretation of the deformation ξ follows from acting with the Cartan element $A^z_i(\xi)$ on the lowest weight state $|d_i(\xi), -d_i(\xi)\rangle$. It follows that

$$d_i(\xi) = \frac{1}{4\xi}\Omega_i - \frac{1}{2}v_i. \tag{2.47}$$

This means that as $\xi \to 0$, the effective degeneracy of the state i increases. The renormalized structure is only valid for $\xi > 0$, but in the limit $\xi = 0$ it is easily observed that the degeneracy is infinite, or that the state is bosonic. This physical interpretation is only strictly valid if

$$\xi = \frac{1}{1+\frac{2k}{\Omega_i}} \tag{2.48}$$

for some positive integer k.

Now that we have an algebraic structure in the three cases $\xi = 1$, $0 < \xi \leq 1$, and $\xi = 0$, let's look at the Hamiltonian $\hat{H}_{BCS}(\xi)$ in the three cases. The first case we already know. The second case follows from the deformed Hamiltonian

$$\hat{H}_{BCS}(\xi) = \frac{1}{2}\sum^N_{i=1}\varepsilon_i\hat{n}_i - g\sum_{ij}S^+_i(\xi)S^-_j(\xi) \tag{2.49}$$

which can be diagonalized with the Bethe ansatz

$$|\{\lambda(\xi)\}\rangle = \prod_{a=1}^{N_P} \left(\sum_{i=1}^{N} \frac{S_i^+(\xi)}{\lambda(\xi) - \varepsilon_i} \right) |\theta\rangle . \tag{2.50}$$

The pseudo-vacuum is similarly defined

$$|\theta\rangle = \bigotimes_{i=1}^{N} |d_i(\xi), -d_i(\xi)\rangle . \tag{2.51}$$

In an approach similar to above, we could act with the Hamiltonian (2.49) on the state (2.51) and move (2.49) to the right until it acts on the pseudo-vacuum. However, if we just substitute eq. (2.42) in the Hamiltonian (2.49)

$$\hat{H}_{BCS}(\xi) = \frac{1}{2} \sum_{i=1}^{N} \varepsilon_i \hat{n}_i - g\xi \sum_{ij} A_i^+(\xi) A_j^-(\xi), \tag{2.52}$$

which is equivalent to the reduced BCS Hamiltonian with the scaled interaction $g\xi$. Thus (2.51) is an eigenvector of (2.49) provided that the rapidities satisfy the non-linear equations

$$\Lambda(\lambda_a, \xi) = -\frac{1}{g} - 2 \sum_{i=1}^{N} \frac{\xi d_i(\xi)}{\lambda_a - \varepsilon_i} + 2\xi \sum_{b \neq a} \frac{1}{\lambda_a - \lambda_b} = 0. \tag{2.53}$$

This construction is not valid when $\xi = 0$, so this case must be treated separately. The BCS Hamiltonian in the contraction limit becomes:

$$\hat{H}_{BCS}(0) = \sum_{ij}^{N} \left(\delta_{ij} \varepsilon_i - \frac{1}{2} g \sqrt{\Omega_i \Omega_j} \right) b_i^\dagger b_j + \sum_{i=1}^{N} \varepsilon_i v_i. \tag{2.54}$$

This is a bosonic one-body Hamiltonian which may be diagonalized by a unitary transformation

$$b_i^\dagger \to \mathfrak{b}_i^\dagger = \sum_{k=1}^{N} U_i^k b_k^\dagger \tag{2.55}$$

so that

$$\hat{H}_{BCS}(0) = \sum_{k=1}^{N} \hbar\omega_k \mathfrak{b}_k^\dagger \mathfrak{b}_k + \sum_{i=1}^{N} \varepsilon_i v_i. \tag{2.56}$$

The harmonic modes $\hbar\omega_k$ are the roots of

$$-\frac{1}{g} - \frac{1}{2}\sum_{i=1}^{N} \frac{\Omega_i}{\hbar\omega - \varepsilon_i} = 0. \tag{2.57}$$

We now turn to the near-contraction limit, i.e. for $\xi \ll 1$. First assume that the response of the rapidities can be written:

$$\lambda_\alpha(\xi) = \hbar\omega_{k(\alpha)} + \sqrt{\xi}\lambda_\alpha^{(1)} + \mathcal{O}(\xi) \tag{2.58}$$

Here the notation is more complicated than the concept: $k(\alpha)$ notes which ω is to be used. The first order change $\lambda_\alpha^{(1)}$ is obtained by plugging (2.58) into (2.53) and collecting terms proportional to $\sqrt{\xi}$.

$$\begin{aligned} -\frac{1}{g} + \sum_{i=1}^{N} \frac{\xi v_i - \frac{1}{2}\Omega_i}{\hbar\omega_{k(\alpha)} + \sqrt{\xi}\lambda_\alpha^{(1)} - \varepsilon_i} + 2\sqrt{\xi} \sum_{\substack{b\neq\alpha \\ k(b)=k(\alpha)}} \frac{1}{\lambda_\alpha^{(1)} - \lambda_b^{(1)}} \\ + 2\xi \sum_{\substack{b\neq\alpha \\ k(b)\neq k(\alpha)}} \frac{1}{\hbar\omega_{k(\alpha)} - \hbar\omega_{k(b)} + \sqrt{\xi}(\lambda_\alpha^{(1)} - \lambda_b^{(1)})} = 0 \end{aligned} \tag{2.59}$$

Since $\xi \approx 0$, a Taylor expansion is appropriate

$$-\frac{1}{g} + \sum_{i=1}^{N} \frac{\xi v_i - \frac{1}{2}\Omega_i}{\hbar\omega_{k(\alpha)} - \varepsilon_i} \left(1 - \frac{\sqrt{\xi}\lambda_\alpha^{(1)}}{\hbar\omega_{k(\alpha)} - \varepsilon_i}\right) + 2\sqrt{\xi} \sum_{\substack{b\neq\alpha \\ k(b)=k(\alpha)}} \frac{1}{\lambda_\alpha^{(1)} - \lambda_b^{(1)}}$$
$$+ 2\xi \sum_{\substack{b\neq\alpha \\ k(b)\neq k(\alpha)}} \frac{1}{\hbar\omega_{k(\alpha)} - \hbar\omega_{k(b)}} \left(1 - \frac{\sqrt{\xi}(\lambda_\alpha^{(1)} - \lambda_b^{(1)})}{\hbar\omega_{k(\alpha)} - \hbar\omega_{k(b)}}\right) = 0 \tag{2.60}$$

and we can collect terms in powers of ξ

$$-\frac{1}{g} - \frac{1}{2}\sum_{i=1}^{N} \frac{\Omega_i}{\hbar\omega_{k(\alpha)} - \varepsilon_i} \left(1 - \frac{\sqrt{\xi}\lambda_\alpha^{(1)}}{\hbar\omega_{k(\alpha)} - \varepsilon_i}\right) + 2\sqrt{\xi} \sum_{\substack{b\neq\alpha \\ k(b)=k(\alpha)}} \frac{1}{\lambda_\alpha^{(1)} - \lambda_b^{(1)}} + \mathcal{O}(\xi) = 0 \tag{2.61}$$

The first two terms are precisely Eq. (2.57), and hence vanish. The remaining $\mathcal{O}(\xi)$ terms give

$$c_k \lambda_\alpha^{(1)} = -2 \sum_{b\neq\alpha} \frac{1}{\lambda_\alpha^{(1)} - \lambda_b^{(1)}} \tag{2.62}$$

where

$$c_k = \frac{1}{2}\sum_{i=1}^{N} \frac{\Omega_i}{(\hbar\omega_{k(\alpha)} - \varepsilon_i)^2} \tag{2.63}$$

The summation in eq. (2.62) only goes over terms originating from the same $\hbar\omega$. The resulting equations are decoupled for $k(\alpha) \neq k(b)$ and hence may be solved independently. Only bosonic states that are multiply occupied need to be considered here since otherwise it is easily observed that $\lambda^{(1)} = 0$. Equation (2.62) can be solved for the first-order responses with a clever construction known as the Heine-Stieltjes correspondence. Define a polynomial $P(x)$ with roots the first-order responses

$$P(x) = \prod_{a=1}^{\nu} (x - \lambda_a^{(1)}) \tag{2.64}$$

with ν the number of bosons assigned to the corresponding $\hbar\omega$. The derivatives of $P(x)$ are easily shown to be:

$$P'(x) = \sum_{a=1}^{\nu} \prod_{b \neq a} (x - \lambda_b^{(1)}), \quad P'(\lambda_\alpha^{(1)}) = \prod_{b \neq \alpha} (\lambda_\alpha^{(1)} - \lambda_b^{(1)}) \tag{2.65}$$

$$P''(x) = \sum_{\substack{a=1 \\ b \neq a}}^{\nu} \prod_{c \neq a,b} (x - \lambda_c^{(1)}), \quad P''(\lambda_\alpha^{(1)}) = 2 \sum_{b \neq \alpha} \prod_{c \neq \alpha, b} (\lambda_\alpha^{(1)} - \lambda_c^{(1)}) \tag{2.66}$$

and without too much effort:

$$\frac{P''(\lambda_\alpha^{(1)})}{P'(\lambda_\alpha^{(1)})} = \sum_{b \neq \alpha} \frac{2}{\lambda_\alpha^{(1)} - \lambda_b^{(1)}}. \tag{2.67}$$

Eq. (2.62) then becomes

$$c_k \lambda_\alpha^{(1)} P'(\lambda_\alpha^{(1)}) + P''(\lambda_\alpha^{(1)}) = 0. \tag{2.68}$$

The left hand side is a polynomial of the same degree as $P(x)$ with the same roots, which means that they are identical up to a scaling factor. Comparing the leading terms of the two polynomials shows that the constant is $c_k \nu$, and we obtain the ODE

$$P''(x) + c_k x P'(x) - c_k \nu P(x) = 0. \tag{2.69}$$

Rescaling the variable $x = i\sqrt{\frac{2}{c_k}}z$ yields Hermite's equation

$$H''(z) - 2zH'(z) + 2\nu H(z) = 0 \tag{2.70}$$

for which the roots may be obtained.

The result is that near the contraction limit, the rapidities are

$$\lambda_\alpha(\xi) = \hbar\omega_{k(\alpha)} + i\sqrt{\frac{2\xi}{c_{k(\alpha)}}}z_{\nu_{k(\alpha)},l(\alpha)} + \mathcal{O}(\xi). \tag{2.71}$$

$z_{\nu,l}$ is the l-th root of the ν-th Hermite polynomial $H_\nu(z)$. The label $l(\alpha)$ is to ensure that distinct rapidities evolving from identical $\hbar\omega$'s are given distinct Hermite roots.

We now have a set of rapidities which satisfy Richardson's equations with a scaled interaction $g\xi$ for very small ξ. The strategy is now to increase ξ slowly until $\xi = 1$ while at each step solving the non-linear equations (2.53) with Newton's method. That is, provided a set $\boldsymbol{\lambda}_{n-1} = \{\lambda\}$ of rapidities at some scaling $0 < \xi < 1$, the next set $\boldsymbol{\lambda}_n$ is obtained by solving the system of equations

$$\frac{\partial\Lambda(\boldsymbol{\lambda}_{n-1},\xi)}{\partial\boldsymbol{\lambda}_{n-1}}(\boldsymbol{\lambda}_n - \boldsymbol{\lambda}_{n-1}) = -\Lambda(\boldsymbol{\lambda}_{n-1}). \tag{2.72}$$

The elements of the Jacobian are:[2]

$$\frac{\partial\Lambda(\lambda_a,\xi)}{\partial\lambda_b} = \begin{cases} -\sum_{i=1}^{N}\frac{\xi v_i - \frac{1}{2}\Omega_i}{(\lambda_a-\varepsilon_i)^2} - 2\xi\sum_{c\neq a}\frac{1}{(\lambda_a-\lambda_c)^2} & a = b \\ \frac{2\xi}{(\lambda_a-\lambda_b)^2} & a \neq b \end{cases} \tag{2.73}$$

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[2] Since Λ is a function of complex variables we should check Cauchy-Riemann conditions to ensure that differentiation is valid. A tedious exercise confirms this assumption.

2.5 Scalar Products

2.5.1 Slavnov's Theorem

To employ the state $|\{\lambda\}\rangle$ as a variational ansatz we need to be able to evaluate the energy functional

$$E[\{\varepsilon\}, g] = \min_{\{\varepsilon\},g} \frac{\langle\{\lambda\}|\hat{H}_C|\{\lambda\}\rangle}{\langle\{\lambda\}|\{\lambda\}\rangle} \tag{2.74}$$

with a reasonable cost. The free parameters are the set of single particle energies $\{\varepsilon\}$ and the pairing strength g. Given that one of the free parameters will define the energy scale, we keep the pairing strength fixed. If we were to expand the state $|\{\lambda\}\rangle$ in terms of configurations we would find a combinatorial sum

$$|\{\lambda\}\rangle = \sum_{\omega} \left(\sum_{\sigma} \prod_{\alpha=1}^{N_P} \frac{1}{\lambda_\alpha - \varepsilon_{\omega_{\sigma(\alpha)}}} \right) \prod_{a=1}^{N_P} S^+_{\omega_a} |\theta\rangle \tag{2.75}$$

where the inner sum is taken over all permutations σ, and ω labels a set of doubly-occupied spatial orbitals. There are $\binom{N}{N_P}$ configurations ω. Individually the permanents in this expression (the bracketed terms) may be expressed as a ratio of determinants due to Borchardt's theorem, so a projected approach is certainly possible. More structure is required for a variational approach however. The key result for deriving the norm and reduced density matrices is Slavnov's theorem. The scalar product between two states $|\{\lambda\}\rangle$ and $|\{\mu\}\rangle$, where at least one set of rapidities satisfies Richardson's equations may be written as a single determinant of size N_P. Explicitly, for the present case with $\{\lambda\}$ a solution of Richardson's equations and $\{\mu\}$

arbitrary [Sla89, ZLMG02],

$$\langle\{\lambda\}|\{\mu\}\rangle = \frac{\prod_{a\neq b}(\lambda_b-\mu_a)}{\prod_{b<a}(\mu_b-\mu_a)\prod_{a<b}(\lambda_b-\lambda_a)}\det J\left(\{\mu\},\{\lambda\}\right), \tag{2.76}$$

where the elements of the matrix J are

$$J_{ab} = \frac{\lambda_b-\mu_b}{\lambda_a-\mu_b}\left(\sum_{i=1}^{N}\frac{1}{(\lambda_a-\varepsilon_i)(\mu_b-\varepsilon_i)} - 2\sum_{c\neq a}\frac{1}{(\lambda_a-\lambda_c)(\mu_b-\lambda_c)}\right). \tag{2.77}$$

2.5.2 Norm

The norm of the state $|\{\lambda\}\rangle$ is obtained by taking the limit $\{\mu\}\to\{\lambda\}$:

$$\langle\{\lambda\}|\{\lambda\}\rangle = \lim_{\{\mu\}\to\{\lambda\}}\langle\{\lambda\}|\{\mu\}\rangle \tag{2.78}$$

Thus, we can express it as the single determinant:

$$\langle\{\lambda\}|\{\lambda\}\rangle = \det G \tag{2.79}$$

with the elements of the so-called Gaudin matrix

$$G_{ab} = \begin{cases} \sum_{i=1}^{N}\frac{1}{(\lambda_a-\varepsilon_i)^2} - 2\sum_{c\neq a}^{N_P}\frac{1}{(\lambda_a-\lambda_c)^2} & a=b \\ \frac{2}{(\lambda_a-\lambda_b)^2} & a\neq b \end{cases}. \tag{2.80}$$

It is worth noting that the elements of the Gaudin matrix are partial derivatives of Richardson's equations

$$G_{ab} = \frac{\partial \Lambda(\lambda_a)}{\partial \lambda_b}. \tag{2.81}$$

We can now consider reduced density matrices by sandwiching operators between $\langle\{\lambda\}|$ and $|\{\mu\}\rangle$. The result can then be expressed in terms of contributions for which Slavnov's theorem is appropriate and the limit $\{\mu\} \to \{\lambda\}$ is then to be taken. Since $\langle\{\lambda\}|$ and $|\{\mu\}\rangle$ contain the same number of pairs, only operators which conserve the number of pairs will have non-vanishing contributions. Considering the quasi-spin representation, the only contributions to the 1-RDM are due to S^z_i, while the 2-RDM has contributions from $S^+_i S^-_j$ and $S^z_i S^z_j$. Practical expressions for these elements is due entirely to Faribault, Calabrese, and Caux, [FCC08, FCC10].

2.5.3 1-RDM

Given that we are working under a seniority zero assumption, the 1-RDM is doubly-degenerate or diagonal in a spatial basis, i.e.

$$\gamma_{i\frac{1}{2}} = \langle\{\lambda\}|a^{\dagger}_{i\frac{1}{2}} a^{i\frac{1}{2}}|\{\lambda\}\rangle = \gamma_{i-\frac{1}{2}} \tag{2.82}$$

and so we will simply label the 1-RDM with a single index. In the final energy expression we will scale the single particle contribution by the appropriate factor of two. The expectation value of S^z_i is

$$\begin{aligned}
\langle\{\lambda\}|S^z_i|\{\lambda\}\rangle &= \langle\{\lambda\}|\frac{1}{2}\left(a^\dagger_{i\frac{1}{2}}a^{i\frac{1}{2}} + a^\dagger_{i-\frac{1}{2}}a^{i-\frac{1}{2}} - 1\right)|\{\lambda\}\rangle \\
&= \frac{1}{2}\gamma_{i\frac{1}{2}} + \frac{1}{2}\gamma_{i-\frac{1}{2}} - \frac{1}{2}\langle\{\lambda\}|\{\lambda\}\rangle \\
&= \gamma_i - \frac{1}{2}\langle\{\lambda\}|\{\lambda\}\rangle \qquad (2.83)
\end{aligned}$$

To obtain an expression for $\langle\{\lambda\}|S^z_i|\{\lambda\}\rangle$ we will first evaluate $\langle\{\lambda\}|S^z_i|\{\mu\}\rangle$ and take the limit $\{\mu\} \to \{\lambda\}$. By observing

$$[S^z_i, \mathbb{S}^+(\mu)] = \sum_{k=1}^{N} \frac{[S^z_i, S^+_k]}{\mu - \varepsilon_k} = \frac{S^+_i}{\mu - \varepsilon_i}, \qquad (2.84)$$

the operator S^z_i can be moved to the right until it acts on the vacuum. The result is:

$$\langle\{\lambda\}|S^z_i|\{\mu\}\rangle = \sum_{a=1}^{N_P} \frac{1}{\mu_a - \varepsilon_i} \langle\{\lambda\}|S^+_i|\{\mu\}_a\rangle - \frac{1}{2}\langle\{\lambda\}|\{\mu\}\rangle. \qquad (2.85)$$

The notation $\{\mu\}_a$ denotes the set of μ with the a-th element left out. The crucial observation to make is that the local spin operator S^+_i is the residue of the simple pole of $\mathbb{S}^+(\mu)$ when $\mu \to \varepsilon_i$

$$S^+_i = \lim_{\mu\to\varepsilon_i}(\mu - \varepsilon_i)\mathbb{S}^+(\mu). \qquad (2.86)$$

This means that the form factor $\langle\{\lambda\}|S^+_i|\{\mu\}_a\rangle$ can be evaluated as the residue of the pole $\mu_a \to \varepsilon_i$ of the scalar product $\langle\{\lambda\}|\{\mu\}\rangle$ for which Slavnov's theorem, Eq.

(2.76), applies.

$$\langle\{\lambda\}|S^+_i|\{\mu\}_a\rangle = \lim_{\mu_a\to\varepsilon_i}(\mu_a-\varepsilon_i)\langle\{\lambda\}|\{\mu\}\rangle \tag{2.87}$$

The final result for the 1-RDM elements is

$$\gamma_i = \frac{1}{2}\left(1-\frac{2^{N_P}}{\|\{\lambda\}\|^2}\frac{\det(Q_i)}{\prod_{a=1}^{N_P}\prod_{b\neq a}(\lambda_a-\lambda_b)}\right) \tag{2.88}$$

where the matrix Q_i is defined:

$$(Q_i)_{ba} = \begin{cases} \prod_{c\neq a}(\lambda_c-\lambda_a)\left(\frac{1}{2}\sum_{k=1}^{N_{SP}}\frac{1}{(\varepsilon_k-\lambda_a)^2}-\sum_{d\neq a}\frac{1}{(\lambda_d-\lambda_a)^2}-\frac{1}{(\varepsilon_i-\lambda_a)^2}\right) & a=b \\ \prod_{c\neq a}(\lambda_c-\lambda_a)\left(\frac{1}{(\lambda_b-\lambda_a)^2}-\frac{1}{(\varepsilon_i-\lambda_b)^2}\right) & a\neq b \end{cases} \tag{2.89}$$

2.5.4 2-RDM

We proceed as in the previous section for the 1-RDM. There are two contributions to consider. The first is the *pair-correlation function* (D2P) $\mathfrak{P}_{ij}$:

$$\mathfrak{P}_{ij} \equiv \langle\{\lambda\}|a^\dagger_{i\frac{1}{2}}a^\dagger_{i-\frac{1}{2}}a^{j-\frac{1}{2}}a^{j\frac{1}{2}}|\{\lambda\}\rangle \tag{2.90}$$

$$= \langle\{\lambda\}|S^+_iS^-_j|\{\lambda\}\rangle \tag{2.91}$$

and the second is the *diagonal correlation function* (D2D) $\mathfrak{D}_{ij}$:

$$\mathfrak{D}_{ij} \equiv \langle\{\lambda\}|\left(\frac{1}{2}a^\dagger_{i\frac{1}{2}}a^{i\frac{1}{2}}+\frac{1}{2}a^\dagger_{i-\frac{1}{2}}a^{i-\frac{1}{2}}\right)\left(\frac{1}{2}a^\dagger_{j\frac{1}{2}}a^{j\frac{1}{2}}+\frac{1}{2}a^\dagger_{j-\frac{1}{2}}a^{j-\frac{1}{2}}\right)|\{\lambda\}\rangle \tag{2.92}$$

$$= \langle\{\lambda\}|S^z_iS^z_j|\{\lambda\}\rangle+\frac{1}{2}\gamma_i+\frac{1}{2}\gamma_j-\frac{1}{4}\langle\{\lambda\}|\{\lambda\}\rangle. \tag{2.93}$$

The strategy is again to move S^z_i and S^-_i to the right until they act on the vacuum. The results are:

$$\begin{aligned}\langle\{\lambda\}|S^+_i S^-_j|\{\mu\}\rangle &= \sum^{N_P}_{a=1} \frac{1}{\mu_a - \varepsilon_j} \langle\{\lambda\}|S^+_i|\{\mu\}_a\rangle \\ &- \sum^{N_P}_{a\neq b} \frac{1}{(\mu_a - \varepsilon_j)(\mu_b - \varepsilon_j)} \langle\{\lambda\}|S^+_i S^+_j|\{\mu\}_{a,b}\rangle \end{aligned} \tag{2.94}$$

and

$$\begin{aligned}\langle\{\lambda\}|S^z_i S^z_j|\{\mu\}\rangle &= \frac{1}{4}\langle\{\lambda\}|\{\mu\}\rangle + \sum^{N_P}_{a\neq b} \frac{\langle\{\lambda\}|S^+_i S^+_j|\{\mu\}_{a,b}\rangle}{(\mu_a - \varepsilon_i)(\mu_b - \varepsilon_j)} \\ &- \frac{1}{2}\sum^{N_P}_{a=1} \frac{1}{\mu_a - \varepsilon_i}\langle\{\lambda\}|S^+_i|\{\mu\}_a\rangle - \frac{1}{2}\sum^{N_P}_{a=1} \frac{1}{\mu_a - \varepsilon_j}\langle\{\lambda\}|S^+_j|\{\mu\}_a\rangle \end{aligned} \tag{2.95}$$

The form factors $\langle\{\lambda\}|S^+_i S^+_j|\{\mu\}_{a,b}\rangle$ may be evaluated similar to those above

$$\langle\{\lambda\}|S^+_i S^+_j|\{\mu\}_{a,b}\rangle = \lim_{\mu_a\rightarrow\varepsilon_i} \lim_{\mu_b\rightarrow\varepsilon_j} (\mu_a - \varepsilon_i)(\mu_b - \varepsilon_j)\langle\{\lambda\}|\{\mu\}\rangle\,. \tag{2.96}$$

The final results for the 2-RDM can be expressed as single sums of determinants:

$$\mathfrak{P}_{ij} = \sum^{N_P}_{q=1} \frac{\lambda_q - \varepsilon_i}{\lambda_q - \varepsilon_j} \det D^{(i,j)}_q \tag{2.97}$$

$$\mathfrak{D}_{ij} = -\frac{1}{2}\sum^{N_P}_{q=1}\left(\det D^{(i,j)}_q + \det D^{(j,i)}_q\right) + \frac{1}{2}(\gamma_i + \gamma_j) \tag{2.98}$$

The double sum of form factors is reduced by performing elementary column operations until the resulting matrices differ by a single column and hence may be combined into a single sum of determinants. The matrices D_q thus appear bizarre at first sight:

$$D_q^{(i,j)} = \begin{cases} \vec{G}_c - \frac{(\varepsilon_i-\lambda_c)(\lambda_q-\lambda_{c+1})}{(\varepsilon_i-\lambda_{c+1})(\lambda_q-\lambda_c)}\vec{G}_{c+1} & c < q-1 \\ \vec{G}_c + \frac{2(\varepsilon_j-\lambda_q)(\varepsilon_i-\lambda_{q-1})}{\lambda_{q-1}-\lambda_q}\vec{B} & c = q-1 \\ \vec{C} & c = q \\ \vec{G}_c & c > q \end{cases} \tag{2.99}$$

where $\vec{G}_c$ denotes the cth column of the Gaudin matrix Eq. (2.80), $\vec{B}$ is the column vector:

$$\vec{B}_k = \frac{(2\lambda_k - \varepsilon_i - \varepsilon_j)}{(\lambda_k - \varepsilon_i)^2(\lambda_k - \varepsilon_j)^2}, \tag{2.100}$$

and $\vec{C}$ is the column vector:

$$\vec{C}_k = \frac{1}{(\lambda_k - \varepsilon_i)^2}. \tag{2.101}$$

It is important to note that the diagonal terms $\mathfrak{P}_{ii}$ and $\mathfrak{D}_{ii}$ coincide, so to avoid double-counting we will define $\mathfrak{D}_{ii} \equiv 0$.

2.6 Results

2.6.1 Atoms

With all the results of the previous sections, we can now evaluate an energy expression:

$$E = 2\sum_{i=1}^{N} h^i_i \gamma_i + \sum_{ij}[(2V^{ij}_{ij} - V^{ij}_{ji})\mathfrak{D}_{ij} + V^{ii}_{jj}\mathfrak{P}_{ij}] \tag{2.102}$$

where the summations are performed over only the spatial orbital index. The elements of the Coulomb Hamiltonian h^i_j and V^{ij}_{kl} are taken as input. For molecular calculations, an orbital optimization has a substantial effect.

We have performed calculations for a series of four- and ten-electron systems, and the results are presented here. There are two sets of results based on two different approaches. The first, labelled 1-RDM, is based on matching the 1-RDM from a full-CI calculation to that from a reduced BCS Hamiltonian and evaluating the energy obtained. The second, labelled VAR, is just a variational calculation using the Richardson wavefunction as an ansatz. The results are summarized in tables (2.1) through (2.4).

Table 2.1: Absolute energies (a.u.) for four-electron systems

	Li^-	B^+	N^{3+}	O^{4+}	Ne^{6+}	Ar^{14+}
HF	-7.40394	-24.21606	-50.86070	-67.84432	-109.12177	-371.63840
1-RDM	-7.43631	-24.27477	-50.93964	-67.93159	-109.22067	-371.76177
VAR	-7.43632	-24.27479	-50.93965	-67.93159	-109.22067	-371.76177
DOCI	-7.43664	-24.27543	-50.94071	-67.93169	-109.22075	-371.76190
CI	-7.43706	-24.27568	-50.94091	-67.93190	-109.22078	-371.76263

Table 2.2: Relative Correlation energies (%) for four-electron systems

	Li^-	B^+	N^{3+}	O^{4+}	Ne^{6+}	Ar^{14+}
1-RDM	97.74	98.47	98.41	99.65	99.88	99.31
VAR	97.75	98.51	98.43	99.65	99.88	99.31
DOCI	98.74	99.57	99.75	99.76	99.96	99.41

The results are nearly exact for the four-electron systems presented. This is not to be taken too seriously however. The systems are essentially two-electron problems as one pair is deeply entrenched in the core. A seniority-zero description is nearly exact, as evidenced by both the DOCI data and our results. For the ten electron systems presented, there is a sharp Fermi gap and hence most of the correlation energy is due

Table 2.3: Absolute energies (a.u.) for ten-electron systems

	F^-	Ne	Mg^{2+}	Ar^{8+}
HF	-99.3663	-128.4888	-198.7021	-504.7797
1-RDM	-99.3553	-128.4836	-198.6987	-504.7794
VAR	-99.4054	-128.5225	-198.7364	-504.8060
DOCI	-99.4305	-128.5503	-198.7530	-504.8144
CI	-99.5624	-128.6809	-198.8631	-504.8828

Table 2.4: Relative Correlation energies (%) for ten-electron systems

	F^-	Ne	Mg^{2+}	Ar^{8+}
1-RDM	-5.63	-2.71	-2.09	-0.35
VAR	19.93	17.57	21.30	25.48
DOCI	32.74	32.01	31.61	33.62

to weak correlation. We are satisfied that we get most of the DOCI energy, as that is the best case scenario in this approach.

2.6.2 Diatomics

We have recently reported curves for some diatomic species as well.[TBJ$^+$14] The curves represent fit Morse potentials based on a discrete set of points for which the energy was calculated with a cc-pVDZ basis. Each curve is shifted so that they have a common dissociation energy. The present approach is labelled APr2G-A (with canonical Hartree-Fock orbitals) and APr2G-B (with optimized AP1roG[LAJ$^+$13] orbitals). For a discussion of each method treated the reader is referred to the original paper. The present treatment does quite well for Lithium Hydride (LiH), Figure 2.1 as there is only a single bond to break. The treatment is rather poor for the other diatomics, with the Carbon dimer being particularly poorly treated. It should be emphasized that the set of orbitals used strongly influences the quality of the result. A curve could not be drawn with the Hartree-Fock orbitals except for LiH.

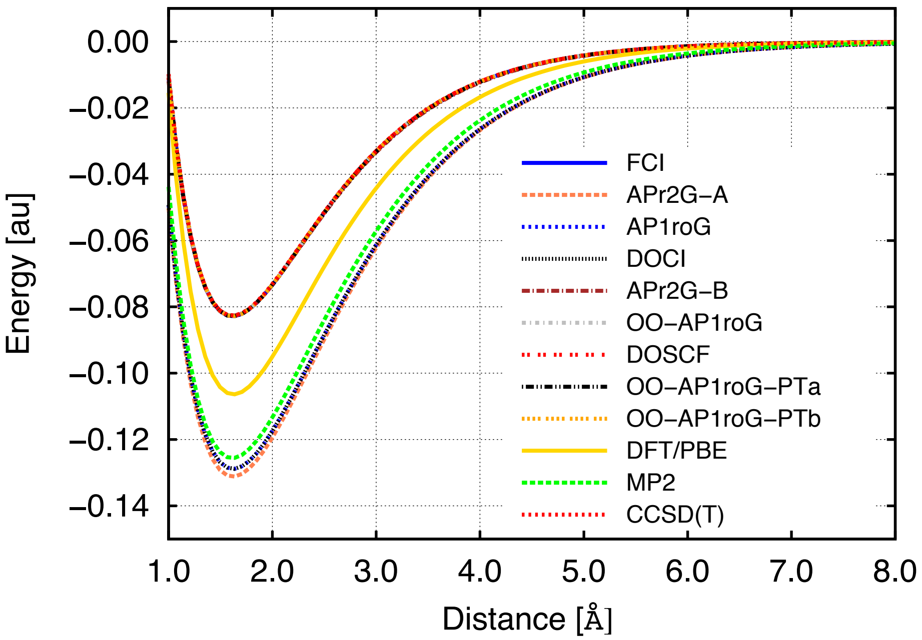

Figure 2.1: Lithium Hydride

In this chapter we have employed the eigenvectors of the reduced BCS Hamiltonian as a variational wavefunction ansatz. We were able to capture most of the "seniority zero correlation", i.e. DOCI. In the next chapter we will look at the same wavefunction form, but we will not restrict ourselves to eigenvectors of the reduced BCS Hamiltonian.

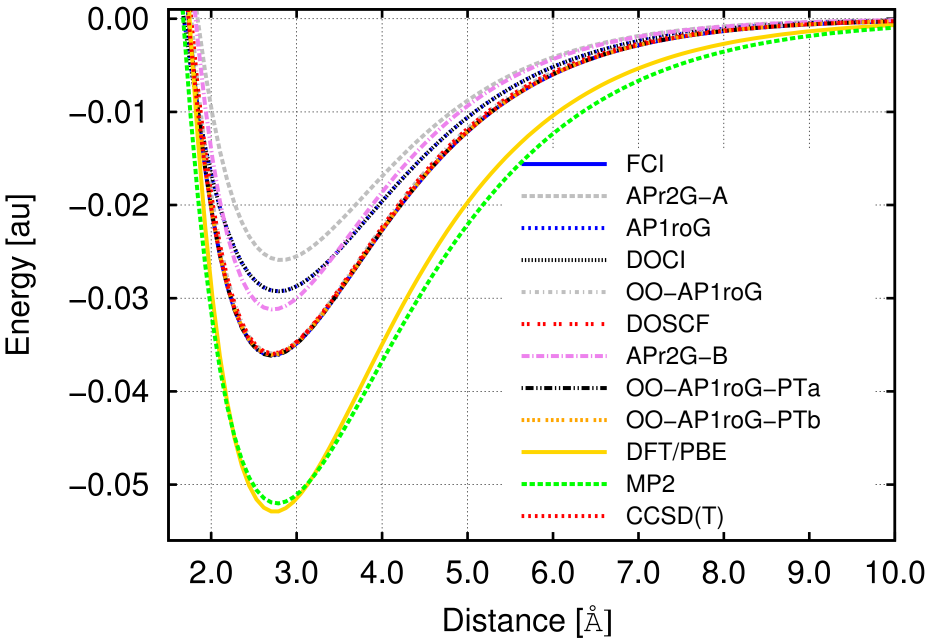

Figure 2.2: Lithium dimer

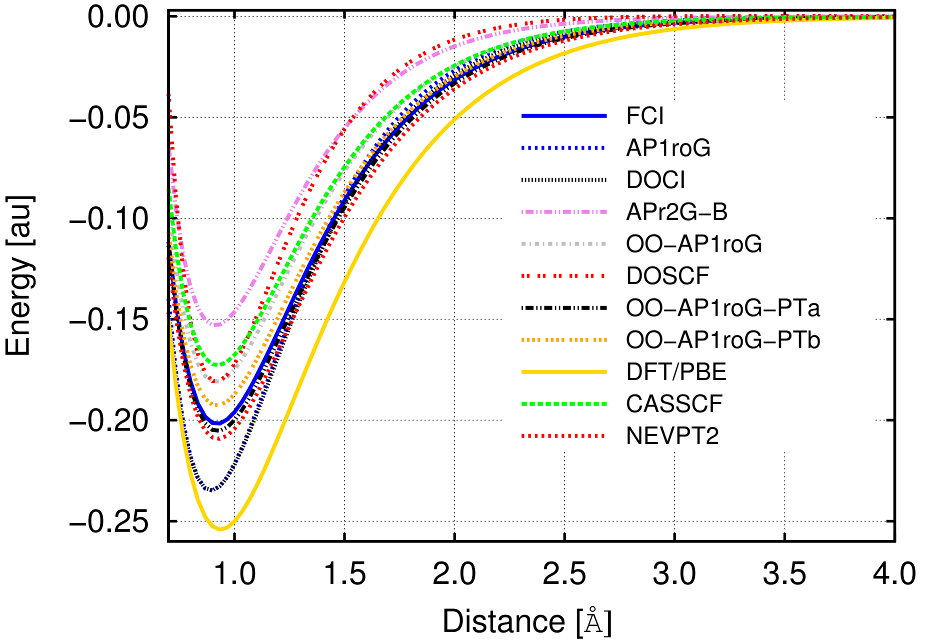

Figure 2.3: Hydrogen Fluoride

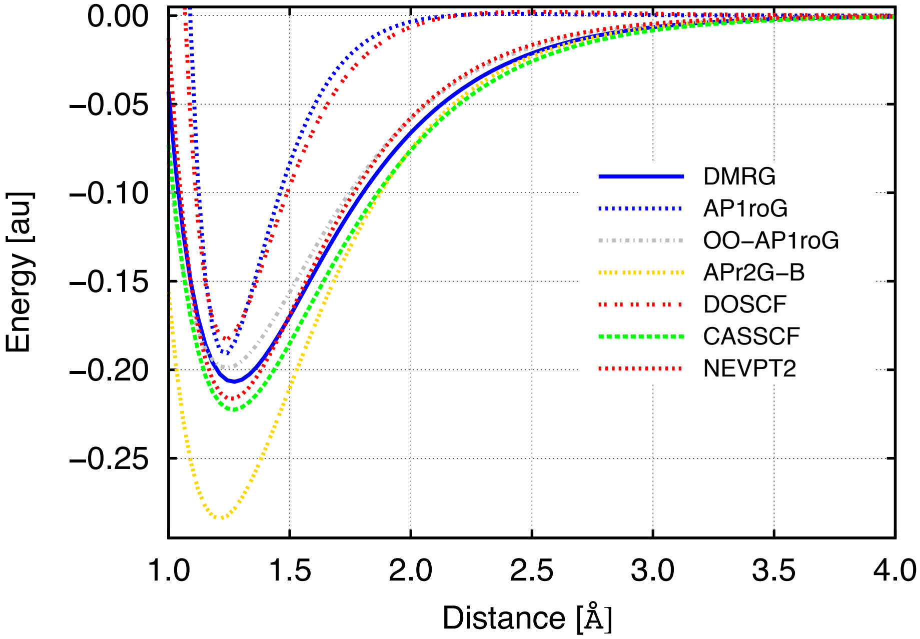

Figure 2.4: Carbon dimer

Chapter 3

Generalized Wavefunction Form: $\mathfrak{su}(2)$

[1]

We develop a variational principle for an antisymmetric product of nonorthogonal geminals. Special cases of this method include the antisymmetric product of strongly orthogonal geminals (APSG), generalized valence bond-perfect pairing (GVB-PP), and antisymmetrized geminal power (AGP) wavefunctions. The method itself uses a wavefunction that is a special case of the antisymmetric product of Cauchy geminals (APr2G). The general idea is to introduce an additional wavefunction, and then optimize the energy expression, $\langle\Phi|\hat{H}|\Psi\rangle$. The method is rigorously variational if the normalization constraint, $\langle\Phi|\Psi\rangle = 1$, and the requirement that the wavefunctions in the bra and the ket be equal, $|\Phi\rangle = |\Psi\rangle$, are satisfied. This general approach may be useful in other contexts also, for example, for the purposes of deriving a

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[1] This chapter is a complete manuscript we will be submitting shortly, hence there is some piecemeal repetition of the previous chapter.

computationally feasible variational coupled cluster method.

3.1 Introduction

Most computational methods for the electronic theory of molecules and solids are based on the orbital (for molecules) or band (for solids) picture [HJO00, RA96, HG96, HCJ$^+$12]. In this picture, the ground-state wavefunction is approximated by a Slater determinant of the single-electron eigenfunctions (orbitals) from a mean-field model (e.g., Hartree-Fock, Kohn-Sham). Physically, the electrons are assumed to move quasi-independently, with each electron feeling only an average repulsion from the other electrons in the system. While electrons do not move independently, in many systems electrons move quasi-independently, and a Slater determinant wavefunction is a good starting point for further approximations. The orbital picture is particularly reliable for equilibrium thermodynamic properties of organic molecules and is less accurate for chemical transition states (ergo for chemical kinetics), electronic excited states, and inorganic substances containing d-block and f-block elements.

When even a qualitatively correct description of a system requires many Slater determinants, it is said to be strongly correlated. [CS11, AI10] Conventional density-based and wavefunction-based methods are usually unreliable for strong correlation, and the methods that are appropriate are usually computationally expensive. While large molecules and complex materials with thousands of valence electrons can be routinely modelled with the orbital picture, no such tools exist when the orbital picture fails. Our goal is to develop new models for strongly correlated substances with hundreds of valence electrons.

Because modelling strongly correlated substances is so difficult, computational physicists usually model these systems by introducing model Hamiltonians that are easily solved and which capture the key qualitative features of the system in question. We have recently shown how these model Hamiltonians can also be used to provide quantitative predictions for real physical systems [JAL$^+$13, LAJ$^+$13]. The basic idea is to (1) find a model Hamiltonian that reproduces the key qualitative features of the system of interest, (2) use the wavefunction-form of that model Hamiltonian to model the substance.

In our previous work we have addressed two approaches. First, one can choose wavefunctions that are eigenvectors of the model Hamiltonian,

$$\hat{H}_{model}(\boldsymbol{\eta}) \left|\Psi_{model}(\boldsymbol{\eta})\right\rangle = E_{model} \left|\Psi_{model}(\boldsymbol{\eta})\right\rangle \tag{3.1}$$

and minimize the parameters, $\boldsymbol{\eta}$, in the model Hamiltonian,

$$E_{GS} \approx \min_{\boldsymbol{\eta}} \left\langle \Psi_{model}(\boldsymbol{\eta}) \middle| \hat{H} \middle| \Psi_{model}(\boldsymbol{\eta}) \right\rangle . \tag{3.2}$$

Because the Hamiltonians we are interested in give rise to Schrödinger equations that can be exactly solved by the (nested) Bethe ansatz, we will refer to the eigenfunctions of the model Hamiltonian as on-shell Bethe vectors. A variational method based on on-shell Bethe vectors is specified in section 3.3. One can relax the requirement that the wavefunction be an eigenfunction of the model Hamiltonian and merely use the model Hamiltonian to make a suitable choice for the wavefunction form [JAL$^+$13, LAJ$^+$13]. The resulting wavefunctions are called off-shell Bethe vectors. Variational optimization of off-shell Bethe vectors is more challenging (and perhaps often impossible), so our previous work used the projected Schrödinger equation to establish a system of nonlinear equations that can be solved for the parameters in the off-shell Bethe vectors,

$$\langle\Phi|\hat{H}|\Psi(\boldsymbol{\eta})\rangle = E\,\langle\Phi|\Psi(\boldsymbol{\eta})\rangle \tag{3.3}$$

The primary goal of this paper is to present a variational principle for off-shell Bethe vectors; this is presented in section 3.4. The basic idea is to rewrite the variational principle as,

$$E_{GS} = \min_{\{|\Psi(\boldsymbol{\eta})\rangle,|\tilde{\Psi}(\boldsymbol{\eta})\rangle:\langle\tilde{\Psi}(\boldsymbol{\eta})|\Psi(\boldsymbol{\eta})\rangle=1,|\Psi(\boldsymbol{\eta})\rangle=|\tilde{\Psi}(\boldsymbol{\eta})\rangle\}} \langle\tilde{\Psi}(\boldsymbol{\eta})|\hat{H}|\Psi(\boldsymbol{\eta})\rangle \tag{3.4}$$

The general approach we take should be applicable to most, if not all, algebraically-solvable model Hamiltonians. We focus, however, on the Richardson-Gaudin family of Hamiltonians and the Bethe-ansatz solution built using the associated $\mathfrak{su}(2)$ or (what is essentially the same) $\mathfrak{gl}(2,\mathbb{C})$ quasi-spin algebra [Gau76, Ric63, RS64, DPS04]. The necessary background material is presented in section 3.2. After discussing the on-shell and off-shell formulations, we discuss the extension to nonorthogonal orbitals in section 3.6. The variational version of the projected APr2G (antisymmetric product of rank-2 geminals) and a different approach to the antisymmetrized geminal power wavefunction are presented in sections 3.7 and 3.8, respectively. Notes on the computational algorithm are presented in section 3.9, and we discuss possible generalizations in section 3.10.

3.2 Background

We consider systems of fermions that are described by a Hamiltonian with at most 2-body terms,

$$\hat{H} = \sum_{ij} h^i_j a^\dagger_i a^j + \frac{1}{2} \sum_{ijkl} V^{ij}_{kl} a^\dagger_i a^\dagger_j a^l a^k, \tag{3.5}$$

where $a^\dagger_i(a^i)$ are the operators for creating (destroying) a single-particle state. The electronic Hamiltonian is of this form and the single-particle states of electrons are spin-orbitals. In Eq. (3.5), the direct two-body integrals are expressed in so-called physicists' notation,

$$V^{ij}_{kl} = \int d\mathbf{r}_1 d\mathbf{r}_2 \; \phi^*_i(\mathbf{r}_1)\phi^*_j(\mathbf{r}_2) V(\mathbf{r}_1, \mathbf{r}_2) \phi_k(\mathbf{r}_1)\phi_l(\mathbf{r}_2) \tag{3.6}$$

The energy of a normalized wavefunction can be computed from the wavefunction,

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle \, , \tag{3.7}$$

or, alternatively, from the 1- and 2-electron reduced density matrices (DM),

$$E[\Psi] = \sum_{ij} h^i_j \gamma^j_i[\Psi] + \frac{1}{2} \sum_{ijkl} V^{ij}_{kl} \Gamma^{kl}_{ij}[\Psi]. \tag{3.8}$$

The 1DM and 2DM are, respectively,

$$\gamma^j_i[\Psi] = \langle \Psi | a^\dagger_i a^j | \Psi \rangle \tag{3.9}$$

$$\Gamma^{kl}_{ij}[\Psi] = \langle \Psi | a^\dagger_i a^\dagger_j a^l a^k | \Psi \rangle \, . \tag{3.10}$$

Because it is extremely difficult to determine, much less optimize, $E[\Psi]$ for arbitrary wavefunction forms, most practical approaches to the quantum many-body problem simplify the form of either the Hamiltonian or the wavefunction. We do not want to surrender our ability to accurately model real physical systems, so we will only approximate the wavefunction in this paper. In particular, the wavefunctions we consider are geminal-product wavefunctions, a subclass of fully-paired states. [HLJP53, MS63, PEL56, PP58, Sur99, SSJZ12, SMR70, MRS70, SRM70, Kut65, MR65, Col65, Col97]. It is therefore convenient to work with the pseudospin representation of $\mathfrak{su}(2)$:

$$S^+_i = a^\dagger_{i\frac{1}{2}} a^\dagger_{i-\frac{1}{2}}, \; S^-_i = a^{i-\frac{1}{2}} a^{i\frac{1}{2}}, \; S^z_i = \frac{1}{2} \left(a^\dagger_{i\frac{1}{2}} a^{i\frac{1}{2}} + a^\dagger_{i-\frac{1}{2}} a^{i-\frac{1}{2}} - 1 \right) . \tag{3.11}$$

with the implied commutation relations,

$$\begin{aligned} [S^z_i, S^\pm_j] &= \pm \delta_{ij} S^\pm_i \\ [S^+_i, S^-_j] &= 2\delta_{ij} S^z_i . \end{aligned} \tag{3.12}$$

The indices $\{i, \bar{i}\} = \{i\frac{1}{2}, i-\frac{1}{2}\}$ denote a pair of spin-orbitals. The pair is ordinarily (but not always [LAJ$^+$13, SJHH$^+$11, BMWS08]) chosen as the two spin-orientations of the spatial orbital indexed by i. The operators $S^\pm_i$ create/destroy a pair in state i, while S^z_i counts the number of electrons in state i, the result being $2S^z + 1$.

The wavefunction-form we consider consists of N_P electron pairs, with each pair built from N_{orb} spatial orbitals,

$$|\text{APIG}\rangle = \prod_{\alpha=1}^{N_P} \sum_{i=1}^{N_{orb}} g_{\alpha,i} S_i^+ |\theta\rangle \tag{3.13}$$

The state $|\theta\rangle$ represents the vacuum; it ordinarily represents the physical vacuum (the zero-electron state) but it is only required to be a vacuum with respect to the removal of electron pairs. When the amplitudes $g_{\alpha,i}$ are allowed to be completely general, this wavefunction is called is an antisymmetric product of interacting geminals (APIG) [Sil70, Sil69].

Equation (13) can be expanded as a linear combination of $\binom{N_{orb}}{N_P}$ Slater determinants

$$|\text{APIG}\rangle = \sum_{\{m_i=\{0,1\} | \sum_{i=1}^{N_{orb}} m_i = N_P\}} |\mathbf{C}(\mathbf{m})|^+ \prod_{c=1}^{N_P} \left(a_c^\dagger a_{\bar{c}}^\dagger \right)^{m_c} |\theta\rangle \, . \tag{3.14}$$

Each expansion coefficient is the permanent of an $N_P \times N_P$ matrix consisting of the geminal amplitudes of the occupied (i.e., $m_i = 1$) orbital pairs,

$$|\mathbf{C}(\mathbf{m})|^+ = \begin{vmatrix} g_{1,i_1} & g_{1,i_2} & \cdots & g_{1,i_{N_P}} \\ g_{2,i_1} & g_{2,i_2} & \cdots & g_{2,i_{N_P}} \\ \vdots & & \ddots & \vdots \\ g_{N_P,i_1} & g_{N_P,i_2} & \cdots & g_{N_P,i_{N_P}} \end{vmatrix}^+ \tag{3.15}$$

$$1 = m_{i_1} = m_{i_2} = \cdots = m_{i_{N_P}}$$

Evaluating the permanent of a matrix is #P-hard [Val79], so the APIG wavefunction is computationally intractable for large N_P. For certain special forms of $g_{\alpha,i}$, however, the permanents may be efficiently evaluated [JAL$^+$13, LAJ$^+$13, Bor55, CL60].

It has long been recognized that for antisymmetric products of geminals (Eq. (3.13)) [Kut64] and doubly-occupied configuration interaction wavefunctions (Eq. (3.14)) [WW67] have especially simple formulas for the reduced density matrices. Specifically, the 1DM is completely diagonal,

$$\gamma_i^j = \delta_{ij} \langle\Psi|a_i^\dagger a^j|\Psi\rangle \tag{3.16}$$

and the 2DM has only two types of non-zero terms: the diagonal terms (D2D) (for $i \neq j$)

$$\mathfrak{D}_{ij} \equiv \Gamma^{ij}_{ij} = \langle\Psi|a_i^\dagger a^i a_j^\dagger a^j|\Psi\rangle \tag{3.17}$$

and the pair correlation terms (D2P)

$$\mathfrak{P}_{ij} \equiv \Gamma^{j\bar{j}}_{i\bar{i}} = \langle\Psi|a_i^\dagger a_{\bar{i}}^\dagger a^{\bar{j}} a^j|\Psi\rangle . \tag{3.18}$$

These nonvanishing matrix elements can all be expressed in terms of the $\mathfrak{su}(2)$ operators, Eq. (3.11). Specifically,

$$\gamma_i = \frac{1}{\langle\Psi|\Psi\rangle}(\langle\Psi|S_i^z|\Psi\rangle + \frac{1}{2}\langle\Psi|\Psi\rangle) \tag{3.19}$$

$$\mathfrak{D}_{ij} = \frac{1}{\langle\Psi|\Psi\rangle}\langle\Psi|S_i^z S_j^z|\Psi\rangle + \frac{1}{2}\gamma_i + \frac{1}{2}\gamma_j - \frac{1}{4}, \quad i \neq j \tag{3.20}$$

$$\mathfrak{P}_{ij} = \frac{1}{\langle \Psi | \Psi \rangle} \langle \Psi | S_i^+ S_j^- | \Psi \rangle \, . \tag{3.21}$$

The diagonal terms of D2D and D2P are identical, so in order to avoid double counting we arbitrarily choose to include the diagonal in D2P, and set D2Ds diagonal elements to zero. Elements of the 1DM represent the probability of occupying the ith orbital. Elements of the D2D matrix represent the probability of occupying the ith and jth orbitals simultaneously. Elements of the D2P matrix capture the correlation between an electron pair in the state i and an electron pair in state j.

The density matrices in Eqs. (3.19)-(3.21) are not easily evaluated for arbitrary amplitudes $g_{\alpha,i}$. In the following sections we will consider simple, but increasingly complicated, forms for the amplitudes $g_{\alpha,i}$ and evaluate the resulting z-form factor $\langle S_i^z \rangle$, the zz-form factor $\langle S_i^z S_j^z \rangle$, and the pair-correlation function $\langle S_i^+ S_j^- \rangle$. The energy can then be evaluated using Eqs. (3.8),(3.19)-(3.21).

3.3 On-Shell Bethe Vectors of the Richardson Hamiltonian (Cauchy Geminals)

Our paradigm for modeling electronic matter is to (a) select a readily solvable model system and then (b) use the wavefunction-form of this model to evaluate the energy of the system. Since we are interested in systems that are well-described by pairing wavefunctions of the form (3.13), we need Hamiltonians whose eigenstates are of this form. One such Hamiltonian is the reduced BCS Hamiltonian [Gau76, Ric63, RS64],

$$\hat{H}_{BCS} = \sum_{i=1}^{N_{orb}} \varepsilon_i S_i^z - g \sum_{ij} S_i^+ S_j^- . \tag{3.22}$$

(The Hamiltonian (22) differs from the reduced BCS Hamiltonian by an additive constant.) The Richardson Hamiltonian is believed to provide qualitative insights into strongly correlated systems like superconducting nanograins [DPS04, DS00, KN12]. The eigenvectors of the Richardson Hamiltonian are

$$|\{\lambda\}\rangle = \prod_{\alpha=1}^{N_P} \mathbb{S}^+(\lambda_\alpha)\,|\theta\rangle \tag{3.23}$$

where the operators $\mathbb{S}^+(\lambda_\alpha)$ create a pair delocalized over the entire single particle space, i.e.

$$\mathbb{S}^+(\lambda_\alpha) = \sum_{i=1}^{N_{orb}} \frac{S_i^+}{\lambda_\alpha - \varepsilon_i} \tag{3.24}$$

There are many normalization conventions for the Richardson wavefunction in the literature though it makes only an aesthetic difference. The complex-valued parameters $\{\lambda_\alpha\}_{\alpha=1}^{N_P}$ are called by various names, including rapidities, quasimomenta, spectral parameters, and pairing energies. The parameters in the Richardson Hamiltonian, $\{\varepsilon_i\}_{i=1}^{N_{orb}}$ and g, represent single-particle energies and the pairing strength (cf. Eq. (3.22)). The two-electron states generated by Eq. (3.24) are called Cauchy geminals because $1/(\lambda_\alpha - \varepsilon_i)$ are the elements of a Cauchy matrix. The form of the solution, Eq. (3.23)-(3.24), is also referred to as the rational solution to the XXX (isotropic) Richardson-Gaudin Hamiltonian.

The wavefunction-form (3.23) is analogous to Bethe's hypothesis for the eigenvectors of the 1-dimensional Heisenberg model Hamiltonian [Bet31, Hei28]. The Bethe ansatz replaces the problem of solving a high-dimensional partial differential equation (the Schrödinger equation) with the problem of solving a system of nonlinear equations. For the Richardson Hamiltonian, substituting the Bethe ansatz wavefunction, Eqs. (3.23)-(3.24), into the Schrödinger equation reveals that Eq. (3.23) is an eigenvector of the reduced BCS Hamiltonian whenever the rapidities satisfy Richardson's equations,

$$\Lambda(\lambda_a) = -\frac{1}{g} - \sum_{i=1}^{N} \frac{1}{\lambda_a - \varepsilon_i} + 2 \sum_{b \neq a} \frac{1}{\lambda_a - \lambda_b} = 0. \tag{3.25}$$

Solving these equations generally requires that at least some of the rapidities be complex-valued. There are several algorithms available for solving Richardson's equations; we have used the method of De Baerdemacker in our previous work [DB12].

Computationally practical expressions for the z-form factor, the zz-form factor and the pair correlation function of a Richardson eigenstate have been derived previously, so we will only present the main ideas. The engine driving all of these results is Slavnov's theorem [Sla89], which gives a formula for the inner product of two states of the Richardson wavefunction-form, Eqs. (3.23)-(3.24), where one of the sets of rapidities (say, $\{\lambda\}$) is required to satisfy the Richardson equations (3.25), but the other is not. Specifically,

$$\langle \{\mu\} | \{\lambda\} \rangle = \frac{\prod_{a \neq b} \left(\lambda_b - \mu_a\right)}{\prod_{b<a} \left(\mu_b - \mu_a\right) \prod_{a<b} \left(\lambda_b - \lambda_a\right)} \det J\left(\{\mu\}, \{\lambda\}\right). \tag{3.26}$$

The most computationally demanding aspect evaluating Eq. (26) is evaluating the determinant of the matrix **J**, with elements

$$J_{ab} = \frac{\lambda_b - \mu_b}{\lambda_a - \mu_b} \left(\sum_{i=1}^{N} \frac{1}{(\lambda_a - \varepsilon_i)(\mu_b - \varepsilon_i)} - 2 \sum_{c \neq a} \frac{1}{(\lambda_a - \lambda_c)(\mu_b - \lambda_c)} \right). \tag{3.27}$$

Choosing $\{\mu\} = \{\lambda\}$ gives a formula for the norm of a Richardson eigenfunction,

$$\langle \{\lambda\} | \{\lambda\} \rangle = \det G \tag{3.28}$$

where the elements of the matrix G are

$$G_{ab} = \begin{cases} \sum_{i=1}^{N} \frac{1}{(\lambda_a - \varepsilon_i)^2} - 2 \sum_{c \neq a}^{N_P} \frac{1}{(\lambda_a - \lambda_c)^2} & a = b \\ \frac{2}{(\lambda_a - \lambda_b)^2} & a \neq b \end{cases}. \tag{3.29}$$

(The formula for the norm of the Richardson eigenstates was originally derived by Richardson by an alternative method.) The Gaudin matrix, G, is the Jacobian for the transformation from a set of arbitrary (”uncorrelated”) rapidities to one where the rapidities are related to each other by the Richardson equations. I.e.,

$$G_{ab} = \frac{\partial \Lambda(\lambda_a)}{\partial \lambda_b} \tag{3.30}$$

where $\Lambda(\lambda_\alpha)$ is one of Richardson’ nonlinear equations, cf. Eq. (3.25). The expressions for the various form factors are corollaries to Slavnov’s theorem. To derive the z-form factor, $\{\lambda\} \rightarrow \{\mu\}$, one can use the commutation relations (3.12) to move S^z_i

to the right until it acts on the vacuum, obtaining

$$\langle\{\mu\}|S^z_i|\{\lambda\}\rangle = \sum_{a=1}^{N_P} \frac{1}{\lambda_a - \varepsilon_i} \langle\{\mu\}|S^+_i|\{\lambda\}_a\rangle - \frac{1}{2} \langle\{\mu\}|\{\lambda\}\rangle . \tag{3.31}$$

Here $|\{\lambda\}_a\rangle$ denotes the $(N_P - 1)$-pair state with the rapidity λ_a removed.

Other form factors are derived by the same technique: one uses the commutation relations of the quasi-spin algebra to shift the operators all the way to the right. The resulting formulas for the elements of the zz-form factor and the pair correlation function are, respectively,

$$\begin{aligned}\langle\{\mu\}|S^z_i S^z_j|\{\lambda\}\rangle = \frac{1}{4} \langle\{\mu\}|\{\lambda\}\rangle + \sum_{a\neq b}^{N_P} \frac{\langle\{\mu\}|S^+_i S^+_j|\{\lambda\}_{a,b}\rangle}{(\lambda_a - \varepsilon_i)(\lambda_b - \varepsilon_j)} \\ - \frac{1}{2}\sum_{a=1}^{N_P} \frac{\langle\{\mu\}|S^+_i|\{\lambda\}_a\rangle}{\lambda_a - \varepsilon_i} - \frac{1}{2}\sum_{a=1}^{N_P} \frac{\langle\{\mu\}|S^+_j|\{\lambda\}_a\rangle}{\lambda_a - \varepsilon_j}\end{aligned} \tag{3.32}$$

and

$$\langle\{\mu\}|S^+_i S^-_j|\{\lambda\}\rangle = \sum_{a=1}^{N_P} \frac{\langle\{\mu\}|S^+_i|\{\lambda\}_a\rangle}{\lambda_a - \varepsilon_j} - \sum_{a\neq b}^{N_P} \frac{\langle\{\mu\}|S^+_i S^+_j|\{\lambda\}_{a,b}\rangle}{(\lambda_a - \varepsilon_j)(\lambda_b - \varepsilon_j)} \tag{3.33}$$

where

$$|\{\lambda\}_a\rangle = \prod_{\eta\neq a} \mathbb{S}^+(\lambda_\eta)\,|\theta\rangle \tag{3.34}$$

$$|\{\lambda\}_{a,b}\rangle = \prod_{\eta\neq a,b} \mathbb{S}^+(\lambda_\eta)\,|\theta\rangle . \tag{3.35}$$

Notice that the geminal-creation operators, Eq. (3.24), have simple poles whenever the rapidity coincides with a single-particle energy. The residues of the poles are simply the orbital-pair creation operators,

$$S_i^+ = \lim_{\lambda \to \varepsilon_i} (\lambda - \varepsilon_i) \mathbb{S}^+(\lambda). \tag{3.36}$$

The matrix elements that appear in Eqs. (3.31)-(3.33) can therefore be represented in terms of the scalar product, $\langle \{\mu\} | \{\lambda\} \rangle$

$$\langle \{\mu\} | S_i^+ | \{\lambda\}_a \rangle = \lim_{\lambda_a \to \varepsilon_i} (\lambda_a - \varepsilon_i) \langle \{\mu\} | \{\lambda\} \rangle \tag{3.37}$$

$$\langle \{\mu\} | S_i^+ S_j^+ | \{\lambda\}_{a,b} \rangle = \lim_{\lambda_a \to \varepsilon_i} \lim_{\lambda_b \to \varepsilon_j} (\lambda_a - \varepsilon_i)(\lambda_b - \varepsilon_j) \langle \{\mu\} | \{\lambda\} \rangle . \tag{3.38}$$

Expressions for $\langle S_i^z \rangle$, $\langle S_i^z S_j^z \rangle$, and $\langle S_i^+ S_j^- \rangle$ are then obtained by using Slavnov's theorem (Eq. (3.26)) and making the substitution $\{\mu\} \to \{\lambda\}$. One then obtains expressions involving sums over determinants. To evaluate $\langle S_i^z \rangle$, one needs to compute N_P determinants of $(N_P - 1)$-dimensional matrices. These matrices differ by single-row-replacements, so low-rank updates can be used to reduce the computational cost. Similarly, to evaluate $\langle S_i^z S_j^z \rangle$ and $\langle S_i^+ S_j^- \rangle$ one needs to compute N_P determinants of $(N_P - 1)$-dimensional matrices and N_P^2 determinants of $(N_P - 2)$-dimensional matrices. All the determinants to be evaluated differ by single-row-replacements and thus may be evaluated efficiently.

3.4 Off-Shell Bethe Vectors of the Richardson Form (Cauchy Geminals)

In the previous section we considered wavefunctions that are eigenfunctions of the Richardson Hamiltonian; such states are called on-shell Bethe vectors. There are $N_{orb} - 1$ free parameters in an on-shell Bethe vector (because the zero of energy and energy scale for the Richardson Hamiltonian is arbitrary). A more flexible wavefunction can be obtained by not requiring that the rapidities satisfy Richardson's equations. Wavefunctions of this form are *off-shell* Bethe vectors; there are $N_P + N_{orb} - 1$ free parameters in an off-shell Bethe vector.

Although Slavnov's theorem for the scalar product only applies when at least one of the states is an on-shell Bethe vector, the expressions (3.31)-(3.33) and (3.36)-(3.38) remain valid for off-shell Bethe vectors [FS12]. Therefore, in order to evaluate the energy of an off-shell Bethe vector, we only require an expression for the scalar product $\langle\{\mu\}|\{\lambda\}\rangle$. One could attempt to evaluate this scalar product by expanding the states $|\{\mu\}\rangle$ and $|\{\lambda\}\rangle$ in Slater determinants (cf. Eq. (3.14)), but this is impractical because (a) there are a factorial number of terms in the sum and (b) evaluating the permanent is #P hard. The second problem is circumvented because $\mathbf{C}(\mathbf{m})$ is a Cauchy matrix. Borchardt's theorem establishes that the permanent of such a Cauchy matrix can be computed as a ratio of determinants [Bor55],

$$|\mathbf{C}(\mathbf{m})|^{+} = \frac{|\mathbf{C}(\mathbf{m}) \circ \mathbf{C}(\mathbf{m})|}{|\mathbf{C}(\mathbf{m})|} = |\mathbf{C}^{-1}(\mathbf{m}) \cdot (\mathbf{C}(\mathbf{m}) \circ \mathbf{C}(\mathbf{m}))| \tag{3.39}$$

where $\mathbf{A} \circ \mathbf{B}$ denotes the Hadamard (i.e., elementwise) product of two matrices and $\mathbf{A} \cdot \mathbf{B}$ denotes the conventional (Binet) form of matrix multiplication. However, we still need to find a method to avoid summing over the factorial number of terms in the Slater determinant expansion.

To this end, we *assume* that there exists a dual representation for the state of interest. That is, we assume that the state of interest can be written either as the creation of N_P pairs on a physical vacuum,

$$|\{\lambda\}\rangle = \prod_{a=1}^{N_P} \mathbb{S}^+(\lambda_a) \, |\theta\rangle \tag{3.40}$$

or as the annihilation of $N_{orb} - N_P$ pairs from the pseudovacuum, $|\tilde{\theta}\rangle$, in which every orbital is doubly-occupied,

$$|\{\lambda\}\rangle = \prod_{a=1}^{N_{orb}-N_P} \mathbb{S}^-(\tilde{\mu}^*_a) \, |\tilde{\theta}\rangle \,, \tag{3.41}$$

where

$$\mathbb{S}^-(\tilde{\mu}^*_a) = \sum_{i=1}^{N_{orb}} \frac{S^-_i}{\tilde{\mu}^*_a - \varepsilon_i} = (\mathbb{S}^+(\tilde{\mu}_a))^\dagger \tag{3.42}$$

The inner product can therefore be written as

$$\langle\{\tilde{\mu}\}|\{\lambda\}\rangle = \langle\tilde{\theta}| \prod_{a=1}^{N_{orb}-N_P} \mathbb{S}^+(\tilde{\mu}_a) \prod_{b=1}^{N_P} \mathbb{S}^+(\lambda_b)|\theta\rangle \tag{3.43}$$

which is the projection of a state with N_{orb} pairs onto the Slater determinant $|\tilde{\theta}\rangle = |1\bar{1}2\bar{2}\dots N_{orb}\bar{N}_{orb}\rangle$. The coefficient in Eq. (3.14) corresponds to a vector $\boldsymbol{m}$ in which every element is 1, and $|\mathbf{C}(\mathbf{1})|^+$ can be evaluated in $\mathcal{O}(N^3_{orb})$ cost using Eq. (3.39). Faribault and Schuricht worked out an explicit formula for this permanent, namely

[FS12],

$$\langle\{\tilde{\mu}\}|\{\lambda\}\rangle = \det \mathbf{K} \tag{3.44}$$

where the elements of the matrix $\mathbf{K}$ are given by

$$k_{ab} = \begin{cases} \sum_{k\neq a} \frac{1}{\varepsilon_a-\varepsilon_k} - \sum_{\beta=1}^{N_P} \frac{1}{\varepsilon_a-\lambda_\beta} - \sum_{\beta=1}^{N_{orb}-N_P} \frac{1}{\varepsilon_a-\tilde{\mu}_\beta} & a=b \\ \frac{1}{\varepsilon_a-\varepsilon_b} & a\neq b \end{cases} \tag{3.45}$$

If $\langle\{\tilde{\mu}\}| = \langle\{\lambda\}|$, then Eq. (3.44) is a formula for the scalar product, $\langle\{\lambda\}|\{\lambda\}\rangle = \langle\{\tilde{\mu}\}|\{\lambda\}\rangle$. It is important that the orbital energies, $\{\varepsilon\}$, be the same in both $\mathbb{S}^+(\{\lambda\})$ and $\mathbb{S}^-(\{\tilde{\mu}^*\})$; if this were not true, then a factorial number of permanents would need to be evaluated to compute the norm, and any hope of favourable scaling would be lost. When there is one set of single-particle energies, there is a clear physical interpretation: pairs of electrons travelling through the lattice of orbital energies with rapidities $\{\lambda\}$ is equivalent to pairs of holes travelling in the opposite direction, with rapidities $\{\tilde{\mu}\}$.

Assuming that $\langle\{\tilde{\mu}\}| = \langle\{\lambda\}|$, the expressions for the form factors are obtained by methods very similar to those in the previous section. Analogous to Eq. (3.37), one has

$$\langle\{\tilde{\mu}\}|S_i^+|\{\lambda\}_\alpha\rangle = \lim_{\lambda_\alpha\to\varepsilon_i} (\lambda_\alpha-\varepsilon_i)\det\mathbf{K} = \det\mathbf{K}_{i\alpha} \tag{3.46}$$

where $\mathbf{K}_{i\alpha}$ is the $N_{orb}-1 \times N_{orb}-1$ matrix with elements

$$[k_{i\alpha}]_{ab} = \begin{cases} \sum_{k\neq i,a} \frac{1}{\varepsilon_a-\varepsilon_k} - \sum_{\gamma\neq\alpha} \frac{1}{\varepsilon_a-\lambda_\gamma} - \sum_{\beta=1}^{N_{orb}-N_P} \frac{1}{\varepsilon_a-\tilde{\mu}_\beta} & a=b\neq i \\ \frac{1}{\varepsilon_a-\varepsilon_b} & a\neq b(\neq i) \end{cases} \tag{3.47}$$

To derive Eq. (3.47), one Laplace-expands the determinant from Eq. (3.46) along the ith row. The only non-vanishing cofactor is proportional to k_{ii} . From $(j\neq i)$

$$\lim_{\lambda_\alpha\to\varepsilon_i} k_{jj} = \sum_{k\neq j} \frac{1}{\varepsilon_j-\varepsilon_k} - \sum_{\gamma\neq\alpha} \frac{1}{\varepsilon_a-\lambda_\gamma} - \sum_{\beta=1}^{N_{orb}-N_P} \frac{1}{\varepsilon_a-\tilde{\mu}_\beta} - \frac{1}{\varepsilon_j-\varepsilon_i} \tag{3.48}$$

and

$$\lim_{\lambda_\alpha\to\varepsilon_i} (\lambda_\alpha-\varepsilon_i)k_{ii} = 1, \tag{3.49}$$

one obtains Eq. (3.47). Analogous to Eq. (3.38) one has,

$$\langle\{\tilde{\mu}\}|S_i^+S_j^+|\{\lambda\}_{\alpha,\beta}\rangle = \lim_{\lambda_\alpha\to\varepsilon_i}\lim_{\lambda_\beta\to\varepsilon_j} (\lambda_a-\varepsilon_i)(\lambda_b-\varepsilon_j)\,\langle\{\mu\}|\{\lambda\}\rangle \det\mathbf{K} = \det\mathbf{K}_{i\alpha,j\beta}, \tag{3.50}$$

where $\mathbf{K}_{i\alpha,j\beta}$ is the $N_{orb}-2 \times N_{orb}-2$ matrix with elements

$$[k_{i\alpha,j\beta}]_{ab} = \begin{cases} \sum_{k\neq i,j,a} \frac{1}{\varepsilon_a-\varepsilon_k} - \sum_{\gamma\neq\alpha,\beta} \frac{1}{\varepsilon_a-\lambda_\gamma} - \sum_{\beta=1}^{N_{orb}-N_P} \frac{1}{\varepsilon_a-\tilde{\mu}_\beta} & a=b\neq i,j \\ \frac{1}{\varepsilon_a-\varepsilon_b} & a\neq b(\neq i,j) \end{cases} \tag{3.51}$$

For on-shell Bethe vectors, the matrices required to compute the form factors differ by a single column, and can be rewritten as a single matrix. This is unfortunately not the case for off-shell Bethe vectors.

We can now write the expressions for the nonzero elements of the 1- and 2-electron reduced density matrices. The elements of the 1DM are

$$\begin{aligned}\gamma_i &= \frac{\langle\{\tilde{\mu}\}|S^z_i|\{\lambda\}\rangle + \frac{1}{2}\langle\{\tilde{\mu}\}|\{\lambda\}\rangle}{\langle\{\tilde{\mu}\}|\{\lambda\}\rangle} \\ &= \frac{1}{\langle\{\tilde{\mu}\}|\{\lambda\}\rangle}\sum_{\alpha=1}^{N_P}\frac{\langle\{\tilde{\mu}\}|S^+_i|\{\lambda\}_\alpha\rangle}{(\lambda_\alpha-\varepsilon_i)} \\ &= \frac{1}{\det\mathbf{K}}\sum_{\alpha=1}^{N_P}\frac{\det\mathbf{K}_{i\alpha}}{(\lambda_\alpha-\varepsilon_i)} \end{aligned} \tag{3.52}$$

The off-diagonal elements of the D2D matrix are

$$\begin{aligned}\mathfrak{D}_{ij} &= \frac{\langle\{\tilde{\mu}\}|S^z_iS^z_j|\{\lambda\}\rangle + \frac{1}{2}\gamma_i + \frac{1}{2}\gamma_j - \frac{1}{4}\langle\{\tilde{\mu}\}|\{\lambda\}\rangle}{\langle\{\tilde{\mu}\}|\{\lambda\}\rangle} \\ &= \frac{1}{\langle\{\tilde{\mu}\}|\{\lambda\}\rangle}\sum_{\alpha=1}^{N_P}\sum_{\beta\neq\alpha}\frac{\langle\{\tilde{\mu}\}|S^+_iS^+_j|\{\lambda\}_{\alpha,\beta}\rangle}{(\lambda_\alpha-\varepsilon_i)(\lambda_\beta-\varepsilon_j)} \\ &= \frac{1}{\det\mathbf{K}}\sum_{\alpha=1}^{N_P}\sum_{\beta\neq\alpha}\frac{\det\mathbf{K}_{i\alpha,j\beta}}{(\lambda_\alpha-\varepsilon_i)(\lambda_\beta-\varepsilon_j)} \end{aligned} \tag{3.53}$$

Recall that, by convention, we define $\mathfrak{D}_{ii} = 0$. The D2P matrix has elements

$$\begin{aligned}\mathfrak{P}_{ij} &= \frac{\langle\{\tilde{\mu}\}|S^+_iS^-_j|\{\lambda\}\rangle}{\langle\{\tilde{\mu}\}|\{\lambda\}\rangle} \\ &= \frac{1}{\langle\{\tilde{\mu}\}|\{\lambda\}\rangle}\left(\sum_{\alpha=1}^{N_P}\frac{\langle\{\tilde{\mu}\}|S^+_i|\{\lambda\}_\alpha\rangle}{(\lambda_\alpha-\varepsilon_j)} - \sum_{\alpha=1}^{N_P}\sum_{\beta\neq\alpha}\frac{\langle\{\tilde{\mu}\}|S^+_iS^+_j|\{\lambda\}_{\alpha,\beta}\rangle}{(\lambda_\alpha-\varepsilon_j)(\lambda_\beta-\varepsilon_j)}\right) \\ &= \frac{1}{\det\mathbf{K}}\left(\sum_{\alpha=1}^{N_P}\frac{\det\mathbf{K}_{i\alpha}}{(\lambda_\alpha-\varepsilon_j)} - \sum_{\alpha=1}^{N_P}\sum_{\beta\neq\alpha}\frac{\det\mathbf{K}_{i\alpha,j\beta}}{(\lambda_\alpha-\varepsilon_j)(\lambda_\beta-\varepsilon_j)}\right) \end{aligned} \tag{3.54}$$

If these formulas are implemented directly, then evaluating the 1DM has computational cost $\mathcal{O}(N_P N_{orb}^4)$ (to compute each nonzero element of the 1DM one must evaluate N_P determinants of $N_{orb} - 1 \times N_{orb} - 1$ matrices). The cost of constructing D2D and D2P is controlled by the cost of evaluating the double-sum, with cost $\mathcal{O}(N_P^2 N_{orb}^5)$. (For each element of D2D and D2P, one must evaluate N_P^2 determinants of $N_{orb} - 2 \times N_{orb} - 2$ matrices.) The actual cost is reduced because the orbitals, in methods like this, tend to be localized (so $\mathfrak{D}_{ij}$ and $\mathfrak{P}_{ij}$ tend rapidly to zero when orbitals i and j are localized more than a few Angstroms away from each other) and because the matrices $\mathbf{K}_{i\alpha,j\beta}$ and $\mathbf{K}_{k\alpha,l\beta}$ differ only by two rows/columns. Using rank-1 updates (cf. ref. [JAL+13]), one can evaluate each determinant of the form $|\mathbf{K}_{i\alpha,j\beta}|$ with cost $\mathcal{O}(N_{orb}^2)$. The cost of evaluating D2D and D2P is therefore reduced to $\mathcal{O}(N_P^2 N_{orb}^4)$.

The variational principle for the energy may be written as

$$\begin{aligned} E_{GS} &= \min_{\{\{\lambda\};\{\varepsilon\} \| \{\tilde{\mu}\}\rangle = |\{\lambda\}\rangle\}} \frac{\langle\{\tilde{\mu}\}|\hat{H}|\{\lambda\}\rangle}{\langle\{\tilde{\mu}\}|\{\lambda\}\rangle} \\ &= \min_{\{\{\lambda\};\{\varepsilon\} \| \{\tilde{\mu}\}\rangle = |\{\lambda\}\rangle\}} 2\sum_{i=1}^{N_{orb}} h_i^i \gamma_i + \sum_{i,j=1}^{N_{orb}} [(2V_{ij}^{ij} - V_{ji}^{ij})\mathfrak{D}_{ij} + V_{jj}^{ii}\mathfrak{P}_{ij}] \end{aligned} \tag{3.55}$$

where the summation is performed so that i runs through each spatial orbital once. Notice the explicit requirement that the wavefunction be the same in its particle $|\{\lambda\}\rangle$ and hole $|\{\tilde{\mu}\}\rangle$ representations.

It should be clear from the preceding discussion that expressions for higher-order reduced density matrices can be derived by the same approach, although the procedures quickly become tedious.

3.5 Hyperbolic On- and Off-Shell Bethe Vectors

The reduced BCS Hamiltonian, (3.22), represents a completely isotropic interaction between the pairs. There are more general Hamiltonians, with anisotropic interactions, that also have eigenvectors which may be determined using a Bethe ansatz. For example, the XXZ Hamiltonian,

$$\hat{H}_{XXZ} = \sum_{i=1}^{N_{orb}} \varepsilon_i S_i^z + g \sum_{i,j=1}^{N_{orb}} \sqrt{\varepsilon_i \varepsilon_j} S_i^+ S_j^- \tag{3.56}$$

has eigenvectors of the geminal-product form,

$$|\{\lambda\}, \{\eta\}\rangle = \prod_{\alpha=1}^{N_P} \mathfrak{S}^+(\lambda_\alpha) \, |\theta\rangle \tag{3.57}$$

where

$$\mathfrak{S}^+(\lambda_\alpha) = \sum_{i=1}^{N_{orb}} \frac{\eta_i}{\lambda_\alpha - \varepsilon_i} S_i^+ \tag{3.58}$$

(Compare Eqs. (3.22)-(3.24). Eq. (3.58) is called the hyperbolic Bethe vector; Eq. (3.24) is the rational Bethe vector.) In this special case, $\eta_i = \sqrt{\varepsilon_i}$ and the rapidities satisfy the Bethe ansatz conditions,

$$-\frac{1}{\lambda_\alpha}\left(\frac{1}{g} + N_{orb} - 2(N_P - 1)\right) + \sum_{i=1}^{N_{orb}} \frac{1}{\lambda_\alpha - \varepsilon_i} - 2\sum_{\beta \neq \alpha} \frac{1}{\lambda_\alpha - \lambda_\beta} = 0 \tag{3.59}$$

It is not difficult to see that the solutions of Eqs. (3.25) and (3.59) must be distinct. However, the eigenvector has no additional parameters, so there is only a limited improvement in flexibility over the Richardson wavefunction. The off-shell case, with arbitrary $\{\eta\}$, is more interesting. There are now $2N_{orb}+N_P$ free parameters. Defining the dual state,

$$\langle\{\tilde{\mu}\},\{\eta\}| = \langle\tilde{\theta}| \prod_{\alpha=1}^{N_{orb}-N_P} \mathfrak{S}^+(\tilde{\mu}_\alpha), \tag{3.60}$$

expressions for the scalar product and form factors can be worked out with the same techniques employed in the previous section. Specifically,

$$\langle\{\tilde{\mu}\},\{\eta\}|\{\lambda\},\{\eta\}\rangle = \prod_{k=1}^{N_{orb}} \eta_k \,\langle\{\tilde{\mu}\}|\{\lambda\}\rangle \tag{3.61}$$

$$\langle\{\tilde{\mu}\},\{\eta\}|S^+_i|\{\lambda\}_\alpha,\{\eta\}\rangle = \prod_{k\neq i}^{N_{orb}} \eta_k \,\langle\{\tilde{\mu}\}|S^+_i|\{\lambda\}_\alpha\rangle \tag{3.62}$$

$$\langle\{\tilde{\mu}\},\{\eta\}|S^+_iS^+_j|\{\lambda\}_{\alpha,\beta},\{\eta\}\rangle = \prod_{k\neq i,j}^{N_{orb}} \eta_k \,\langle\{\tilde{\mu}\}|S^+_iS^+_j|\{\lambda\}_{\alpha,\beta}\rangle \tag{3.63}$$

$$\langle\{\tilde{\mu}\},\{\eta\}|S^z_i|\{\lambda\},\{\eta\}\rangle = \prod_{k=1}^{N_{orb}} \eta_k \,\langle\{\tilde{\mu}\}|S^z_i|\{\lambda\}\rangle \tag{3.64}$$

$$\langle\{\tilde{\mu}\},\{\eta\}|S^z_iS^z_j|\{\lambda\},\{\eta\}\rangle = \prod_{k=1}^{N_{orb}} \eta_k \,\langle\{\tilde{\mu}\}|S^z_iS^z_j|\{\lambda\}\rangle \tag{3.65}$$

$$\langle\{\tilde{\mu}\},\{\eta\}|S^+_iS^-_j|\{\lambda\},\{\eta\}\rangle = \eta_j \prod_{k\neq i}^{N_{orb}} \eta_k \,\langle\{\tilde{\mu}\}|S^+_iS^-_j|\{\lambda\}\rangle \tag{3.66}$$

Using the expressions for the reduced density matrices in Eqs. (3.19)-(3.21), it is clear that only the D2P elements of the 2DM change,

$$\mathfrak{P}^\eta_{ij} = \frac{\eta_j}{\eta_i}\frac{1}{\det\mathbf{K}}\left(\sum_{\alpha=1}^{N_P}\frac{\det\mathbf{K}_{i\alpha}}{(\lambda_\alpha-\varepsilon_j)} - \sum_{\alpha=1}^{N_P}\sum_{\beta\neq\alpha}\frac{\det\mathbf{K}_{i\alpha,j\beta}}{(\lambda_\alpha-\varepsilon_j)(\lambda_\beta-\varepsilon_j)}\right) = \frac{\eta_j}{\eta_i}\mathfrak{P}_{ij} \tag{3.67}$$

The parameters $\{\eta\}$ introduce a bias into a lattice of otherwise equivalent orbitals.

For example, if $\varepsilon_i = \varepsilon_j$, then in the rational model, $\mathfrak{P}_{ij} = \mathfrak{P}_{ji}$. However, in the hyperbolic model the hopping term from pair i to pair j is generally different from the hopping term from pair j to pair i. (Specifically, $\mathfrak{P}^{\eta}_{ij} \neq \mathfrak{P}^{\eta}_{ji}$ unless $\eta_i = \eta_j$.)

One can generalize the wavefunction in Eqs. (3.57)-(3.58) by considering the most general form for which Borchardt's theorem holds,

$$|\{\lambda\},\{\eta\},\{\tau\}\rangle = \prod_{\alpha=1}^{N_P} \sum_{i=1}^{N_{orb}} \frac{\eta_i \tau_\alpha}{\lambda_\alpha - \varepsilon_i} S^+_i \,|\theta\rangle \tag{3.68}$$

However, this only changes the normalization of the wavefunction,

$$|\{\lambda\},\{\eta\},\{\tau\}\rangle = \prod_{\beta=1}^{N_P} \tau_\beta \prod_{\alpha=1}^{N_P} \sum_{i=1}^{N_{orb}} \frac{\eta_i}{\lambda_\alpha - \varepsilon_i} S^+_i \,|\theta\rangle = \prod_{\beta=1}^{N_P} \tau_\beta \,|\{\lambda\},\{\eta\}\rangle \tag{3.69}$$

so none of the density matrix components change.

3.6 Nonorthogonal Orbitals

An alternative perspective on the hyperbolic model wavefunction, Eqs. (3.57)-(3.58), is that it relaxes the constraint that the orbitals be orthonormal. Specifically, the hyperbolic model is equivalent to a rational model where the normalization of the orbitals is changed to η_i, but the orbitals are still orthogonal. Can one generalize the rational model to general, nonorthogonal, nonnormalized, single-particle states? Such a formulation is especially interesting because electron-pair wavefunctions constructed from nonorthogonal orbitals are the fundamental building block of elementary valence-bond calculations [SH11, WSSH11, SH08, Gal02].

The preceding procedure for deriving the matrix elements of reduced density matrices still works, but there are additional nonvanishing matrix elements that occur because

$$a_i^\dagger a^j + a^j a_i^\dagger = \langle \phi_i | \phi_j \rangle \neq \delta_{ij} \tag{3.70}$$

Denoting the elements of the overlap matrix with $\Omega_{ij} = \langle \phi_i | \phi_j \rangle$, the scalar product is

$$\det \mathbf{\Omega} = \langle \{\tilde{\mu}\} | \{\lambda\} \rangle \tag{3.71}$$

This factor appears in the numerator and denominator of all the expressions for the density matrices, so it does not affect the final result. In this section, the single-particle states are numbered sequentially, such that: $S^+_m = a^\dagger_{(2m-1)} a^\dagger_{(2m)}$. The final expressions are

$$\gamma^j_i = \begin{cases} \Omega_{ji} \sum_{\alpha=1}^{N_P} \frac{1}{\lambda_\alpha - \varepsilon_{\frac{i+1}{2}}} \langle \{\tilde{\mu}\} | S^+_{\frac{i+1}{2}} | \{\lambda\}_\alpha \rangle & \text{i odd} \\ \Omega_{ji} \sum_{\alpha=1}^{N_P} \frac{1}{\lambda_\alpha - \varepsilon_{\frac{i}{2}}} \langle \{\tilde{\mu}\} | S^+_{\frac{i}{2}} | \{\lambda\}_\alpha \rangle & \text{i even} \end{cases} \tag{3.72}$$

$$\Gamma^{kl}_{ij} = \begin{cases} \sum_{\alpha=1}^{N_P} \sum_{\beta\neq\alpha} \frac{\Omega_{ki}\Omega_{lj}-\Omega_{li}\Omega_{kj}}{\left(\lambda_\alpha-\varepsilon_{\frac{j+1}{2}}\right)\left(\lambda_\beta-\varepsilon_{\frac{i+1}{2}}\right)} \langle\{\tilde{\mu}\}|S^+_{\frac{i+1}{2}}S^+_{\frac{j+1}{2}}|\{\lambda\}_{\alpha\beta}\rangle & \text{i odd, j odd} \\ \delta_{i(j-1)} \sum_{\alpha=1}^{N_P} \sum_{m=1}^{N_{orb}} \frac{\Omega_{l(2m-1)}\Omega_{k(2m)}-\Omega_{k(2m-1)}\Omega_{l(2m)}}{\lambda_\alpha-\varepsilon_m} \langle\{\tilde{\mu}\}|S^+_{\frac{i+1}{2}}|\{\lambda\}_{\alpha}\rangle & \\ +\sum_{\alpha=1}^{N_P} \sum_{\beta\neq\alpha} \frac{\Omega_{ki}\Omega_{lj}-\Omega_{li}\Omega_{kj}}{\left(\lambda_\alpha-\varepsilon_{\frac{i+1}{2}}\right)\left(\lambda_\beta-\varepsilon_{\frac{j}{2}}\right)} \langle\{\tilde{\mu}\}|S^+_{\frac{i+1}{2}}S^+_{\frac{j}{2}}|\{\lambda\}_{\alpha\beta}\rangle & \text{i odd, j even} \\ \delta_{i(j+1)} \sum_{\alpha=1}^{N_P} \sum_{m=1}^{N_{orb}} \frac{\Omega_{k(2m-1)}\Omega_{l(2m)}-\Omega_{l(2m-1)}\Omega_{k(2m)}}{\lambda_\alpha-\varepsilon_m} \langle\{\tilde{\mu}\}|S^+_{\frac{i}{2}}|\{\lambda\}_{\alpha}\rangle & \\ +\sum_{\alpha=1}^{N_P} \sum_{\beta\neq\alpha} \frac{\Omega_{ki}\Omega_{lj}-\Omega_{li}\Omega_{kj}}{\left(\lambda_\alpha-\varepsilon_{\frac{i}{2}}\right)\left(\lambda_\beta-\varepsilon_{\frac{j+1}{2}}\right)} \langle\{\tilde{\mu}\}|S^+_{\frac{i}{2}}S^+_{\frac{j+1}{2}}|\{\lambda\}_{\alpha\beta}\rangle & \text{i even, j odd} \\ \sum_{\alpha=1}^{N_P} \sum_{\beta\neq\alpha} \frac{\Omega_{ki}\Omega_{lj}-\Omega_{li}\Omega_{kj}}{\left(\lambda_\alpha-\varepsilon_{\frac{j}{2}}\right)\left(\lambda_\beta-\varepsilon_{\frac{i}{2}}\right)} \langle\{\tilde{\mu}\}|S^+_{\frac{i}{2}}S^+_{\frac{j}{2}}|\{\lambda\}_{\alpha\beta}\rangle & \text{i even, j even} \end{cases} \tag{3.73}$$

3.7 Numerical Considerations

3.7.1 Preliminaries

The results from sections 3.2-3.6 indicate that one may variationally optimize the off-shell Bethe vectors associated with the Richardson Hamiltonian. In order to give explicit procedures for doing this, it is useful to write the rapidities of the dual state as

$$\lambda_{N_P+i} = \tilde{\mu}_i \tag{3.74}$$

With this notational convention, the wavefunction and its dual are written as

$$|\{\lambda_\alpha\}_{\alpha=1}^{N_P}, \{\varepsilon_i, \eta_i\}_{i=1}^{N_{orb}}\rangle = \prod_{\alpha=1}^{N_P} \sum_{i=1}^{N_{orb}} \frac{\eta_i}{\lambda_\alpha - \varepsilon_i} S^+_i |\theta\rangle \tag{3.75}$$

and

$$|\{\lambda_\alpha\}_{\alpha=N_P+1}^{N_{orb}}, \{\varepsilon_i, \eta_i\}_{i=1}^{N_{orb}}\rangle = \prod_{\alpha=N_P+1}^{N_{orb}} \sum_{i=1}^{N_{orb}} \frac{\eta_i^*}{\lambda_\alpha^* - \varepsilon_i} S_i^- |\tilde{\theta}\rangle \,, \tag{3.76}$$

respectively.

3.7.2 Bivariational Principle

The bivariational principle was introduced to quantum chemistry by Boys and Handy [BH69], and is relatively well-known in (albeit rarely used by) the coupled-cluster community [Ber73, Kut91, Arp83, Kva13, Kva12, BP87, Pal86]. It indicates that the asymmetric energy expectation value expression,

$$E[\Psi, \tilde{\Psi}] = \frac{\langle\tilde{\Psi}|\hat{H}|\Psi\rangle}{\langle\tilde{\Psi}|\Psi\rangle} \tag{3.77}$$

is stationary with respect to variations of both $|\Psi\rangle$ and $|\tilde{\Psi}\rangle$

$$\frac{\delta E[\Psi, \tilde{\Psi}]}{\delta \Psi} = \frac{\delta E[\Psi, \tilde{\Psi}]}{\delta \tilde{\Psi}} = 0 \tag{3.78}$$

only when $|\Psi\rangle$ and $|\tilde{\Psi}\rangle$ are equal to each other (i.e., they are dual) and they are equal to an eigenstate of the Hamiltonian. (Matters are slightly more complicated for degenerate states.) Applying this principle to our *approximate* $\mathfrak{su}(2)$ wavefunction ansatz, and using the notation from the previous section, one needs to solve $3N_{orb}$

nonlinear equations in $3N_{orb}$ unknowns,

$$\begin{aligned}\frac{\partial E[\{\lambda_i,\eta_i,\varepsilon_i\}_{i=1}^{N_{orb}}]}{\partial \lambda_i} &= 0\\ \frac{\partial E[\{\lambda_i,\eta_i,\varepsilon_i\}_{i=1}^{N_{orb}}]}{\partial \eta_i} &= 0\\ \frac{\partial E[\{\lambda_i,\eta_i,\varepsilon_i\}_{i=1}^{N_{orb}}]}{\partial \varepsilon_i} &= 0\end{aligned} \tag{3.79}$$

In practical calculations, one would also optimize over the choice of orbitals. This could be done together with the optimization of the wavefunction-parameters or alternately, iteratively optimizing the wavefunction parameters (Eq. (3.79)) and then minimizing the resulting energy expression with respect to the orbitals until convergence.

The bivariational principle does not provide a lower bound to the true energy; the energy expression in Eq. (3.77) is not bounded from below. It is not even guaranteed that the stationary values for the energy are real (though this could be added as a variational constraint). If, however, the solution of Eqs. (3.79) gives wavefunctions that are dual,

$$\prod_{\alpha=1}^{N_P}\sum_{i=1}^{N_{orb}}\frac{\eta_i}{\lambda_\alpha-\varepsilon_i}S_i^+\left|\theta\right\rangle = \prod_{\alpha=N_P+1}^{N_{orb}}\sum_{i=1}^{N_{orb}}\frac{\eta_i^*}{\lambda_\alpha^*-\varepsilon_i}S_i^-\left|\tilde{\theta}\right\rangle, \tag{3.80}$$

then the stationary-value for the energy is an upper bound to the true ground-state energy.

3.7.3 Dual-Constrained Minimization

The failsafe method for variationally optimizing the $\mathfrak{su}(2)$ wavefunction is to minimize the energy expression subject to the duality constraint, Eq. (3.80). (See, for example, Eq. (3.55).) We have been unable to find any practical way to exactly enforce the duality constraint. Notice, however, that the duality constraint is valid if and only if

$$\left\langle \Phi \left| \prod_{\alpha=1}^{N_P} \sum_{i=1}^{N_{orb}} \frac{\eta_i}{\lambda_\alpha - \varepsilon_i} S_i^+ \right| \theta \right\rangle = \left\langle \Phi \left| \prod_{\alpha=N_P+1}^{N_{orb}} \sum_{i=1}^{N_{orb}} \frac{\eta_i^*}{\lambda_\alpha^* - \varepsilon_i} S_i^- \right| \tilde{\theta} \right\rangle \quad \forall \Phi \tag{3.81}$$

Equation (3.81) can be easily evaluated if Φ is a Slater determinant. Specifically, both sides of the equation are zero if any electron in the Slater determinant is unpaired. If the Slater determinant has the same pairing structure as the $\mathfrak{su}(2)$ wavefunction, then Eq. (3.81) is an identity about the permanents of the coefficient matrices,

$$|\mathbf{C}_\Phi|^+ = |\tilde{\mathbf{C}}_\Phi|^+ \tag{3.82}$$

where the $N_P \times N_P$ matrix $\mathbf{C}_\Phi$ includes orbitals that are occupied in Φ and the $(N_{orb} - N_P) \times (N_{orb} - N_P)$ matrix $\tilde{\mathbf{C}}_\Phi$ includes orbitals that are not occupied in Φ. I.e.,

$$\mathbf{C}_\Phi = \begin{bmatrix} \frac{\eta_{i_1 \in \Phi}}{\lambda_1 - \varepsilon_{i_1 \in \Phi}} & \frac{\eta_{i_2 \in \Phi}}{\lambda_1 - \varepsilon_{i_2 \in \Phi}} & \cdots & \frac{\eta_{i_{N_P} \in \Phi}}{\lambda_1 - \varepsilon_{i_{N_P} \in \Phi}} \\ \frac{\eta_{i_1 \in \Phi}}{\lambda_2 - \varepsilon_{i_1 \in \Phi}} & \frac{\eta_{i_2 \in \Phi}}{\lambda_2 - \varepsilon_{i_2 \in \Phi}} & \cdots & \frac{\eta_{i_{N_P} \in \Phi}}{\lambda_2 - \varepsilon_{i_{N_P} \in \Phi}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\eta_{i_1 \in \Phi}}{\lambda_{N_P} - \varepsilon_{i_1 \in \Phi}} & \frac{\eta_{i_2 \in \Phi}}{\lambda_{N_P} - \varepsilon_{i_2 \in \Phi}} & \cdots & \frac{\eta_{i_{N_P} \in \Phi}}{\lambda_{N_P} - \varepsilon_{i_{N_P} \in \Phi}} \end{bmatrix} \tag{3.83}$$

$$\tilde{\mathbf{C}}_\Phi = \begin{bmatrix} \frac{\eta^*_{i_1 \notin \Phi}}{\lambda^*_{N_P+1} - \varepsilon_{i_1 \notin \Phi}} & \frac{\eta^*_{i_2 \notin \Phi}}{\lambda^*_{N_P+1} - \varepsilon_{i_2 \notin \Phi}} & \cdots & \frac{\eta^*_{i_{N_{orb}-N_P} \notin \Phi}}{\lambda^*_{N_P+1} - \varepsilon_{i_{N_{orb}-N_P} \notin \Phi}} \\ \frac{\eta^*_{i_1 \notin \Phi}}{\lambda^*_{N_P+2} - \varepsilon_{i_1 \notin \Phi}} & \frac{\eta^*_{i_2 \notin \Phi}}{\lambda^*_{N_P+2} - \varepsilon_{i_2 \notin \Phi}} & \cdots & \frac{\eta^*_{i_{N_{orb}-N_P} \notin \Phi}}{\lambda^*_{N_P+2} - \varepsilon_{i_{N_{orb}-N_P} \notin \Phi}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\eta^*_{i_1 \notin \Phi}}{\lambda^*_{N_{orb}} - \varepsilon_{i_1 \notin \Phi}} & \frac{\eta^*_{i_2 \notin \Phi}}{\lambda^*_{N_{orb}} - \varepsilon_{i_2 \notin \Phi}} & \cdots & \frac{\eta^*_{i_{N_{orb}-N_P} \notin \Phi}}{\lambda^*_{N_{orb}} - \varepsilon_{i_{N_{orb}-N_P} \notin \Phi}} \end{bmatrix} \tag{3.84}$$

The permanents of these rank-2 matrices can be efficiently evaluated. Specifically, Eq. (3.82) reduces to the constraint,

$$\mathfrak{d}[\Phi] = \frac{|\mathbf{C}_\Phi \circ \mathbf{C}_\Phi|}{|\mathbf{C}_\Phi|} - \frac{|\tilde{\mathbf{C}}_\Phi \circ \tilde{\mathbf{C}}_\Phi|}{|\tilde{\mathbf{C}}_\Phi|} = 0 \tag{3.85}$$

where $\circ$ denotes the Hadamard (element-wise) product.

It is not practical to impose the duality constraint in Eq. (3.85) for all Slater determinants. In the spirit of our recent work using the projected Schrödinger equation to optimize the parameters in the $\mathfrak{su}(2)$ wavefunction, we only require Eq. (3.85) to hold for a reference determinant

$$|\Phi_0\rangle = |1\bar{1}2\bar{2}\dots N_P\bar{N}_P\rangle \tag{3.86}$$

and its one-pair excitations,

$$|\Phi^{a\bar{a}}_{i\bar{i}}\rangle = S^+_a S^-_i |1\bar{1}2\bar{2}\dots N_P\bar{N}_P\rangle, \quad 1 \leq i \leq N_P \leq a \leq N_{orb} \tag{3.87}$$

In comparison to our previous work, we are using an approximate expression for duality instead of approximately forcing the wavefunction to satisfy the Schrödinger equation. Even with this restriction, Eq. (3.85) represents $N_P(N_{orb} - N_P)$ equations with only $3N_P$ unknowns; we believe that it is very unlikely to find a solution to this equation that are not true dual vectors. If one is suspicious that spurious false-dual vectors have been found, one can add consider pair-excitations from additional reference Slater determinants.

Introducing Lagrange multipliers for the duality constraints, the duality constrained variational principle corresponds to optimizing the Lagrangian

$$\mathcal{L}[\{\lambda, \varepsilon, \eta\}; \{\xi\}] = E[\{\lambda, \varepsilon, \eta\}] + \xi_0 \mathfrak{d}[\Phi_0] + \sum_{i=1}^{N_P} \sum_{a=N_P+1}^{N_{orb}} \xi_i^a \mathfrak{d}[\Phi_{i\bar{i}}^{a\bar{a}}]. \tag{3.88}$$

Even though the equations we use to force duality are overdetermined, solutions always exist because every eigenstate of a Richardson-like Hamiltonian, Eqs. (3.22) or (3.56), has a dual representation. Specifically, given an eigenvector of Richardson's equations, $|\{\lambda\}\rangle$, the dual vector is the solution of the overdetermined set of nonlinear equations [TF14],

$$\sum_{j=N_P+1}^{N_{orb}} \frac{\eta_i}{\varepsilon_i - \lambda_j} = \sum_{j=1}^{N_P} \frac{\eta_i}{\varepsilon_i - \lambda_j} - \frac{2}{g}, \quad \forall i \tag{3.89}$$

It is unclear whether Eqs. (3.89) are necessary and sufficient for duality. Given an arbitrary off-shell eigenvector, however, one could construct a near-dual state by solving the equations,

$$\sum_{j=1}^{N_P} \frac{\eta_i}{\varepsilon_i - \lambda_j} - \sum_{j=N_P+1}^{N_{orb}} \frac{\eta_i}{\varepsilon_i - \lambda_j} = \bar{c} \tag{3.90}$$

where

$$\bar{c} = \frac{1}{N_{orb}} \sum_{i=1}^{N_{orb}} \left(\sum_{j=1}^{N_P} \frac{\eta_i}{\varepsilon_i - \lambda_j} - \sum_{j=N_P+1}^{N_{orb}} \frac{\eta_i}{\varepsilon_i - \lambda_j} \right). \tag{3.91}$$

3.7.4 Projected Schrödinger Equation

These approaches can be contrasted with the approach we have used previously, based on the projected Schrödinger equation. In the projected Schrödinger equation, we examine the weak formulation of the eigenvalue problem, namely,

$$\langle \tilde{\Psi} | \hat{H} | \{\lambda, \varepsilon, \eta\} \rangle = E \langle \tilde{\Psi} | \{\lambda, \varepsilon, \eta\} \rangle , \quad \forall \tilde{\Psi}. \tag{3.92}$$

That is, one projects the Schrödinger equation against all possible wavefunctions, and forces the expected value of the energy to be the same in all cases.

In our previous work, we projected wavefunctions with the form (3.13) against Slater determinants [JAL$^+$13, LAJ$^+$13]. Since the action of the Hamiltonian on a Slater determinant is just a linear combination of Slater determinants, this procedure had computational cost $\mathcal{O}(N_P^3(N_{orb} - N_P)N_{orb})$. Now it is clear, however, that we could also project against off-shell XXZ wavefunctions,

$$\langle \{\tilde{\mu}, \varepsilon, \eta\} | \hat{H} | \{\lambda, \varepsilon, \eta\} \rangle = E \langle \{\tilde{\mu}, \varepsilon, \eta\} | \{\lambda, \varepsilon, \eta\} \rangle \tag{3.93}$$

Evaluating each of these nonlinear equations is just as difficult as evaluating the energy itself, and one needs at least one equation for each unknown parameter in the wavefunction. (Often one would choose more equations than unknowns, and then determine the least-squares solution to the overdetermined system of equations.) The cost of this procedure is at least $\mathcal{O}(N_P^2 N_{orb}^5)$, but it will be more robust than projection against Slater determinants when the orbital picture breaks down so completely that it is difficult to pick a suitable set of Slater determinants to project against.

3.8 Special Case: The Antisymmetrized Geminal Power

The antisymmetrized geminal power (AGP) wavefunction arises when all the geminals are equal [Col65]. Referring to the wavefunction form (3.57)-(3.58), we must set all the rapidities equal to each other. However, it is convenient to retain both $\{\varepsilon\}$ and $\{\eta\}$ as (redundant) free parameters,

$$|\mathrm{AGP}\rangle = \left(\sum_{i=1}^{N_{orb}} \frac{\eta_i S_i^+}{\lambda - \varepsilon_i} \right)^{N_P} |\theta\rangle \equiv \left(\sum_{i=1}^{N_{orb}} c_i S_i^+ \right)^{N_P} |\theta\rangle \tag{3.94}$$

To obtain an explicit energy expression, we need to find the dual representation of this state. We will demonstrate, later, that the dual representation is also an AGP, i.e.,

$$|\mathrm{AGP}\rangle = \left(\sum_{i=1}^{N_{orb}} \frac{\eta_i^* S_i^-}{\mu - \varepsilon_i} \right)^{N_{orb}-N_P} |\tilde{\theta}\rangle \equiv \left(\sum_{i=1}^{N_{orb}} \tilde{c}_i S_i^- \right)^{N_{orb}-N_P} |\tilde{\theta}\rangle \tag{3.95}$$

The two representations of the wavefunction are equivalent if, for any Slater determinant in which all electrons are paired, the following equation holds:

$$\left\langle \Phi \left| \left(\sum_{i=1}^{N_{orb}} c_i S_i^+ \right)^{N_P} \right| \theta \right\rangle = \left\langle \Phi \left| \left(\sum_{i=1}^{N_{orb}} \tilde{c}_i S_i^- \right)^{N_{orb}-N_P} \right| \tilde{\theta} \right\rangle . \tag{3.96}$$

Referring to section 3.7.2, this implies an identity about the permanents of the coefficient matrices, with the simplifying feature that every row in the matrices (3.83) and (3.84) is the same. Using the formula for the permanent of a rank-one matrix, Eq. (3.96) can be rewritten as

$$N_P! \prod_{i \in \Phi} c_i = (N_{orb} - N_P)! \prod_{i \notin \Phi} \tilde{c}_i \tag{3.97}$$

The solution to this equation is

$$\tilde{c}_i \frac{\left(\frac{N_P!}{(N_{orb}-N_P)!} \prod_{k=1}^{N_{orb}} c_k \right)^{\frac{1}{N_{orb}-N_P}}}{c_i} \tag{3.98}$$

as may be verified by direct substitution into Eq. (3.97). Note that the existence of this explicit solution confirms that the dual representation of an AGP, Eq. (3.94), is also an AGP, Eq. (3.95). The numerator of Eq. (3.98) is a constant, which is arbitrary since choosing its value is controlled by the phase and normalization of the wavefunction. The duality constraint is therefore

$$\tilde{c}_i c_i = \mathcal{K} \tag{3.99}$$

Finding the dual representation in the XXZ form of the AGP is equivalent to solving two equations and two unknowns. For convenience, fix the scale and zero of energy by setting $\lambda = 0$ and $\mu = 1$. Then, from Eqs. (3.94), (3.95), and (3.99),

$$\begin{aligned} c_i &= -\frac{\eta_i}{\varepsilon_i} \\ c_i\tilde{c}_i &= \frac{|\eta|^2}{\varepsilon_i(1-\varepsilon_i^*)} = \mathcal{K} \end{aligned} \tag{3.100}$$

The solution to these equations is

$$\begin{aligned} \varepsilon_i &= \frac{\mathcal{K}^*}{|c_i|^2 + \mathcal{K}^*} \\ \eta_i &= -\frac{\mathcal{K}^* c_i}{|c_i|^2 + \mathcal{K}^*} \end{aligned} \tag{3.101}$$

This gives an explicit expression for the energy that can be minimized as a function of c_i. It is simpler, mathematically, to derive expressions if one chooses $\{\varepsilon_i\}$ to be real-valued variational parameters, imposes the duality condition

$$\eta_i = \sqrt{\varepsilon_i(1-\varepsilon_i)}, \tag{3.102}$$

and minimizes the energy as a function of $\{\varepsilon_i\}$.

3.9 Discussion

In the quantum theory of electronic structure, there are very few wavefunction-families that lend themselves to variational optimization. We believe that an ideal variational method should be size-consistent and that its computational requirements should grow only as a (preferably small) polynomial in the size of the system. While there is some debate about whether size-consistent variational methods exist [HG14], we believe that the approaches presented here meet these requirements. Not many previous methods do, and one could argue that aside from full-CI, the only variational size-consistent methods are mean-field models for (quasi)particles, like the methods considered in this paper. Other polynomial-scaling and variational post-Hartree-Fock methods (e.g., limited configuration interaction) tend not to be size-consistent. Polynomial and size-consistent post Hartree-Fock methods (e.g., coupled cluster methods, many body perturbation theory) tend not to be variational. The density matrix renormalization group (DMRG) algorithm for optimizing matrix product states is variational and size-consistent, but has exponentially-growing computational cost for most three-dimensional molecular systems [CS11, Whi92, Whi93, CHG02].

Our approach fits best into the hierarchy of geminal-based approaches. The antisymmetric product of strongly orthogonal geminals wavefunction (and the generalized valence bond-perfect pairing wavefunction, which is a special case of that method), are also size-consistent, variational, and polynomial-scaling post-Hartree-Fock methods. The antisymmetric geminal power wavefunction is variational and polynomial-scaling, but not size-consistent. The question arises: can we stretch the geminals formulation while retaining (a) a polynomial-cost variational method, (b) size-consistency, and (c) a theory that includes all of the more traditional geminal-based wavefunctions as special cases? The methods presented here, based on the variational optimization of off-shell Cauchy geminals, do exactly this. To what extent can the results in this paper be generalized even further? For example, in reference [JAL$^+$13], we used the superalgebras, $\mathfrak{gl}(m|n)$, to develop approaches for open-shell atoms and molecules. The treatment presented in this paper can be extended to these superalgebras, but the associated method has factorial computational scaling. We have explored many other algebras also, but factorial computational cost seems to arise for all algebras except $\mathfrak{su}(2)$.

Can we variationally optimize more general wavefunctions based on $\mathfrak{su}(2)$? For example, in reference [LAJ+13], we used the projected Schrödinger equation to explore an $\mathfrak{su}(2)$-based wavefunction with the form,

$$|\text{AP1roG}\rangle = \prod_{\alpha=1}^{N_P} \left(\delta_{\alpha i} + \sum_{i=N_P+1}^{N_{orb}} g_{\alpha,i} \right) S_i^+ \, |\theta\rangle \tag{3.103}$$

This wavefunction, which we call AP1roG (antisymmetric product of 1-reference-orbital geminals) has proved to be highly effective for many systems, including some that are strongly correlated. Can we use the methods in this paper to formulate a variational version of that theory?

A variational version of AP1roG indeed exists. It even has the desirable property that the dual vector is easily constructed. Specifically, the dual vectors are,

$$\langle \text{AP1roG}| = \langle \tilde{\theta}| \prod_{\alpha=N_P+1}^{N_{orb}} \left(\delta_{i\alpha} + \sum_{i=1}^{N_P} g_{i,\alpha}^* \right) S_i^- \tag{3.104}$$

Unfortunately, evaluating permanents of matrices with the form

$$\boldsymbol{G}_{\text{AP1roG}} = \begin{bmatrix} \boldsymbol{I}_{N_P \times N_P} & \boldsymbol{G}_{N_P \times (N_{orb}-N_P)} \\ \boldsymbol{G}^\dagger_{(N_{orb}-N_P)\times N_P} & \boldsymbol{I}_{(N_{orb}-N_P)\times(N_{orb}-N_P)} \end{bmatrix} \tag{3.105}$$

is computational intractable, so variational optimization of the AP1roG wavefunction has factorial scaling.

3.10 Recapitulation

This chapter develops variational approaches for geminal product wavefunctions from the algebraic structure of $\mathfrak{su}(2)$. More specifically, it shows how the 1-electron and 2-electron reduced density matrices can be determined for quasi-spin wavefunctions, Eq. (3.13), of increasing generality. After considering the case where the wavefunction is an eigenfunction of the Richardson-Gaudin Hamiltonian (on-shell; section 3.3), we note that the reduced density matrices between wavefunctions that have the Richardson-Gaudin wavefunction form can also be evaluated (off-shell, section 3.4). We then generalize this wavefunction form to unnormalized (hyperbolic case, section 3.5) and nonorthogonal (section 3.6) orbitals. All of these methods are based on the same key "tricks:" elements of the reduced density matrices are written as expectation values of quasi-spin operators. These expectation values are then rewritten as projections onto the fully-filled Slater determinant. This trick allows us to exploit the only result that we know for a general quasi-spin wavefunction: the projection of a quasi-spin wavefunction onto a Slater determinant is a permanent (cf. Eq. (3.14)).

In section 3.6, we use the expressions for the density matrices to propose variational methods for determining the energy. The alternative, and more rigorous, approach is to minimize the energy subject to the constraint that the wavefunction expression in the ket (which generates electrons from the vacuum) and the wavefunction expression in the bra (which generates holes in the fully-filled Slater determinant) are equal. Both of these variational approaches have higher computational scaling than previously proposed methods based on the projected Schrdinger equation. As an application of this result, we developed a new, direct, and explicit, variational optimization procedure for the antisymmetrized geminal power (AGP) wavefunction.

Chapter 4

Open-shell Singlets and Triplets: $\mathfrak{sp}(n)$ and $\mathfrak{so}(4n)$

Previous chapters considered only seniority zero pairs. In this chapter we deal with operators coupled to produce open-shell singlets and triplets across several levels. Accordingly, the representation theory becomes substantially more involved. Coupled pair creators close the special orthogonal and symplectic Lie algebras, and integrable models could be constructed, but their eigenvectors obey too many symmetries to be physically reasonable.

4.1 Coupled Pairs of Fermions

Since upper and lower indices were included primarily for this chapter, let us briefly recall their properties. In a $SU(2) \supset U(1)$ basis with labels jm, annihilators with upper and lower indices are related as:

$$a^{jm} = (-1)^{j-m} a_{j(-m)}, \quad a_{jm} = (-1)^{j+m} a^{j(-m)} \tag{4.1}$$

One usually thinks of an annihilator as having *upper* indices, so any final expression to be used will employ upper indices. The usual anticommutation relations are expressed:

$$\left[a^{jm}, a^{j'm'}\right]_+ = \left[a^\dagger_{jm}, a^\dagger_{j'm'}\right]_+ = 0, \quad \left[a^{jm}, a^\dagger_{j'm'}\right]_+ = \delta_{jj'}\delta_{mm'} \tag{4.2}$$

This particular choice is made to emphasize the transformation of such operators in a spherical basis. A state with good $SU(2) \supset U(1)$ quantum numbers jm transforms through an $\Omega \in SU(2)$ rotation as:

$$|jm\rangle \rightarrow \hat{R}(\Omega)\,|jm\rangle = \sum_n D^j_{nm}\,|jn\rangle \tag{4.3}$$

where $D^j_{nm}(\Omega)$ are the matrix elements of the rotation

$$D^j_{nm}(\Omega) = \langle jn|\hat{R}(\Omega)|jm\rangle \tag{4.4}$$

and are called Wigner D-matrices. The resulting creation operators transform in a covariant manner, and are hence labelled by lower indices

$$a^\dagger_{jm} \rightarrow \hat{R}(\Omega) a^\dagger_{jm} \hat{R}(\Omega^{-1}) = \sum_n D^j_{nm}(\Omega) a^\dagger_{jn}. \tag{4.5}$$

Conversely, annihilators transform in a contravariant manner, which is obtained by taking the adjoint of the previous result

$$a^{jm} \to \hat{R}(\Omega) a^{jm} \hat{R}(\Omega^{-1}) = \sum_{n} (D^{j}_{nm})^{*}(\Omega) a^{jn}. \tag{4.6}$$

The choice of upper and lower indices is helpful in the coupling of individual operators to good jm numbers for two fermions. In a left-to-right coupling scheme[1] we can define a coupling to JM for two second quantized operators c_j with lower indices in terms of Clebsch-Gordan coefficients:

$$[c_j \otimes c_{j'}]^{J}_{M} = \sum_{mm'} (jm; j'm'|JM) c_{jm} c_{j'm'}. \tag{4.7}$$

As we are dealing with electrons (i.e. spin one-half fermions) the j label will be suppressed and only the $U(1)$ label (m) will be written. Now we will describe different couplings, the Lie algebras they close, and their corresponding irreducible representations (irreps).

4.1.1 Closed Shell Singlets

To clarify the notation, let us reconsider the treatment of $\mathfrak{su}(2)$ result of the previous chapters. In one (spatial) orbital, there are four possible occupations: $|jm\rangle =$

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[1] This is to say that angular momenta are coupled sequentially from left to right. Alternatively, see [RW10] where the convention is right-to-left. The results are the same up to phase transformations.

$\{|0,0\rangle, |\frac{1}{2},\frac{1}{2}\rangle, |\frac{1}{2},-\frac{1}{2}\rangle, |1,0\rangle\}$. The only Clebsch-Gordan coefficient we require for singlets are:

$$(j_1m_1;j_2m_2|00) = \delta_{j_1j_2}\delta_{m_1(-m_2)}\frac{(-1)^{j_1-m_1}}{\sqrt{2j_1+1}} \tag{4.8}$$

A substitution then yields $(\frac{1}{2}\frac{1}{2};\frac{1}{2}-\frac{1}{2}|00) = \frac{1}{\sqrt{2}}$, and $(\frac{1}{2}-\frac{1}{2};\frac{1}{2}\frac{1}{2}|00) = -\frac{1}{\sqrt{2}}$. The couplings are then:

$$\begin{aligned}
\left[a_i^\dagger \otimes a_i^\dagger\right]^0_0 &= \frac{1}{\sqrt{2}}\left(a^\dagger_{i\frac{1}{2}}a^\dagger_{i-\frac{1}{2}} - a^\dagger_{i-\frac{1}{2}}a^\dagger_{i\frac{1}{2}}\right) = \sqrt{2}S_i^+ && (4.9)\\
\left[a_i \otimes a_i\right]^0_0 &= \frac{1}{\sqrt{2}}\left(a_{i\frac{1}{2}}a_{i-\frac{1}{2}} - a_{i-\frac{1}{2}}a_{i\frac{1}{2}}\right) = \sqrt{2}a_{i\frac{1}{2}}a_{i-\frac{1}{2}} = -\sqrt{2}a^{i-\frac{1}{2}}a^{i\frac{1}{2}}\\
&= -\sqrt{2}S_i^- && (4.10)\\
\left[a_i^\dagger \otimes a_i\right]^0_0 &= \frac{1}{\sqrt{2}}\left(a^\dagger_{i\frac{1}{2}}a_{i-\frac{1}{2}} - a^\dagger_{i-\frac{1}{2}}a_{i\frac{1}{2}}\right) = \frac{1}{\sqrt{2}}\left(a^\dagger_{i\frac{1}{2}}a^{i\frac{1}{2}} + a^\dagger_{i-\frac{1}{2}}a^{i-\frac{1}{2}}\right)\\
&= \sqrt{2}\left(S_i^Z + \frac{1}{2}\right) && (4.11)
\end{aligned}$$

For each spatial orbital index i, the operators $\{S_i^+, S_i^-, S_i^Z\}$ close a copy of $\mathfrak{su}(2)$. Taken together, with N spatial orbitals, the Lie algebra is $\bigoplus_{i=1}^N \mathfrak{su}(2)_i$.

4.1.2 Open Shell Singlets in two orbitals

It is impossible to have an open shell singlet in a single spatial orbital. In two spatial orbitals (labelled 1 and 2), we have two copies of $\mathfrak{su}(2)$ defined in the same way as above. That is, for $i = 1, 2$:

$$S_i^+ = \frac{1}{\sqrt{2}} \left[a_i^\dagger \otimes a_i^\dagger \right]_0^0 \tag{4.12a}$$

$$S_i^- = -\frac{1}{\sqrt{2}} \left[a_i \otimes a_i \right]_0^0 \tag{4.12b}$$

$$S_i^Z = \frac{1}{\sqrt{2}} \left[a_i^\dagger \otimes a_i \right]_0^0 - \frac{1}{2} \tag{4.12c}$$

Taken together, these objects close $\mathfrak{so}(4) \cong \mathfrak{su}(2) \oplus \mathfrak{su}(2)$ with structure constants

$$[S_i^+, S_j^-] = 2\delta_{ij} S_i^Z, \quad [S_i^Z, S_j^\pm] = \pm \delta_{ij} S_i^\pm. \tag{4.13}$$

The four remaining couplings can be arranged into a bi-spinor:

$$A_{\frac{1}{2}\frac{1}{2}} = \frac{1}{\sqrt{2}} \left[a_1^\dagger \otimes a_2^\dagger \right]_0^0 = \frac{1}{2} \left(a^\dagger_{1\frac{1}{2}} a^\dagger_{2-\frac{1}{2}} - a^\dagger_{1-\frac{1}{2}} a^\dagger_{2\frac{1}{2}} \right) \tag{4.14a}$$

$$A_{-\frac{1}{2}-\frac{1}{2}} = \frac{1}{\sqrt{2}} \left[a_1 \otimes a_2 \right]_0^0 = -\frac{1}{2} \left(a^{2-\frac{1}{2}} a^{1\frac{1}{2}} - a^{2\frac{1}{2}} a^{1-\frac{1}{2}} \right) \tag{4.14b}$$

$$A_{\frac{1}{2}-\frac{1}{2}} = -\frac{1}{\sqrt{2}} \left[a_1^\dagger \otimes a_2 \right]_0^0 = -\frac{1}{2} \left(a^\dagger_{1\frac{1}{2}} a^{2\frac{1}{2}} + a^\dagger_{1-\frac{1}{2}} a^{2-\frac{1}{2}} \right) \tag{4.14c}$$

$$A_{-\frac{1}{2}\frac{1}{2}} = -\frac{1}{\sqrt{2}} \left[a_2^\dagger \otimes a_1 \right]_0^0 = -\frac{1}{2} \left(a^\dagger_{2\frac{1}{2}} a^{1\frac{1}{2}} + a^\dagger_{2-\frac{1}{2}} a^{1-\frac{1}{2}} \right) \tag{4.14d}$$

$[-,-]$	$A_{-\frac{1}{2}-\frac{1}{2}}$	$A_{\frac{1}{2}-\frac{1}{2}}$	$A_{-\frac{1}{2}\frac{1}{2}}$	$A_{\frac{1}{2}\frac{1}{2}}$
$A_{-\frac{1}{2}-\frac{1}{2}}$	0	$\frac{1}{2}S_2^-$	$\frac{1}{2}S_1^-$	$\frac{1}{2}\left(S_1^Z+S_2^Z\right)$
$A_{\frac{1}{2}-\frac{1}{2}}$	$-\frac{1}{2}S_2^-$	0	$\frac{1}{2}\left(S_1^Z-S_2^Z\right)$	$-\frac{1}{2}S_1^+$
$A_{-\frac{1}{2}\frac{1}{2}}$	$-\frac{1}{2}S_1^-$	$\frac{1}{2}\left(S_2^Z-S_1^Z\right)$	0	$-\frac{1}{2}S_2^+$
$A_{\frac{1}{2}\frac{1}{2}}$	$-\frac{1}{2}\left(S_1^Z+S_2^Z\right)$	$\frac{1}{2}S_1^+$	$\frac{1}{2}S_2^+$	0

Table 4.1: Structure constants of the bi-spinor of the open-shell singlet $\mathfrak{so}(5)$, elements in the left column appear *first* in the commutator.

The subscript labelling in the bi-spinor is employed to simplify the structure constants, the non-zero ones being:

$$[S_1^Z, A_{\sigma\tau}] = \sigma A_{\sigma\tau}, \quad [S_2^Z, A_{\sigma\tau}] = \tau A_{\sigma\tau} \tag{4.15a}$$

$$[S_1^\pm, A_{\sigma\tau}] = \sqrt{\left(\frac{1}{2}\mp\sigma\right)\left(\frac{1}{2}\pm\sigma+1\right)}A_{(\sigma\pm1)\tau} \tag{4.15b}$$

$$[S_2^\pm, A_{\sigma\tau}] = \sqrt{\left(\frac{1}{2}\mp\tau\right)\left(\frac{1}{2}\pm\tau+1\right)}A_{\sigma(\tau\pm1)} \tag{4.15c}$$

and those between the elements of the bi-spinor are tabulated in Table 4.1.

These ten operators close the Lie algebra $\mathfrak{so}(5)$. Let's classify the irreducible representations according to the labels of the group chain

$$\underset{[l_1 l_2]}{SO(5)} \supset SO(4) \cong \underset{J_1}{SO(3)_1} \times \underset{J_2}{SO(3)_2} \supset \underset{M_1}{SO(2)_1} \times \underset{M_2}{SO(2)_2}.$$

The chosen $SO(5)$ labels denote the values of the Cartan elements on the highest weight in each irrep, sorted so that $l_1 > l_2$. Other choices are possible [CSM10]. Note: while there is an equivalence of the Lie algebras $\mathfrak{so}(4) \cong \mathfrak{so}(3)\oplus\mathfrak{so}(3) \cong \mathfrak{su}(2)\oplus\mathfrak{su}(2)$, the Lie groups are *not* equivalent. Instead, $SU(2)\times SU(2)$ is a double-cover of

$SO(4) \cong SO(3) \times SO(3)$.[2]

The 16 possible states in two spatial orbitals are split into five irreps, see Table 4.1.2.

4.1.3 Triplets in two levels

Once again we consider two spatial orbitals, but now we couple products of second-quantized operators to spin-one. The Clebsch-Gordan coefficients required are:

$$\left(\frac{1}{2}\frac{1}{2};\frac{1}{2}\frac{1}{2}\middle| 11\right) = \left(\frac{1}{2}-\frac{1}{2};\frac{1}{2}-\frac{1}{2}\middle| 1\ -1\right) = 1 \tag{4.16}$$

$$\left(\frac{1}{2}\frac{1}{2};\frac{1}{2}-\frac{1}{2}\middle| 11\right) = \left(\frac{1}{2}-\frac{1}{2};\frac{1}{2}\frac{1}{2}\middle| 10\right) = \frac{1}{\sqrt{2}} \tag{4.17}$$

Coupled operators are then:

$$X^{+} = \left[a_1^{\dagger} \otimes a_2^{\dagger}\right]^1_1 = a^{\dagger}_{1\frac{1}{2}}a^{\dagger}_{2\frac{1}{2}} \tag{4.18a}$$

$$X^{-} = \left[a_2 \otimes a_1\right]^1_{-1} = a^{2\frac{1}{2}}a^{1\frac{1}{2}} \tag{4.18b}$$

$$Y^{+} = \left[a_1^{\dagger} \otimes a_2^{\dagger}\right]^1_{-1} = a^{\dagger}_{1-\frac{1}{2}}a^{\dagger}_{2-\frac{1}{2}} \tag{4.18c}$$

$$Y^{-} = \left[a_2 \otimes a_1\right]^1_{1} = a^{2-\frac{1}{2}}a^{1-\frac{1}{2}} \tag{4.18d}$$

---

[2] That is to say there is a projective mapping $\phi : SU(2) \rightarrow SO(3)$. Each element $g \in SO(3)$, there are two elements in the preimage $\phi^{-1}(g)$.

$[l_1, l_2]$	(J_1, J_2)	M_1	M_2	
$[\frac{1}{2}, \frac{1}{2}]$	$(\frac{1}{2}, \frac{1}{2})$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\|\theta\rangle$
		$\frac{1}{2}$	$-\frac{1}{2}$	$S^+_1 \|\theta\rangle$
		$-\frac{1}{2}$	$\frac{1}{2}$	$S^+_2 \|\theta\rangle$
		$\frac{1}{2}$	$\frac{1}{2}$	$S^+_1 S^+_2 \|\theta\rangle$
	$(0, 0)$	0	0	$A_{\frac{1}{2}\frac{1}{2}} \|\theta\rangle$
$[\frac{1}{2}, 0]$	$(\frac{1}{2}, 0)$	$\frac{1}{2}$	0	$a^\dagger_{2\frac{1}{2}} \|\theta\rangle$
		$-\frac{1}{2}$	0	$S^+_1 a^\dagger_{2\frac{1}{2}} \|\theta\rangle$
	$(0, \frac{1}{2})$	0	$-\frac{1}{2}$	$a^\dagger_{1\frac{1}{2}} \|\theta\rangle$
		0	$\frac{1}{2}$	$S^+_2 a^\dagger_{1\frac{1}{2}} \|\theta\rangle$
$[\frac{1}{2}, 0]$	$(\frac{1}{2}, 0)$	$\frac{1}{2}$	0	$a^\dagger_{2-\frac{1}{2}} \|\theta\rangle$
		$-\frac{1}{2}$	0	$S^+_1 a^\dagger_{2-\frac{1}{2}} \|\theta\rangle$
	$(0, \frac{1}{2})$	0	$-\frac{1}{2}$	$a^\dagger_{1-\frac{1}{2}} \|\theta\rangle$
		0	$\frac{1}{2}$	$S^+_2 a^\dagger_{1-\frac{1}{2}} \|\theta\rangle$
$[0, 0]$	$(0, 0)$	0	0	$a^\dagger_{1\frac{1}{2}} a^\dagger_{2\frac{1}{2}} \|\theta\rangle$
$[0, 0]$	$(0, 0)$	0	0	$a^\dagger_{1-\frac{1}{2}} a^\dagger_{2-\frac{1}{2}} \|\theta\rangle$
$[0, 0]$	$(0, 0)$	0	0	$\frac{1}{2}\left(a^\dagger_{1\frac{1}{2}} a^\dagger_{2-\frac{1}{2}} + a^\dagger_{1-\frac{1}{2}} a^\dagger_{2\frac{1}{2}}\right) \|\theta\rangle$

Table 4.2: Irreps of $\mathfrak{so}(5)$ singlet

$$\begin{aligned}
X^0 &= \frac{1}{2\sqrt{2}}\left(\left[a_1^\dagger \otimes a_1\right]^0_0 + \left[a_2^\dagger \otimes a_2\right]^0_0 + \left[a_1^\dagger \otimes a_1\right]^1_0 + \left[a_2^\dagger \otimes a_2\right]^1_0 - \sqrt{2}\right) \\
&= \frac{1}{2}\left(a^\dagger_{1\frac{1}{2}} a^{1\frac{1}{2}} + a^\dagger_{2\frac{1}{2}} a^{2\frac{1}{2}} - 1\right) && (4.18e) \\
Y^0 &= \frac{1}{2\sqrt{2}}\left(\left[a_1^\dagger \otimes a_1\right]^0_0 + \left[a_2^\dagger \otimes a_2\right]^0_0 - \left[a_1^\dagger \otimes a_1\right]^1_0 - \left[a_2^\dagger \otimes a_2\right]^1_0 - \sqrt{2}\right) \\
&= \frac{1}{2}\left(a^\dagger_{1-\frac{1}{2}} a^{1-\frac{1}{2}} + a^\dagger_{2-\frac{1}{2}} a^{2-\frac{1}{2}} - 1\right) && (4.18f)
\end{aligned}$$

It is easily verified that individually these two sets $\{X^+, X^-, X^0\}$, and $\{Y^+, Y^-, Y^0\}$ close $\mathfrak{su}(2)$ algebras:

$$[X^0, X^\pm] = \pm X^\pm, \quad [X^+, X^-] = 2X^0 \tag{4.19}$$

$$[Y^0, Y^\pm] = \pm Y^\pm, \quad [Y^+, Y^-] = 2Y^0 \tag{4.20}$$

$$[X^a, Y^b] = 0, \;\; a, b \in \{+, -, 0\} \tag{4.21}$$

and together close $\mathfrak{so}(4) \cong \mathfrak{su}(2) \oplus \mathfrak{su}(2)$ as before. A bi-spinor is obtained from the remaining couplings:

$$\begin{aligned}
T_{\frac{1}{2}\frac{1}{2}} &= \frac{1}{\sqrt{2}}\left[a_1^\dagger \otimes a_2^\dagger\right]^1_0 = \frac{1}{2}\left(a^\dagger_{1\frac{1}{2}} a^\dagger_{2-\frac{1}{2}} + a^\dagger_{1-\frac{1}{2}} a^\dagger_{2\frac{1}{2}}\right) && (4.22a) \\
T_{-\frac{1}{2}-\frac{1}{2}} &= \frac{1}{\sqrt{2}}\left[a_2 \otimes a_1\right]^1_0 = -\frac{1}{2}\left(a^{2\frac{1}{2}} a^{1-\frac{1}{2}} + a^{2-\frac{1}{2}} a^{1\frac{1}{2}}\right) && (4.22b) \\
T_{\frac{1}{2}-\frac{1}{2}} &= \frac{1}{2}\left(\left[a_1^\dagger \otimes a_1\right]^1_1 + \left[a_2^\dagger \otimes a_2\right]^1_1\right) = -\frac{1}{2}\left(a^\dagger_{1\frac{1}{2}} a^{1-\frac{1}{2}} + a^\dagger_{2\frac{1}{2}} a^{2-\frac{1}{2}}\right) && (4.22c) \\
T_{-\frac{1}{2}\frac{1}{2}} &= -\frac{1}{2}\left(\left[a_1^\dagger \otimes a_1\right]^1_{-1} + \left[a_2^\dagger \otimes a_2\right]^1_{-1}\right) = -\frac{1}{2}\left(a^\dagger_{1-\frac{1}{2}} a^{1\frac{1}{2}} + a^\dagger_{2-\frac{1}{2}} a^{2\frac{1}{2}}\right) && (4.22d)
\end{aligned}$$

These ten operators close the Lie algebra $\mathfrak{so}(5)$, and the structure constants are essentially identical with those for the open-shell singlet case with the "letter isomorphism", i.e. replace $\{S_1, S_2, A\}$ with $\{X, Y, T\}$. Explicitly, the structure constants of

$[-,-]$	$T_{-\frac{1}{2}-\frac{1}{2}}$	$T_{\frac{1}{2}-\frac{1}{2}}$	$T_{-\frac{1}{2}\frac{1}{2}}$	$T_{\frac{1}{2}\frac{1}{2}}$
$T_{-\frac{1}{2}-\frac{1}{2}}$	0	$\frac{1}{2}Y^-$	$\frac{1}{2}X^-$	$\frac{1}{2}(X^0+Y^0)$
$T_{\frac{1}{2}-\frac{1}{2}}$	$-\frac{1}{2}Y^-$	0	$\frac{1}{2}(X^0-Y^0)$	$-\frac{1}{2}X^+$
$T_{-\frac{1}{2}\frac{1}{2}}$	$-\frac{1}{2}X^-$	$\frac{1}{2}(Y^0-X^0)$	0	$-\frac{1}{2}Y^+$
$T_{\frac{1}{2}\frac{1}{2}}$	$-\frac{1}{2}(X^0+Y^0)$	$\frac{1}{2}X^+$	$\frac{1}{2}Y^+$	0

Table 4.3: Structure constants of the bi-spinor of the triplet $\mathfrak{so}(5)$, elements in the left column appear *first* in the commutator.

the $\mathfrak{su}(2)$ copies with the bi-spinor are:

$$[X^0, T_{\sigma\tau}] = \sigma T_{\sigma\tau}, \quad [Y^0, T_{\sigma\tau}] = \tau T_{\sigma\tau} \tag{4.23a}$$

$$[X^\pm, T_{\sigma\tau}] = \sqrt{\left(\frac{1}{2} \mp \sigma\right)\left(\frac{1}{2} \pm \sigma + 1\right)} T_{(\sigma\pm1)\tau} \tag{4.23b}$$

$$[Y^\pm, T_{\sigma\tau}] = \sqrt{\left(\frac{1}{2} \mp \tau\right)\left(\frac{1}{2} \pm \tau + 1\right)} T_{\sigma(\tau\pm1)} \tag{4.23c}$$

and those of the bi-spinor elements are summarized in Table 4.3.

The same possible 16 states are present, but decompose into different irreps than in the singlet case. With the group chain

$$\underset{[\mu_1\mu_2]}{SO(5)} \supset SO(4) \cong \underset{X}{SO(3)_X} \times \underset{Y}{SO(3)_Y} \supset \underset{M_X}{SO(2)_X} \times \underset{M_Y}{SO(2)_Y},$$

the irreps are as in Table 4.1.3. The $SO(5)$ labels are again of Cartan highest weight.

$[\mu_1, \mu_2]$	(X, Y)	M_X	M_Y	
$[\frac{1}{2}, \frac{1}{2}]$	$(\frac{1}{2}, \frac{1}{2})$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\vert\theta\rangle$
		$\frac{1}{2}$	$-\frac{1}{2}$	$X^+\vert\theta\rangle$
		$-\frac{1}{2}$	$\frac{1}{2}$	$Y^+\vert\theta\rangle$
		$\frac{1}{2}$	$\frac{1}{2}$	$X^+Y^+\vert\theta\rangle$
	$(0, 0)$	0	0	$T_{\frac{1}{2}\frac{1}{2}}\vert\theta\rangle$
$[\frac{1}{2}, 0]$	$(\frac{1}{2}, 0)$	$\frac{1}{2}$	0	$a^\dagger_{1-\frac{1}{2}}\vert\theta\rangle$
		$-\frac{1}{2}$	0	$X^+a^\dagger_{1-\frac{1}{2}}\vert\theta\rangle$
	$(0, \frac{1}{2})$	0	$-\frac{1}{2}$	$a^\dagger_{1\frac{1}{2}}\vert\theta\rangle$
		0	$\frac{1}{2}$	$Y^+a^\dagger_{1\frac{1}{2}}\vert\theta\rangle$
$[\frac{1}{2}, 0]$	$(\frac{1}{2}, 0)$	$\frac{1}{2}$	0	$a^\dagger_{2-\frac{1}{2}}\vert\theta\rangle$
		$-\frac{1}{2}$	0	$X^+a^\dagger_{2-\frac{1}{2}}\vert\theta\rangle$
	$(0, \frac{1}{2})$	0	$-\frac{1}{2}$	$a^\dagger_{2\frac{1}{2}}\vert\theta\rangle$
		0	$\frac{1}{2}$	$Y^+a^\dagger_{2\frac{1}{2}}\vert\theta\rangle$
$[0, 0]$	$(0, 0)$	0	0	$a^\dagger_{1\frac{1}{2}}a^\dagger_{1-\frac{1}{2}}\vert\theta\rangle$
$[0, 0]$	$(0, 0)$	0	0	$a^\dagger_{2\frac{1}{2}}a^\dagger_{2-\frac{1}{2}}\vert\theta\rangle$
$[0, 0]$	$(0, 0)$	0	0	$\frac{1}{2}\left(a^\dagger_{1\frac{1}{2}}a^\dagger_{2-\frac{1}{2}} - a^\dagger_{1-\frac{1}{2}}a^\dagger_{2\frac{1}{2}}\right)\vert\theta\rangle$

Table 4.4: Irreps of $\mathfrak{so}(5)$ triplet

4.1.4 Open-Shell Singlets in N Levels

Taking N levels together, we can couple second quantized operators to produce all possible singlets in these N spatial orbitals. Each spatial orbital gets a copy of $\mathfrak{su}(2)$, and each pair of spatial orbitals gets a four-element bi-spinor like Eqs. (4.14). In total, there are

$$3N + 4\binom{N}{2} = N(2N+1) \tag{4.24}$$

operators, which is the dimension of both $\mathfrak{sp}(N)$ and $\mathfrak{so}(2N+1)$. Aside from the "accidental isomorphisms" $\mathfrak{sp}(1) \cong \mathfrak{so}(3)(\cong \mathfrak{su}(2))$, and $\mathfrak{sp}(2) \cong \mathfrak{so}(5)$, the Lie algebras $\mathfrak{sp}(N)$ and $\mathfrak{so}(2N+1)$ are dual, and correspond to a rotation of the long roots. The correct Lie algebra in our case is $\mathfrak{sp}(N)$. Given that $\mathfrak{sp}(N)$ has N conserved quantities, it is in general intractable to label and classify irreps.

4.1.5 Open-Shell Singlets and Triplets in N levels

Whereas it is possible to close a Lie algebra with only triplet operators for two spatial orbitals as $\mathfrak{so}(5)$, this is only a low-dimensional coincidence. Constructing the set of triplet operators in N levels is indeed possible, but evaluating commutators produces linear combinations of *singlet* operators. These operators close $\mathfrak{so}(4N)$ for N spatial orbitals. Employing coupled operators in this algebra is tedious, cumbersome, and unnecessary. It is *much* simpler to use instead all quadratic combinations of second quantized operators, which is equivalent in this case.

Worse than the case above, $\mathfrak{so}(4N)$ has $2N$ conserved quantities, and its representation theory is just as tedious as one might expect.

4.2 Geminals

In the previous section, several couplings of second quantized operators to singlet and triplet pair creators were presented and the Lie algebras they closed were discussed. We now look at what may be usefully done with these pair creators. In previous chapters, many-electron states were constructed as quasi-particles of closed shell singlet pair creators. Many-body states will now be described in terms of more elaborate open shell singlet and triplet quasi-particles. As expected, the resulting states are much more complete in their representation of physical states. Also as expected, practical calculations seem to be impossible. Internal degrees of freedom make the projections of these states onto sets of chosen states intractable. There is no free lunch.

We consider direct sums of several copies of the Lie algebras described in the previous section. Distinct copies of each Lie algebra will commute as they act on different spaces and consist of even numbers of second quantized operators. For each type of coupling we expand a $2N_P$ electron wavefunction in terms of N_P geminals. As in chapter 2, it is possible to construct integrable models for each Lie algebra. There is always at least a rational version of a transfer matrix (which looks like the quadratic Casimir element of the Lie algebra) but the eigenvectors have too many symmetries. In addition, for an exactly solvable Hamiltonian built upon a Lie algebra of rank n, there will be n sets of coupled non-linear equations to solve which characterize the quasi-particles. Finally, while Slavnov's theorem is the engine that makes the results in chapter 2 possible, there is no nice known formulae for higher-order Lie algebras, though there is much work for the simplest rank-2 algebra: $\mathfrak{su}(3)$ [BPRS12].

Define an arbitrary geminal as a two-electron state to be expressed in a given single-particle basis:

$$G^{\dagger}_{\alpha} = \sum_{ij} g^{ij}_{\alpha} a^{\dagger}_{i} a^{\dagger}_{j} \tag{4.25}$$

The upper indices are employed to reflect that if the state $|kl\rangle$ is transformed, then the (direct) matrix element

$$g^{kl}_{\alpha} = (kl|G^{\dagger}_{\alpha}|\theta\rangle \tag{4.26}$$

is transformed in a contravariant manner. We will look at states of the form

$$\prod_{\alpha=1}^{N_P} G^{\dagger}_{\alpha} \left|\theta\right\rangle \tag{4.27}$$

restricting the pair-creators to those defined in the previous section. We will therefore look at a projected Schrödinger equation approach: the geminal products will be expanded in symmetry-adapted $2N_P$ electron basis functions, called configuration state functions (CSFs). The task of the chapter is to calculate the projections of the $2N_P$ electron state on individual CSFs so that a projected approach may be considered. Unfortunately, CSFs are not in general orthogonal (or even linearly independent), which makes the choice of which CSFs to include significant.

Similar to the approach in chapter 3, we can also evaluate scalar products between many-electron states provided that one is written in terms of particles and the other is written in terms of holes. In this case, the scalar product is just the projection of a $2N$ electron state on the fully occupied "vacuum", a single Slater determinant.

4.2.1 Closed Shell Singlets: $\mathfrak{su}(2)$

The results for closed-shell singlets will be rewritten in a more convenient notation to clarify the procedure. Restricting the summation to closed shell singlets, the geminal creator is

$$G^{\dagger}_{\alpha}[\mathfrak{su}(2)] = \sum^{N}_{i=1} f^i_{\alpha} S^+_i. \tag{4.28}$$

In other chapters, we were primarily interested in the algebraic structure of these objects, and consequently this geminal was labelled $\mathbb{S}^+(\lambda)$. We now seek to expand a many-body state $|\mathfrak{su}(2)\rangle$ in terms of many-body basis functions (in this case Slater determinants). I.e. for the state

$$|\mathfrak{su}(2)\rangle = \prod^{N_P}_{\alpha=1} \sum^{N}_{i=1} f^i_{\alpha} S^+_i \left|\theta\right\rangle = \sum_{\omega} C_{\omega} \left|\Phi_{\omega}\right\rangle, \tag{4.29}$$

we want to identify the many-electron basis functions $|\Phi_{\omega}\rangle$ and their respective expansion coefficients C_{ω}. The $2N_P$ electron basis functions $|\Phi_{\omega}\rangle$ are Slater determinants which are conveniently form an orthonormal set. Consequently, the projection in which we are interested is just the respective expansion coefficient

$$\langle \Phi_{\omega} | \mathfrak{su}(2)\rangle = \sum_{\omega'} C_{\omega'} \left\langle \Phi_{\omega} | \Phi_{\omega'} \right\rangle = C_{\omega}. \tag{4.30}$$

From here a projected Schrödinger equation approach follows easily.

Consider the monomials of S^+_i's in Eq. (4.29). Can a monomial contain the same

S_i^+ more than once? In chapter 2, the quasi-spin representation was defined

$$S_i^+ = \sum_{m_i > 0} a^\dagger_{m_i} a^\dagger_{\bar{m}_i} \tag{4.31}$$

to allow for degeneracies in the single-particle spectrum, which was convenient to maintain spherical symmetry while solving Richardson's equations. For the purposes of this chapter each spatial orbital is considered separately, so

$$S_i^+ = a^\dagger_{i\frac{1}{2}} a^\dagger_{i-\frac{1}{2}} \tag{4.32}$$

and hence

$$S_i^+ S_i^+ = 0. \tag{4.33}$$

This means that a particular S_i^+ can appear in a monomial in Eq. (4.29) once. Further, the ordering doesn't matter since

$$[S_i^+, S_j^+] = 0. \tag{4.34}$$

The state (4.29) is then a sum of $\binom{N}{N_P}$ Slater determinants $|\Phi_\omega\rangle$ characterised by their occupation of the spatial orbitals ω, where ω is an ordered set of N_P integers, such that $1 \leq \omega_1 < \omega_2 < \dots < \omega_{N_P} \leq N$. The corresponding coefficient is a sum over all permutations σ:

$$C_\omega = \sum_\sigma \prod_{a=1}^{N_P} f^{\omega_a}_{\sigma(a)} \tag{4.35}$$

The symmetric sum can be thought of as the *permanent* of the matrix

$$C_\omega = \begin{vmatrix} f_1^{\omega_1} & & f_1^{\omega_{N_P}} \\ & \ddots & \\ f_{N_P}^{\omega_1} & & f_{N_P}^{\omega_{N_P}} \end{vmatrix}^+ . \tag{4.36}$$

4.2.2 Open Shell Singlets: $\mathfrak{so}(5)_S$

Provided that the number of spatial orbitals (N) is even, we may divide them into groups of two such that each spatial orbital has a definite partner. We will refer to such groupings as "$\mathfrak{so}(5)_S$ copies". In the case that N is odd, one spatial orbital can be chosen to be "privileged" with no partner, with the most obvious choices being those with the highest and lowest single-particle energies, i.e. those which are expected to be either completely empty or fully occupied. Such a choice is inevitably ad-hoc and must be made *a priori*. From now on we will assume that N is an even integer. In addition, it is convenient to assume that the basis has been arranged such that pairs of spatial orbitals occur sequentially in the numbering scheme.

Singlets in two spatial orbitals (labelled "1" and "2") are constructed with the three operators $\{S^+_1, S^+_2, A^+_{12}\}$, where the first two are closed shell singlets, and the open shell singlet creator is a relabelling of an operator defined in eq. (4.14); i.e. $A^+_{12} \equiv A_{\frac{1}{2}\frac{1}{2}}$ for the specific $\mathfrak{so}(5)_S$ copy for the set 1 and 2.

A geminal is then of the form

$$G^\dagger_\alpha[\mathfrak{so}(5)_S] = \sum_{i=1}^{N} f^{ii}_\alpha S^+_i + \sum_{j=1}^{N/2} f^{(2j-1)(2j)}_\alpha A^+_{(2j-1)(2j)}, \tag{4.37}$$

where the first term is just the closed shell $\mathfrak{su}(2)$ treatment as above. If only one pair is considered, then there always exists a unitary transformation which transforms the geminal (4.37) into the closed shell singlet (4.28). If more than one pair is considered there does not necessarily exist such a transformation.

Expanding the state

$$|\mathfrak{so}(5)_S\rangle = \prod_{a=1}^{N_P} G^\dagger_a[\mathfrak{so}(5)_S]\,|\theta\rangle = \sum_{\eta\omega} C^\eta_\omega\,|\Phi^\eta_\omega\rangle \tag{4.38}$$

in a basis of $2N_P$ electron functions composed of $\mathfrak{so}(5)$ generators involves the use of configuration state functions (CSFs):

$$|\Phi^\eta_\omega\rangle = \prod_{a=1}^{\eta} S^+_{\omega_a} \prod_{b=\eta+1}^{N_P} A^+_{(2\omega_b-1)(2\omega_b)}\,|\theta\rangle \tag{4.39}$$

If we restrict ourselves to states below half-filling, there are N_P+1 types of CSF which contribute (for $\eta = 0\ldots N_P$). The value of η (*i.e.* the number of closed shell singlets in the CSF) is a symmetry label of each CSF that contributes to the state (4.38), but the state itself has no such symmetry. The definition of ω, which labels the occupied states, needs to be updated: the first η entries label the fully occupied spatial orbitals, while the remaining labels are one-half of the upper spatial orbital in each $\mathfrak{so}(5)_S$ copy contributing to the CSF.

The representation theory is a little more difficult than it was for $\mathfrak{su}(2)$. The square of the open shell singlet creators are non-zero:

$$A^+_{ij}A^+_{ij} = -\frac{1}{2}S^+_i S^+_j \tag{4.40}$$

therefore we will only consider basis CSFs in which an open shell singlet creator A^+_{ij}

occurs at most once. Since distinct copies of $\mathfrak{so}(5)_S$ all act on distinct sets of spatial orbitals, this new basis is still orthogonal, with inner product

$$\langle \Phi^{\eta}_{\omega} | \Phi^{\eta'}_{\omega'} \rangle = 2^{-(N_P-\eta)} \delta_{\eta\eta'} \delta_{\omega\omega'}. \tag{4.41}$$

Once the expansion coefficients are known, the projections on the basis follow easily through Eq. (4.41). The coefficients can be worked out noting that

$$S^+_i A^+_{ij} = S^+_j A^+_{ij} = 0 \tag{4.42}$$

and for $\{ij\} \neq \{i'j'\}$

$$[S^+_i, A^+_{i'j'}] = [S^+_j, A^+_{i'j'}] = [A^+_{ij}, A^+_{i'j'}] = 0 \tag{4.43}$$

Therefore, each CSF in the expansion (4.38) has one of four possible contributions from each $\mathfrak{so}(5)_S$ copy:

1. Nothing, if the particular $\mathfrak{so}(5)_S$ copy is empty in the CSF
2. Half-occupied closed shell singlet: either $S^+_{(2j-1)}$ or $S^+_{(2j)}$
3. Half-occupied open shell singlet: $A^+_{(2j-1)(2j)}$
4. Fully occupied: contributions from both $S^+_{(2j-1)} S^+_{(2j)}$ and $A^+_{(2j-1)(2j)} A^+_{(2j-1)(2j)}$

The first case is trivial. For the second and third cases, each geminal $G^{\dagger}_{\alpha}$ contributes the corresponding f^{ii}_{α} or $f^{(2j-1)(2j)}_{\alpha}$ respectively. For the fourth case, each geminal contributes both $f^{(2j-1)(2j-1)}_{\alpha}$ and $f^{(2j)(2j)}_{\alpha}$ and each pair of geminals contributes $-\frac{1}{2} f^{(2j-1)(2j)}_{\alpha} f^{(2j-1)(2j)}_{\beta}$.

This is best illustrated by an example, e.g. the CSF

$$|\Phi^{(2)}_{\{1,2,2\}}\rangle = S^+_1 S^+_2 A^+_{34} |\theta\rangle \tag{4.44}$$

The coefficient is

$$C^{(2)}_{\{1,2,2\}} = \begin{vmatrix} f^{11}_1 & f^{22}_1 & f^{34}_1 \\ f^{11}_2 & f^{22}_2 & f^{34}_2 \\ f^{11}_3 & f^{22}_3 & f^{34}_3 \end{vmatrix}^+ - \frac{1}{2} \begin{vmatrix} f^{12}_1 & f^{12}_1 & f^{34}_1 \\ f^{12}_2 & f^{12}_2 & f^{34}_2 \\ f^{12}_3 & f^{12}_3 & f^{34}_3 \end{vmatrix}^+ \tag{4.45}$$

$$= \sum_{\sigma} \left(f^{11}_{\sigma(1)} f^{22}_{\sigma(2)} - \frac{1}{4} f^{12}_{\sigma(1)} f^{12}_{\sigma(2)} \right) f^{34}_{\sigma(3)} \tag{4.46}$$

where the sum is performed over all permutations σ. In general, each fully occupied $\mathfrak{so}(5)_S$ copy contributes a binomial like the bracketed term in Eq. (4.46) and evaluating the respective coefficient has combinatorial complexity.

4.2.3 Triplets: $\mathfrak{so}(5)_T$

The treatment is similar to the previous subsection with a few minor distinctions. The triplets in each $\mathfrak{so}(5)_T$ copy are constructed from the vector of spin-1 operators $\{X^+_{12}, Y^+_{12}, T^+_{12}\}$ where like the case for $\mathfrak{so}(5)_S$, the $J = 1, M = 0$ creator is a relabelling of an operator defined in eq. (**??**); i.e. $T^+_{12} \equiv T_{\frac{1}{2}\frac{1}{2}}$ for the specific $\mathfrak{so}(5)_T$ copy. The geminal considered is then

$$G^\dagger_\alpha[\mathfrak{so}(5)_T] = \sum_{j=1}^{N/2} \left(g^{(2j-1)(2j)}_\alpha X^+_{(2j-1)(2j)} + h^{(2j-1)(2j)}_\alpha Y^+_{(2j-1)(2j)} + k^{(2j-1)(2j)}_\alpha T^+_{(2j-1)(2j)} \right) \tag{4.47}$$

Similar to the singlet case, we have

$$X^+_{ij}T^+_{ij} = Y^+_{ij}T^+_{ij} = 0 \tag{4.48a}$$

$$T^+_{ij}T^+_{ij} = -\frac{1}{2}X^+_{ij}Y^+_{ij} \tag{4.48b}$$

Expanding a geminal product in terms of CSFs is not difficult, the only complication arises from the fully occupied $\mathfrak{so}(5)_T$ copies. In these cases, there are binomial contributions just like in the previous subsection. As a particular example, the CSF $X^+_{12}Y^+_{12}\left|\theta\right\rangle$ has coefficient

$$C = \sum_{\sigma}\left(g^{12}_{\sigma(1)}h^{12}_{\sigma(2)} - \frac{1}{4}k^{12}_{\sigma(1)}k^{12}_{\sigma(2)}\right) \tag{4.49}$$

Classifying CSFs in this basis is not difficult, but notationally cumbersome (and serves little purpose here, so it will be avoided).

4.2.4 Open Shell Singlets and Triplets: $\mathfrak{so}(8)$

In a straightforward generalization of the previous two sections, a relevant geminal is

$$G^\dagger_\alpha[\mathfrak{so}(8)] = G^\dagger_\alpha[\mathfrak{so}(5)_S] + G^\dagger_\alpha[\mathfrak{so}(5)_T], \tag{4.50}$$

and one easily verifies the additional identities

$$S^+_iX^+_{ij} = S^+_iY^+_{ij} = S^+_iT^+_{ij} = 0 \tag{4.51a}$$

$$A^+_{ij}X^+_{ij} = A^+_{ij}Y^+_{ij} = A^+_{ij}T^+_{ij} = 0 \tag{4.51b}$$

$$T^+_{ij}T^+_{ij} = -\frac{1}{2}X^+_{ij}Y^+_{ij} = \frac{1}{2}S^+_iS^+_j \tag{4.51c}$$

Once again, expanding a geminal product in terms of CSFs yields complications only when an $\mathfrak{so}(8)$ copy is fully occupied. For example, the CSF $S^+_1 S^+_2 \left|\theta\right\rangle$ has coefficient

$$C = \sum_{\sigma} \left(f^{11}_{\sigma(1)} f^{22}_{\sigma(2)} - g^{12}_{\sigma(1)} h^{12}_{\sigma(2)} - \frac{1}{4} f^{12}_{\sigma(1)} f^{12}_{\sigma(2)} + \frac{1}{4} k^{12}_{\sigma(1)} k^{12}_{\sigma(2)} \right), \tag{4.52}$$

similar to the previous two subsections.

4.3 Open Shell Singlets: $\mathfrak{sp}(N)$

Before looking at geminals it is worth reviewing some basic properties of the symmetric group.

4.3.1 The Symmetric Group and Some Elementary Properties of Groups

The *symmetric group* on N elements, $\mathfrak{S}_N$, consists of the set of all permutations of N objects.[3] For N objects, there are $N!$ ways of rearranging them, and hence $\mathfrak{S}_N$ has $N!$ elements. A *cycle* is a permutation $\sigma \in \mathfrak{S}_N$ such that acting on a set of objects $\{i_1, i_2, \dots, i_k\}$

$$\sigma(i_1) = i_2, \quad \sigma(i_2) = i_3, \quad \dots, \quad \sigma(i_k) = i_1 \tag{4.53}$$

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[3] A standard notation for the symmetric group would be S_N, but given how much S is already being overused, the fraktur character is employed.

In this case, the cycle σ can be written

$$\sigma = (1, 2, 3, \dots, k) \tag{4.54}$$

Any permutation can be written as a product of disjoint cycles with each integer up to N appearing in a single cycle. To be a group, we require a well-defined associative binary operation, an identity element, and inverses. The multiplication of permutations is defined by applying them sequentially from right to left. For example, with the three permutations $\sigma_1 = (1, 6)(2, 4, 3),\ \sigma_2 = (1, 3, 5, 4, 6),\ \sigma_3 = (1, 2, 5)$ the product is

$$\begin{aligned} \sigma_1\sigma_2\sigma_3 &= (1, 6)(2, 4, 3)(1, 3, 5, 4, 6)(1, 2, 5) \\ &= (1, 4)(2, 3, 5)(6). \end{aligned} \tag{4.55}$$

It is evaluated by starting with 1 and sequentially performing each permutation

$$\begin{aligned} &1 \xrightarrow{\sigma_3} 2 \xrightarrow{\sigma_2} 2 \xrightarrow{\sigma_1} 4 \\ &4 \xrightarrow{\sigma_3} 4 \xrightarrow{\sigma_2} 6 \xrightarrow{\sigma_1} 1 \\ &2 \xrightarrow{\sigma_3} 5 \xrightarrow{\sigma_2} 4 \xrightarrow{\sigma_1} 3 \\ &3 \xrightarrow{\sigma_3} 3 \xrightarrow{\sigma_2} 5 \xrightarrow{\sigma_1} 5 \\ &5 \xrightarrow{\sigma_3} 1 \xrightarrow{\sigma_2} 3 \xrightarrow{\sigma_1} 2 \\ &6 \xrightarrow{\sigma_3} 6 \xrightarrow{\sigma_2} 1 \xrightarrow{\sigma_1} 6 \end{aligned}$$

which can be written as a product of the three disjoint cycles $(1, 4)(2, 3, 5)(6)$ as above. An exercise shows that $(\sigma_1\sigma_2)\sigma_3 = \sigma_1(\sigma_2\sigma_3)$. The identity element is just the identity permutation, which is generally denoted (1). The inverse of any cycle is just the cycle with the elements listed in the reverse order, and the convention is to list the smallest element first. For example, the cycle $(1, 3, 2, 5, 7)$ has inverse $(7, 5, 2, 3, 1) = (1, 7, 5, 2, 3)$. For any permutation written as disjoint cycles, the inverse permutation is the product of the inverses of the disjoint cycles. $\mathfrak{S}_N$ is therefore a group.

A two-element cycle (i_1, i_2) is called a transposition, and any cycle can be written as a product of transpositions. The decomposition of a cycle into transpositions is not unique, nor is the number of transpositions. However, the parity of the number of transpositions is unique. Hence any permutation is unambiguously even or odd corresponding to whether the number of transpositions is even or odd.

If $(G, \circ, e)$ is a group (i.e. a set G with associative binary operation $\circ$ and identity element e), then $(H, \circ, e)$ is a *subgroup* of G if as a set $H \subset G$, $e \in H$, and H is closed under the operation $\circ$. The number of elements in G is called the order of G, and denoted $|G|$. Lagrange's theorem states that for any subgroup $H \subset G$,

$$|G| = |H| \cdot [G : H] \tag{4.56}$$

where $[G : H]$ is called the index of H in G. For $H \subset G$, the (left) cosets of H are the sets $gH \; \forall g \in G$. Cosets are either disjoint or identical, and a fundamental result is that the number of distinct cosets is $[G : H]$. Right cosets are defined similarly: $Hg \; \forall g \in G$. If the left and right cosets of H are identical, then H is called a normal subgroup and the set of cosets is called the factor or quotient group G/H.

Consider the example $\mathfrak{S}_4$, which has the $4! = 24$ elements:

$$\begin{aligned}\mathfrak{S}_4 = \{&(1),(1,2),(1,3),(1,4),(2,3),(2,4),(3,4),(1,2)(3,4),(1,3)(2,4),(1,4)(2,3)\\ &(1,2,3),(1,3,2),(1,2,4),(1,4,2),(1,3,4),(1,4,3),(2,3,4),(2,4,3),\\ &(1,2,3,4),(1,2,4,3),(1,3,2,4),(1,3,4,2),(1,4,2,3),(1,4,3,2)\}\end{aligned} \tag{4.57}$$

and the subgroup $H = \{(1),(2,3),(2,4),(3,4),(2,3,4),(2,4,3)\}$. $|\mathfrak{S}_4| = 24$ and $|H| = 6$, so there should be 4 distinct (left) cosets. They are:

$$H = \{(1),(2,3),(2,4),(3,4),(2,3,4),(2,4,3)\} \tag{4.58a}$$

$$(1,2)H = \{(1,2),(1,2,3),(1,2,4),(1,2)(3,4),(1,2,3,4),(1,2,4,3)\} \tag{4.58b}$$

$$(1,3)H = \{(1,3),(1,3,2),(1,3)(2,4),(1,3,4),(1,3,4,2),(1,3,2,4)\} \tag{4.58c}$$

$$(1,4)H = \{(1,4),(1,4)(2,3),(1,4,2),(1,4,3),(1,4,2,3),(1,4,3,2)\} \tag{4.58d}$$

The right cosets are not identical and hence H is not normal. A basic property of $\mathfrak{S}_N$, $N > 4$, is that the only normal subgroup is $\mathfrak{A}_N$, the alternating group on N elements (the set of all even permutations).

4.3.2 Geminals

We now consider all possible open shell singlets in the basis. With

$$A^{+}_{ij} = \frac{1}{2}\left(a^{\dagger}_{i\frac{1}{2}}a^{\dagger}_{j-\frac{1}{2}} - a^{\dagger}_{i-\frac{1}{2}}a^{\dagger}_{j\frac{1}{2}}\right), \tag{4.59}$$

it is readily observed that $A^+_{ji} = A^+_{ij}$ and $A^+_{ii} = S^+_i$. An appropriate geminal is then

$$G^\dagger_\alpha[\mathfrak{sp}(N)] = \sum_{ij} f^{ij}_\alpha A^+_{ij}. \tag{4.60}$$

If we make the assumption that $f^{ij}_\alpha = f^{ji}_\alpha$ then this geminal may be rewritten

$$G^\dagger_\alpha[\mathfrak{sp}(N)] = \sum_i f^{ii}_\alpha S^+_i + 2\sum_{i<j} f^{ij}_\alpha A^+_{ij} \tag{4.61}$$

which emphasizes the fact that each off-diagonal term occurs twice. A geminal product is once again written in terms of CSFs with symmetry label η denoting the number of closed shell pairs:

$$|\mathfrak{sp}(N)\rangle = \prod^{N_P}_{a=1} G^\dagger_a[\mathfrak{sp}(N)] \, |\theta\rangle = \sum_{\eta\omega} C^\eta_\omega \, |\Phi^\eta_\omega\rangle \tag{4.62}$$

The labelling ω is now a set of N_P pairs of index labels (i, j). For example, the CSF

$$A^+_{i_1,j_1} A^+_{i_2,j_2} A^+_{i_3,j_3} \, |\theta\rangle \tag{4.63}$$

has $\omega = \{(i_1, j_1), (i_2, j_2), (i_3, j_3)\}$. There are then η repeated indices. Without any loss of generality, we can list the η repeated indices first such that

$$\omega = \{(i_1, i_1), \dots, (i_\eta, i_\eta), (i_{\eta+1}, j_{\eta+1}), \dots, (i_{N_P}, j_{N_P})\}. \tag{4.64}$$

Projecting the state (4.62) onto a CSF is now more complicated since the CSFs themselves do not form an orthogonal basis. Specifically, for

$$\langle \Phi^{\eta'}_{\omega'} | \mathfrak{sp}(N) \rangle = \sum_{\eta\omega} C^{\eta}_{\omega} \langle \Phi^{\eta'}_{\omega'} | \Phi^{\eta}_{\omega} \rangle \tag{4.65}$$

both the coefficient C^{η}_{ω} and the overlap $\langle \Phi^{\eta'}_{\omega'} | \Phi^{\eta}_{\omega} \rangle$ are non-trivial. We'll deal first with the coefficient. There are two complications. The first is that any repeated index has the effect:

$$A^{+}_{ij} A^{+}_{ik} = -\frac{1}{2} S^{+}_{i} A^{+}_{jk} \tag{4.66}$$

and the second is that there is a braiding of the generators[4]

$$A^{+}_{ij} A^{+}_{kl} + A^{+}_{ik} A^{+}_{jl} + A^{+}_{il} A^{+}_{jk} = 0. \tag{4.67}$$

Eq. (4.66) makes the coefficients and the overlaps non-trivial but can be dealt with. We do not however know how to deal with eq. (4.67).

We'll consider the two extreme cases of $\eta = 0$ and $\eta = N_P$ first before presenting the general result. For $\eta = 0$, a typical CSF in the expansion (4.62) will look like

$$A^{+}_{i_1 j_1} \dots A^{+}_{i_{N_P} j_{N_P}} |\theta\rangle . \tag{4.68}$$

Since all the indices $\{(i,j)\}$ are distinct, no rearrangement of the indices will yield the same CSF. Therefore, for each A^{+}_{ij} in the CSF, each geminal will contribute $2 f^{ij}_{\alpha}$

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[4] Note the similarity with the classical Yang-Baxter equation in chapter 2.

to the coefficient. The result is just a permanent scaled by 2^{N_P}:

$$C^{(0)}_{(i_1j_1),\dots,(i_{N_P}j_{N_P})} = 2^{N_P} \begin{vmatrix} f^{i_1j_1}_1 & & f^{i_{N_P}j_{N_P}}_1 \\ & \ddots & \\ f^{i_1j_1}_{N_P} & & f^{i_{N_P}j_{N_P}}_{N_P} \end{vmatrix}^+ \tag{4.69}$$

$$= 2^{N_P} \sum_{\sigma} \prod_{a=1}^{N_P} f^{i_aj_a}_{\sigma(a)} \tag{4.70}$$

for every $\sigma \in \mathfrak{S}_{N_P}$. The permanent has been expressed algebraically (4.70) to compare with the result for the closed shell $\eta = N_P$. In that case, there is not only a contribution from the term

$$S^+_{i_1} \dots S^+_{i_{N_P}} \left|\theta\right> \equiv A^+_{i_1i_1} \dots A^+_{i_{N_P}i_{N_P}} \left|\theta\right>, \tag{4.71}$$

but also from every permutation π of the second lower indices. From (4.66), each transposition gives a factor of $-\frac{1}{2}$, but each of the A^+_{ij} occurs twice in the summation (4.60) so the contribution is just the sign of the permutation. The expression for the coefficient is then

$$C^{(N_P)}_{(i_1i_1),\dots,(i_{N_P}i_{N_P})} = \sum_{\pi} \sum_{\sigma} \text{sgn}(\pi) \prod_{a=1}^{N_P} f^{i_ai_{\pi(a)}}_{\sigma(a)}. \tag{4.72}$$

Before proceeding, a little comment on this object is warranted. The object f^{ij}_{α} is a rank-3 tensor (a sort of generalized matrix) and eq. (4.72) is a sort of generalized determinant or permanent of a rank-3 object. Are there results for such objects? Given the general difficulty of two dimensional permanents we are not optimistic and we are unaware of any results.[5]

Now consider $0 < \eta < N_P$, and arrange ω such that the distinct indices are at the end (as in eq. (4.64)). The set of permutations of all the $j \neq i$ forms a subgroup $H \subset \mathfrak{S}_{N_P}$ which is easily seen to be isomorphic to $H \cong \mathfrak{S}_{N_P-\eta}$. By Lagrange's theorem, there are $\frac{N_P!}{(N_P-\eta)!}$ distinct (left) cosets, which are labelled πH. For a CSF

$$|\Phi^{\eta}_{\omega}\rangle = \prod_{a=1}^{N_P} S^+_{\omega_a} \prod_{b=\eta+1}^{N_P} A^+_{\omega_b} |\theta\rangle \,, \tag{4.73}$$

any of the permutations $h \in H$ generate a different CSF. The remaining permutations which generate the same CSF (with of course the requisite $-\frac{1}{2}$ for each transposition) each label distinct cosets σH and there are $\frac{N_P!}{(N_P-\eta)!}$ of them. To write the final expression for the coefficient, we need to define an operation on a coset, labelled $\natural$ which takes the "smallest" element of a specific coset. For example, with the cosets (4.58), $\natural(H) = (1)$, and $\natural((1,2)H) = (1,2)$. For arbitrary η, the coefficient in the expansion (4.62) is then

$$C^{(\eta)} = 2^{N_P-\eta} \sum_{\{\pi H\}} \sum_{\sigma} \operatorname{sgn}(\natural(\pi H)) \prod_{a=1}^{N_P} f^{i_a j_{\natural(\pi H)(a)}}_{\sigma(a)}. \tag{4.74}$$

The first sum should be understood as being taken over the set of distinct (left) cosets. Let's check the limiting cases. For $\eta = 0$, then $H = \mathfrak{S}_{N_P}$ and there is a single coset. The identity is the smallest element, and has even signature, so this reduces to eq. (4.70). For $\eta = N_P$, then $H = \{(1)\}$, and there are then $N_P!$ distinct cosets,[6] and the result is eq. (4.72). Also, for $\eta = N_P - 1$, $H = \{(1)\}$ and there are still $N_P!$ distinct

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[5] Although our search has admittedly been *very* brief.

[6] that is, if we accept the idea that $\mathfrak{S}_0$, the symmetric group on zero elements can be considered a good object

cosets. This reduces to eq. (4.72) with a factor of 2 reflecting that the lone f^{ij} with $i \neq j$ occurs twice in each geminal.

We will close the section with a worked out example for 4 pairs of electrons, but we need to state the overlap between CSFs first. For two CSFs

$$\langle \Phi^{\eta'}_{\omega'} | \Phi^{\eta}_{\omega} \rangle = \frac{\delta_{\eta\eta'}}{2^{N_P - \eta}} \sum_{h \in H} \delta_{\{h(\omega')\}\{\omega\}} \left(-\frac{1}{2} \right)^{\flat(h)} \tag{4.75}$$

where the sum is taken over the subgroup H defined above. Non-vanishing results are only obtained if as a set, acting with h on the indices in ω' results in the set ω. The positive integer $\flat(h)$ is the *minimum* number of transpositions required to write h.

4.3.3 Example: $N_P = 4$

We'll project the state

$$|\mathfrak{sp}(N)\rangle = \prod_{a=1}^{4} G^{\dagger}_{a}[\mathfrak{sp}(N)] \tag{4.76}$$

against arbitrary CSFs. For $\eta = 4$, $H = \{(1)\}$ and there is only one term in the scalar product:

$$\langle \Phi^{(4)}_{\omega'} | \mathfrak{sp}(N) \rangle = \sum_{\eta\omega} C^{\eta}_{\omega} \langle \Phi^{\eta'}_{\omega'} | \Phi^{\eta}_{\omega} \rangle = C^{(4)}_{\omega'} \tag{4.77}$$

which is just eq. (4.72). The case $\eta = 3$ is similar, with

$$\langle \Phi^{(3)}_{\omega'} | \mathfrak{sp}(N) \rangle = \frac{1}{2} C^{(3)}_{\omega'} = \sum_{\pi} \sum_{\sigma} \text{sgn}(\pi) \prod_{a=1}^{N_P} f^{i_a j_{\pi(a)}}_{\sigma(a)}. \tag{4.78}$$

The factor of $\frac{1}{2}$ disappears since $C^{(3)}$ is similarly scaled with a factor of 2.

For $\eta = 2$, $\omega' = \{(i_1, i_1), (i_2, i_2), (i_3, j_3), (i_4, j_4)\}$, gives $H = \{(1), (3, 4)\}$. The twelve distinct cosets are:

$$\begin{aligned}
H &= \{(1), (3,4)\} & (1,2,3)H &= \{(1,2,3), (1,2,3,4)\} \\
(1,2)H &= \{(1,2), (1,2)(3,4)\} & (1,3,2)H &= \{(1,3,2), (1,3,4,2)\} \\
(1,3)H &= \{(1,3), (1,3,4)\} & (1,2,4)H &= \{(1,2,4), (1,2,4,3)\} \\
(1,4)H &= \{(1,4), (1,4,3)\} & (1,4,2)H &= \{(1,4,2), (1,4,3,2)\} \\
(2,3)H &= \{(2,3), (2,3,4)\} & (1,3)(2,4)H &= \{(1,3)(2,4), (1,3,2,4)\} \\
(2,4)H &= \{(2,4), (2,4,3)\} & (1,4)(2,3)H &= \{(1,4)(2,3), (1,4,2,3)\}
\end{aligned}$$

The permutations that will be summed over are thus

$$\begin{aligned}
\{\natural(\pi H)\} = \{&(1), (1,2), (1,3), (1,4), (2,3), (2,4), (1,2,3), \\
&(1,3,2), (1,2,4), (1,4,2), (1,3)(2,4), (1,4)(2,3)\}.
\end{aligned} \tag{4.79}$$

So, projecting a CSF we get

$$\langle \Phi^{(2)}_{\omega'} | \mathfrak{sp}(N) \rangle = \frac{1}{4} C^{(2)}_{(i_1,i_1),(i_2,i_2),(i_3,j_3),(i_4,j_4)} - \frac{1}{8} C^{(2)}_{(i_1,i_1),(i_2,i_2),(i_3,j_4),(i_4,j_3)} \tag{4.80}$$

and each coefficient may be evaluated with eq. (4.74).

For $\eta = 1$, $\omega' = \{(i_1, i_1), (i_2, j_2), (i_3, j_3), (i_4, j_4)\}$, gives

$$H = \{(1), (2, 3), (2, 4), (3, 4), (2, 3, 4), (2, 4, 3)\} \tag{4.81}$$

and the left cosets are already worked out in eq. (4.58). In evaluating coefficients, the permutations summed will be

$$\{\natural(\pi H)\} = \{(1), (1, 2), (1, 3), (1, 4)\}. \tag{4.82}$$

Projecting a CSF then yields

$$\begin{aligned}\langle \Phi^{(1)}_{\omega'} | \mathfrak{sp}(N) \rangle =& \frac{1}{8} C^{(1)}_{(i_1,i_1),(i_2,j_2),(i_3,j_3),(i_4,j_4)} - \frac{1}{16} C^{(1)}_{(i_1,i_1),(i_2,j_3),(i_3,j_2),(i_4,j_4)} \\ &- \frac{1}{16} C^{(1)}_{(i_1,i_1),(i_2,j_4),(i_3,j_3),(i_4,j_2)} - \frac{1}{16} C^{(1)}_{(i_1,i_1),(i_2,j_2),(i_3,j_4),(i_4,j_3)} \\ &+ \frac{1}{32} C^{(1)}_{(i_1,i_1),(i_2,j_4),(i_3,j_2),(i_4,j_3)} + \frac{1}{32} C^{(1)}_{(i_1,i_1),(i_2,j_3),(i_3,j_4),(i_4,j_2)} \end{aligned} \tag{4.83}$$

and once again each coefficient may be evaluated with eq. (4.74).

The last case, for which $\eta = 0$, follows easily, but writing it out serves little purpose. Note: in all of the last three cases, we are left with a set of restricted sums over the symmetric group. It looks like its possible to rescale portions of the object f^{ij}_{α} so that the final expression is a single unrestricted sum over the symmetric group.

In this chapter we have looked at different ways of coupling the spatial orbitals to describe open shell singlets and triplets. If it turns out to be possible to evaluate the "generalized determinants" in eq. (4.74), then wavefunctions composed of $\mathfrak{sp}(N)$ geminals would be an effective treatment of open shell singlets.

Chapter 5

Generalized Wavefunction Forms: $\mathfrak{gl}(m|n)$

[1] 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 wavefunction 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 $\mathcal{O}(N^5)$ scaling if all electrons are assumed to be paired, and with $\mathcal{O}(N^6)$ scaling otherwise. Based on the analogy with coupled-cluster theory, methods for computing spectroscopic properties, molecular forces, and response properties are proposed.

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[1] This chapter was originally published as [JAL$^+$13]

5.1 Motivation

Modern quantum chemistry, at both the conceptual and computational levels, is dominated by the orbital paradigm [HG96, HJO00]. 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 [HJO00, SO89]. 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 [CS11].

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 [BCS57].

The purpose of this chapter 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 [HLJP53, Sur99]. Our approach is different: in Section (5.2.1) 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 (APr2G), and the equations for determining the wavefunction are computationally tractable (Section 5.2.3). The APr2G form was inspired by the eigenfunctions of the Richardson Hamiltonian, which can be determined by a Bethe ansatz (Section 5.3.1) [Ric63, RS64].

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 5.3.2, 5.3.3, 5.3.4, wavefunctions that are appropriate for systems with unpaired electrons are derived by considering algebras of higher degree, $\mathfrak{gl}(n|k)$. $\mathfrak{gl}(n|k)$ is the general linear *super*-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 5.4; these methods are similar to those in coupled-cluster theory. Section 5.5

provides a summary of the main results in the paper. Readers who are primarily interested in the key results may safely skip Section 5.3, which is focused on the mathematical tools needed to derive the results in Section 5.2 and extend them to systems with unpaired electrons.

5.2 Pairing Models for the Wavefunction; gl(2,ℂ)

5.2.1 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

$$\hat{G}^{\dagger}_{p} = \sum^{2K}_{i,j=1} c_{ij;p} a^{\dagger}_{j} a^{\dagger}_{i} \tag{5.1}$$

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 [HLJP53, Low55], the pair-creation operator may be rewritten in as a sum over pairs of spin-orbitals,

$$\hat{G}^{\dagger}_{p} = \sum^{K}_{i=1} c_{i;p} a^{\dagger}_{2i} a^{\dagger}_{2i-1} = \sum^{K}_{i=1} c_{i;p} a^{\dagger}_{i} a^{\dagger}_{\bar{i}} \tag{5.2}$$

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 [SJHH$^+$11, BMWS08]. (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,

$$|\Psi\rangle = \prod_{q=1}^{P} \hat{G}_q^\dagger |\theta\rangle = \left(\sum_{i_1=1}^{K} c_{i_1;p} a_{i_1}^\dagger a_{\bar{i}_1}^\dagger\right)\left(\sum_{i_2=1}^{K} c_{i_2;p} a_{i_2}^\dagger a_{\bar{i}_2}^\dagger\right)\dots\left(\sum_{i_P=1}^{K} c_{i_P;p} a_{i_P}^\dagger a_{\bar{i}_P}^\dagger\right)|\theta\rangle \quad (5.3)$$

where P is the number of electron pairs and where $|\theta\rangle$ denotes the vacuum state. The vacuum state doesn't 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 [NS73, NS75, Sil71]. 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. (5.3) 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. (5.1) to the form in Eq. (5.2) for all the geminals, $p = 1, 2, \dots P$.) Without this assumption, geminal product theories are very complicated mathematically and very expensive computationally [CC06, CCI12].

The wavefunction in Eq. (5.3) can be expanded in terms of Slater determinants,

$$|\Psi\rangle = \sum_{[\{P_i\}_P]} \phi_{[\{P_i\}_P]} \left(\hat{g}_1^\dagger\right)^{P_1} \left(\hat{g}_2^\dagger\right)^{P_2} \dots \left(\hat{g}_K^\dagger\right)^{P_K} \tag{5.4}$$

where

$$\hat{g}_i^\dagger = a_i^\dagger a_{\bar{i}}^\dagger \tag{5.5}$$

generates an electron pair in the ith 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,

$$\sum_{i=1}^{K} P_i = P \qquad 0 \leqslant P_i. \tag{5.6}$$

The expansion coefficient is

$$\phi_{[\{P_i\}_P]} = \frac{1}{P_1! P_2! \dots P_K!} \left|\mathbf{C}_{[\{P_i\}_P]}\right|^+ \tag{5.7}$$

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 list the coefficients of $\hat{g}_i^\dagger$, each of which appears

P_i times,

$$\mathbf{C}_{[\{P_i\}_P]} \equiv \begin{array}{cccccccccc} c_{1,1} & \cdots & c_{1,1} & c_{2,1} & \cdots & c_{2,1} & \cdots & c_{K,1} & \cdots & c_{K,1} \\ c_{1,2} & \cdots & c_{1,2} & c_{2,2} & \cdots & c_{2,2} & \cdots & c_{K,2} & \cdots & c_{K,2} \\ & \vdots & & & \vdots & & & & \vdots & \\ c_{1,P} & \cdots & c_{1,P} & c_{2,P} & \cdots & c_{2,P} & \cdots & c_{K,P} & \cdots & c_{K,P} \end{array} \tag{5.8}$$

Eq. (5.7) is valid for the general boson case, where it is possible to put multiple bosons into a single state. We will not derive Eq. (5.7) 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 $\hat{o}_{k_1}\hat{o}_{k_2}\ldots\hat{o}_{k_p}$ in the polynomial

$$\prod_{l=1}^{L} \left(\sum_{k=1}^{K} c_{k;l}\hat{o}_{k_l} \right) \tag{5.9}$$

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. (5.7) 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 $\hat{o}_{k_1}\hat{o}_{k_2}\ldots\hat{o}_{k_L}$ would be the determinant, $|\mathbf{C}|^-$. (This will be useful in section (5.3), where the open-shell case is treated.)

Equation (5.7) 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 Borchardt's theorem [Bor55], which implies that if the geminal coefficients have the form,

$$c_{i;p} = \frac{1}{\varepsilon_i - \lambda_p}, \tag{5.10}$$

then the permanent is just a ratio of determinants,

$$\left|\mathbf{C}_{[\{P_i\}_P]}\right|^+ = \frac{\left|\mathbf{C}_{[\{P_i\}_P]} \circ \mathbf{C}_{[\{P_i\}_P]}\right|^-}{\left|\mathbf{C}_{[\{P_i\}_P]}\right|^-} \tag{5.11}$$

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, $\mathbf{C}_{[\{P_i\}_P]} \circ \mathbf{C}_{[\{P_i\}_P]} \equiv [c^2_{i;p}]$.[MM65, Min78] (N.B. There is an analogue of Borchardt's theorem that allows Hafnians to be converted to Pfaffians [IKO05], which may be useful given the recent interest in Pfaffian wavefunctions in the quantum Monte Carlo community [BMD$^+$06, BMWS08, NUC12].)

Borchardt's result was generalized to generic rank-two matrices by Carlitz and Levine [CL60]: 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. (5.2) are the reciprocal of the elements in a rank-two matrix,

$$c_{i,p} = \frac{1}{a_p \varepsilon_i + b_i \lambda_p}, \tag{5.12}$$

then Eq. (5.11) still holds. This is the type of coefficients we will use. Our wavefunction ansatz is then,

$$\left|\Psi\left(\boldsymbol{a}, \boldsymbol{\varepsilon}, \boldsymbol{b}, \boldsymbol{\lambda}\right)\right\rangle = \prod_{p=1}^P \left(\sum_{i=1}^K \frac{a^\dagger_i a^\dagger_{\bar{i}}}{a_p \varepsilon_i + b_i \lambda_p}\right) \left|\theta\right\rangle . \tag{5.13}$$

We call this the antisymmetric product of rank-two geminals, APr2G. It can be expanded in terms of Slater determinants, (5.4), where the coefficients in the expansion have the form of a ratio of determinants,

$$\phi_{[\{P_i\}_P]} = \frac{\left|\left[\frac{1}{(a_p\varepsilon_i+b_i\lambda_p)^2}\right]\right|^-}{\left|\left[\frac{1}{a_p\varepsilon_i+b_i\lambda_p}\right]\right|^-} \tag{5.14}$$

where only the columns corresponding to the occupied orbitals appear in the matrix (cf. Eq. (5.8)).

5.2.2 Links to other models

In order to elucidate the relationship between the APr2G wavefunction and previous models, it is helpful to rewrite Eq. (5.13) in the form

$$|\Psi\left(\boldsymbol{\nu},\boldsymbol{\zeta},\tilde{\boldsymbol{\varepsilon}},\tilde{\boldsymbol{\lambda}}\right)\rangle = \prod_{p=1}^{P}\nu_p\left(\sum_{i=1}^{K}\frac{\zeta_i a_i^\dagger a_{\bar{i}}^\dagger}{\tilde{\varepsilon}_i+\tilde{\lambda}_p}\right)|\theta\rangle \tag{5.15}$$

with

$$\tilde{\varepsilon}_i = \frac{\varepsilon_i}{b_i},\ \ \zeta_i = \frac{1}{b_i},\ \ \tilde{\lambda}_p = \frac{\lambda_p}{a_p},\ \ \nu_p = \frac{1}{a_p} \tag{5.16}$$

The constant prefactors, ν_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,

$$\left|\tilde{\Psi}_\nu\left(\boldsymbol{\zeta},\tilde{\boldsymbol{\varepsilon}},\tilde{\boldsymbol{\lambda}}\right)\right\rangle = \prod_{q=1}^{K}\nu_q\prod_{p=1}^{K}\left(\sum_{i=1}^{K}\frac{\zeta_i}{\tilde{\varepsilon}_i+\tilde{\lambda}_p}a_i^\dagger a_{\bar{i}}^\dagger\right)|\theta\rangle \tag{5.17}$$

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

$$\left|\tilde{\Psi}_{\nu}\left(\boldsymbol{\zeta},\tilde{\boldsymbol{\varepsilon}},\tilde{\boldsymbol{\lambda}}\right)\right\rangle = \prod_{q=1}^{P}\nu_q \sum_{\{m_i=\{0,1\}|\sum_{i=1}^{K} m_i=P\}} \left|\left[\frac{\zeta_i}{\tilde{\varepsilon}_i+\tilde{\lambda}_p}\right]\right|^{+} \prod_{c=1}^{K}\left(a_c^{\dagger}a_{\bar{c}}^{\dagger}\right)^{m_c}|\theta\rangle \tag{5.18}$$

where $\left|\left[\frac{\zeta_i}{\tilde{\varepsilon}_i+\tilde{\lambda}_p}\right]\right|^{+}$ is a permanent of a matrix that includes only the contributions from the orbitals with $m_i = 1$ (cf. Eq. (5.8)). The wavefunction in Eq. (5.15) is a generalization of the wavefunction form one obtains from a completely factorizable interaction [PDO98], i.e. an interaction that may be decomposed

$$\hat{V} = \sum_{ij}\left(C^{i}a_i^{\dagger}a_{\bar{i}}^{\dagger}\right)\left(C_j a^{\bar{j}}a^{j}\right) \tag{5.19}$$

Examples of such models include $p+ip$ wave [ILSZ09, DIL+10, LHRDO11] and $d+id$ wave superconductors [ML13], along with related models for heavy nuclei [DLR+11]. 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) [DPS04].

Eq. (5.17) 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. For example, the antisymmetrized geminal power wavefunction (AGP, [Bla60, Col65, Col97, Kut65, BD65]) is the special case where $\tilde{\boldsymbol{\varepsilon}} = 0$, $\tilde{\boldsymbol{\lambda}} = 1$. AGP is an antisymmetrized product of rank-one geminals: APr1G = AGP. A special case of AGP is the Slater determinant wavefunction, which arises when $\tilde{\boldsymbol{\varepsilon}} = \tilde{\boldsymbol{\lambda}} = 1$, 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, [HLJP53, PEL56, PP58]) form was proposed and explored [Kut65, McW59, MO60, Kut64, AK68, SRM70, MRS70, SMR70, KM65, PP60, MS63, AS62, MR65, MR68, SF65, Pal72, PSC72] as a wavefunction form in the 1950s and 1960s, and use of the APSG wavefunction form continues to the present day [Sur99, SSJZ12, Ras02, RX07, RXG04, CCR10, SKS98, RS02, KSNS10, Kut12, Sur84, SML85, Sur94, Sur95]. (The generalized-valence bond (GVB) wavefunction, "perfect pairing" wavefunction, and Piris natural orbital functional version 5 (PNOF5) are special cases of APSG [HLJP53, Sur99, GDHH73, GH78, HHG72b, HHG72a, PLR+11, MPU+12, VVHG00, Per13].) The APSG is a limiting case of the present form: choose $\boldsymbol{\zeta} = 1$, 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. (5.13), 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 ($\Delta \to \infty$), each geminal is built from a distinct orbital subspace, which is the characteristic feature of strongly orthogonal geminal product wavefunctions [Ara60, Lo61]. The APSG wavefunction is also a special case of the Richardson wavefunction, which arises from APr2G when $\boldsymbol{\zeta} = 1$, with $\tilde{\boldsymbol{\lambda}}$ and $\tilde{\boldsymbol{\varepsilon}}$ related to each other by Richardson's equations [Ric63, RS64].

There is also a link to the variation-after-projection Hartree-Fock Bogoliubov (PHFB) method [SLR01, SR00, SRLR02, SDK+07, SDNT04, OFAB07, MSGR11, LG12] that Scuseria et al. [SJHH+11, RGSJHS12, JHHTS12, SJHS12] 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 $\tilde{\boldsymbol{\varepsilon}} = \tilde{\boldsymbol{\lambda}} = 1$ case of Eq. (5.15). Just as in PHFB, we can consider cases where the orbital-pairing scheme is increasingly flexible. If we write our geminals in the form

$$\hat{G}_p^\dagger = \sum_{i=1}^{K} c_{i;p} a_i^\dagger a_{K+i}^\dagger \tag{5.20}$$

and build the orbital basis for Eq. (5.20) as a unitary transformation of the orthonormal spin-orbitals,

$$a_i^\dagger = \sum_{\kappa=1}^{2K} u_{i;\kappa} \tilde{a}_\kappa^\dagger \tag{5.21}$$

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

$$\mathbf{U} = \begin{bmatrix} \mathbf{U}_{\alpha\alpha} & \mathbf{U}_{\alpha\beta} \\ \mathbf{U}_{\alpha\beta}^\dagger & \mathbf{U}_{\beta\beta} \end{bmatrix}. \tag{5.22}$$

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

$$\mathbf{Q} = \begin{bmatrix} \mathbf{Q}_{\alpha\alpha} & \mathbf{Q}_{\alpha\beta} \\ \mathbf{Q}_{\alpha\beta}^T & \mathbf{Q}_{\beta\beta} \end{bmatrix} \tag{5.23}$$

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 S^z (“G”,$\mathbf{Q}_{\alpha\beta} \neq 0$; $\mathbf{Q}_{\alpha\alpha} \neq \mathbf{Q}_{\beta\beta}$). Projecting the RHFB, UHFB, and GHFB functions onto the N-electron space (NRHFB, NUHFB, NGHFB) gives antisymmetrized geminal power wavefunctions with unbroken (NRHFB = AGP) or broken (NUHFB = UAGP; NGHFB = GAGP) symmetry geminals [BMD+06, BMWS08, NUC12, WJO84]. NGHFB is the most general APr1G wavefunction, and is thus a special case of the APr2G wavefunction. The NUHFB and NGHFB wavefunctions are generally not spin eigenfunctions, but spin symmetry can be restored by projection (i.e., SNGHFB).

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

$$\left|\tilde{\Psi}_\nu\left(\boldsymbol{\zeta}, \tilde{\boldsymbol{\varepsilon}}, \tilde{\boldsymbol{\lambda}}\right)\right\rangle = \prod_{q=1}^{K} \nu_q \prod_{p=1}^{K} \left(\sum_{i=1}^{K} \left(1 + \frac{\zeta_i}{\tilde{\varepsilon}_i + \tilde{\lambda}_p} a_i^\dagger a_{\bar{i}}^\dagger \right) \right) |\theta\rangle \tag{5.24}$$

without a debilitating increase in computational expense. The link between APr2G and other popular wavefunction forms is summarized in Fig. 5.1.

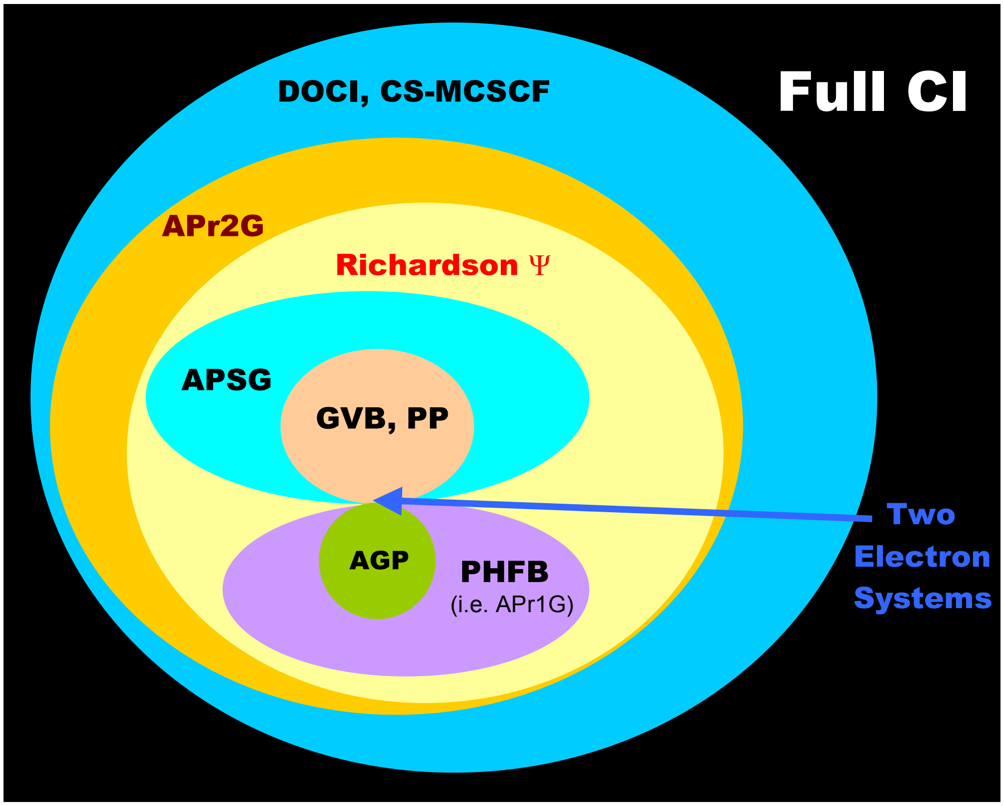

Figure 5.1: The antisymmetrized product of rank-2 geminals wavefunction (APr2G; cf. Eq. (5.15)) and its relationship to other, more common, wavefunction forms in quantum chemistry. See Section 5.2.2 for details. The coefficients in the Richardson wavefunction have the form of Eq. (5.10). APSG is the antisymmetric product of strongly orthogonal geminals, which includes the generalized valence bond (GVB) wavefunction (and hence 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.

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 [MS63]. This most general form of geminals is computationally daunting and mathematically intimidating [CC06], 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 [Sil70, Sil69], who calls the wavefunction in Eq. (5.3) an antisymmetric product of interacting geminals (APIGs). Even the APIG form is not computationally facile [NH71], however; the appearance of the permanent in the expansion coefficients (cf. Eq. (5.7)) indicates that directly employing the APIG wavefunction is likely to be challenging. The restricted form of APIG in Eq. (5.13) 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 [WW67]. 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 [VC67, Cle67], doubly-occupied MCSCF [Coo75], pair-excited MCSCF [Coo75, BHJH$^+$11, CH77, CH97, SCJK90, RDH79, KH03, KH04], even-replacement MCSCF [RDH79], closed-shell-MCSCF [Kol04], and seniority-zero MCSCF [BHJH$^+$11]. These methods are CI (or MCSCF, where the spin-orbitals are optimized) calculations including all the Slater determinants in which every orbital pair is either unoccupied or doubly occupied. The unpaired electron configurations contribute most of the correlation energy in larger molecules, and the APr2G wavefunction anstz, like DOCI and its APSG wavefunction special case, is not expected to recover dynamical correlation effects [BHJH$^+$11]. 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 product 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 [Sur99, RS02, KSNS10, Kut12, Roe99] will be even more effective if the APr2G wavefunction is used as a starting point.

In agreement with Bytautas et al.'s results [BHJH^{+}11], 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 [LAJ^{+}13]. While APIG is not computationally tractable, these results encouraged us to develop computational procedures for determining the parameters in the APr2G wavefunction.

5.2.3 The projected Schrödinger equations for the APr2G wavefunction

To optimize the parameters in the wavefunction (5.17), we use the projected Schrödinger equation,

$$\left\langle \Phi_{test} \middle| \hat{H} \middle| \Psi_{\nu}\left(\boldsymbol{\zeta}, \tilde{\boldsymbol{\varepsilon}}, \tilde{\boldsymbol{\lambda}}\right) \right\rangle = E \left\langle \Phi_{test} \middle| \Psi_{\nu}\left(\boldsymbol{\zeta}, \tilde{\boldsymbol{\varepsilon}}, \tilde{\boldsymbol{\lambda}}\right) \right\rangle \tag{5.25}$$

or, equivalently,

$$\left\langle \hat{H}\Phi_{test} \middle| \Psi_{\nu}\left(\boldsymbol{\zeta}, \tilde{\boldsymbol{\varepsilon}}, \tilde{\boldsymbol{\lambda}}\right) \right\rangle = E \left\langle \Phi_{test} \middle| \Psi_{\nu}\left(\boldsymbol{\zeta}, \tilde{\boldsymbol{\varepsilon}}, \tilde{\boldsymbol{\lambda}}\right) \right\rangle \tag{5.26}$$

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 [Ciz66]. In the context of geminal product wavefunctions, the idea of using the projected Schrödinger equation was proposed by Cullen [Cul96] and developed further by the Head-Gordon group [VVHG00, SHG11, PHG10].

Because the overlaps between $\Psi_\nu(\boldsymbol{\zeta}, \tilde{\boldsymbol{\varepsilon}}, \tilde{\boldsymbol{\lambda}})$ and Slater determinants can be computed efficiently, we choose Φ_{test} in Eq. (5.25) to be Slater determinants. It seems logical to choose the determinant defined by occupying the lowest-energy pairs (Hartree-Fock) and a subset of its pair-excited determinants,

$$|\Phi_{i\bar{i}}^{a\bar{a}}\rangle = a_a^\dagger a_{\bar{a}}^\dagger a^{\bar{i}} a^i \, |\Phi_{HF}\rangle \, , \tag{5.27}$$

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 $\left\langle \Phi_{i\bar{i}\,j\bar{j}\,k\bar{k}\,\dots}^{a\bar{a}\,b\bar{b}\,c\bar{c}\,\dots} \middle| \Psi_\nu(\boldsymbol{\zeta}, \tilde{\boldsymbol{\varepsilon}}, \tilde{\boldsymbol{\lambda}}) \right\rangle$, 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. (5.14) 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 $\boldsymbol{e}_k$ 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,

$$\left|\mathbf{C}^{a\bar{a}}_{i\bar{i}}\right|^{-} = \left|\mathbf{C} + \left(\boldsymbol{c}_{a\bar{a}} - \boldsymbol{c}_{i\bar{i}}\right)\boldsymbol{e}_k^T\right|^{-} = \left(1 + \boldsymbol{e}_k^T \mathbf{C}^{-1}\left(\boldsymbol{c}_{a\bar{a}} - \boldsymbol{c}_{i\bar{i}}\right)\right)\left|\mathbf{C}\right|^{-}. \tag{5.28}$$

This means that, for a given electron configuration, the cost of Eq. (5.14) is just $\mathcal{O}(P^2)$, instead of the naively expected $\mathcal{O}(P^3)$.

The number of determinants that appear depends on the choice of test functions. If $\mathcal{O}(K)$ 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 $\mathcal{O}((K-P)PK)$ of the two-pair excited determinants, $\Phi^{a\bar{a}\,b\bar{b}}_{i\bar{i}\,j\bar{j}}$. The overall computational cost per iteration will then be $\mathcal{O}(P^3(K-P)K)$, which grows as the fifth power of the systems size.

Alternatively, one could use $\mathcal{O}(K)$ single-excited Slater determinants, denoted Φ^{a}_{i} or $\Phi^{\bar{a}}_{\bar{i}}$, 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 $\mathcal{O}(P^3(K-P))$, 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. Brillouins theorem indicates that $\langle \Phi_i^a | \hat{H} | \Phi_{HF} \rangle = \langle \Phi_i^a | \Phi_{HF} \rangle = 0$, so the Hartree-Fock wavefunction is a solution to the projected-Schrdinger 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, Newtons 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

$$\frac{\partial \left| \mathbf{C} \right|^{-}}{\partial q} = \left| \mathbf{C} \right|^{-} \left(\mathrm{Tr} \left[\mathbf{C}^{-1} \frac{\partial \mathbf{C}}{\partial q} \right] \right) \tag{5.29}$$

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

$$\left(\mathbf{C}_{i\bar{i}}^{a\bar{a}} \right)^{-1} = \mathbf{C}^{-1} + \frac{\mathbf{C}^{-1} \left(\boldsymbol{c}_{a\bar{a}} - \boldsymbol{c}_{i\bar{i}} \right) \boldsymbol{e}_k^T \mathbf{C}^{-1}}{1 + \boldsymbol{e}_k^T \mathbf{C}^{-1} \left(\boldsymbol{c}_{a\bar{a}} - \boldsymbol{c}_{i\bar{i}} \right)}, \tag{5.30}$$

the derivative can be efficiently evaluated,

$$\begin{aligned}\frac{\partial \left|\mathbf{C}^{a\bar{a}}_{i\bar{i}}\right|^{-}}{\partial q} &= |\mathbf{C}^{a\bar{a}}_{i\bar{i}}|^{-}\left(\mathrm{Tr}\left[\mathbf{C}^{-1}\frac{\partial \mathbf{C}}{\partial q}\right]-1\right)\\ &+ |\mathbf{C}^{a\bar{a}}_{i\bar{i}}|^{-}\left(1+\frac{\boldsymbol{e}_k^T\mathbf{C}^{-1}\left(\boldsymbol{c}_{a\bar{a}}-\boldsymbol{c}_{i\bar{i}}\right)}{1+\boldsymbol{e}_k^T\mathbf{C}^{-1}\left(\boldsymbol{c}_{a\bar{a}}-\boldsymbol{c}_{i\bar{i}}\right)}\right)\\ &\times\left(1+\boldsymbol{e}_k^T\mathbf{C}^{-1}\left(\frac{\partial\left(\boldsymbol{c}_{a\bar{a}}-\boldsymbol{c}_{i\bar{i}}\right)}{\partial q}\right)\right). \end{aligned} \tag{5.31}$$

5.3 Generalization to open shells; gl$(n|k)$

5.3.1 Bethe ansatz wavefunctions

The wavefunction in Eq. (5.13) 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. (5.13) (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 [Yan67, Gau67]. The Richardson wavefunction, which is commonly written in the form of Eq. (5.15) with $\zeta = 1$, 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 kth orbital pair occupied, $|k\bar{k}\rangle$.We denote this ladder of states as a vector,

$$\begin{bmatrix} |k\bar{k}\rangle \\ |\theta\rangle \end{bmatrix} \tag{5.32}$$

The operator that creates a pair of electrons in the kth orbital pair is denoted $\hat{E}_{12}(k)$ and its adjoint, $\hat{E}_{21}(k) = \hat{E}^{\dagger}_{12}(k)$ 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 mnth element of the matrix is,

$$\left[\hat{E}_{fi}(j)\right]_{mn} = \delta_{mf}\delta_{ni} \tag{5.33}$$

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,

$$\begin{aligned} \hat{H}_{BCS} &= \sum_{k=1}^{K} \varepsilon_k \left(a^{\dagger}_{k} a^{k} + a^{\dagger}_{\bar{k}} a^{\bar{k}}\right) + g \sum_{k,k'}^{K} \hat{E}_{12}(k)\hat{E}_{21}(k') \\ &= \sum_{k=1}^{K} \varepsilon_k \left(a^{\dagger}_{k} a^{k} + a^{\dagger}_{\bar{k}} a^{\bar{k}}\right) + g \sum_{k,k'}^{K} a^{\dagger}_{k} a^{\dagger}_{\bar{k}} a^{\bar{k}'} a^{k'} \end{aligned} \tag{5.34}$$

The manner in which this Hamiltonian can be systematically constructed is presented by Cambiaggio et al. [CRS97] building on previous work of Gaudin [Gau76]. 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

$$|\Psi_{\mathfrak{gl}(2,\mathbb{C})}\rangle = \prod_{p=1}^{P}\left(\sum_{k=1}^{K}\frac{\hat{E}_{12}(k)}{\lambda_p - \varepsilon_k}\right)|\theta\rangle = \prod_{p=1}^{P}\left(\sum_{k=1}^{K}\frac{a_k^\dagger a_{\bar{k}}^\dagger}{\lambda_p - \varepsilon_k}\right)|\theta\rangle \tag{5.35}$$

(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. (5.12) generalizes Eq. (5.10)) 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 these wavefunction forms, but those approaches work only for the eigenfunctions of the model Hamiltonian (e.g., Eq. (5.34)). 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. (5.26)) after one generalizes the wavefunction form. (Our initial *variational* calculations using the eigenfunctions of the Richardson Hamiltonian (Eq. (5.34)) have given promising results - see Chapter 2.) 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

$$|\Psi^{(m)}_{\mathfrak{gl}(2,\mathbb{C})}\rangle = \prod_{p=Q_{m-1}+1}^{Q_m} \left(\sum_{k=L_{m-1}+1}^{L_m} \frac{a^\dagger_k a^\dagger_{\bar{k}}}{\lambda_p - \varepsilon_k} \right) |\theta\rangle \, . \tag{5.36}$$

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

$$|\Psi_{\mathfrak{gl}(2,\mathbb{C})}\rangle = \lim_{\Delta\to\infty} \prod_{p=1}^{P} \left(\sum_{k=1}^{K} \frac{a^\dagger_k a^\dagger_{\bar{k}}}{(\lambda_p + m_p\Delta) - (\varepsilon_k + n_k\Delta)} \right) |\theta\rangle \tag{5.37}$$

where m_p and n_k indicate which fragment the pair p and orbital k belong to. I.e., $Q_{m_p-1} < p \leqslant Q_{m_p}$ and $L_{n_k-1} < k \leqslant L_{n_k}$. (In chemical systems, where the fragments are never entirely noninteracting, one never needs to go all the way to the $\Delta \to \infty$ 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. (5.37). 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 [NSM05].

5.3.2 All unpaired electrons have the same spin; $\mathbf{gl}(2|1)$

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,

$$\begin{bmatrix} |k\rangle \\ |k\bar{k}\rangle \\ |\theta\rangle \end{bmatrix} \tag{5.38}$$

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 $\hat{E}_{fi}(k) = \hat{E}^{\dagger}_{if}(k) = \delta_{mf}\delta_{ni}$. Notice that the $\hat{E}_{fi}(k)$ operators have a different meaning in this algebra. (Now, for example, $\hat{E}_{12}|k\bar{k}\rangle = |k\rangle$. 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

$$\hat{E}_{23}(k) = a^{\dagger}_{k} a^{\dagger}_{\bar{k}}, \quad \hat{E}_{13}(k) = a^{\dagger}_{k}, \quad \hat{E}_{12} = a^{\bar{k}} \tag{5.39}$$

The Hamiltonian is of the form

$$\begin{aligned} \hat{H}_{\mathfrak{gl}(2|1)} = & \sum_{i=1}^{K} \varepsilon_i \left(a^{\dagger}_{i} a^{i} + a^{\dagger}_{\bar{i}} a^{\bar{i}} \right) \\ & + g \sum_{i,i'}^{K} \left(\hat{E}_{12}(i)\hat{E}_{21}(i') + \hat{E}_{13}(i)\hat{E}_{31}(i') + \hat{E}_{23}(i)\hat{E}_{32}(i') \right) \end{aligned} \tag{5.40}$$

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

$$|\Psi_{\mathfrak{gl}(2|1)}\rangle = \prod_{p=1}^{P} \left(\sum_{i=1}^{K} \frac{\hat{E}_{23}(i)}{\lambda_p - \varepsilon_i} \right) \prod_{q=1}^{Q} \left(\sum_{p'=1}^{P} \frac{\hat{I}(p')}{\mu_q - \lambda_{p'}} \right) |\theta\rangle \tag{5.41}$$

$\hat{I}(p')$ is a notational convenience introduced by Dukelsky et al. [DGVI$^+$06]. 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,

$$\begin{aligned} \prod_{p=1}^{P} \left(\sum_{i=1}^{K} \frac{\hat{E}_{23}(i)}{\lambda_p - \varepsilon_i} \right) \frac{\hat{I}(p')}{\mu_q - \lambda_{p'}} |\theta\rangle = & \frac{1}{\mu_q - \lambda_{p'}} \left(\sum_{i=1}^{K} \frac{\hat{E}_{23}(i)}{\lambda_1 - \varepsilon_i} \right) \dots \left(\sum_{i=1}^{K} \frac{\hat{E}_{23}(i)}{\lambda_{p'-1} - \varepsilon_i} \right) \\ \times \left(\sum_{i=1}^{K} \frac{\hat{E}_{13}(i)}{\lambda_{p'} - \varepsilon_i} \right) \left(\sum_{i=1}^{K} \frac{\hat{E}_{23}(i)}{\lambda_{p'+1} - \varepsilon_i} \right) \dots \left(\sum_{i=1}^{K} \frac{\hat{E}_{23}(i)}{\lambda_{P} - \varepsilon_i} \right) & \end{aligned} \tag{5.42}$$

Eq. (5.41) 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 $a_{\bar{i}}^\dagger$ and typically β-spin), respectively. Ensuring that there are the correct number of electrons of each type in the wavefunction (5.41) 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 (5.41) is superior to the conventional approach of choosing the vacuum state in the APr2G wavefunction (Eq. (5.17)) as a wavefunction for the unpaired electrons. In the conventional approach, the unpaired electrons are not correlated with the electron pairs. In Eq. (5.41), the unpaired electrons and the electron pairs are coupled together.

To use the projection algorithm from Section 5.2.3, we need to write $\Psi_{\mathfrak{gl}(2|1)}$ as a linear combination of Slater determinants. Using the relationship between a product of a sum and permanents/determinants (cf. Eq. (5.9) and the surrounding discussion), we can rewrite Eq. (5.41) as:

$$\begin{aligned} |\Psi_{\mathfrak{gl}(2|1)}\rangle = {} & \prod_{p=1}^{P}\left(\sum_{i=1}^{K}\frac{\hat{E}_{23}(i)}{\lambda_p-\varepsilon_i}\right) \\ & \times \left(\sum_{\{m_p\in\{0,1\}|\sum_{p=1}^{P} m_p=Q\}} \left|\frac{1}{\mu_q-\lambda_p}\right| \prod_{p'=1}^{P}\hat{I}^{m_{p'}}(p')\right)|\theta\rangle . \end{aligned} \tag{5.43}$$

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,[2]

$$\sum_{i=1}^{K} \frac{\hat{E}_{23}(i)\hat{I}^{m_p}}{\lambda_p - \varepsilon_i} = \begin{cases} \sum_{i=1}^{K} \frac{\hat{E}_{23}(i)}{\lambda_p - \varepsilon_i} & m_p = 0 \\ \sum_{i=1}^{K} \frac{\hat{E}_{13}(i)}{\lambda_p - \varepsilon_i} & m_p = 1 \\ 0 & m_p > 1 \end{cases} \tag{5.44}$$

the remaining product of pair creators is decomposed in two pieces, corresponding to the two cases in Eq. (5.44),

$$\begin{aligned} |\Psi_{\mathfrak{gl}(2|1)}\rangle = & \sum_{\{m_p \in \{0,1\} | \sum_{p=1}^{P} m_p = Q\}} \left| \frac{1}{\mu_q - \lambda_p} \right| \left(\prod_{\{p|m_p=1\}}^{P} \sum_{i=1}^{K} \frac{\hat{E}_{13}(i)}{\lambda_p - \varepsilon_i} \right) \\ & \times \left(\prod_{\{p|m_p=0\}}^{P} \sum_{i=1}^{K} \frac{\hat{E}_{23}(i)}{\lambda_p - \varepsilon_i} \right) |\theta\rangle \end{aligned} \tag{5.45}$$

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

$$\begin{aligned} |\Psi_{\mathfrak{gl}(2|1)}\rangle = & \sum_{\{m_p \in \{0,1\} | \sum_{p=1}^{P} m_p = Q\}} \sum_{\{k_i \in \{0,1\} | \sum_{i=1}^{K} k_i = Q\}} \sum_{\{l_i \in \{0,1\} | \sum_{i=1}^{K} l_i = P-Q\}} \\ & \times \left| \frac{1}{\mu_q - \lambda_p} \right| \left| \frac{1}{\lambda_p - \varepsilon_i} \right|^{-}_{\{m_q=1\}} \left| \frac{1}{\lambda_p - \varepsilon_i} \right|^{+}_{\{m_q=0\}} \\ & \times \hat{E}^{k_1}_{13}(1)\hat{E}^{k_2}_{13}(2)\dots\hat{E}^{k_K}_{13}(K)\hat{E}^{l_1}_{23}(1)\hat{E}^{l_2}_{23}(2)\dots\hat{E}^{l_K}_{23}(K)\,|\theta\rangle \end{aligned} \tag{5.46}$$

---

[2] Since this paper has been published, Dukelsky has asked that we do not refer to these objects in this way.

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 P choose Q ways of combining paired (generated by $\hat{E}_{23}$) and unpaired (generated by $\hat{E}_{13}$) states).

Eq. (5.46) 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,

$$|\Psi_{\mathfrak{gl}(2|1)}\rangle = \sum_{q=1}^{P} \prod_{p=1}^{P} \left(\delta_{qp} \sum_{j=1}^{K} b_{j;q} a^{j} \right) \left(\sum_{i=1}^{K} c_{i;p} a_i^\dagger a_{\bar{i}}^\dagger \right) |\theta\rangle \,, \tag{5.47}$$

with $P = \frac{1}{2}(N+1)$. The Slater determinant expansion of Eq. (5.47) is

$$\begin{aligned} |\Psi_{\mathfrak{gl}(2|1)}\rangle = &\sum_{q=1}^{P} \sum_{\{k_i \in \{0,1\} | \sum_{i=1}^{K} k_i = 1\}} \sum_{\{l_i \in \{0,1\} | \sum_{i=1}^{K} l_i = P-1\}} b_{i;q} \left| c_{i;p\neq q} \right|^{+} \\ &\times \prod_{m=1}^{K} \left(a_m^\dagger \right)^{k_m} \prod_{n=1}^{K} \left(a_n^\dagger a_{\hat{n}}^\dagger \right)^{l_n} \end{aligned} \tag{5.48}$$

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

$$
\begin{aligned}
\left|\tilde{\Psi}_{\mathfrak{gl}(2|1)}\right\rangle = & \left(\prod_{p=1}^{P_{12}}\left(\sum_{i=1}^{K} c^{(12)}_{i,p}\hat{E}_{12}(i)\right)\right)\left(\prod_{p=1}^{P_{13}}\left(\sum_{i=1}^{K} c^{(13)}_{i,p}\hat{E}_{13}(i)\right)\right) \\
& \times\left(\prod_{p=1}^{P_{23}}\left(\sum_{i=1}^{K} c^{(23)}_{i,p}\hat{E}_{23}(i)\right)\right)|\theta\rangle
\end{aligned}
\tag{5.49}
$$

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,

$$
\begin{aligned}
\left|\tilde{\Psi}_{\mathfrak{gl}(2|1)}\right\rangle = & \sum_{\left\{ m^{(12)}_i, m^{(13)}_i, m^{(23)}_i \in\{0,1\} \;\middle|\; \begin{array}{l} \sum_{i=1}^{K} m^{(12)}_i = P_{12} \\ \sum_{i=1}^{K} m^{(13)}_i = P_{13} \\ \sum_{i=1}^{K} m^{(23)}_i = P_{23} \end{array} \right\}} \\
& \left|\mathbf{C}^{(12)}_{i,p}\right|^{-}\left|\mathbf{C}^{(13)}_{i,p}\right|^{-}\left|\mathbf{C}^{(23)}_{i,p}\right|^{+}\prod_{i=1}^{K}\left(a^{\bar{i}}\right)^{m^{(12)}_i}\left(a^{\dagger}_{i}\right)^{m^{(13)}_i}\left(a^{\dagger}_{i}a^{\dagger}_{\bar{i}}\right)^{m^{(23)}_i}|\theta\rangle
\end{aligned}
\tag{5.50}
$$

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

$$
c^{(23)}_{i;p} = \frac{\zeta_i}{\tilde{\varepsilon}_i + \tilde{\lambda}_p}. \tag{5.51}
$$

The projection method in Section 5.2.3 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. (5.49) can still be viewed as a "mean-field" wavefunction ansatz, but one with two different types of quasi-particles.

$\tilde{\Psi}_{\mathfrak{gl}(2|1)}$ (Eq. (5.49)) 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

$$|\Psi\rangle = \left(g_1^\dagger g_2^\dagger \left(a^{\bar{i}} g_3^\dagger\right) + g_1^\dagger \left(a^{\bar{i}} g_2^\dagger\right) g_3^\dagger + \left(a^{\bar{i}} g_1^\dagger\right) g_2^\dagger g_3^\dagger\right) |\theta\rangle \tag{5.52}$$

where $g_k^\dagger$ is the operator for creating the kth electron pair. If there were only one term in Eq. (5.52), 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. (5.52) 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. (5.49).

The wavefunction form from the nested Bethe ansatz has additional correlation: in Eq. (5.47), the form of the single-particle state depends on which pair the electron is removed from, while in Eq. (5.49) the same single particle state is removed from all pairs, regardless of their structure.

5.3.3 Unpaired electrons of both spins; $\mathfrak{gl}(2|2)$

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 $\mathfrak{gl}(2|2)$ (the general linear algebra of 4×4 matrices with two boson states and two fermion states). With $\mathfrak{gl}(2|2)$ 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:

$$\begin{bmatrix} |k\rangle \\ |\bar{k}\rangle \\ |k\bar{k}\rangle \\ |\theta\rangle \end{bmatrix} \tag{5.53}$$

and define the operators for moving between the states,

$$\begin{aligned} \hat{E}_{34}(i) &= a_i^\dagger a_{\bar{i}}^\dagger \\ \hat{E}_{24}(i) &= a_{\bar{i}}^\dagger \left(1 - \hat{n}_i\right) \\ \hat{E}_{14}(i) &= a_i^\dagger \left(1 - \hat{n}_{\bar{i}}\right) \\ \hat{E}_{23}(i) &= a^i \hat{n}_{\bar{i}} \\ \hat{E}_{13}(i) &= a^{\bar{i}} \hat{n}_i \\ \hat{E}_{12}(i) &= a_i^\dagger a^{\bar{i}}. \end{aligned} \tag{5.54}$$

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

The Hamiltonian is of the form

$$\begin{aligned}\hat{H}_{\mathfrak{gl}(2|2)} = \sum_{i=1}^{K} \varepsilon_i \left(a_i^\dagger a^i + a_{\bar{i}}^\dagger a^{\bar{i}}\right) + g \sum_{i,i'}^{K} \Big(&\hat{E}_{12}(i)\hat{E}_{21}(i') + \hat{E}_{13}(i)\hat{E}_{31}(i') \\ &+\hat{E}_{14}(i)\hat{E}_{41}(i') + \hat{E}_{23}(i)\hat{E}_{32}(i') + \hat{E}_{24}(i)\hat{E}_{42}(i') + \hat{E}_{34}(i)\hat{E}_{43}(i')\Big)\end{aligned} \tag{5.55}$$

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

$$\left|\Psi_{\mathfrak{gl}(2|2)}\right\rangle = \prod_{p=1}^{P}\left(\sum_{i=1}^{K}\frac{\hat{E}_{34}(i)}{\lambda_p - \varepsilon_i}\right)\prod_{q=1}^{Q}\left(\sum_{p=1}^{P}\frac{\hat{I}(p)}{\mu_q - \lambda_p}\right)\prod_{r=1}^{R}\left(\sum_{q=1}^{Q}\frac{\hat{J}(q)}{\nu_r - \mu_q}\right)|\theta\rangle \tag{5.56}$$

where the Dukelsky operators have the effect,

$$\sum_{i=1}^{K}\sum_{p=1}^{P}\frac{\hat{E}_{34}(i)\hat{I}^{m_p}(p)\hat{J}^{n_q}(q)}{(\lambda_p - \varepsilon_i)(\mu_q - \lambda_p)} = \begin{cases} 0 & m_p > 1 \\ 0 & n_q > m_p \\ \sum_{i=1}^{K}\sum_{p=1}^{P}\frac{\hat{E}_{34}(i)}{(\lambda_p-\varepsilon_i)(\mu_q-\lambda_p)} & m_p = n_q = 0 \\ \sum_{i=1}^{K}\sum_{p=1}^{P}\frac{\hat{E}_{24}(i)}{(\lambda_p-\varepsilon_i)(\mu_q-\lambda_p)} & m_p = 1,\ n_q = 0 \\ \sum_{i=1}^{K}\sum_{p=1}^{P}\frac{\hat{E}_{14}(i)}{(\lambda_p-\varepsilon_i)(\mu_q-\lambda_p)} & m_p = n_q = 1 \end{cases} \tag{5.57}$$

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

$$\begin{aligned} R &= n \\ Q &= \bar{n} + n \\ P &= \frac{1}{2}(N + n + \bar{n}) \end{aligned} \tag{5.58}$$

Similar to the nested Bethe ansatz wavefunction for $\mathfrak{gl}(2|1)$ (cf. Eq. (5.50)), in the expansion of $\Psi_{\mathfrak{gl}(2|2)}$, 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,

$$\left|\Psi_{\mathfrak{gl}(2|2)}\right\rangle = \sum_{r=1}^{P} \sum_{q=1}^{P} \prod_{p=1}^{P} \left(\delta_{rp} \sum_{k=1}^{K} b_{k;r} a^{\bar{k}} a^{\dagger}_{k} \right) \left(\delta_{qp} \sum_{j=1}^{K} \bar{b}_{j;q} a^{j} \right) \left(\sum_{i=1}^{K} c_{i;p} a^{\dagger}_{i} a^{\dagger}_{\bar{i}} \right) |\theta\rangle \tag{5.59}$$

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

$$\left|\Psi_{\mathfrak{gl}(2|2)}\right\rangle = \sum_{q,r=1}^{P} \sum_{\left\{ j_i,k_i,l_i \in \{0,1\} \,\middle|\, \begin{array}{c} \sum_{i=1}^{K} j_i = 1 \\ \sum_{i=1}^{K} k_i = 1 \\ \sum_{i=1}^{K} l_i = P-2 \end{array} \right\}} \left(b_{i,r}\right) \left(\bar{b}_{i,q}\right) \left|c_{i,p\neq q,p\neq r}\right|^{+}$$
$$\left(a^{\dagger}_{1} a^{\bar{1}} a^{\dagger}_{\bar{1}}\right)^{j_1} \dots \left(a^{\dagger}_{K} a^{\bar{K}} a^{\dagger}_{\bar{K}}\right)^{j_K} \left(a^{\dagger}_{\bar{1}}\right)^{k_1} \dots \left(a^{\dagger}_{\bar{K}}\right)^{k_K} \left(a^{\dagger}_{1} a^{\dagger}_{\bar{1}}\right)^{l_1} \dots \left(a^{\dagger}_{K} a^{\dagger}_{\bar{K}}\right)^{l_K} |\theta\rangle \tag{5.60}$$

Notice that Eq. (5.60) 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,

$$\left|\Psi_{\mathfrak{gl}(2|2)}\right\rangle = \sum_{r=1}^{P} \sum_{q=1}^{P} \prod_{p=1}^{P} \left(\delta_{rp} \sum_{k=1}^{K} b_{k;r} a^{\bar{k}} \right) \left(\delta_{qp} \sum_{j=1}^{K} \bar{b}_{j;q} a^{j} \right) \left(\sum_{i=1}^{K} c_{i;p} a^{\dagger}_{i} a^{\dagger}_{\bar{i}} \right) |\theta\rangle \tag{5.61}$$

$$\left|\Psi_{\mathfrak{gl}(2|2)}\right\rangle = \sum_{q,r=1}^{P} \sum_{\left\{ j_i,k_i,l_i\in\{0,1\} \;\middle|\; \begin{array}{c} \sum_{i=1}^{K} j_i = 1 \\ \sum_{i=1}^{K} k_i = 1 \\ \sum_{i=1}^{K} l_i = P-2 \end{array} \right\}} \left(b_{i,r}\right)\left(\bar{b}_{i,q}\right)\left|c_{i,p\neq q,p\neq r}\right|^{+}$$
$$\left(a_1^\dagger\right)^{j_1}\dots\left(a_K^\dagger\right)^{j_K}\left(a_{\bar{1}}^\dagger\right)^{k_1}\dots\left(a_{\bar{K}}^\dagger\right)^{k_K}\left(a_1^\dagger a_{\bar{1}}^\dagger\right)^{l_1}\dots\left(a_K^\dagger a_{\bar{K}}^\dagger\right)^{l_K}|\theta\rangle \qquad (5.62)$$

This is expected to be an extremely good model for static correlation in strongly correlated systems [BHJH+11].

To use the projection algorithm from Section 5.2.3 for systems with many unpaired electrons, we need an alternative to $\Psi_{\mathfrak{gl}(2|2)}$ that has a compact expansion in terms of Slater determinants. The wavefunction ansatz we choose is,

$$\begin{aligned}\left|\tilde{\Psi}_{\mathfrak{gl}(2|2)}\right\rangle &= \left(\prod_{p=1}^{P_{12}}\left(\sum_{i=1}^{K} c_{i,p}^{(12)}\hat{E}_{12}(i)\right)\right)\left(\prod_{p=1}^{P_{13}}\left(\sum_{i=1}^{K} c_{i,p}^{(13)}\hat{E}_{13}(i)\right)\right) \\ &\times\left(\prod_{p=1}^{P_{23}}\left(\sum_{i=1}^{K} c_{i,p}^{(23)}\hat{E}_{23}(i)\right)\right)\left(\prod_{p=1}^{P_{14}}\left(\sum_{i=1}^{K} c_{i,p}^{(14)}\hat{E}_{14}(i)\right)\right) \\ &\times\left(\prod_{p=1}^{P_{24}}\left(\sum_{i=1}^{K} c_{i,p}^{(24)}\hat{E}_{24}(i)\right)\right)\left(\prod_{p=1}^{P_{34}}\left(\sum_{i=1}^{K} c_{i,p}^{(34)}\hat{E}_{34}(i)\right)\right)|\theta\rangle \qquad (5.63)\end{aligned}$$

The constants must be chosen so that:

$$\begin{aligned} n &= P_{12} + P_{13} + P_{14} \\ \bar{n} &= P_{23} + P_{24} - P_{12} \\ N &= 2P_{34} - P_{23} - P_{13} + P_{24} + P_{14} \end{aligned} \tag{5.64}$$

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

$$\begin{aligned} \left|\tilde{\Psi}_{\mathfrak{gl}(2|2)}\right\rangle = & \sum_{\substack{m_k^{(fi)}\in\{0,1\} \\ \sum_{k=1}^{K} m_k^{(fi)}=P_{fi}}} \left|\mathbf{C}_{k,p}^{(12)}\right|^{+} \left|\mathbf{C}_{k,p}^{(13)}\right|^{-} \left|\mathbf{C}_{k,p}^{(23)}\right|^{-} \left|\mathbf{C}_{k,p}^{(14)}\right|^{-} \left|\mathbf{C}_{k,p}^{(24)}\right|^{-} \left|\mathbf{C}_{k,p}^{(34)}\right|^{+} \\ & \prod_{i=1}^{K} \left(a_k^{\dagger} a^{\bar{k}}\right)^{m_k^{(12)}} \left(a^{\bar{k}} \hat{n}_k\right)^{m_k^{(13)}} \left(a^{k} \hat{n}_{\bar{k}}\right)^{m_k^{(23)}} \left(a_k^{\dagger}\right)^{m_k^{(14)}} \left(a_{\bar{k}}^{\dagger}\right)^{m_k^{(24)}} \left(a_k^{\dagger} a_{\bar{k}}^{\dagger}\right)^{m_k^{(34)}} \left|\theta\right\rangle \end{aligned} \tag{5.65}$$

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. (5.65) 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. (5.63) with forms that allow unpaired electrons to combine into pairs. This can be achieved by the following reassignment,

$$\begin{aligned}
\hat{E}_{24}(i) &= a^{\dagger}_{\bar{i}} \\
\hat{E}_{14}(i) &= a^{\dagger}_{i} \\
\hat{E}_{23}(i) &= a^{i} \\
\hat{E}_{13}(i) &= a^{\bar{i}}
\end{aligned} \tag{5.66}$$

5.3.4 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 increasingly dimensionality. For example, if one wishes to include coupling between pairs of fermions, one could consider $\mathfrak{gl}(8|8)$ based on the states,

$$\begin{array}{llllll}
|j\rangle & |\bar{j}\rangle & |J\rangle & |\bar{J}\rangle & & \\
|J\bar{J}\rangle & |\bar{j}\bar{J}\rangle & |j\bar{J}\rangle & |\bar{j}J\rangle & |jJ\rangle & |j\bar{j}\rangle \\
|\bar{j}J\bar{J}\rangle & |jJ\bar{j}\rangle & |j\bar{j}\bar{J}\rangle & |j\bar{j}J\rangle & & \\
|j\bar{j}J\bar{J}\rangle & |\theta\rangle & & & &
\end{array} \tag{5.67}$$

namely,

$$\left|\tilde{\Psi}_{\mathfrak{gl}(8|8)}\right\rangle = \prod_{(i=2,f<i)}^{16} \prod_{p=1}^{P_{fi}} \left(\sum_{k=1}^{K} c^{(fi)}_{k,p} \hat{E}_{fi}(k) \right) |\theta\rangle \tag{5.68}$$

The coefficient matrices for operators that transfer between states separated by an even number of rows in Eq. (5.67) (zero or two, e.g., $\hat{E}_{5,15}(k), \hat{E}_{6,10}(k)$) 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., $\hat{E}_{1,7}(k), \hat{E}_{5,13}(k)$) anticommute, so they enter the Slater determinant expansion as a determinant, and can be chosen arbitrarily. There are 120 operators in Eq. (5.68), 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.

5.3.5 Other generalizations

The wavefunction one obtains using these methods depends on how one chooses the order of the operators. For example, placing $\hat{E}_{24}(i)$ before $\hat{E}_{12}(i)$ in Eq. (5.63) 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

$$
\begin{aligned}
\left|\tilde{\Psi}_{\mathfrak{gl}(2|1)}\right\rangle = &\left(\prod_{p=1}^{P_{32}}\left(\sum_{i=1}^{K} c^{(32)}_{i,p}\hat{E}_{32}(i)\right)\right)\left(\prod_{p=1}^{P_{31}}\left(\sum_{i=1}^{K} c^{(31)}_{i,p}\hat{E}_{31}(i)\right)\right) \\
&\times\left(\prod_{p=1}^{P_{21}}\left(\sum_{i=1}^{K} c^{(21)}_{i,p}\hat{E}_{21}(i)\right)\right)\left(\prod_{p=1}^{P_{12}}\left(\sum_{i=1}^{K} c^{(12)}_{i,p}\hat{E}_{12}(i)\right)\right) \\
&\times\left(\prod_{p=1}^{P_{13}}\left(\sum_{i=1}^{K} c^{(13)}_{i,p}\hat{E}_{13}(i)\right)\right)\left(\prod_{p=1}^{P_{23}}\left(\sum_{i=1}^{K} c^{(23)}_{i,p}\hat{E}_{23}(i)\right)\right)|\theta\rangle \qquad (5.69)
\end{aligned}
$$

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. (5.12) (equivalently, Eq. (5.15)) 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 (APrkG). 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.

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 [LAJ$^+$13].

5.4 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. (5.25). This leads to a set of nonlinear equations for the wavefunction parameters that can, at least in principle, be solved at low ($\mathcal{O}(K^4)$ or $\mathcal{O}(K^5)$) computational cost. The equations we must solve are strongly reminiscent of coupled-cluster theory [HJO00, CS00, PL99, Bar81, Bar10, Bar12, BM07], 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 [BHJH$^+$11, EP66, PCS71, LYMG94]. 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 [SS87]. The Lagrangian approach to constraints in coupled-cluster theory is especially useful here: one rewrites the problem as the minimization of an energy expression,

$$\tilde{E}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \equiv \frac{\left\langle \Phi \middle| \hat{H} \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \right\rangle}{\left\langle \Phi \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \right\rangle} \tag{5.70}$$

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

$$\begin{aligned}\Lambda_{\mathfrak{gl}(2|k)}[\boldsymbol{\eta};\boldsymbol{\lambda}] &= \tilde{E}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \\ &+ \sum_i \lambda_i \left(\left\langle \Phi_i \middle| \hat{H} \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \right\rangle - \tilde{E}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \left\langle \Phi_i \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \right\rangle \right)\end{aligned} \tag{5.71}$$

After solving the equations,

$$\begin{aligned}\nabla_{\eta}\Lambda_{\mathfrak{gl}(2|k)}[\boldsymbol{\eta};\boldsymbol{\lambda}] &= 0 \\ \nabla_{\lambda}\Lambda_{\mathfrak{gl}(2|k)}[\boldsymbol{\eta};\boldsymbol{\lambda}] &= 0\end{aligned} \tag{5.72}$$

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

$$\begin{aligned}\left.\frac{\partial \tilde{E}_{\mathfrak{gl}(2|k)}}{\partial \eta_j}\right|_{\boldsymbol{\eta}=\boldsymbol{\eta}_{opt}} &= \left.\frac{\partial \tilde{E}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta})}{\partial \eta_j}\right|_{\boldsymbol{\eta}=\boldsymbol{\eta}_{opt}} \\ &+ \boldsymbol{\lambda}_{opt} \left.\frac{\partial \left[\left\langle \Phi_i \middle| \hat{H} \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \right\rangle - \tilde{E}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \left\langle \Phi_i \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta}) \right\rangle \right]}{\partial \eta_j}\right|_{\boldsymbol{\eta}=\boldsymbol{\eta}_{opt}}\end{aligned} \tag{5.73}$$

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 [Bar12, SB93]. For example, ionization potentials and electron affinities can be computed using equations that are reminiscent of the extended Koopmans' theorem [DSM75, SF65, MPL75, VVNA$^+$09, Ern09],

$$\left\langle \Phi_i \middle| a^\dagger_k \left[\hat{H}, a^j\right] \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}\left(\boldsymbol{\eta}\right) \right\rangle \approx -I_\lambda \left\langle \Phi_i \middle| a^\dagger_k a^j \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}\left(\boldsymbol{\eta}\right) \right\rangle \tag{5.74}$$

$$\left\langle \Phi_i \middle| a^k \left[\hat{H}, a^\dagger_j\right] \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}\left(\boldsymbol{\eta}\right) \right\rangle \approx -A_\lambda \left\langle \Phi_i \middle| a^k a^\dagger_j \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}\left(\boldsymbol{\eta}\right) \right\rangle \tag{5.75}$$

or its generalizations to higher-order operators like [AM07]

$$\begin{aligned} \left\langle \Phi_i \middle| a^\dagger_{j'} a^\dagger_{k'} a^{l'} \left[\hat{H}, a^\dagger_l a^k a^j\right] \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}\left(\boldsymbol{\eta}\right) \right\rangle &\approx \\ -I_\lambda \left\langle \Phi_i \middle| a^\dagger_{j'} a^\dagger_{k'} a^{l'} a^\dagger_l a^k a^j \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}\left(\boldsymbol{\eta}\right) \right\rangle &. \end{aligned} \tag{5.76}$$

Eq. (5.76) changes the computational scaling, but Eqs. (5.74) and (5.75) can be evaluated with negligible computational cost after the projected Schrödinger equation for $\tilde{\Psi}_{\mathfrak{gl}(2|k)}(\boldsymbol{\eta})$ has been solved. Excitation energies can be computed in several ways, including

$$\left\langle \Phi_i \middle| a^\dagger_j a^k \left[\hat{H}, a^\dagger_{k'} a^{j'}\right] \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}\left(\boldsymbol{\eta}\right) \right\rangle \approx \omega_{0\lambda} \left\langle \Phi_i \middle| a^\dagger_j a^k a^\dagger_{k'} a^{j'} \middle| \tilde{\Psi}_{\mathfrak{gl}(2|k)}\left(\boldsymbol{\eta}\right) \right\rangle \tag{5.77}$$

In designing formulas like Eqs. (5.74)-(5.77), it is important to choose Hermitian operators: it is impractical to act directly on ket (the geminal product wavefunction) with an operator, so one needs to be able to apply operators to the bra (the Slater determinant test functions).

5.5 Summary

This paper presents a new wavefunction form, an antisymmetrized product of nonorthogonal geminals (Section 5.2), and discusses its extensions to open shells (Section 5.3) and molecular property calculations (Section 5.4). 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. Eg. (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) $\frac{1}{2}N_{electrons} + N_{basis}$ 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 paramters in APr2G can be determined by solving the projected Schrödinger equation with computational scaling of $\mathcal{O}(N_{basis}^5)$ and perhaps even $\mathcal{O}(N_{basis}^4)$.

Chapter 6

Summary, Conclusions, and Outlook

6.1 Summary and Conclusions

The goal of quantum chemistry is to develop accurate approximations to the solutions of the Schrödinger equation. For atoms and molecules, this involves making a guess for the wavefunction, $|\tilde{\Psi}\rangle$, and proceeding by variational, projected, or perturbative methods.

The approaches in this thesis are mostly efficient approximations to the doubly-occupied configuration interaction (DOCI), i.e. a complete expansion in terms of closed shell states. Approximations to DOCI are phrased in terms of geminals, or two-electron functions, and the expansion coefficients are symmetric sums over permutations (permanents).

In the second chapter we employed Richardson's solution to the reduced BCS

Hamiltonian as a wavefunction ansatz in a variational approach. Richardson's equations had to be solved numerically several times to produce any results. Practical expressions for scalar products are possible due to Slavnov's theorem, and hence the 1- and 2-RDMs are tractable. We have observed that while for four-electron systems the results are essentially exact, for ten-electron systems with a sharp Fermi gap there is substantial dynamic correlation to be added. Results are in reasonable agreement with DOCI.

In the third chapter we looked at wavefunctions of the same form as the Bethe ansatz in chapter 2, but we did not require them to be eigenvectors of the reduced BCS Hamiltonian, hence avoiding Richardson's equations altogether. Provided dual descriptions of the same state in terms of particles and holes, practical expressions for the 1- and 2-RDMs are available. In general this problem is rather difficult, so we outlined a bivariational principle and projection approaches. In both cases, the energy is not variationally bound, and complex energies are possible.

In the fourth chapter we considered couplings of second-quantized operators into open shell singlets and triplets. Geminals were constructed and expanded in bases of the corresponding configuration state functions. The final formulae looked to be intractable in general, though restrictions on the geminal coefficients may produce tractable computational approaches.

In the fifth chapter, we looked at wavefunction forms with non-zero seniorities and odd-numbers of electrons based on the Lie superalgebras $\mathfrak{gl}(m|n)$. It was possible to frame these wavefunctions as eigenvectors of model Hamiltonians, though the non-linear equations become difficult. These wavefunctions have the form of a nested Bethe ansatz, i.e. quasi-particles on top of quasi-particles. In general this type of description quickly becomes intractable, though for few unpaired electrons such approaches are feasible. Unfortunately, in these states seniority is a conserved quantity, making it impossible to have both seniority zero and seniority two simultaneously. There are too many non-physical symmetries conserved: the exact wavefunction in general does not have a good seniority. A reasonable approximation to an open shell state needs to have an expansion in several seniorities.

6.2 The Future

We have looked at several wavefunction forms while adhering to our golden rules for possible ansätze:

- Non-trivial result: not a single Slater determinant
- Tractable: we must be able to evaluate either RDMs (variational) or scalar products (projection) by polynomially scaling algorithms (ideally $\mathcal{O}(N^4)$ or $\mathcal{O}(N^5)$, no worse than $\mathcal{O}(N^7)$)
- Size-consistent / extensive: if not present, the fraction of the correlation energy recovered reduces with increasing system size
- No active spaces: it is generally only easy to identify active spaces when they are essentially not needed, otherwise no active space method can be considered a black box (unless the active space is exhaustive)

Our experiences have pointed out further guidelines to follow:

- It is nice to use Lie algebra symmetries, but restrict yourselves to ones which are physical.

- Seniority zero and seniority two are required. To be extensive, either everything must be seniority zero, or every seniority from zero to the maximum is strictly required.
- Stay away from nesting quasi-particles.

We are confident that we have solid approaches for seniority zero strong correlation (in a non-relativistic framework). It remains to generalize to non-zero seniorities and to include weak correlation. How would one account for relativistic effects? Scalar approaches are essentially free and require only a rescaling of the matrix elements. Two-component wavefunction approaches are certainly more interesting and we would like to explore this line of thought. Should one use distinct algebras for each component? Is a wavefunction ansatz written in terms of *spin* $\mathfrak{su}(2)$ generators more appropriate?

Appendix A

Abstract Nonsense

The terms direct product, direct sum, and tensor product are used liberally both in the text, and in the literature in general. Though similar, they are often distinct constructions. It is convenient to have precise (though certainly obtuse) definitions. They will be given in a general form: categorical constructions with universal properties.

A.1 Direct Product

A direct product is an example of a *product* in category theory. The *product* of two objects X_1 and X_2, denoted $X_1 \times X_2$, is defined to be surjective onto each individual object. There are therefore surjective mappings $\pi_1 : X_1 \times X_2 \to X_1$ and $\pi_2 : X_1 \times X_2 \to X_2$. The product is *universal*: if Y is any other product of X_1 and X_2 (i.e. there are surjective mappings $f_1 : Y \to X_1$ and $f_2 : Y \to X_2$), then there exists a unique mapping f such that $f_1 = \pi_1 \circ f$ and $f_2 = \pi_2 \circ f$.

$$\begin{tikzcd}
 & Y \arrow[dl, "f_1"'] \arrow[d, dotted, "f"] \arrow[dr, "f_2"] & \\
X_1 & X_1 \times X_2 \arrow[l, "\pi_1"] \arrow[r, "\pi_2"'] & X_2
\end{tikzcd}$$

A.2 Direct Sum

Similarly, the direct sum is an example of a *coproduct* in category theory. It is a dual notion to that of product. For the same X_1 and X_2, but equipped with *injective* mappings $i_1 : X_1 \to X_1 \oplus X_2$ and $i_2 : X_2 \to X_1 \oplus X_2$. It is universal in the sense that if $f_1 : X_1 \to Y$ and $f_2 : X_2 \to Y$, then both mappings factor uniquely through the coproduct: there exists a unique f such that $f \circ i_1 = f_1$ and $f \circ i_2 = f_2$.

$$\begin{tikzcd}
 & Y & \\
X_1 \arrow[ur, "f_1"] \arrow[r, "i_1"'] & X_1 \oplus X_2 \arrow[u, dotted, "f"] & X_2 \arrow[ul, "f_2"'] \arrow[l, "i_2"]
\end{tikzcd}$$

A.3 Tensor Product

We give a definition for the case where the objects have at least the structure of a vector space. More general constructions are possible when there is less structure, e.g. when the scalar multiplication by the field is not commutative there is a corresponding construction for modules.

Provided two vector spaces X and Y, the *tensor product* $X \otimes Y$, is a vector space along with a map $\varphi : X \times Y \to X \otimes Y$ which is universal: for any vector space Z and *bilinear* mapping $f : X \times Y \to Z$, there is a unique *linear* mapping $\tilde{f} : X \otimes Y \to Z$ such that $f = \tilde{f} \circ \varphi$.

$$\begin{tikzcd}
X \times Y \arrow[r, "\varphi"] \arrow[dr, "f"'] & X \otimes Y \arrow[d, dotted, "\tilde{f}"] \\
& Z
\end{tikzcd}$$

The tensor product $X \otimes Y$ is constructed by taking all the individual symbols $\{x \otimes y | x \in X, y \in Y\}$ and imposing the equivalence relations:

$$(x_1 + x_2) \otimes y = x_1 \otimes y + x_2 \otimes y \tag{A.1}$$

$$x \otimes (y_1 + y_2) = x \otimes y_1 + x \otimes y_2 \tag{A.2}$$

$$c\,(x \otimes y) = x \otimes (cy) = (cx) \otimes y. \tag{A.3}$$

While the above definitions are certainly not the most intuitive, let us consider the distinction between the vector spaces $X \times Y$, $X \oplus Y$, and $X \otimes Y$. Both the direct product $X \times Y$, and the direct sum $X \oplus Y$ have as basis the union of the original bases $\{x\} \cup \{y\}$, whereas the tensor product $X \otimes Y$ has as basis the set of objects $\{x \otimes y\}$. The dimensions of the spaces are then $\dim(X \times Y) = \dim(X \oplus Y) = \dim(X) + \dim(Y)$, and $\dim(X \otimes Y) = \dim(X) \times \dim(Y)$. The distinction between the direct product and direct sum of vector spaces arises only when there are an infinite number of elements. Specifically, the direct sum

$$\bigoplus_{i=1}^{\infty} X_i$$

consists of vectors with only a *finite* number of non-zero elements, whereas the direct product

$$\prod_{i=1}^{\infty} X_i$$

includes vectors with infinitely many non-zero elements as well. In other categories, the direct product and direct sum are often distinct constructions.

A.4 Fock Space

Second quantized operators reside in the so-called Fock space. As electrons are fermions, the relevant states are elements of the *anti-symmetric* Fock space

$$\mathfrak{F}_- = \bigoplus_{n=0}^{\infty} \Lambda^n \left(\mathfrak{H}\right) \tag{A.4}$$

where $\mathfrak{H}$ is the single-particle Hilbert space, and Λ^n its *nth* exterior power. The exterior power is obtained from the tensor product of the spaces with the additional relation that the tensor product is alternating:

$$x_{\sigma(1)} \otimes \ldots \otimes x_{\sigma(n)} = \mathrm{sgn}\left(\sigma\right) x_1 \otimes \ldots \otimes x_n \tag{A.5}$$

for each permutation $\sigma \in S_n$.

Alternatively, bosonic states reside in the *symmetric* Fock space:

$$\mathfrak{F}_+ = \bigoplus_{n=0}^{\infty} Sym^n \left(\mathfrak{H}\right). \tag{A.6}$$

The symmetric power is defined analogously to the antisymmetric power. It is the tensor product of the spaces with the additional relation:

$$x_{\sigma(1)} \otimes \ldots \otimes x_{\sigma(n)} = x_1 \otimes \ldots \otimes x_n. \tag{A.7}$$

A.5 Hopf Algebra

A.5.1 Algebras

A unital, associative *algebra* is a triple (A, μ, η) of a vector space A; a mapping $\mu : A \otimes A \to A$ called the *multiplication*; a mapping $\eta : k \to A$ called the *unit.* k is the ground field of A. The multiplication is associative, i.e. $\mu \circ (\mu \otimes \mathrm{id}) = \mu \circ (\mathrm{id} \otimes \mu)$, or as a commutative diagram:

$$\begin{tikzcd}
A \otimes A \otimes A \arrow[r, "\mu\otimes\mathrm{id}"] \arrow[d, "\mathrm{id}\otimes\mu"'] & A \otimes A \arrow[d, "\mu"] \\
A \otimes A \arrow[r, "\mu"'] & A
\end{tikzcd}$$

There is also the *unital* property $\mu \circ (\eta \otimes \mathrm{id}) = \mu \circ (\mathrm{id} \otimes \eta)$, or:

$$\begin{tikzcd}
k \otimes A \arrow[r, "\eta\otimes\mathrm{id}"] \arrow[dr, "\cong"'] & A \otimes A \arrow[d, "\mu"] & A \otimes k \arrow[l, "\mathrm{id}\otimes\eta"'] \arrow[dl, "\cong"] \\
& A &
\end{tikzcd}$$

Multiplication is deductive, i.e. it takes an element of $A \otimes A$ and produces an element of A. The algebra is *commutative* if $\mu = \mu \circ \tau$, where $\tau(a \otimes a') = a' \otimes a$, or:

$$\begin{tikzcd}
A \otimes A \arrow[rr, "\tau"] \arrow[dr, "\mu"'] & & A \otimes A \arrow[dl, "\mu"] \\
& A &
\end{tikzcd}$$

A.5.2 Coalgebras

The axioms for *coassociative, counital coalgebras* are obtained simply by reversing all the arrows in the previous section. A coalgebra is a triple (C, Δ, ε) of a vector space C, a mapping $\Delta : A \to A \otimes A$ called the *comultiplication* (or coproduct), and a mapping $\varepsilon : A \to k$ called the counit. The comultiplication is coassociative $(\Delta \otimes \mathrm{id}) \circ \Delta = (\mathrm{id} \otimes \Delta) \circ \Delta$, or:

$$\begin{tikzcd}
C \otimes C \otimes C & C \otimes C \arrow[l, "\Delta\otimes\mathrm{id}"'] \\
C \otimes C \arrow[u, "\mathrm{id}\otimes\Delta"] & C \arrow[l, "\Delta"] \arrow[u, "\Delta"']
\end{tikzcd}$$

The counit satisfies the counital property $(\varepsilon \otimes \mathrm{id}) \circ \Delta = (\mathrm{id} \otimes \varepsilon) \circ \Delta$, or:

$$\begin{tikzcd}
k \otimes C & C \otimes C \arrow[l, "\varepsilon\otimes\mathrm{id}"'] \arrow[r, "\mathrm{id}\otimes\varepsilon"] & C \otimes k \\
& C \arrow[ul, "\cong"] \arrow[u, "\Delta"] \arrow[ur, "\cong"'] &
\end{tikzcd}$$

Comultiplication is inductive, i.e. it takes an element of C and produces a linear combination of elements in $C \otimes C$. The comultiplication is cocommutative if $\tau \circ \Delta = \Delta$, or:

$$\begin{tikzcd}
C \otimes C & & C \otimes C \arrow[ll, "\tau"'] \\
& C \arrow[ul, "\Delta"] \arrow[ur, "\Delta"'] &
\end{tikzcd}$$

A.5.3 Bialgebras

A vector space B with both algebra and coalgebra structures is a *bialgebra* provided that the two sets of structures are compatible:

- $\Delta \circ \mu = (\mu \otimes \mu) \circ (\mathrm{id} \otimes \tau \otimes \mathrm{id}) \circ (\Delta \otimes \Delta)$

$$\begin{tikzcd}
B \otimes B \arrow[r, "\mu"] \arrow[d, "\Delta\otimes\Delta"'] & B \arrow[r, "\Delta"] & B \otimes B \\
B \otimes B \otimes B \otimes B \arrow[rr, "\mathrm{id}\otimes\tau\otimes\mathrm{id}"'] & & B \otimes B \otimes B \otimes B \arrow[u, "\mu\otimes\mu"']
\end{tikzcd}$$

- $\varepsilon \circ \mu = \mathrm{id} \circ (\varepsilon \otimes \varepsilon)$

$$\begin{tikzcd}
B \otimes B \arrow[r, "\varepsilon\otimes\varepsilon"] \arrow[d, "\mu"'] & k \otimes k \arrow[d, "\mathrm{id}"] \\
B \arrow[r, "\varepsilon"'] & k
\end{tikzcd}$$

- $\Delta \circ \eta = (\eta \otimes \eta) \circ \mathrm{id}$

$$\begin{tikzcd}
k \arrow[r, "\eta"] \arrow[d, "\mathrm{id}"'] & B \arrow[d, "\Delta"] \\
k \otimes k \arrow[r, "\eta\otimes\eta"'] & B \otimes B
\end{tikzcd}$$

- $\varepsilon \circ \eta = \mathrm{id}$

$$\begin{tikzcd}
k \arrow[rr, "\eta"] \arrow[dr, "\mathrm{id}"'] & & B \arrow[dl, "\varepsilon"] \\
& k &
\end{tikzcd}$$

A.5.4 Hopf Algebras

A Hopf algebra is a bialgebra (with vector space H) with a mapping $S : H \to H$ called the antipode such that $\mu \circ (\mathrm{id} \otimes S) \circ \Delta = \mu \circ (S \otimes \mathrm{id}) \circ \Delta$

$$\begin{tikzcd}
& H \otimes H \arrow[rr, "S\otimes\mathrm{id}"] & & H \otimes H \arrow[dr, "\mu"] & \\
H \arrow[ur, "\Delta"] \arrow[dr, "\Delta"'] \arrow[rr, "\varepsilon"] & & k \arrow[rr, "\eta"] & & H \\
& H \otimes H \arrow[rr, "\mathrm{id}\otimes S"'] & & H \otimes H \arrow[ur, "\mu"'] &
\end{tikzcd}$$

A.6 Lie Algebras

A Lie algebra $\mathfrak{g}$ is a vector space of objects $\{X_a\}$ over the complex numbers $\mathbb{C}$. Objects in the Lie algebra will be denoted with lower indices though both upper and lower conventions seem to appear in the literature. What is important is that there *is a distinction* between upper and lower indices. The multiplication $[\cdot,\cdot] : \mathfrak{g} \times \mathfrak{g} \to \mathfrak{g}$, called the Lie bracket, which is bilinear $\forall a, b \in \mathbb{C}$, and $X_\alpha, X_\beta, X_\gamma \in \mathfrak{g}$

$$[aX_\alpha + bX_\beta, X_\gamma] = a[X_\alpha, X_\gamma] + b[X_\beta, X_\gamma] \tag{A.8}$$

and is antisymmetric

$$[X_\alpha, X_\beta] = -[X_\beta, X_\alpha]. \tag{A.9}$$

Additionally, for any three generators there is the Jacobi identity:

$$[X_\alpha, [X_\beta, X_\gamma]] + [X_\beta, [X_\gamma, X_\alpha]] + [X_\gamma, [X_\alpha, X_\beta]] = 0 \tag{A.10}$$

which ensures that the algebra is defined consistently. For Gaudin algebras, the Jacobi identity dictates the (classical) Yang-Baxter equations, which in turn ensure that the transfer matrix commutes with itself for distinct choices of its argument.

The Lie bracket has the action

$$[X_\alpha, X_\beta] = \sum_\gamma C^\gamma_{\alpha\beta} X_\gamma \tag{A.11}$$

where the scalars $C^\gamma_{\alpha\beta}$ are called the structure constants. The most prevalent example of the Lie bracket is the commutator defined

$$[X_\alpha, X_\beta] := X_\alpha X_\beta - X_\beta X_\alpha. \tag{A.12}$$

A subset $\mathfrak{h} \subset \mathfrak{g}$ is a Lie subalgebra if $\mathfrak{h}$ is closed under the Lie bracket, i.e. $[\mathfrak{h}, \mathfrak{h}] \subset \mathfrak{h}$. Further, if $[\mathfrak{h}, \mathfrak{g}] \subset \mathfrak{h}$, then $\mathfrak{h}$ is called an *ideal* of $\mathfrak{g}$. For non-commutative rings, left- and right-sided ideals may be distinct objects and it is necessary to check if a given ideal is two-sided. For Lie algebras the antisymmetry of the Lie bracket (A.9) ensures that $[\mathfrak{h}, \mathfrak{g}] \subset \mathfrak{h} \iff [\mathfrak{g}, \mathfrak{h}] \subset \mathfrak{h}$. A Lie algebra is called *simple* if its only ideals are the trivial ones: $\mathfrak{g}, \{0\}$, and *semi-simple* if it is the direct sum of simple Lie algebras.

It is an accepted convention to refer to Lie algebras with the lower case fraktur alphabet, while using upper case Roman letters to refer to the corresponding Lie group.[1]

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[1] Also prevalent in the literature is the convention of using lower case Roman characters to denote a Lie algebra, though this may or may not be a dodge for optimal kerning.

Appendix B

Dirty Tricks

> *I was not lying. I said things that later on seemed to be untrue.*
>
> – Richard M. Nixon

By “dirty trick” we mean a procedure that is rigorously true while seeming to be entirely too easy. The thesis is primarily concerned with the evaluation of scalar products of complicated objects. These scalar products are generally seen as functions of several complex variables. Additionally, the goal is to express these objects as determinants, which may be evaluated with $\mathcal{O}(N^3)$ computational scaling.

As stated in the introduction, molecular electronic structure methods are clever sequences of linear algebra operations applied to wavefunctions expanded in basis sets of Gaussian functions. This is because only Gaussian integrals and linear algebra operations are especially efficient to evaluate with conventional computers. Our job is to think hard about complicated objects and to reduce everything to those two operations.

B.1 Complex Analysis

Functions of a complex variable are characterized by their poles, the points at which they diverge. Functions are *holomorphic* (within a region) if they are infinitely differentiable at every point (within that region), and *analytic* if they can be expressed as a convergent power series (within that region). A fundamental result is that these properties are equivalent. An *entire* function is one that is holomorphic everywhere.

B.1.1 Liouville's Theorem

A bounded, entire function is a constant. That is, given $f(z)$ holomorphic and some positive constant M such that for all $z \in \mathbb{C}$,

$$|f(z)| \leq M \tag{B.13}$$

then $f(z)$ is a constant. Liouville's theorem is especially useful in proving identities. To show that a right hand side is equal to a given left hand side, the strategy is either to show that either $LHS - RHS$ or $\frac{LHS}{RHS}$ is bounded and entire, and hence a constant. Further analysis then will show that this constant is 0, or 1. Slavnov's theorem is proved in this manner.

B.1.2 Residue Theorem

Rather than Taylor series, functions of complex variables are expressed as *Laurent series* with both positive and negative powers:

$$f(z) = \sum_{n=-\infty}^{\infty} a_n (z-c)^n \tag{B.14}$$

If f has a pole at c, regardless of degree, the coefficient a_{-1} is called the *residue* of f at c. For simple poles, the residues are easily calculated:

$$\mathrm{Res}(f,c) = \lim_{z\to c}(z-c)f(z) \tag{B.15}$$

For poles of order n, the residue is

$$\mathrm{Res}(f,c) = \frac{1}{(n-1)!}\lim_{z\to c}\frac{d^{n-1}}{dz^{n-1}}((z-c)^n f(z)). \tag{B.16}$$

The residue theorem is that for a positively oriented (counter-clockwise) closed curve γ which circles around each of the poles $\{a_k\}$, $I(\gamma, a_k)$ times, then the contour integral is easily evaluated

$$\oint_\gamma f(z)dz = 2\pi i \sum_{k=1}^{N} I(\gamma, a_k)\mathrm{Res}(f, a_k). \tag{B.17}$$

$I(\gamma, a_k)$ is called the winding number. Why is this result remarkable? First, it immediately implies Cauchy's integral theorem, if $f(z)$ is holomorphic in the interior of γ,

$$\oint_\gamma f(z)dz = 0 \tag{B.18}$$

which is the analogue of the fundamental theorem of calculus.

Further, the residue theorem is useful in real analysis. Given a difficult integral on the real line, one can extend the integration domain to the complex plane and draw a contour connecting finite points on the real line. This integral is trivial (by the residue theorem), and then one shows that the arc between the real points vanishes as they approach ±∞.

B.1.3 Cauchy's Integral Formula

A holomorphic function defined on a disk is entirely determined by its values on the boundary of the disk. Specifically

$$f(a) = \frac{1}{2\pi i}\oint_\gamma \frac{f(z)}{z-a}dz \tag{B.19}$$

where γ is the boundary of disk containing a over which f is holomorphic. Further, the n-th derivative of f at a is

$$f^{(n)}(a) = \frac{n!}{2\pi i}\oint_\gamma \frac{f(z)}{(z-a)^{n+1}}dz. \tag{B.20}$$

In complex analysis then "integration and differentiation are equivalent" as opposed to real analysis.

B.2 Linear Algebra

B.2.1 Permanents

The *permanent* of a matrix A is the symmetric sum of entries a_{ij}

$$\begin{aligned} \mathrm{per}A &= |A|^+ \\ &= \sum_\sigma \prod_{i=1}^N a_{i\sigma(i)}. \end{aligned} \tag{B.21}$$

While this may be symbolically thought of as linear algebra, the difficulty in computing permanents is not communicated. A determinant, has a similar expression in terms of permutations, where $\mathrm{sgn}(\sigma)$ is the sign or signature of the permutation (even or odd)

$$\begin{aligned} \det A &= |A| \\ &= \sum_\sigma \prod_{i=1}^N \mathrm{sgn}(\sigma) a_{i\sigma(i)}. \end{aligned} \tag{B.22}$$

However, determinants have the nice property of being invariant to linear transformations, i.e. for any linear T,

$$\det A = \det(TAT^{-1}). \tag{B.23}$$

Hence A can be triangularized with Gaussian elimination in $\mathcal{O}(N^3)$ operations and the resulting permanent is trivially obtained. For permanents, this is only true if T is a permutation matrix. Thus, to evaluate the permanent of an arbitrary matrix A of size N requires taking a sum of $N!$ elements, though there exist Monte Carlo algorithms of approximating permanents in something like $\mathcal{O}(N^{10})$ time. In either case it is intractable for the purposes of the electronic structure problem.

The most relevant form of matrix to be considered is a Cauchy matrix, where the elements a_{ij} are rational functions of two variables, i.e.,

$$a_{ij} = \frac{1}{\lambda_i - \varepsilon_j}. \tag{B.24}$$

Borchardt's theorem[Bor55] states that, for a Cauchy matrix A,

$$\det A \ \cdot \mathrm{per} A = \det(A \circ A) \tag{B.25}$$

here $\circ$ is the element-wise or Hadamard product.

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