RICE UNIVERSITY

Variational approaches to the molecular electronic structure problem based on symmetry-projected Hartree–Fock configurations

by

Carlos A. Jiménez-Hoyos

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy

Approved, Thesis Committee:

Gustavo E. Scuseria, Chair
Robert A. Welch Professor of Chemistry and Physics and Astronomy

Cecilia Clementi
Wiess Career Development Chair, Professor of Chemistry and Chemical and Biomolecular Engineering

Anatoly B. Kolomeisky
Professor of Chemistry and Chemical and Biomolecular Engineering

Andrij Nevidomskyy
Assistant Professor of Physics and Astronomy

Houston, Texas

December, 2013
Variational approaches to the molecular electronic structure problem based on symmetry-projected Hartree–Fock configurations

by

Carlos A. Jiménez-Hoyos

Approximate wavefunctions such as Hartree–Fock (HF) states need not respect the symmetries of the molecular electronic Hamiltonian. In certain cases such as in bond-breaking processes, the lowest-energy HF solution obtained by a variational scheme corresponds to a symmetry-broken Slater determinant. This broken symmetry HF solution captures some of the correlations associated with near-degeneracies in a symmetry-adapted construction. Broken-symmetry HF solutions are, nevertheless, unphysical and cannot accurately represent the stationary states of a molecular system. By using projection operators, one can restore the physical character of the wavefunction while accessing the relevant correlations introduced by the broken symmetry mean field description.

In this work, we consider a single symmetry-projected Slater determinant as a working wave function ansatz. Originally proposed by Löwdin in 1955, the idea was mostly abandoned in the quantum chemistry community after decades of work. By borrowing techniques successful in the nuclear physics community, we use a rigorous, yet efficient mathematical apparatus to perform the projection before the variation of broken symmetry wavefunctions. The wavefunctions thus obtained have a multi-determinantal
character and can account for significantly more correlations than a broken-symmetry
HF state in finite systems. The symmetry-projected HF approach is, nonetheless, not
free of vices. The approach is neither size-consistent nor size-extensive.

In order to go beyond the symmetry-projected HF wavefunction, we construct multi-
reference wavefunctions written as a linear combination of symmetry-projected con-
figurations constructed out of a set of non-orthogonal Slater determinants. Chains of
variational calculations are used to optimize wavefunctions suitable for an accurate
description of ground and excited states, with well defined quantum numbers, which
can account for both strong and weak correlation effects. Our results indicate that
such expansions can produce fairly accurate results for small molecular systems. We
hope our approach will eventually become yet another tool for the quantum chemist
useful in situations where both strong and weak correlation effects are important.
In memory of my beloved grandparents, Augusto and Carmen.
Acknowledgments

I would like to thank Prof. Gustavo Scuseria for welcoming me into his group and for supporting a stimulating research environment. I have greatly enjoyed the many science discussions that we have held during these past years and I profoundly acknowledge him for his patience and wise guidance.

I am deeply grateful to Prof. Benjamin Janesko, Dr. Thomas Henderson, and Dr. Rayner R. Rodríguez-Guzmán, all of whom helped mentor me during my time at Rice University. I am also grateful to Ireneusz Bulik, Jason Ellis, Takashi Tsuchimochi, Laimis Bytautas, and Kousik Samanta for continuous stimulating discussions.

Along the course of my graduate studies, I have enjoyed collaborations that resulted in published work with Dr. L. Bytautas, Dr. J. K. Ellis, A. J. Garza, Dr. R. Haunschild, Dr. T. M. Henderson, Prof. B. G. Janesko, Prof. J. P. Perdew, Dr. P. Rivero, Dr. R. R. Rodríguez-Guzmán, Dr. K. Samanta, Prof. K. W. Schmid, R. Schutski, Prof. V. N. Staroverov, and T. Tsuchimochi.

I have had the pleasure to share office with a number of people, Ed Brothers, Griffin Canning, Mi Kyung Lee, Laimutis Bytautas, Kousik Samanta, Roman Schutski, and Jacob Wahlen-Strothman. The daily interactions with all of them have been fruitful. I am also grateful to all other former and current members of the Scuseria research group with whom I have overlapped.

Prof. Cecilia Clementi, Prof. Anatoly Kolomeisky, and Prof. Andriy Nevidomskyy have taken the time to carefully evaluate this work. I am indebted to them for this kind gesture.
I would like to express my deepest gratitude to Prof. Seiichi Matsuda for all his support. I will be always grateful to my undergraduate advisors, Prof. Marcelo Videa and Prof. Michael Hall, for their advise and encouragement during the early part of my career. I will remain indebted to all the Professors that I interacted with at the Universidad Nacional Autónoma de México and the friends I met during my participation in the chemistry olympiads as they helped foster my interest in science.

During my graduate studies, I have been supported by the Attwell-Welch Graduate Fellowship, the Stephen C. Hofmann Fellowship, and the Lodieska Stockbridge Vaugh Fellowship.

I am grateful to my friends here at Rice for making all these years more enjoyable. I have found in my family a continuous source of inspiration and encouragement. I finally wish to thank my wife, Melisa, for without her love and patience this work would have not been completed.
# Contents

List of Figures .......................... x
List of Tables .......................... xii

## 1 Introduction

1

## 2 Preliminaries

2.1 The molecular Hamiltonian ................. 4
2.2 The LCAO approach .......................... 5
2.3 Second-quantized formulation ............... 6
2.4 The one-dimensional periodic Hubbard Hamiltonian .... 7
2.5 Hartree–Fock-type transformation of fermion operators .... 8
2.6 The Hartree–Fock method ........................ 11

## 3 Symmetry-projected Hartree–Fock

3.1 Symmetry breaking in HF ........................ 15
3.1.1 The symmetry dilemma ...................... 17
3.1.2 Self-consistent symmetries ................. 18
3.1.3 Classification of broken-symmetry HF solutions .... 20
3.1.4 Symmetry-adapted expansion of broken symmetry HF states .... 22
3.2 Projection operators .......................... 23
3.2.1 Spin projection .......................... 24
3.2.2 Spatial symmetry projection ......... 26
3.2.3 Complex conjugation projection .......... 27
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>The symmetry-projected HF ansatz</td>
<td>28</td>
</tr>
<tr>
<td>3.4</td>
<td>Variational optimization of the symmetry-projected HF wavefunction</td>
<td>33</td>
</tr>
<tr>
<td>3.5</td>
<td>Optimization based on a Thouless parametrization</td>
<td>35</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Restoration of the normalization condition</td>
<td>38</td>
</tr>
<tr>
<td>3.5.2</td>
<td>Global gradient</td>
<td>39</td>
</tr>
<tr>
<td>3.6</td>
<td>Application to molecular systems</td>
<td>41</td>
</tr>
<tr>
<td>3.6.1</td>
<td>Implementation details</td>
<td>41</td>
</tr>
<tr>
<td>3.6.2</td>
<td>Nomenclature</td>
<td>42</td>
</tr>
<tr>
<td>3.6.3</td>
<td>VAP vs PAV</td>
<td>43</td>
</tr>
<tr>
<td>3.6.4</td>
<td>Dissociation curves of small systems</td>
<td>44</td>
</tr>
<tr>
<td>3.6.5</td>
<td>Basis set dependence</td>
<td>47</td>
</tr>
<tr>
<td>3.6.6</td>
<td>Singlet-triplet splittings</td>
<td>47</td>
</tr>
<tr>
<td>3.7</td>
<td>Concluding remarks</td>
<td>49</td>
</tr>
<tr>
<td>4</td>
<td>Configuration-mixing approaches to account for ground-state correlations</td>
<td>51</td>
</tr>
<tr>
<td>4.1</td>
<td>Configuration Interaction based on symmetry-projected determinants</td>
<td>52</td>
</tr>
<tr>
<td>4.2</td>
<td>Generalized fermion coherent states</td>
<td>53</td>
</tr>
<tr>
<td>4.3</td>
<td>Multi-configuration approaches</td>
<td>55</td>
</tr>
<tr>
<td>4.3.1</td>
<td>The few-determinant (FED) approach</td>
<td>57</td>
</tr>
<tr>
<td>4.3.2</td>
<td>The resonating (RES) approach</td>
<td>59</td>
</tr>
<tr>
<td>4.4</td>
<td>Application to molecular systems</td>
<td>60</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Ground-state energy of ( N_2 )</td>
<td>60</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Dissociation profiles</td>
<td>63</td>
</tr>
<tr>
<td>4.4.3</td>
<td>The copper oxide ([\text{Cu}_2\text{O}_2]^{2+}) core</td>
<td>67</td>
</tr>
<tr>
<td>4.5</td>
<td>Concluding remarks</td>
<td>69</td>
</tr>
<tr>
<td>5</td>
<td>Excited states</td>
<td>73</td>
</tr>
<tr>
<td>5.1</td>
<td>The excited VAMP strategy</td>
<td>74</td>
</tr>
</tbody>
</table>
5.2 Correlations in excited states ........................................ 78
5.3 Applications to molecular systems .................................. 80
  5.3.1 Dissociation profile of the carbon dimer ....................... 80
  5.3.2 Vertical excitation spectrum of formaldehyde ................. 82
5.4 Concluding remarks .................................................... 84

6 The one-dimensional Hubbard model 89
  6.1 The symmetries of the Hubbard Hamiltonian .................... 90
  6.2 Size-extensivity and symmetry-projected HF ..................... 90
  6.3 Spin-spin correlation function .................................... 95
  6.4 Structure of the reference determinants .......................... 100
  6.5 Low-lying spectrum of small lattices ............................ 101
  6.6 Concluding remarks ................................................. 102

7 Conclusions and outlook 105

A Thouless’ theorem 109

B Matrix elements between non-orthogonal Slater determinants 113
  B.1 Norm overlap ...................................................... 114
  B.2 Operator matrix elements ....................................... 115

C Stability condition for symmetry-projected HF solutions 119

D Reduced density matrices of spin-projected states 122
  D.1 Tensorial character of individual fermion operators ........... 124
  D.2 One-particle density operators \( \hat{\Gamma}_i^k = c_i^\dagger c_k \) ....... 124
  D.3 Two-particle density operators \( \hat{\Gamma}_i^k \hat{\Gamma}_j^l = c_i^\dagger c_k c_j^\dagger c_l \) ...... 125
  D.4 Density matrix elements for \( m = 0 \) states .................... 127

Bibliography 130
List of Figures

3.1 Symmetry-adapted (sa) and broken-symmetry (bs) HF description of the molecular dissociation profile of the H$_2$ molecule. ....................... 15
3.2 Potential energy curve for H$_2$ dissociation predicted by S-UHF (PAV) and S-UHF (VAP). ................................................................. 43
3.3 Potential energy curve for the isotropic dissociation of an H$_3$ equilateral triangle. ................................................................. 45
3.4 Potential energy curve for the dissociation of the nitrogen molecule. . 46
3.5 Relative energy with respect to UHF across the dissociation profile of N$_2$ with different basis sets. ................................. 48

4.1 Ground-state energy of N$_2$ predicted by a variety of FED approaches at $r = r_{eq}$ and $r = 1.5\, r_{eq}$ as a function of the number of symmetry-projected configurations. ......................... 62
4.2 Dissociation profile for the ground state of the N$_2$ molecule obtained with a FED $D_{2h}$S-UHF approach as a function of the number of HF transformations. ................................................................. 65
4.3 Symmetric dissociation profile of the water molecule as predicted with a variety of multi-configuration symmetry-projected approaches. 67
4.4 Relative total energy of (Cu$_2$O$_2$)$^{2+}$ along a linear isomerization path from B to A. ................................. 72
5.1 Dissociation profiles for low-lying singlet states of the C$_2$ molecule computed with the $D_{4h}$-S-UHF / 6-31G(d) method. 

5.2 Evolution of the $^1A_1$ spectrum of formaldehyde as computed with the excited $C_{2v}$-S-UHF method with increasing number of symmetry-projected configurations.

5.3 Low-lying singlet and triplet states of the formaldehyde molecule predicted with the $C_{2v}$-S-UHF method.

6.1 Energy per site and total correlation energy with respect to UHF predicted by a variety of symmetry-projected HF methods on Hubbard lattices of increasing size $L$.

6.2 Energy per site predicted by FED SG-UHF expansions for Hubbard lattices of increasing size $L$.

6.3 Absolute value of the overlap among states in the Goldstone manifold defined by spin projection (S-UHF) for Hubbard lattices of increasing size.

6.4 Absolute value of the overlap among states in the Goldstone manifold defined by space-group (SG-UHF) projection for Hubbard lattices of increasing size.

6.5 Magnetic structure factor computed with a variety of symmetry-projected HF methods on Hubbard lattices of increasing size $L$.

6.6 Structure of the underlying deformed determinant obtained from a variety of symmetry-projected HF methods for a Hubbard lattice of $L = 128$ sites at half-filling and $U/t = 4$.

6.7 Low-lying spectrum of a 10-site Hubbard lattice at half-filling and $U/t = 4$ as predicted with SG-SGHF and deviations from the exact diagonalization energies.
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Singlet triplet splittings predicted by symmetry-projected methods for a variety of small molecules.</td>
<td>48</td>
</tr>
<tr>
<td>4.1</td>
<td>Ground-state energy of N(_2) predicted with the FED S-UHF and RES S-UHF approaches as a function of the number of transformations.</td>
<td>64</td>
</tr>
<tr>
<td>D.1</td>
<td>Irreducible tensor components from one-particle density operators.</td>
<td>125</td>
</tr>
<tr>
<td>D.2</td>
<td>Spin-blocks of one-particle density operators as linear combinations of irreducible tensor components.</td>
<td>126</td>
</tr>
<tr>
<td>D.3</td>
<td>Irreducible tensor components from two-particle density operators.</td>
<td>129</td>
</tr>
<tr>
<td>D.4</td>
<td>Spin-blocks of two-particle density operators as linear combinations of irreducible tensor components.</td>
<td>130</td>
</tr>
</tbody>
</table>
Preface

This thesis is based on some of the research conducted with Prof. Gustavo E. Scuseria at Rice University between December 2010 and February 2013. Most of the results and ideas included in this document are discussed in a series of papers:


The application of symmetry-projected HF approaches to the Hubbard Hamiltonian, as opposed to molecular systems, has been published in:

Our work has motivated the following series of papers:


Additional research efforts related to the topic of this work have been published in:


Chapter 1

Introduction

In the last few decades, advancements in the methods used in quantum chemistry and other fields of many-body physics have allowed for an efficient description of weakly-correlated systems, that is, those systems that have a Fermi-liquid character. On the other hand, the description of strongly correlated systems has proven much more challenging. Successful methods typically need to expand the wavefunction in terms of a number of configurations that increases combinatorially with the size of the system. It was early realized, however, that a symmetry-broken HF approach can account for some fraction of the strong correlations that are otherwise very costly to build into an approximate solution. The resulting wavefunction is, nevertheless, unphysical (as it does not respect the symmetries of the Hamiltonian) and may lead to an incorrect qualitative description of certain observables.

A symmetry-projected HF ansatz, first proposed by Löwdin [1], provides a very attractive shortcut. On the one hand, the strong correlations introduced by a broken-symmetry mean field are captured and, on the other hand, the wavefunction remains physical as it possesses a good set of quantum numbers. Furthermore, even more correlations can be captured when the optimization of the ansatz is carried out self-consistently, as symmetries that were not originally broken in the HF wavefunction can be deliberately broken. Note that, additionally, the wavefunction is still defined by a single set of occupied (hole) states, which facilitates the understanding of the
physics behind the approximation. Despite the merits of the ansatz and after decades of work, quantum chemists payed little attention to it due to the complications in the evaluation of the energy and the realization that the resulting wavefunction is neither size-consistent nor size-extensive.

In this work, we describe an efficient implementation of the symmetry-projected HF approach to the molecular electronic Hamiltonian. We emphasize that all symmetries of the Hamiltonian (save for the particle number symmetry) have been broken and restored. This differs from most early work in quantum chemistry, where most efforts were put into a spin-projected approach [2]. The key to the efficient implementation that we present lies in the form of the projection operator used; for angular momentum (including spin), the form we use was introduced by Villars [3] in the nuclear physics community.

As shown in this work (and noted by other authors previously [4]), projected HF is neither size-consistent nor size extensive. Even though it provides an efficient description of the strong correlations associated with bond-breaking, it often misses a large part of the dynamical, instantaneous electron correlation. We have considered two approaches, devised by Schmid et al. [5, 6] and Fukutome [7] to introduce correlations beyond the symmetry-projected ground state. A multi-configurational expansion based on symmetry-projected configurations can efficiently capture all correlations in molecular systems, as our work clearly shows. These approaches have the merit of becoming exact in the limit of an infinite number of configurations.

A multi-configurational expansion can be used not only to build ground state correlations, but also to variationally optimize excited states with the same quantum numbers as the ground state. The approach we use was first proposed by Schmid
and co-workers [8]. The methods presented in this work can be used to construct, through a chain of variational calculations, the full low-lying spectrum of a molecular system where each state has well-defined quantum numbers. In light of this, we believe this methods deserve further consideration among the quantum chemists, as the robustness of the approach can at least prove complementary to other methods used in the field.

This work is organized as follows. In Chapter 2 we briefly introduce the molecular electronic Hamiltonian and the one-dimensional periodic Hubbard Hamiltonian, culminating with a short discussion about the HF method. Chapter 3 provides an extensive description of the symmetry-projected HF approach and it discusses some applications of the method in molecular systems. In Chapter 4, we introduce the approach used to build ground state correlations (beyond symmetry-projected HF) by considering a multi-configurational ansatz. We then show, in Chapter 5, how a similar approach can be used to access all states in the low-lying spectrum, including those with the same quantum numbers as the ground state. We discuss the application of the previous methods to the one-dimensional Hubbard Hamiltonian in Chapter 6, with emphasis on exploring the quality of the approximation rather than the physics of the model system. We provide some conclusions and outlook in the last Chapter (7) of this document.
Chapter 2

Preliminaries

Our purpose in this chapter is to very briefly describe the molecular electronic structure problem for which we aim to provide accurate solutions throughout the rest of the thesis. Our presentation culminates with a brief discussion of the Hartree–Fock method.

2.1 The molecular Hamiltonian

A molecule is a quantum mechanical system where a collection of charged nuclei and electrons interact electromagnetically through the Hamiltonian (in atomic units)

\[ \hat{H}_{\text{molecular}} = -\sum_A \frac{1}{2 M_A} \nabla_A^2 - \sum_i \frac{1}{2} \nabla_i^2 + \sum_{AB} \frac{Z_A Z_B}{r_{AB}} + \sum_{ij} \frac{1}{r_{ij}} - \sum_A \frac{Z_A}{r_{iA}}, \]  

where the indices \( A \) and \( B \) are used for the nuclei while \( i \) and \( j \) are used for electrons. Here, \( M_A \) and \( Z_A \) represent the mass and the charge of the nuclei, respectively. The first two terms in the Hamiltonian represent the kinetic energy of the nuclei and electrons, while the last three terms represent the Coulombic repulsion among nuclei and electrons and the nuclear-electron attraction.

We shall not attempt to consider such Hamiltonian in this work. Rather, we use the Born-Oppenheimer or clamped-nuclei approximation. This is most often justified in terms of the relative masses of the nuclei and protons. The electronic Hamiltonian
depends only on the electronic degrees of freedom, although it has a parametric
dependence on the nuclear positions. It is given by

\[ \hat{H}_{\text{elec}} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_{Ai} \frac{Z_A}{r_{iA}} + \sum_{ij} \frac{1}{r_{ij}}. \]  

(2.2)

Given this Hamiltonian, solutions to the time-independent Schrödinger equation,

\[ \hat{H}_{\text{elec}} |\Psi\rangle = E |\Psi\rangle, \]

(2.3)
yield the wavefunctions that characterize the stationary states of the system. We aim
in this work to obtain high-quality approximate solutions to this equation.

### 2.2 The LCAO approach

We shall consider a further approximation to the electronic Hamiltonian before at-
ttempting to solve it. In order to render the problem more amenable to computation,
we do not attempt to find wavefunctions \(|\Psi\rangle\) of arbitrary form (satisfying the appro-
priate boundary conditions).

A basis set is commonly introduced in quantum chemistry. One-electron wavefunc-
tions obtained by linear combinations of the basis states are the only ones allowed in
this approximation. The basis set is commonly chosen in terms of atomic orbitals,
thus yielding the linear combination of atomic orbitals (LCAO) approach. Because
Gaussian basis functions are easier to handle computationally, each atomic orbital
is commonly written as a linear expansion of a few atom-centered Gaussian basis
functions.

A basis set composed of atom-centered basis functions is not orthonormal. That is,
if \(|\mu\rangle\) and \(|\nu\rangle\) are two different basis states, then in general

\[ \langle \nu | \mu \rangle \neq \delta_{\mu\nu}. \]  

(2.4)
The rest of this work assumes orthonormality conditions among the basis states for convenience. We note that a transformation from the standard, non-orthogonal atomic orbital basis to an orthonormal basis can be easily accomplished by means of a canonical orthogonalization, using a transformation matrix

\[ X = U s^{-1/2}, \quad (2.5) \]

where \( U \) is the matrix of eigenvectors of the overlap matrix among basis states, and \( s \) is used for the diagonal matrix with its eigenvalues.

### 2.3 Second-quantized formulation

The single-particle Hilbert space is spanned by a set of \( M \) orthonormal one-particle states \( |j\rangle \) (spin-orbitals). In second-quantization, we introduce a set of \( M \) creation \( \{c^\dagger_j\} \) and annihilation \( \{c_j\} \) operators satisfying standard anti-commutation relations

\[
\begin{align*}
\left[ c_k, c_j \right]_+ &= 0, \quad (2.6a) \\
\left[ c_{k}^{\dagger}, c_{j}^{\dagger} \right]_+ &= 0, \quad (2.6b) \\
\left[ c_{k}, c_{j}^{\dagger} \right]_+ &= \langle k|j \rangle = \delta_{jk}, \quad (2.6c)
\end{align*}
\]

where |k\rangle (\langle k|) is a single-particle ket (bra) state.

Properly antisymmetrized many-electron wavefunctions can be written in terms of creation operators acting upon the fermion vacuum state. These are called Slater determinants.

In a second-quantized framework, the molecular electronic Hamiltonian takes the form

\[
\hat{H} = \sum_{ik} \langle i|\hat{h}|k \rangle c_{i}^{\dagger} c_{k} + \frac{1}{4} \sum_{ijkl} \langle ij|\hat{v}|kl \rangle c_{i}^{\dagger} c_{j}^{\dagger} c_{l} c_{k}, \quad (2.7)
\]
where
\[ \hat{h} = \frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{r_A} \] (2.8)
is the core Hamiltonian operator and
\[ \hat{v} = \frac{1}{r_{12}} \] (2.9)
is the electron-electron repulsion operator. \( \langle i | \hat{h} | k \rangle \) and \( \langle ij | \hat{v} | kl \rangle \) constitute core Hamiltonian and antisymmetrized electron-repulsion integrals, respectively, over the set of basis states.

In a given basis set, the exact solution to the molecular electronic structure problem can be obtained by diagonalization of the Hamiltonian operator (Eq. 2.7) over the set of all possible Slater determinants constructed from the basis states. Such an approach is known as full configuration interaction (full CI) in the quantum chemistry jargon.

### 2.4 The one-dimensional periodic Hubbard Hamiltonian

In previous sections we introduced the molecular electronic Hamiltonian, on which most of this work is based. Here, we briefly introduce a simpler Hamiltonian, namely, the one-dimensional, single-band periodic Hubbard model, which is used in Ch. 6 due to its simplicity. This Hamiltonian describes a set of spin-\( \frac{1}{2} \) fermions (electrons) in a lattice of \( L \) sites interacting through

\[ \hat{H} = -t \sum_{j,\sigma} \left( c_{j,\sigma}^\dagger c_{j+1,\sigma} + c_{j+1,\sigma}^\dagger c_{j,\sigma} \right) + U \sum_j c_{j,\uparrow}^\dagger c_{j,\uparrow} c_{j,\downarrow}^\dagger c_{j,\downarrow} \] (2.10)

Here, \( c_{j,\sigma}^\dagger \) creates an electron on site \( j \) of the lattice with \( \sigma = \{\uparrow, \downarrow\} \) z-projection of spin. The first term in the Hamiltonian accounts for a negative (\( t > 0 \)) kinetic energy that the electrons gain when they hop from one site to a neighbor. The second term
accounts for the \( (U > 0) \) repulsion that opposite-spin electrons feel when they are in the same site. Periodic boundary conditions are assumed, which make the site \( L + k \) equivalent to the site \( k \).

The Hubbard Hamiltonian can be regarded as a simplified model of the Hamiltonian of a collection of atoms located in a lattice, when only one-band (one-orbital per atom) is sufficient to account for the physics of the system. Hopping is allowed only to nearest-neighbors reflecting the fact that the kinetic-energy integrals decay exponentially fast with interatomic distance. On the other hand, only the Coulomb repulsion within the atom is accounted for.

We point the interested reader to the comprehensive book on the 1D Hubbard Hamiltonian by Essler et al. [9]. We also refer the reader to the work of Lieb and Wu [10], where the authors derived a set of equations from which the exact solutions to the 1D Hubbard Hamiltonian of Eq. 2.10 can be obtained.

### 2.5 Hartree–Fock-type transformation of fermion operators

The Hartree–Fock (HF) and Hartree–Fock–Bogoliubov (HFB) mean-field methods can be written as product states built from quasi-particle operators resulting from a linear canonical transformation of the basic fermion operators. Here, a *canonical* transformation is defined as that preserving the commutation (or anti-commutation) rules of the fermionic operators [11]. In the case of HFB, this is commonly referred to as the Bogoliubov–Valatin [12, 13] transformation. Berezin [14] systematized the study of general linear transformations of fermion operators within a second-quantized framework.
An arbitrary $N$-electron Slater determinant is constructed out of a set of $N$ hole (occupied) creation ($\{b_h^\dagger\}$) and $M-N$ particle (virtual) annihilation ($\{b_p\}$) operators, each of them resulting from a linear combination of the elementary operators $\{c_k, c_k^\dagger\}$.

$$b_h^\dagger = \sum_j D_{jh}^* c_j^\dagger,$$

$$b_p = \sum_j D_{jp} c_j.$$  

We will refer to these relations as a HF-type transformation. Using standard notation, the first $N$ columns in $D$ (which we write as $D_h$) represent the hole states, while the last $M-N$ columns (which we write as $D_p$) represent the particle states.

In the diagram below we show pictorially how states (here denoted by $\chi$) are classified into hole and particle. The coefficients $D$ correspond to the expansion of $\chi$ in the chosen single-particle basis. Typically, an energy criterion is used to decide which states are to become occupied and which are left empty.

![Diagram](image)

The transformation from the elementary operators to the set of HF-type operators...
constructed above can be compactly written as
\[
\begin{pmatrix}
  b_h^\dagger \\
  b_p \\
  b_h \\
  b_p^\dagger
\end{pmatrix}
= \begin{pmatrix}
  0_{N \times M} & D_h^\dagger \\
  D_p^T & 0_{(M-N) \times M} \\
  D_h^T & 0_{N \times M} \\
  0_{(M-N) \times M} & D_p^\dagger
\end{pmatrix}
\begin{pmatrix}
  c \\
  c^\dagger
\end{pmatrix},
\] (2.12)
where we have implicitly assumed the transformation to be unitary\(^*\).

The above transformation is canonical if the HF-type operators satisfy the (non-trivial) anti-commutation relations
\[
\begin{align*}
[b_h, b_h^\dagger]_+ &= \delta_{h' h}, & \quad [b_p, b_p^\dagger]_+ &= \delta_{p' p}, & \quad [b_p, b_h^\dagger]_+ &= 0. & \quad (2.13)
\end{align*}
\]
These conditions restrict the form of the matrix \(D\) according to
\[
\begin{align*}
[b_h, b_{h'}^\dagger]_+ &= \sum_{jk} D_{j h} D_{h' k}^* \delta_{j k} = (D^\dagger D)_{h' h} = \delta_{h' h}, & \quad (2.14a) \\
[b_p, b_{p'}^\dagger]_+ &= \sum_{jk} D_{j p} D_{p' k}^* \delta_{j k} = (D^\dagger D)_{p' p} = \delta_{p' p}, & \quad (2.14b) \\
[b_p, b_h^\dagger]_+ &= \sum_{jk} D_{j p} D_{k h}^* \delta_{j k} = (D^\dagger D)_{h p} = 0. & \quad (2.14c)
\end{align*}
\]
The first equation implies orthonormality of the hole states, the second one orthonormality of the particle states, and the last one corresponds to orthogonality between hole and particle states. All these conditions are summarized in the requirement \(D^\dagger D = 1\).

Let us remark that, if the HF-type operators \(\{b_h^\dagger, b_p\}\) are defined by a canonical
\[^*\text{A unitary transformation is here understood as that for which } b_h = (b_h^\dagger)^\dagger \text{ and } b_p^\dagger = (b_p)^\dagger.\]
transformation, the inverse transformation is given by

\[
\begin{pmatrix}
  c \\
  c^\dagger
\end{pmatrix} =
\begin{pmatrix}
  0_{M\times N} & D_p^* & D_h^* & 0_{M\times(M-N)} \\
  D_h & 0_{M\times(M-N)} & 0_{M\times N} & D_p
\end{pmatrix}
\begin{pmatrix}
  b_p^\dagger \\
  b_p \\
  b_h \\
  b_h^\dagger
\end{pmatrix},
\] (2.15)

as it can be easily verified by substituting the r.h.s. of Eq. 2.11 into the above equality.

2.6 The Hartree–Fock method

We are now in a position to introduce the Hartree–Fock ansatz of the many-body wavefunction. In HF, the ansatz of the wavefunction is a single Slater determinant (SD) built from a HF-type transformation of the elementary fermion operators

\[
|\Phi_{SD}\rangle = \prod_h b_h^\dagger | - \rangle,
\] (2.16)

where \(|-\rangle\) is the bare fermion vacuum. The flexibility in the ansatz lies on the coefficients \(D\) defining the HF-type transformation.

In the HF method, the energy associated with the trial state (Eq. 2.16), given by

\[
E[\Phi_{SD}] = \frac{\langle \Phi_{SD}|\hat{H}|\Phi_{SD}\rangle}{\langle \Phi_{SD}|\Phi_{SD}\rangle},
\] (2.17)

is minimized with respect to the coefficients \(D\), subject to the constraint that \(D\) remains unitary. The HF state corresponds to the Slater determinant that minimizes the above energy expression, that is, \(|\Phi_{HF}\rangle \equiv |\Phi_{SD}\rangle_{\text{min}E}^\text{min}E\).
The energy functional of Eq. 2.17 can be written as

\[ E[\Phi_{SD}] = \sum_{ik} \langle i|\hat{h}|k \rangle \rho_{ki} + \frac{1}{2} \sum_{ijkl} \langle ij|\hat{v}|kl \rangle \rho_{ki} \rho_{lj}, \]  

(2.18)

\[ \rho_{ki} = \sum_{h=1}^{N} D_{kh}^* D_{ih}, \]  

(2.19)

which makes explicit the dependence of the energy on the coefficients \( D \) to be optimized. Note that the energy is non-linear in \( D \) (or \( D^* \)). Solving for the optimal \( D \) is therefore non-trivial and one has to use an iterative method, usually referred to as the self-consistent field (SCF) procedure.

We note that there are several ways in which one can optimize the energy functional of Eq. 2.17. Perhaps the most well-known is the Roothaan [15] method. Given an initial guess of the orbital coefficients \( D^* \), one finds an improved set of coefficients by solving the eigenvalue problem

\[ F D^* = D^* \epsilon, \]  

(2.20)

\[ F_{ik} = \langle i|\hat{h}|k \rangle + \sum_{jl} \langle ij|\hat{v}|kl \rangle \rho_{lj}, \]  

(2.21)

where \( F \) is the so-called Fock matrix and \( \epsilon \) is a diagonal matrix of eigenvalues (which can be associated with the energies of the HF orbitals). Note that the Fock matrix depends on \( \rho \), which makes explicit the non-linearity of the problem. An optimal solution is found when the matrix \( D \) obtained by solution of the above eigenvalue problem remains unchanged from iteration to iteration. We note that the Roothaan method is not guaranteed to converge.

Being a product wavefunction, the electrons remain uncorrelated in the Hartree–Fock approximation.† This is to say that the probability of finding an electron in a given

†To be precise, it is only opposite-spin electrons that remain uncorrelated. The antisymmetry of the wavefunction precludes same-spin electrons from occupying the same position in space.
position in space does not depend on the probability of other electrons being nearby. In reality, electrons try to avoid each other dynamically. An accurate description of this electron correlation is the aim of all approximate many-body methods.

The Hartree–Fock method is of paramount importance in quantum chemistry (and in other fields of many-body physics) not only because of its simplicity, but also because more accurate approximations are often built starting from the HF wavefunction.
Chapter 3

Symmetry-projected Hartree–Fock

In the previous chapter we have discussed some of the basic ingredients of quantum chemistry, culminating with the HF approximation. The HF wavefunction constitutes the best single-determinantal description of the electronic structure of a molecular system. Despite its apparent simplicity, HF has been quite successful in chemistry. In this chapter, we will discuss in more detail some aspects of HF theory. We start by considering the spontaneous symmetry breaking of HF solutions. This then takes us on a journey where we discuss the symmetry dilemma [16], self-consistent symmetries, and the expansion of the symmetry broken states in terms of symmetry-projected configurations.

The benefits associated with the broken symmetry solution motivate our consideration of a single symmetry-projected HF state as an ansatz for the many-body wavefunction, as originally done by Löwdin in 1955 [1]. The form of the projection operators that we use is introduced and contrasted with that proposed by Löwdin. This then leads to an extensive discussion of the symmetry-projected ansatz and how the energy of such a state is evaluated. When using a symmetry-projected HF state, the broken symmetry determinant can be optimized before (PAV) or after (VAP) the variation. The latter choice should be preferred, as we discuss in some detail.

We proceed to discuss the alternative optimization strategies that can be used for symmetry-projected HF states. Our preferred choice is a Thouless-based parametriza-
tion, a strategy that is then presented in greater detail. Lastly, we share details of our computational implementations of the optimization of projected Hartree–Fock states as well as some results that we have obtained for molecular systems.

3.1 Symmetry breaking in HF

When performing a HF calculation on a chemical system of interest, one can choose the HF states to preserve the symmetries of the Hamiltonian, or allow them to break symmetry. Early on, authors did not consider this possibility until Slater showed [17] that a symmetry-broken HF state yields lower energy for a stretched hydrogen molecule than the symmetry-adapted solution. This is illustrated in Fig. 3.1.

![Figure 3.1: Symmetry-adapted (sa) and broken-symmetry (bs) HF description of the molecular dissociation profile of the H$_2$ molecule.](image-url)
The failure of the symmetry-adapted HF description for stretched H\textsubscript{2} configurations is explained pictorially below. At the equilibrium distance the bonding 1\(\sigma\) and antibonding 1\(\sigma^*\) orbitals are well-separated in energy. Doubly-occupying the former provides a reasonable approximation to the exact wavefunction. On the other hand, as the molecule is stretched the bonding and anti-bonding orbitals become degenerate. One then expects that the configurations \(|(1\sigma)^2\rangle\) and \(|(1\sigma^*)^2\rangle\) carry similar weights in the exact description. The symmetry-adapted HF description of stretched H\textsubscript{2}, which keeps doubly occupying the bonding orbital, is thus a poor approximation to the correct solution.

![Energy level diagram](https://example.com/diagram.png)

It turns out that symmetry broken solutions are ubiquitous in chemistry, particularly for open-shell systems. It often happens that when the self-consistent method associated with the HF optimization detects near degeneracies, a symmetry-broken solution appears that can partially account for the correlations due to such degeneracies.

Certain symmetries of the Hamiltonian can be shown to become self-consistent solutions of the HF equations [18]. This implies that, in the self-consistent field procedure, an initial broken symmetry state is necessary in order to reach a HF solution that
is symmetry broken. Allowing for symmetry breaking may lead to a solution with lower energy than a symmetry-adapted one, as elegantly summarized by Löwdin in his symmetry dilemma [16]. The broken symmetry solution is not a panacea; it has many undesirable features. Nevertheless, symmetry-breaking allows one to recover correlations that are otherwise difficult to build into a simple wavefunction ansatz.

Projection operators represent a way to obtain the best of both worlds: the correlations introduced by the symmetry breaking of the underlying HF transformation are recovered, while a physical state with good quantum numbers is produced after application of the projector. This is why the idea of symmetry projected configurations has been considered time and again in the quantum chemistry community. We show that, in addition, one can prove that one of the symmetry-adapted states recovered must have an energy lower than the broken symmetry HF solution. It is then natural to consider a symmetry-projected HF ansatz for the ground state of a chemical system.

In this section, we touch upon a variety of issues related to the symmetry breaking of HF solutions in chemical systems and how these motivate us to consider a symmetry-projected ansatz.

3.1.1 The symmetry dilemma

If a Hermitian operator $\hat{\Lambda}$ commutes with the Hamiltonian $\hat{H}$, then eigenstates $|\Psi\rangle$ of the Hamiltonian are also eigenstates of $\hat{\Lambda}$ (or can be chosen to). That is, we have

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

(3.1)

$$\hat{\Lambda}|\Psi\rangle = \lambda|\Psi\rangle,$$

(3.2)
where $\lambda$ is the eigenvalue of $\hat{\Lambda}$ and constitutes a good quantum number to label the eigenstate $|\Psi\rangle$.

Approximate wavefunctions need not have all the symmetries of the eigenstates of the Hamiltonian (they do not need to preserve the quantum numbers). Forcing an approximate wavefunction $|\Phi\rangle$ to be symmetry-adapted introduces constraints which reduce the variational flexibility in the considered manifold. This constitutes the symmetry dilemma first pointed out by Löwdin [16]: one is often forced to choose between finding the variationally optimal wavefunction and one which has the right symmetries.

### 3.1.2 Self-consistent symmetries

Consider an arbitrary single determinantal state $|\Phi_0\rangle$ for a given quantum mechanical system. If the Hamiltonian of such a system commutes with a given symmetry operator (or set of operators), then one could hope that the HF state possesses those symmetries. A HF state commutes with the symmetry operator if and only if the density matrix $((\rho_0)_{ij} = \langle \Phi_0 | c_j^\dagger c_i | \Phi_0 \rangle)$ commutes with the symmetry operator. One can straightforwardly prove that, if this is the case, the mean-field potential $\hat{G}$ given by

$$G_{ik} = \langle i | \hat{h} | k \rangle + \Gamma_{ik}, \quad (3.3a)$$

$$\Gamma_{ik} = \sum_{jl} \langle ij | \hat{v} | kl \rangle \rho_{lj}, \quad (3.3b)$$

commutes also with the same symmetry operator.

There are two important consequences of this property [18]:
• If a given symmetry is desired in the HF solution, one can start with an initial guess \(|\Phi_0\rangle\) that possesses such a symmetry. In general, the computational effort can be reduced by working in a basis of eigenstates of this symmetry. This is commonly done in HF calculations of infinite systems. All periodic codes work use crystalline orbitals with good translation properties as the basis set. This then reduces the computational effort of an otherwise intractable calculation.

• If the initial guess \(|\Phi_0\rangle\) possesses certain symmetry, it will be preserved throughout the self-consistent field procedure. The minimum of energy can then only be found among the wavefunctions that have this symmetry. This is an important property in molecular calculations. If one wishes to converge to the broken-symmetry UHF solution that dissociates the H\(_2\) molecule properly, then one must prepare an initial guess that breaks spatial and spin symmetry.

A final consequence of this property is that if a converged HF solution \(|\Phi\rangle\) breaks a certain symmetry \(\hat{S}\), that is,

\[
\hat{S} \rho \hat{S}^\dagger = \rho_1 \neq \rho,
\]

it can be easily shown that the density matrix \(\rho_1\) characterizes a single-determinantal state \(|\Phi_1\rangle\) that is also a solution to the HF equations, with the same energy as \(|\Phi\rangle\). This means that, for continuous symmetries, if one finds a symmetry broken solution then one can form an infinite set of degenerate solutions.

The last property discussed above deserves further consideration as it is not unique to HF states. Consider a group of operations \(\hat{\Lambda}(\alpha)\), where \(\alpha\) is a discrete or con-
tinuous label, that leaves the Hamiltonian unchanged; then, by definition the group characterizes a symmetry of the Hamiltonian. That is,

$$\hat{\Lambda}(\alpha) \hat{H} \hat{\Lambda}^\dagger(\alpha) = \hat{H} \quad (3.5)$$

Consider a deformed state $|\Phi\rangle$ which is not invariant upon the action of $\hat{\Lambda}(\alpha)$. Then, the states

$$|\Phi_\alpha\rangle = \hat{\Lambda}(\alpha)|\Phi\rangle \quad (3.6)$$

are all degenerate:

$$\langle \Phi_\alpha | \hat{H} | \Phi_\alpha \rangle = \langle \Phi | \hat{H} | \Phi \rangle. \quad (3.7)$$

The existence of a degenerate manifold (infinite or discrete) of states is a fingerprint of broken symmetry solutions.

### 3.1.3 Classification of broken-symmetry HF solutions

The molecular Hamiltonian commutes with several symmetry operators. It commutes with the point group defined by the nuclear framework. It behaves as a scalar in spin space and thus eigenfunctions of the Hamiltonian can be chosen to be also eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ simultaneously. It commutes with the time-reversal $\hat{\Theta}$ and complex conjugation operator $\hat{K}$. Lastly, it trivially commutes with the particle number operator $\hat{N}$.

Fukutome [19] was the first to classify the different possible HF solutions according to their symmetry properties. His work was recently reviewed by Stuber and Paldus [20]. We note that HF states do not break particle number symmetry. Symmetry-projected methods that break and restore particle number symmetry require the use
of Hartree–Fock–Bogoliubov determinants [21, 22, 6, 23]. This, however, lies beyond the scope of this work.

Here, we only briefly consider the classification of HF solutions:

1. Restricted Hartree–Fock (RHF) solutions. They preserve the full SU(2) spin symmetry, and may be real (preserving also $\hat{\Theta}$ and $\hat{K}$) or complex.

Mathematically, the spin orbitals $\{|\chi\rangle\}$ in RHF take the following structure

\[
\langle r | \chi_{2i-1} \rangle = u_i(r) | \uparrow \rangle,
\]

\[
\langle r | \chi_{2i} \rangle = u_i(r) | \downarrow \rangle,
\]

where $u(r)$ corresponds to the spatial distribution of the orbital. Note that two spin orbitals (with up and down spin, respectively) share the same spatial distribution.

2. Unrestricted Hartree–Fock (UHF) solutions. These correspond to the different orbitals for different spins (DODS) solutions, where each orbital has a well-defined spin, but the spatial distribution of $\uparrow$ and $\downarrow$ orbitals is allowed to be different. UHF solutions can be further classified into real (preserving $\hat{S}_z$ and $\hat{K}$), paired (preserving $\hat{S}_z$ and $\hat{\Theta}$), or complex (preserving $\hat{S}_z$).

In UHF, the spin orbitals take the form

\[
\langle r | \chi_{2i-1} \rangle = u_i(r) | \uparrow \rangle,
\]

\[
\langle r | \chi_{2i} \rangle = v_i(r) | \downarrow \rangle.
\]

That is, each spin orbital still has a well defined spin. The spatial distributions of up and down orbitals are allowed to be different.
3. Generalized Hartree–Fock (GHF) solutions. In these case, the orbitals are linear combinations of $\uparrow$ and $\downarrow$ components. GHF solutions can be real (preserving $\hat{K}$), paired (preserving $\hat{\Theta}$), or complex.

In GHF, the spin orbitals take the form

$$\langle \mathbf{r} | \chi_j \rangle = u_j(\mathbf{r}) | \uparrow \rangle + v_j(\mathbf{r}) | \downarrow \rangle,$$

where it is explicit that each orbital is a linear combination with up and down spin components.

Real RHF and UHF solutions are the most common in quantum chemistry. Only a few systems are known to have true GHF solutions, i.e., GHF solutions that are not rigid rotations of UHF solutions. For molecular dissociation processes, RHF is size-consistent* only when a singlet system dissociates into singlet fragments. UHF is often size consistent, but it fails in cases such as $\text{O}_2$, where a triplet system should dissociate into two triplet systems. Lastly, GHF is always size consistent [24].

3.1.4 Symmetry-adapted expansion of broken symmetry HF states

We have discussed how allowing the approximate HF wavefunction $|\Phi\rangle$ to break symmetry can lead to lower energies because of the increased variational flexibility in the wavefunction. The resulting broken-symmetry wavefunction has, however, undesirable characteristics.

*In this context, a size-consistent method predicts the energy of the dissociated molecule to be the same as the sum of the energies of the individual fragments.
Consider for the moment a spin symmetry-broken HF solution (of the GHF type). It can be expanded in terms of symmetry-preserving (normalized) wavefunctions as

$$|\Phi\rangle = \sum_{sm} f_{s,m} |s,m\rangle,$$

(3.8)

where $s$ and $m$ are used to label the quantum numbers of $\hat{S}^2$ and $\hat{S}_z$, respectively. Here, $f_{s,m} = \langle s,m|\Phi \rangle$. Note that this symmetry-preserving wavefunctions may have a complicated determinantal structure.

Because the states $\{|s,m\rangle\}$ are orthonormal, the expectation value of the Hamiltonian becomes

$$E_{\Phi} = \langle \Phi | \hat{H} | \Phi \rangle
= \sum_{s,m} |f_{s,m}|^2 \langle s,m|\hat{H}|s,m\rangle
= \sum_{s,m} |f_{s,m}|^2 E_{s,m}.$$

(3.9)

This last equality implies that the energy associated with the symmetry broken state is a weighted average among the energies of the symmetry-preserving states in the expansion. In the general case, where there is more than one term in the expansion, one should be able to find a term in the expansion for which $E_{s,m} \leq E_{\Phi}$.

We then conclude that, besides the fact that good quantum numbers are restored, a symmetry-projection strategy based on a symmetry-broken Slater determinant can yield an approximation to the ground state with lower energy than $|\Phi\rangle$. Both of these features have motivated our consideration of symmetry-projected HF states as variational ansätze for the molecular electronic structure problem.

### 3.2 Projection operators

Projection operators are used in order to recover the good symmetries of the Hamiltonian from a broken-symmetry determinant. The mathematical machinery associated
with symmetry restoration has been discussed extensively in, e.g., Refs. [18, 11]. The structure of the projection operators that we use is borrowed from the nuclear physics community. It was developed in part after the realization by Peierls and Yoccoz [25] that the diagonalization of the Hamiltonian in the set of degenerate states associated with the broken symmetry yields collective states with good symmetry properties.

Before starting our discussion, we emphasize that by a projected Hartree–Fock approach we mean recovering a wavefunction with good quantum numbers from an intrinsically deformed HF state, and do not demand the use of actual projection operators in a strict mathematical sense. In other words, while we require that the wavefunction $\hat{P}|\Phi\rangle$ be an eigenfunction of the relevant symmetry operators, we do not insist that $\hat{P}$ is either Hermitian or idempotent.

### 3.2.1 Spin projection

Our presentation of the spin-projection operator follows that provided by Schmid [6]. We start by introducing the projection-like operator

$$\hat{P}_{mk} = \sum_{\alpha} |s, m; \alpha\rangle \langle s, k; \alpha|$$

(3.10)

in terms of states with good quantum numbers $s$ and $m$, associated with $\hat{S}^z$ and $\hat{S}_z$, respectively. The index $\alpha$ is used to represent all other quantum numbers of the system.

In order to turn the above operator into a more workable form, we note that an arbitrary rotation in spin-space can be parametrized by the set of Euler angles $\Omega = (\alpha, \beta, \gamma)$. Using the commutation relations among $\{\hat{S}_x, \hat{S}_y, \hat{S}_z\}$, one can derive the
form of the spin rotation operator [26]:

\[ \hat{R}(\Omega) = \exp\left(-i\alpha \hat{S}_z\right) \exp\left(-i\beta \hat{S}_y\right) \exp\left(-i\gamma \hat{S}_z\right). \] (3.11)

Multiplying on the left and right by the identity operator in spin-space, we arrive at

\[ \hat{R}(\Omega) \equiv 1 \hat{R} 1 \]

\[ = \sum_{smk,\alpha} |s, m; \alpha\rangle \langle s, m; \alpha| \hat{R}(\Omega) |s, k; \beta\rangle \langle s, k; \beta| \]

\[ = \sum_{smk,\alpha} |s, m; \alpha\rangle D^s_{mk}(\Omega) \langle s, k; \beta| \] (3.12)

where \( D^s_{mk}(\Omega) \equiv \langle s, m| \hat{R}(\Omega)|s, k\rangle \) is Wigner’s D-matrix. Using the orthonormality relation for Wigner’s D-matrix, we arrive at

\[ \frac{2s+1}{8\pi^2} \int d\Omega D^{ss*}_{mk}(\Omega) \hat{R}(\Omega) \]

\[ = \sum_{s'm'k',\alpha} |s', m'; \alpha\rangle \frac{2s+1}{8\pi^2} \int d\Omega D^{ss*}_{mk}(\Omega) D^{s'k'}_{mk'}(\Omega) \langle s', k'; \alpha| \]

\[ = \sum_{\alpha} |s, m; \alpha\rangle \langle s, k; \alpha| . \] (3.13)

We can then conclude that the integral representation of the spin projection-like operator of Eq. 3.10 is given by

\[ \hat{P}^s_{mk} = \frac{2s+1}{8\pi^2} \int d\Omega D^{ss*}_{mk}(\Omega) \hat{R}(\Omega). \] (3.14)

A few words are in order at this point comparing the spin-projection operator presented above (Eq. 3.14) due to Villars [3] with Löwdin’s [1] spin-projection operator

\[ \hat{P}^s = \prod_{l \neq s} \frac{\hat{S}^2 - l(l+1)}{s(s+1) - l(l+1)}. \] (3.15)

Löwdin’s is a many-particle operator and as such it is difficult to manipulate. On the other hand, Villars’ is written as an integral over single-particle rotation operators.
The Löwdin operator restores the desired expectation value of $\hat{S}^2$ and thus it can be used whenever the Hamiltonian commutes with $\hat{S}^2$, even in the presence of magnetic fields. On the other hand, Villars’ operator exploits the SU(2) algebra associated with angular momentum and, as such, requires that the full set of operators \{\hat{S}_x, \hat{S}_y, \hat{S}_z\} commute with the Hamiltonian. In other words, it can only be used whenever the Hamiltonian is a scalar in spin-space. The form of the spin projection operator discussed above was used in quantum chemistry by Lefebvre and Prat [27, 28].

### 3.2.2 Spatial symmetry projection

The nuclear framework defines a group $G = \{\hat{g}\}$ of spatial operations that leave the Hamiltonian invariant. Hence, we can label the symmetry-preserving molecular solutions according to the irreducible representation of the point group that defines how they transform under the symmetry operations.

In general, one can construct the so-called “transfer” operators [26, 29]

$$\hat{P}^j_{\lambda\kappa} = \frac{l_j}{h} \sum_g \Gamma^j(g)^*_{\lambda\kappa} \hat{g},$$

(3.16)

where $h$ is the order of the group $G$, $l_j$ is the dimension of the irreducible representation $\Gamma^j$, and $\Gamma^j(g)_{\lambda\kappa}$ is the element in the $\lambda$-th row and $\kappa$-th column of the matrix associated with $\hat{g}$ in such irreducible representation. This operator yields zero unless the function on which it acts belongs to the $\kappa$-th row of $\Gamma^j$. By using the great orthogonality theorem one can show that

$$\hat{P}^j_{\lambda\kappa} \hat{P}^k_{\mu\nu} = \delta_{jk} \delta_{\kappa\mu} \hat{P}^k_{\lambda\nu},$$

(3.17)

$$\left(\hat{P}^j_{\lambda\kappa}\right)^\dagger = \hat{P}^j_{\kappa\lambda}$$

(3.18)
It is easy to see that $\hat{P}_{\kappa\kappa}^j$ is indeed a projection operator in the mathematical sense: it is Hermitian and idempotent.

Consider the action of $\hat{P}_{\kappa\kappa}^j$ on a deformed wavefunction $|\Phi\rangle$. It extracts the component of $|\Phi\rangle$ which transforms as the $\kappa$-th row of $\Gamma^j$. It is, however, unphysical in the sense that

$$\hat{P}_{\kappa\kappa}^j|\Phi\rangle \neq \hat{P}_{\kappa\kappa}^j|\Phi'\rangle$$

(3.19)

where $|\Phi'\rangle$ is a rotated wavefunction in the subspace of $\Gamma^j$. In order to avoid this unphysical behavior, one can form the linear combination

$$|\Psi\rangle = \sum_{\kappa} f_{\kappa} \hat{P}_{\lambda\kappa}^j|\Phi\rangle.$$  

(3.20)

It is clear that this linear combination produces a wavefunction $|\Psi\rangle$ which transforms as the $\lambda$-th row of $\Gamma^j$, thus having $\lambda$ and $j$ as good quantum numbers. The above form avoids the unphysical behavior: any rotation among the rows of the irreducible representation will change the coefficients $f_{\kappa}$ but will leave the projected state invariant.

### 3.2.3 Complex conjugation projection

We have seen that the molecular Hamiltonian commutes with the complex conjugation operator $\hat{K}$. Because this is an anti-unitary operator, it does not carry good quantum numbers. One can, nevertheless, ensure that a wavefunction $|\Psi\rangle$ is an eigenstate of the complex conjugation operator, that is,

$$\hat{K}|\Psi\rangle = e^{i\chi} |\Psi\rangle$$

(3.21)
Restoration of the complex conjugation symmetry cannot be done straightforwardly. This is because one does not know a priori the eigenvalue $e^{ix}$ that brings the Hamiltonian to a diagonal form in the basis of $\{|\Phi\rangle, \hat{K}|\Phi\rangle\}$. Complex conjugation projection is most easily achieved by the diagonalization of the Hamiltonian in the basis of those two configurations. We note that the same holds true for the time-reversal operator. Complex conjugation symmetry breaking and restoration was carried out in molecular systems by Hendekovic [30] in his complex molecular orbital method. The author did not, however, present the method in the context of symmetry breaking and restoration.

3.3 The symmetry-projected HF ansatz

As early as 1955, Löwdin [1] suggested an extension of the standard Hartree–Fock scheme in order to account for spin or orbital degeneracies. Namely, he proposed to use a variational ansatz of the form

$$\hat{P}|\Phi\rangle,$$

where $\hat{P}$ is a projection operator and $|\Phi\rangle$ is a single Slater determinant. The ansatz is multi-determinantal in nature and can account for correlations beyond the mean-field description. However, the ansatz is still fully characterized by a single set of molecular orbitals. Equivalently, the ansatz is completely determined by the density matrix $\rho$ associated with $|\Phi\rangle$ ($\rho_{ij} = \langle \Phi | c_j^\dagger c_i | \Phi \rangle$) which is Hermitian, idempotent and satisfies $\text{Tr} \rho = N$.

Using the form of the projection operators discussed in previous sections, we write
the variational ansatz for the symmetry-projected HF state as

\[ |\Psi_{j,m}\rangle = \sum_k f_k \hat{P}^j_{mk} |\Phi\rangle, \]  

(3.22)

where \(|\Phi\rangle\) is a symmetry-broken Slater determinant. The superscripts \(j, m\) in \(|\Psi\rangle\) label the irreducible representation as well as the row.\(^\dagger\) The form above is suitable for arbitrary non-Abelian symmetry groups, including spin. The linear variational coefficients \(\{f\}\) are introduced in order to remove unphysical dependencies of the energy with respect to the orientation of the underlying state \(|\Phi\rangle\) [31, 18].

The Hamiltonian expectation value of a symmetry-projected HF state defined by Eq. 3.22 is given by

\[
E^j[\Phi] = \frac{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{H} \hat{P}^j_{mk} \hat{P}^j_{mk'} | \Phi \rangle}{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{P}^j_{mk} \hat{P}^j_{mk'} | \Phi \rangle} = \frac{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{H} \hat{P}^j_{kk'} | \Phi \rangle}{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{P}^j_{kk'} | \Phi \rangle},
\]

(3.23)

where we have used the properties of the projection-like operator and the fact that it commutes with the Hamiltonian. Note that the energy expression given by Eq. 3.23 is explicitly independent of the row of the irrep selected for non-Abelian groups.

In order to provide explicit expressions for the energy associated with the projected HF state, we introduce a generic representation of the projection operator

\[
\hat{P}^j_{mk} = \frac{1}{V} \int d\vartheta \ w^{ij}_{mk}(\vartheta) \hat{R}(\vartheta),
\]

(3.24)

where the integration should be understood in a loose sense as sampling over the elements of the group for finite groups. Additionally, \(V\) is the volume of integration.

\(^\dagger\)Here, the projection operator may be a product of projection operators for say, spin and point group restoration.
\( w_{mk}(\vartheta) \) is the weight associated with the irreducible representation to be recovered, and \( \hat{R}(\vartheta) \) stands for the rotation operator.

In all cases considered (save for complex conjugation), \( \hat{R}(\vartheta) \) is a single-particle rotation operator that transforms the HF operators according to

\[
b_k^\dagger(\vartheta) \equiv \hat{R}(\vartheta) b_k^\dagger \hat{R}^{-1}(\vartheta) = \sum_j D_{jk}^* \hat{R}(\vartheta) c_j^\dagger \hat{R}^{-1}(\vartheta) = \sum_{ij} R_{ij}(\vartheta) D_{jk}^* c_i^\dagger, \tag{3.25}
\]

where \( R_{ij}(\vartheta) = \langle i | \hat{R}(\vartheta) | j \rangle \) is the matrix representation of \( \hat{R}(\vartheta) \) in the single-particle basis. Additionally, \( D \) are the set of coefficients of the HF transformation.

Using Eq. 3.24 as the representation of the projection operator, the energy expression of Eq. 3.23 can then be rewritten as

\[
E^j[\Phi] = \sum_{kk'} f^*_k f_{k'} \int d\vartheta \ w_{kk'}^j(\vartheta) \ y(\vartheta) \ \frac{\langle \Phi | \hat{\mathcal{H}} \hat{R}(\vartheta) | \Phi \rangle}{\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle}, \tag{3.26a}
\]

\[
y(\vartheta) = \frac{\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle}{\sum_{kk'} f^*_k f_{k'} \int d\vartheta' \ w_{kk'}^j(\vartheta') \langle \Phi | \hat{R}(\vartheta') | \Phi \rangle}. \tag{3.26b}
\]

In order to provide explicit expressions for the matrix elements in Eq. 3.26, we assume a two-body Hamiltonian in the usual second-quantized form

\[
\hat{\mathcal{H}} = \sum_{ik} \langle i | \hat{\mathcal{H}} | k \rangle c_i^\dagger c_k + \frac{1}{4} \sum_{ijkl} \langle ij | \hat{v} | kl \rangle c_i^\dagger c_j^\dagger c_l c_k, \tag{3.27}
\]

where \( \langle i | \hat{\mathcal{H}} | k \rangle \) and \( \langle ij | \hat{v} | kl \rangle \) are one- and antisymmetrized two-electron integrals, respectively.

The matrix elements appearing in Eq. 3.26 can be evaluated using the expressions provided in Appendix B. An alternative derivation was provided by Löwdin [32]. We
arrive at

\[ \langle \Phi | \hat{R}(\vartheta) | \Phi \rangle = \det N \left( D^T R(\vartheta) D^* \right), \quad (3.28a) \]

\[ h(\vartheta) \equiv \frac{\langle \Phi | \hat{H} \hat{R}(\vartheta) | \Phi \rangle}{\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle} = \text{Tr} \left( h \rho(\vartheta) + \frac{1}{2} \Gamma(\vartheta) \rho(\vartheta) \right), \quad (3.28b) \]

\[ \rho_{ki}(\vartheta) \equiv \frac{\langle \Phi | c_i^\dagger c_k \hat{R}(\vartheta) | \Phi \rangle}{\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle}, \quad (3.28c) \]

\[ \Gamma_{ik}(\vartheta) = \sum_{jl} (i) j | v | kl \rho_{lj}(\vartheta). \quad (3.28d) \]

Here, the matrix \( D \) of orbital coefficients characterize the state \( | \Phi \rangle \). An explicit expression to evaluate the transition density matrix \( \rho(\vartheta) \) can be found in Appendix B. We point out that the evaluation of matrix elements of arbitrary operators is mostly straightforward because a generalized Wick’s theorem holds [11] between the non-orthogonal Slater determinants \( | \Phi \rangle \) and \( \hat{R}(\vartheta) | \Phi \rangle \) (see Appendix B).

At this point, one faces the all important question of how to carry out the variational optimization of the wavefunction of Eq. 3.22. There are two possibilities:

- In a projection-after-variation (PAV) approach, the broken-symmetry mean-field state \( | \Phi \rangle \) is optimized variationally. The symmetry-projected energy is then computed in a single-shot evaluation.

- In a variation-after-projection (VAP) approach, the Slater determinant \( | \Phi \rangle \) is optimized in the presence of the projection operators.

The PAV approach is appealing for its simplicity. However, it may lead to unphysical behavior. For instance, dissociation profiles evaluated with the PAV approach show derivative discontinuities at the point where the broken-symmetry HF solution collapses back to the symmetry-adapted one [33].
The VAP approach is favored not only because it leads to lower energies, but most importantly because the variation is performed for the actual considered ansatz. As it will be shown below, optimizing the state of Eq. 3.22 in a VAP manner leads to generalized Brillouin-like conditions that characterize the stationary nature of the solution.

A self-consistent VAP approach was the basis of the extended Hartree–Fock method proposed by Löwdin [1]. More often than not, EHF has been associated with the use of a spin-projection operator on a reference unrestricted determinant (the so-called spin-projected EHF [2]). We note that Goddard’s GF method [34] is equivalent to EHF.

Several methodologies have been proposed in the quantum chemistry literature to carry out the self-consistent optimization of the EHF wavefunction. We point the reader to the comprehensive review by Mayer [2]. Mayer’s derivation was based on the Brillouin condition that the EHF state satisfies [35]; his derivation relied heavily on the pairing theorem by Löwdin [36]. Rosenberg and Martino [37], and later Klímo and Tiño [38] used a direct minimization of the energy functional. Recently, Byrman proposed an optimization of the EHF wavefunction based on its connection to the spin-coupled valence bond method [39].

We discuss in the next section the optimization strategy that we follow, borrowing techniques developed in the nuclear physics community and pioneered by, among others, Mang [21] and Onishi [40].
3.4 Variational optimization of the symmetry-projected HF wavefunction

Even though the symmetry-projected HF ansatz is multi-determinantal in character, the wavefunction is fully characterized by the underlying Slater determinant $|\Phi\rangle$. The variational degrees of freedom are thus the same as for a standard HF wavefunction, with possibly a small number of linear variational coefficients for non-Abelian symmetries. At least three different parametrizations of the underlying HF transformation can be used:

1. Treat the coefficients in the matrix $D$ of the associated HF-transformation as variational parameters. That is, one can minimize the Lagrangian

$$\mathcal{L}[D] = E[D] - \sum_{ij} \Lambda_{ji} \left[ (D^T D^*)_{ij} - \delta_{ij} \right], \quad (3.29)$$

where the orthonormality of the spin-orbitals is used as a constraint. Only the occupied orbitals in $D$ have to be considered in the above Lagrangian. The optimization has then $N M$ variational parameters with $N^2$ constraints, leaving $N(M - N)$ free parameters.

2. Treat the elements of the one-particle density matrix ($\rho_{ij} = \langle \Phi | c_j^\dagger c_i | \Phi \rangle$) as variational parameters. This can be done because the one-particle density matrix associated with $|\Phi\rangle$ fully determines the state. One then minimizes the Lagrangian

$$\mathcal{L}[\rho] = E[\rho] - \sum_{ij} \Lambda_{ji} \left[ (\rho^2)_{ij} - \rho_{ij} \right]. \quad (3.30)$$

where the idempotency of the density matrix is used as a constraint.‡

‡Recall that a state $|\Phi\rangle$ has an idempotent density matrix if and only if it has single-determinantal character.
3. Because the Slater determinant $|\Phi\rangle$ can be written as a Thouless rotation with respect to a reference one $|\Phi_0\rangle$ (as long as the two determinants are not orthogonal, see Appendix A), we can use the Thouless matrix $Z$ to parametrize the underlying HF transformation. Note that a Thouless matrix has $N(M - N)$ (complex) free variational parameters (see Sec. 3.5 below).

In Ref. [41], we pursued the second approach, that is, to minimize the elements of the density matrix. This is probably the most convoluted approach as one has to be able to write all matrix elements in the energy expression as functionals of the density matrix.

The first approach was used in Refs. [42] and [43]. A parametrization in terms of a Thouless rotation was used in Refs. [44] and [45]. We also point the reader to the optimization considered by Ikawa [46] in the resonating Hartree–Fock approach (see Chapter 4).

In this work, we will consider the latest approach, where a Thouless rotation is used to parametrize the variation of $|\Phi\rangle$. This has been the preferred variational strategy in the nuclear physics community since Mang [21], among others, suggested it in the context of Hartree–Fock–Bogoliubov states. It has several key advantages:

- The minimization is unconstrained; there are exactly $N(M - N)$ free variational parameters. All the robust optimization algorithms for unconstrained minimization (see, for instance, Ref. [47]) can be used straightforwardly.

- Because the minimization is unconstrained, one can follow always the direction of descent. Safeguarded techniques can be used such that, either convergence to a stationary point is reached, or the optimization is terminated.
• It can be easily extended to the configuration mixing approaches discussed in the next chapters.

We note that, despite the advantages associated with the Thouless parametrization, there is no guarantee that it will converge faster than other approaches. In the next section we discuss in detail the optimization based on the Thouless rotation.

### 3.5 Optimization based on a Thouless parametrization

In this section, we provide a detailed discussion of the optimization of symmetry-projected HF states based on a Thouless parametrization. Our approach follows closely the work of Egido et al. [48], which formulated a conjugate-gradient based optimization for Hartree–Fock–Bogoliubov (HFB) states.

We parametrize the underlying broken symmetry determinant $|\Phi\rangle$ by an arbitrary Thouless rotation. That is, we let

$$|\Phi\rangle \rightarrow \exp(\hat{Z})|\Phi\rangle,$$

(3.31)

$$\hat{Z} = \sum_{ph} Z_{ph} b^\dagger_p b_h,$$

(3.32)

where $p$ runs over particle (virtual) and $h$ over hole (occupied) states. We remind the reader that this is possible because $\exp(\hat{Z})|\Phi\rangle$ is still a Slater determinant, as shown in Appendix A. Making such substitution in the energy functional (Eq. 3.23) yields

$$E^j[Z] = \frac{\sum_k f_k^* f_{k'} \langle \Phi | \exp(\hat{Z}^\dagger) \hat{H} \hat{P}_{kk'}^{ij} \exp(\hat{Z}) | \Phi \rangle}{\sum_k f_k^* f_{k'} \langle \Phi | \exp(\hat{Z}^\dagger) \hat{P}_{kk'}^{ij} \exp(\hat{Z}) | \Phi \rangle}.$$  

(3.33)

Having parametrized the energy functional in terms of the matrix $Z$ of coefficients, we proceed to evaluate the gradient. The local gradient $G$ around $Z = 0$ is defined
as
\[ G_{ph} = -\frac{\partial}{\partial Z_{ph}^*} \frac{E^j[Z]}{Z_{ph} = 0}. \] (3.34)

Note that \( Z_{ph} \) and \( Z_{ph}^* \) can be treated as independent variables. The total derivative of the energy then becomes
\[ dE = -\sum_{ph} [G_{ph} dZ_{ph}^* + \text{c.c.}] . \] (3.35)

Explicit differentiation of the parametrized energy expression, Eq. 3.33, leads to an expression for the local gradient
\[ G_{ph} = -\sum_{kk'} f_k^* f_{k'} \langle \Phi | b_h^\dagger b_p (\hat{H} - E^j) \hat{P}_{kk'}^i | \Phi \rangle \sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{P}_{kk'}^j | \Phi \rangle 
= -\sum_{kk'} f_k^* f_{k'} \int d\vartheta w_{kk'}^j(\vartheta) y(\vartheta) \frac{\langle \Phi | b_h^\dagger b_p (\hat{H} - E^j) \hat{R}(\vartheta) | \Phi \rangle}{\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle} \] (3.36)

where \( E^j \) is the energy of the symmetry-projected HF state. (The term proportional to \( E^j \) results from the differentiation of the denominator of Eq. 3.33.)

Matrix elements appearing in Eq. 3.36 can be evaluated in terms of transition density matrices, as discussed in Appendix B. For the overlap-like terms, we arrive at
\[ \frac{\langle \Phi | b_h^\dagger b_p \hat{R}(\vartheta) | \Phi \rangle}{\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle} = \sum_{mn} D_{mh}^* D_{np} \rho_{nm}(\vartheta), \] (3.37)

while the Hamiltonian-like terms are given by
\[ \frac{\langle \Phi | b_h^\dagger b_p \hat{H} \hat{R}(\vartheta) | \Phi \rangle}{\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle} = \sum_{mn} D_{mh}^* D_{np} h(\vartheta) \rho_{nm}(\vartheta) 
+ \sum_{mn} \sum_{ik} D_{mh}^* D_{np} (h_{ik} + \Gamma_{ik}(\vartheta)) \rho_{km}(\vartheta) (\delta_{ni} - \rho_{ni}(\vartheta)), \] (3.38)

where \( h(\vartheta) \) is given by Eq. 3.28b.
A stationary point has been reached when the local gradient vanishes, \(i.e.,\)

\[ G_{ph} = 0 \quad \forall \quad p, h. \tag{3.39} \]

This, however, is not guaranteed to be a minimum. In order to assess whether the obtained stationary point is a local minimum or not, one has to consider the Hessian of the energy functional (see Appendix C). The generalized Brillouin condition, that is, the stationarity condition of the energy functional, that symmetry-projected HF states satisfy is given by

\[
\sum_{kk'} f_k^* f_{k'} \langle \Phi | | b_{p}^{\dagger} b_{h}^j (\hat{\mathbf{H}} - E_j) \hat{p}_{kk'}^{j} | \Phi \rangle \frac{\langle \Phi | \hat{p}_{kk'}^{j} | \Phi \rangle}{\sum_{kk'} f_k^* f_{k'} \langle \Phi | \hat{P}_{kk'} | \Phi \rangle} = 0. \tag{3.40}
\]

The symmetry-projected HF state obtained by such a variational procedure is invariant with respect to arbitrary mixing among hole states in \(|\Phi\rangle\). Similarly, the wavefunction is invariant with respect to arbitrary variations among the particle operators \(\{b_p\}\) in the HF transformation. We obtain a unique representation of the HF operators by diagonalization of the \(\hat{H}^{11}\) Hamiltonian [6]:

\[
\hat{H}^{11} = h\hat{H}_{hh}^{11} \oplus p\hat{H}_{pp}^{11}, \tag{3.41}
\]

where

\[
h\hat{H}_{hh}^{11} = \frac{\langle \Phi | b_{h}^j \hat{\mathbf{H}} b_{h'}^{\dagger} | \Phi \rangle}{\langle \Phi | \Phi \rangle} - \delta_{hh'} \frac{\langle \Phi | \hat{\mathbf{H}} | \Phi \rangle}{\langle \Phi | \Phi \rangle}, \tag{3.42a}
\]

\[
p\hat{H}_{pp}^{11} = \frac{\langle \Phi | b_{p} b_{p'}^{\dagger} \hat{\mathbf{H}} | \Phi \rangle}{\langle \Phi | \Phi \rangle} - \delta_{pp'} \frac{\langle \Phi | \hat{\mathbf{H}} | \Phi \rangle}{\langle \Phi | \Phi \rangle}. \tag{3.42b}
\]

The eigenvalues obtained from the diagonalization of the \(\hat{H}^{11}\) Hamiltonian can be interpreted as the occupied (hole) and virtual (particle) orbital energies of the deformed determinant.
3.5.1 Restoration of the normalization condition

Consider the situation where, during the optimization process, the state $|\Phi\rangle$ is built by a Thouless rotation from state $|\Phi\rangle$ after moving in the direction of the gradient.

$$|\Phi\rangle = \mathcal{N} \exp \left( \sum_{ph} Z_{ph} b_p^\dagger b_h \right) |\Phi\rangle.$$  \hfill (3.43)

Here, the matrix $Z$ can be chosen as, for instance,

$$Z_{ph} = \eta G_{ph},$$  \hfill (3.44)

with $\eta \geq 0$ being some parameter. We denote with $\{\tilde{d}_h^\dagger, \tilde{d}_p\}$ the set of HF operators produced by such transformations (see Eq. A.9)

$$\tilde{d}_h^\dagger = b_h^\dagger + \sum_p Z_{ph} b_p^\dagger,$$  \hfill (3.45a)

$$\tilde{d}_p = b_p - \sum_h Z_{ph} b_h,$$  \hfill (3.45b)

where the operators $\{b_h^\dagger, b_p\}$ that annihilate the state $|\Phi\rangle$ are assumed to satisfy all the appropriate anti-commutation relations.

We show in Appendix A that the operators $\{\tilde{d}_h^\dagger, \tilde{d}_p\}$ annihilate the state $|\Phi\rangle$. These operators do not, however, satisfy the anti-commutation relations given by Eq. 2.13. In fact, they satisfy

$$\left[ \tilde{d}_p, \tilde{d}_h^\dagger \right]_+ = 0,$$  \hfill (3.46a)

$$\left[ \tilde{d}_h, \tilde{d}_h^\dagger \right]_+ = (I + Z^T Z^*)_{h'h},$$  \hfill (3.46b)

$$\left[ \tilde{d}_p, \tilde{d}_p^\dagger \right]_+ = (I + Z^* Z^T)_{p'p}.$$  \hfill (3.46c)
We can restore the desired anti-commutation relations by performing the transformations

\[
\begin{align*}
&d_h^\dagger = \sum_{h'} L^{-1}_{hh'} d_{h'}^\dagger, \\
&d_p = \sum_{\nu'} M_{\nu\nu'}^{-1} \tilde{d}_{\nu'},
\end{align*}
\]

in terms of the lower triangular matrices \( L \) and \( M \).

The anti-commutation relations among \( \{d_h^\dagger, d_p \} \) become

\[
\begin{align*}
\left[ d_h, d_{h'}^\dagger \right]_+ &= \sum_{\mu\nu} L_{\mu h}^{-1} L_{\nu h'}^{-1} (I + Z^T Z^*)_{\nu\mu} = \delta_{h'h}, \\
\left[ d_p, d_{\nu'}^\dagger \right]_+ &= \sum_{\mu\nu} M_{\mu\nu}^{-1} M_{\nu'\nu}^{-1} (I + Z^* Z^T)_{\nu\mu} = \delta_{\nu'\nu},
\end{align*}
\]

which yield the following equations for determining \( L \) and \( M \):

\[
\begin{align*}
&I + Z^T Z^* = L L^\dagger, \\
&I + Z^* Z^T = M M^\dagger.
\end{align*}
\]

Hence, given the matrix \( Z \), standard Cholesky decompositions (Eq. 3.49) can be performed to obtain the matrices \( L \) and \( M \) [44, 45].

### 3.5.2 Global gradient

In order to use powerful gradient-based optimization methods such as the conjugate gradient or quasi-Newton methods (see Refs. [48], [44], and [45]), one must be able to compute a global gradient. That is, we should be able to compute the gradient of the energy of \( |\Psi_{1}^{i\nu k}\rangle = \sum_{k} f_{k} \hat{P}_{i\mu k}^{j} |\Phi_{1}\rangle \) with respect to variations in \( Z \) defined in terms of the operators \( \{b_{h}^{0\dagger}, b_{p}^{0}\} \) that annihilate the deformed Slater determinant \( |\Phi_{0}\rangle \). Here, we follow Egido et al. [48] in deriving the form of the global gradient.
Consider the Slater determinant $|\Phi_1\rangle$. Provided that $|\Phi_1\rangle$ is not orthogonal to $|\Phi_0\rangle$ we can write

$$|\Phi_1\rangle = \mathcal{N} \exp\left(\sum_{ph} Z_{ph} b_0^\dagger b_0 \right) |\Phi_0\rangle,$$

(3.50)

where $\mathcal{N} = \langle \Phi_0 | \Phi_1 \rangle$ is a normalization constant. Here,

$$Z_{ph} = \sum_{h'} (D^0^T D^1_s)^{ph'} (L^{s-1})_{h'h},$$

(3.51a)

$$L_{h'h'} = (D^0_0^T D^1_1)^{h'h},$$

(3.51b)

where we have used Eqs. A.5 and A.8a to write $Z$ and $L$ in terms of the matrices of orbital coefficients $D^0$ and $D^1$ characterizing the state $|\Phi_0\rangle$ and $|\Phi_1\rangle$, respectively.

A variation in $Z$ leads to a change in energy given by

$$\delta E = \sum_{ph} \frac{\partial E}{\partial Z_{ph}^*} \delta Z_{ph}^* + \text{c.c.}$$

$$= \sum_{ph} -G_{ph} \delta Z_{ph}^* + \text{c.c.,}$$

(3.52)

where we have introduced the global gradient $G$ given by

$$G_{ph} = -\frac{\sum_{kk'} f_k^* f_{k'} \langle \Phi_1 | p_{kk'} (\hat{\mathcal{P}}_{kk'}^j | \Phi_1 \rangle}{\sum_{kk'} f_k^* f_{k'} \langle \Phi_1 | \hat{\mathcal{P}}_{kk'}^j | \Phi_1 \rangle}.$$ (3.53)

In order to evaluate the matrix elements appearing in the global gradient (Eq. 3.53), we need to relate the operators $\{b_0^{0\dagger}, b_0^0\}$ to the operators $\{b_1^{1\dagger}, b_1^1\}$. Combining the results of the previous subsection with Eq. A.9, we arrive at

$$b_1^{1\dagger} = \sum_{h'} L^{h'h} b_0^{0\dagger} b_0^0 = \sum_{h'} L^{h'h} \left( b_0^{0\dagger} + \sum_p Z_{ph} b_0^0 \right),$$

(3.54a)

$$b_1^1 = \sum_{p'} M^{p'0\dagger} b_0^0 = \sum_{p'} M^{p'0\dagger} \left( b_0^0 - \sum_h Z_{p'h} b_0^0 \right),$$

(3.54b)
where the matrices $L$ and $M$ are here determined by the solution to Eq. 3.49.

Because the transformation defined by Eq. 3.54 is canonical (we have explicitly en-
sured that anti-commutation rules are preserved), it can be inverted straightforwardly. We arrive at

$$b^0_h = \sum_{h'} L^*_{h'h} b^1_{h'} - \sum_{pp'} Z_{p'h'} M^*_{pp'} b^1_{p'},$$  \hspace{1cm} (3.55a)

$$b^0_p = \sum_{p'} M_{p'p} b^1_{p'} + \sum_{hh'} Z_{ph'} L^{-1}_{hh'} b^1_{h}. \hspace{1cm} (3.55b)$$

We now use Eq. 3.55 to write the global gradient ($\mathcal{G}$) matrix elements in terms of the
local gradient ($G$) as

$$\mathcal{G}_{ph} = \sum_{p'h'} L^*_{h'h} M^{-1}_{p'h} G_{p'h'} = \left[M^T G L^*-1\right].$$ \hspace{1cm} (3.56)

Equation 3.56 defines the global gradient\(^8\) that can be used in combination with
powerful gradient-based optimization algorithms.

\section*{3.6 Application to molecular systems}

\subsection*{3.6.1 Implementation details}

In our original work \cite{41}, the optimization of symmetry-projected Hartree–Fock states
was implemented in a development version of the GAUSSIAN program \cite{49}. The op-
timization was carried out via a diagonalization-based approach, using the direct-
inversion of the iterative subspace (DIIS) acceleration \cite{50} technique whenever pos-
sible. This code can handle the optimization of spin and/or complex conjugation

\(^8\)Note that the global gradient is the gradient of the energy with respect to $Z^*_{ph}$ at an arbitrary $Z$, as opposed to the local gradient, which is evaluated at $Z = 0$ (see Eq. 3.34.)
projected states. The capability to compute the one- and two-particle reduced density matrices from spin projected states was later completed (see Appendix D).

Recently, we have developed a new computational program, phfmol, that can handle the full variational optimization of symmetry-projected states (as well as configuration mixing approaches) based on a Thouless parametrization. A limited-memory Broyden–Fletcher–Goldfarb–Shanno (BFGS) [51, 52] quasi-Newton method is used as the unconstrained minimization algorithm. The program interfaces with the GAUSSIAN suite [49] to retrieve one- and two-electron integrals. The phfmol program is parallelized (MPI-based) over the grid used to perform the symmetry restoration (spatial and/or spin). Complex conjugation projection is not currently supported.

We use a converged broken-symmetry UHF state as an initial guess for S-UHF calculations. In order to prepare an initial guess for S-GHF and calculations involving complex conjugation symmetry breaking, we mix a few orbitals closest to the Fermi energy according to some predetermined scheme.

### 3.6.2 Nomenclature

Before we discuss our results, let us briefly clarify the nomenclature we use in this document. All symmetry projected methods are written in a notation of the form X-Y. Here, Y = RHF, UHF, or GHF denotes the type of underlying HF transformation used; complex orbitals are used in all cases. In X, we write the collection of symmetries restored in the calculation: K is used for complex conjugation, S is used for spin, and the point group label (like C$_{2v}$) is used to denote the type of spatial symmetry projection.
3.6.3 VAP vs PAV

We start by considering the dissociation profile of the H$_2$ molecule in the cc-pVDZ basis (see Fig. 3.2). Restricted Hartree–Fock (RHF) fails to dissociate the hydrogen molecule correctly, separating to a mix of hydrogen atoms and ionic states. The energetically correct dissociation limit is recovered by breaking spin and spatial symmetry in UHF. The resulting wavefunction is not a pure spin state but rather a linear combination of singlet and triplet states. The term “spin contamination” is used to refer to such unphysical admixtures of spin states.

![Potential energy curve for H$_2$ dissociation predicted by S-UHF (PAV) and S-UHF (VAP). The calculations use the cc-pVDZ basis set. S-UHF (PAV) yields an unphysical curve with a derivative discontinuity at the Coulson-Fischer point.](image)

A spin projection can be applied before (PAV) or after (VAP) the variation. The PAV
curve displays an unphysical derivative discontinuity exactly at the same point where UHF separates from the RHF solution. On the other hand, the VAP scheme yields a curve that is lower than UHF over the entire set of considered bond lengths. Towards dissociation, the PAV and VAP yield very similar results, and they both converge to the exact dissociation (as UHF does) while retaining good quantum numbers. Near equilibrium, S-UHF (VAP) and UHF differ significantly, as can be seen from Fig. 3.2.

3.6.4 Dissociation curves of small systems

Let us now consider a three-electron system, namely H₃. Here, we arrange the three atoms on the corners of an equilateral triangle and stretch the triangle isotropically. The Hartree–Fock ground state in this case is non-collinear due to the frustrated arrangement of the atoms. Figure 3.3 shows the dissociation predicted by S-UHF and S-GHF, projecting onto \( s = 1/2 \). It is evident that spin-projection accounts for significantly more correlation than the broken symmetry mean-field solutions. Interestingly, S-GHF is capable of accounting for significantly more correlations than S-UHF in the equilibrium region. The two curves merge for \( r \geq 2.2 \, \text{Å} \).

While PHF yields excellent results for the dissociation of H₂, it misses some of the effects of dynamical correlation, which we illustrate by considering the dissociation of N₂, as shown in Fig. 3.4. The projected HF methods generally go to a dissociation limit slightly below that of UHF. Spin projected methods (S-UHF and S-GHF) improve significantly over the UHF profile, eliminating the artificial bump observed in the latter. KS-UHF and KS-GHF yield sizable improvements over S-UHF and S-GHF, respectively, making evident the ability of complex-conjugation symmetry-breaking and restoration to account for dynamical correlation. All of these curves,
Figure 3.3: Potential energy curve for the isotropic dissociation of an H$_3$ equilateral triangle. The calculations use the cc-pVDZ basis set. Because the system is spin-frustrated, a GHF solution exists which is lower in energy than the UHF solution.

however, are far above the coupled-cluster singles and doubles (CCSD) [53] based on the UHF reference, even with this small basis set. It is interesting to note that the KS-GHF curve is nearly parallel to the UCCSD one, suggesting that the predicted bond energy is roughly the same.

We note that the PHF dissociation profiles for N$_2$ (and for other systems) are not size-consistent. That is, the energy of two separate fragments computed with a given PHF method will be lower than the energy obtained in the dissociation of the parent system. This is ultimately a consequence of the fact that the ansatz is not factorizable,
Figure 3.4: Potential energy curve for the dissociation of the nitrogen molecule. The calculations use the cc-pVDZ basis set. Complex-conjugation symmetry-breaking and restoration accounts for a significant fraction of the missing dynamical correlation. A reference UCCSD curve is included for comparison.

that is,

$$\hat{P}\Phi_{AB} \neq \hat{P}\Phi_A \otimes \hat{P}\Phi_B,$$

(3.57)
even when the reference state does satisfy this property ($\Phi_{AB} = \Phi_A \otimes \Phi_B$).

Therefore, as the molecular system dissociates, the wavefunction fails to become the product of wavefunctions corresponding to each of the non-interacting fragments.
3.6.5 Basis set dependence

Another interesting aspect is the basis set dependence of the correlation energy recovered by projection methods. In Fig. 3.5, we show the difference of the S-UHF, KS-UHF, and CASSCF(10,8)\(^\dagger\) energies with respect to UHF as a function of the internuclear separation with basis sets of increasing size for the case of the nitrogen molecule. As it is evident from the figure, the correlation energy recovered is almost independent of the basis set size for both S-UHF and CASSCF. This suggests that the correlations recovered are mostly static (or strong) in nature.

3.6.6 Singlet-triplet splittings

Singlet-triplet splittings, or the energy difference between the lowest-lying singlet and triplet states, can often be accurately determined experimentally. These splittings are often used to evaluate the performance of different theoretical methods. Unrestricted Hartree–Fock (UHF) often fails to provide accurate splittings, particularly when spin contamination is large [55].

In Table 3.1 we show the computed singlet-triplet splittings for a variety of small diatomic molecules at the experimental geometries [56]. All calculations use the cc-pVTZ basis set, and we define the singlet-triplet splittings as \(E_{ST} = E_T - E_S\), where \(E_T\) and \(E_S\) are the energies of the triplet and the singlet states, respectively.

For this set of small diatomic molecules, S-UHF provides excellent agreement with experiment and provides a significant improvement over UHF. KS-UHF results are

\(\dagger\)Here, CASSCF stands for complete active-space self-consistent field [54]. The numbers in parenthesis indicate the number of electrons (first) and spatial orbitals (second) that are correlated via an exact diagonalization in the CAS approach.
Figure 3.5: Relative energy with respect to UHF across the dissociation profile of \( \text{N}_2 \) with different basis sets. Notice that both CAS(10/8) and S-UHF results show essentially no dependence on the size of the basis, while KS-UHF shows a small basis set sensitivity. cc-pVQZ results are only shown for S-UHF.

Table 3.1: Singlet triplet splittings (kcal/mol) predicted by symmetry-projected methods for a variety of small molecules. The experimental data was extracted from Ref. [57].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>UHF</th>
<th>S-UHF</th>
<th>KS-UHF</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
<td>19.4</td>
<td>33.6</td>
<td>31.6</td>
<td>39.0</td>
</tr>
<tr>
<td>OH(^+)</td>
<td>25.9</td>
<td>45.8</td>
<td>43.4</td>
<td>50.6</td>
</tr>
<tr>
<td>O(_2)</td>
<td>15.8</td>
<td>20.6</td>
<td>24.2</td>
<td>22.6</td>
</tr>
<tr>
<td>NF</td>
<td>19.7</td>
<td>32.3</td>
<td>31.0</td>
<td>34.3</td>
</tr>
</tbody>
</table>
also in good agreement with the experimental data. We note that there is no reason to expect that a single symmetry-projected configuration will yield states of comparable quality for different symmetries (such as singlets and triplets). The fact that a good agreement is observed for these small systems in the singlet-triplet splittings does not imply that we expect this to remain true for other systems.

### 3.7 Concluding remarks

The molecular electronic Hamiltonian possesses certain symmetries that permit the characterization of the states of a given system, both theoretically and spectroscopically. Unfortunately, approximate variational solutions of the Schrödinger equation need not respect the same symmetry as does the exact solution. Forcing them to do so reduces the variational flexibility in the ansatz, which is not ideal. On the other hand, at the HF level, symmetry breaking indicates the emergence of strong correlations that are otherwise difficult to capture. Despite this, the symmetry broken wavefunction remains qualitatively poor because it lacks the appropriate symmetries. By using projection operators, one can accomplish two goals simultaneously: accounting for the strong correlations included in the symmetry-broken underlying determinant, and restoring the correct set of quantum numbers. Moreover, this can be done without leaving the independent particle picture that allows one to easily grasp the physics contained in the wavefunction.

The self-consistent optimization of a symmetry-projected HF ansatz is formally attractive, but its implementation is not trivial. On the other hand, a projection-after-variation approach is much simpler to handle, but may lead to unphysical behavior in certain situations. In addition, a self-consistent optimization allows one to go beyond
the mean-field description even in situations where HF by itself does not converge to a symmetry-broken solution.

We have presented the application of a numerically robust self-consistent approach for the optimization of symmetry-projected HF wavefunctions in molecular systems. These can account for the strong correlations present in, for instance, molecular dissociation processes. Nevertheless, the wavefunctions obtained are neither size consistent nor size extensive. In addition, a single symmetry-projected configuration remains insufficient to account for the weak correlations also present in molecular systems.
Chapter 4

Configuration-mixing approaches to account for ground-state correlations

In the previous chapter, we explored in detail the symmetry-projected HF approach as an ansatz for the ground state of a system with a given symmetry. We showed how, by deliberate symmetry breaking and restoration performed in a variation-after-projection manner, one can gain access to ground state correlations that may go significantly beyond the broken-symmetry mean-field solution.

In this chapter, we shall consider two approaches to account for even more correlations based on a linear combination of symmetry-projected configurations. We start by considering a configuration interaction ansatz based on symmetry-projected determinants. We then discuss an alternative construction of the exact wavefunction based on generalized fermion coherent states, that is, the set of all non-orthogonal determinants that can be accessed via a Thouless rotation from a reference one.

Our use of multi-reference symmetry-projected states, where the orbital coefficients for each determinant are variationally optimized, is ultimately justified in terms of the coherent state representation of the exact wavefunction. The approaches described in this chapter can be systematically improved towards the exact solution. Nevertheless, we aim to account for as many correlations with as few configurations as possible, thus yielding a fairly compact wavefunction fully characterized by a small set of non-orthogonal symmetry broken Slater determinants.
4.1 Configuration Interaction based on symmetry-projected determinants

Conceptually, the simplest approach to account for the missing correlation in the symmetry-projected HF ansatz is to consider a configuration interaction approach. A full configuration interaction ansatz can be written as

$$\Psi_{jm} = \sum_k \hat{P}_{mk} \left( f_{0;k} |\Phi\rangle + \sum_{ia,k} f_{ia;k} |\Phi^a_i\rangle + \sum_{ijab,k} f_{ia,jb;k} |\Phi^{ab}_{ij}\rangle + \cdots \right)$$

(4.1)

In the above expression, we have used indices $i$ and $j$ to denote occupied (hole) states in the broken-symmetry determinant $|\Phi\rangle$, whereas indices $a$ and $b$ were used for unoccupied (particle) states. The notation $|\Phi^a_i\rangle \equiv b^\dagger_a b^\dagger_i |\Phi\rangle$ has been used. The linear variational coefficients $f$ can be determined by the solution to a generalized eigenvalue problem among all configurations. We note that the above representation of the Hilbert subspace with the appropriate symmetry is overcomplete.

Including only singly excited configurations (of the form $|\Phi^a_i\rangle$) in the configuration-interaction expansion will in general not lead to any improvement in the ground state energy.\(^*\) On the other hand, diagonalization in this space can be used for a

\(^*\)The generalized Brillouin condition that a variationally optimized symmetry-projected HF state satisfies is given by

$$\sum_{kk'} f^*_{0;k} f_{0;k'} \langle \Phi^a_i | (\hat{H} - E_0) \hat{P}_{kk'} |\Phi\rangle = 0,$$

(4.2)

which makes singly-excited configurations orthogonal to the symmetry-projected HF state through the Hamiltonian when using the $f_{0;k}$ variational coefficients.

If the dimension of the irreducible representation associated with the restored symmetry is larger than 1, some energy improvement in the ground state may be obtained by diagonalization in the singly-excited space due to the variational coefficients $f_{ia;k}$.
first-order description of excited states. This corresponds to the symmetry-projected Tamm-Dancoff Approximation discussed by Schmid et al. [58].

If, in addition, one includes doubly-excited configurations, an energy improvement is all but guaranteed unless the symmetry-projected HF state was already exact. Nevertheless, the matrix is large and dense; the evaluation of each matrix element is more expensive than in the standard HF-based approach, where the Slater–Condon rules [59] can be used to simplify the evaluation.

We have not pursued the configuration interaction approach described in this section. We have strived to obtain wavefunctions as compact as possible, in terms of a few number of symmetry-projected configurations. This facilitates, at the same time, the physical insight behind the wavefunction. If the ground state wavefunction is expanded in terms of a few non-orthogonal, symmetry-broken Slater determinants, one may relate the correlation thus gained to the resonance among the different such configurations.

### 4.2 Generalized fermion coherent states

The approach described in the previous section is based on an orthogonal, particle-hole construction of the Hilbert space. An alternative way of constructing wavefunctions in the Hilbert space is based on generalized fermion coherent states. These are built using the symmetry properties of the Lie group associated with the anticommutation rules of the individual fermion operators [11, 60]. Given a reference Slater determinant $|\Phi_0\rangle$, a (normalized) generalized coherent state $|z\rangle$ is generated from a Thouless rotation on $|\Phi_0\rangle$ (see Appendix A). Any wavefunction in the Hilbert
space (including the exact solutions) can be expanded in terms of these coherent states as

$$|\Psi\rangle = \int \prod_{ph} dz_{ph} d\lambda_{ph} \mu(\mathbf{z}) f(\mathbf{z}) |\mathbf{z}\rangle,$$

(4.3)

where \(\mathbf{z}\) is a vector of dimension \(N(M - N)\). Here, \(f(\mathbf{z}) = \langle \mathbf{z} | \Psi \rangle\), while \(\mu(\mathbf{z})\) is a measure guaranteeing that the closure relation equals the identity operator.

This construction is necessarily overcomplete. There are an infinite number of generalized coherent states, while the Hilbert space has a (large) finite number of linearly independent states. Nonetheless, this construction may be useful when there are dynamical symmetries. In fact, it is easy to realize that the symmetry-projected ansatz considered in the previous chapter takes a certain path in the multi-dimensional space of generalized coherent states. Jancovici and Schiff used the coherent state representation to account for small amplitude vibrations around the mean-field solution in their celebrated derivation of the random phase approximation [61].

In the next section, we describe our approach to build-up ground state correlations. We consider states that are linear combinations of variationally optimized (symmetry-projected) non-orthogonal configurations, or generalized coherent states. The ansatz becomes exact when the number of linearly independent states spanned equals the size of the Hilbert space of the problem. It coincides with the coherent state representation of the exact wavefunction when the number of determinants included is infinite.
4.3 Multi-configuration approaches

Let us suppose that we have already optimized a symmetry-projected HF configuration. In this section, we write this as

\[ |^{1}\Psi_{j,m}\rangle = \sum_{k} f_{1k} \hat{P}_{mk}^{j}|\Phi_{1}\rangle, \]  

(4.4)

where the superscript 1 in \(|^{1}\Psi_{j,m}\rangle\) is used to indicate that a single symmetry-projected configuration is used in the ansatz. Similarly, the subscript 1 in the \(f_{1k}\) variational coefficients and in \(|\Phi_{1}\rangle\) indicate that only one determinant is included in the ansatz.

If the description of the ground state was poor, this can be improved by introducing another symmetry-projected configuration. That is, we now consider the ansatz

\[ |^{2}\Psi_{j,m}\rangle = \sum_{k} \hat{P}_{mk}^{j} (f_{1k} |\Phi_{1}\rangle + f_{2k} |\Phi_{2}\rangle), \]  

(4.5)

where two symmetry-projected configurations (constructed from two non-orthogonal determinants) are used in the variational ansatz for the ground state of a given set of quantum numbers.

In the general case, we could describe the ground state with \(n\) symmetry-projected configurations, as in

\[ |^{n}\Psi_{j,m}\rangle = \sum_{k} \hat{P}_{mk}^{j} \sum_{l=1}^{n} f_{lk} |\Phi_{l}\rangle. \]  

(4.6)

One has now to address the issue of how to variationally optimize the \(n\)-configuration ansatz. There are two extreme approaches that we will consider:

- In the FED (few-determinant) approach introduced by Schmid et al. [5], the different configurations are optimized one-at-a-time. That is, the second symmetry-projected configuration is optimized after the first one, leaving the latter untouched, and so on.
We note that there is no need for the FED expansion to be short, as its name would imply. We keep the acronym to remain consistent with the literature.

- In the RES (resonating) approach introduced by Fukutome [7], all the configurations are optimized at the same time.

There are, of course, a number of possible variants in between. For instance, one could optimize two configurations at a time. Each approach has strengths and drawbacks. In particular, we would like to note that

- A RES optimized wavefunction is stationary with respect to changes in any of the underlying determinants. On the other hand, a FED optimized wavefunction is stationary only with respect to particle-hole excitations of the last-added determinant.

This feature makes the RES wavefunction easier to work with for evaluating properties that depend on derivatives of the wavefunction.

- In a RES optimization, $\mathcal{O}(n^2)$ overlap and Hamiltonian matrix elements need to be re-computed at every iteration. In contrast, an efficient implementation of the FED approach requires only $\mathcal{O}(n)$ overlap and Hamiltonian matrix elements to be recomputed.

- The convergence properties of the two approaches can be very different. In the RES approach, for instance, there is no guarantee that any of the configurations will resemble the optimized single-configuration ansatz.

We now proceed to consider each of the two approaches in detail.
4.3.1 The few-determinant (FED) approach

In the few-determinant (FED) approach introduced by Schmid [5, 6], only the last-added symmetry-projected configuration is optimized with respect to the underlying HF transformation. In the quantum chemistry community, a similar approach was proposed by Koch and Dalgaard [62], although the configurations included were limited to a restricted HF-type ansatz. The FED approach has been very successful in the nuclear physics community (see Ref. [6] and references therein).

Let us consider the variational optimization of the \( n \)-th determinant in the ansatz defined by 4.6. The energy functional becomes

\[
E^{j,m}\{\Phi_n, \{f\}\} = \frac{\langle n\Psi^{j,m}|\hat{H}|n\Psi^{j,m}\rangle}{\langle n\Psi^{j,m}|n\Psi^{j,m}\rangle} = \sum_{kl,k'k} f^*_{lk} f_{l'k'} \langle \Phi_l|\hat{H} \hat{P}_{kk'}|\Phi_{l'}\rangle/\sum_{kl,k'k} f^*_{lk} f_{l'k'} \langle \Phi_l|\hat{P}_{kk'}|\Phi_{l'}\rangle.
\] (4.7)

The variation with respect to the coefficients \( f^\dagger \) leads to the generalized eigenvalue problem

\[
(\hat{H} - nE^{n}\mathcal{N}) f = 0,
\] (4.8)

subject to the constraint

\[
f^\dagger n\mathcal{N} f = 1_h,
\] (4.9)

where \( h \leq nd \) is the number of non-zero eigenvalues of \( n\mathcal{N} \) and \( d \) is the dimension of the irreducible representation associated with the projection. Here, the matrices \( n\mathcal{H} \)

\footnote{Note that all \( f \) coefficients are re-optimized, as opposed to the configurations \( |\Phi\rangle \) where only the last one is optimized.}
and $^N\mathcal{N}$ are given by

\[ ^n\mathcal{H}_{kl,k'\ell'} = \langle \Phi_l | \hat{H} \hat{P}^j_{kk'} | \Phi_{\ell'} \rangle, \tag{4.10} \]
\[ ^n\mathcal{N}_{kl,k'\ell'} = \langle \Phi_l | \hat{P}^j_{kk'} | \Phi_{\ell'} \rangle. \tag{4.11} \]

The variational optimization with respect to the last-added underlying HF transformation $|\Phi_n\rangle$ can be done using the Thouless parametrization, in a manner similar to that presented in Section 3.5. The local gradient takes the form

\[ G_{ph} = -\frac{\sum_{k,k'\ell'} f^*_{nk} f_{\ell'k'} \langle \Phi_n | b^*_h b_p \left( \hat{H} - ^nE \right) \hat{P}^j_{kk'} | \Phi_{\ell'} \rangle}{\sum_{k,l,k'\ell'} f^*_{lk} f_{\ell'k'} \langle \Phi_l | \hat{P}^j_{kk'} | \Phi_{\ell'} \rangle}. \tag{4.12} \]

Because the state is prepared variationally, it follows that

\[ ^1E - ^2E \geq ^2E - ^3E \geq \cdots \geq ^{n-1}E - ^nE. \tag{4.13} \]

That is, the last added symmetry-projected configuration will improve the ground state energy by a smaller amount than the previously added one. Of course this is only satisfied if one can guarantee that the global minimum was found in each optimization problem. In practice, as this is difficult to guarantee, small deviations to this rule are observed, yet the overall trend remains valid.

We close this section by noting that Schmid et al. [5] realized that the FED approach is not the most general description using $n$ symmetry-projected configurations. The authors stated, regarding the RES approach discussed in the next section, that they did not believe that “such a fine-tuning will yield improvements with respect to the (FED) approach”.
4.3.2 The resonating (RES) approach

It is perhaps conceptually simpler, though computationally more challenging, to optimize all configurations at the same time. This is the basis of the resonating Hartree–Fock method devised by Fukutome [7]. It has been used by Tomita, Ten-no, and Tanimura [63] in half-projected RES HF calculations on CO (carbon monoxide), and by Ten-no in CI and coupled-cluster approaches based on a RES HF expansion [64]. It has proven very successful in the context of the Hubbard Hamiltonian [65, 66, 46, 67].

Let us consider the variational optimization of the ansatz defined by 4.6. The energy functional becomes

\[ n E^{j,m} \left[ \{ \Phi \}, \{ f \} \right] = \frac{\langle n \Psi^{j,m} | \hat{H} | n \Psi^{j,m} \rangle}{\langle n \Psi^{j,m} | n \Psi^{j,m} \rangle} = \frac{\sum_{kl,k'k''} f^*_l f_{k''} \langle \Phi_l | \hat{P}_{kk'}^{j} | \Phi_{k''} \rangle}{\sum_{kl,k'k''} f^*_l f_{k''} \langle \Phi_l | \hat{P}_{kk'}^{j} | \Phi_{k''} \rangle}, \tag{4.14} \]

where we have emphasized that the full set of determinants is optimized. The variation with respect to the coefficients \( f \) leads to the same generalized eigenvalue problem as in the FED approach (though the matrix elements are necessarily different).

The variational optimization with respect to the set of underlying HF transformations \( \{| \Phi \rangle \} \) can also be done using the Thouless parametrization. The local gradient with respect to the \( l \)-th determinant in the expansion takes the form

\[ G_{ph}^l = - \frac{\sum_{k,k'} f^*_k f_{k'} \langle \Phi_l | b_p^\dagger | b_p \rangle \left( \hat{H} - n \hat{E} \right) \hat{P}_{kk'}^{j} | \Phi_{k'} \rangle}{\sum_{k''k'} f^*_k f_{k''} \langle \Phi_{k'} | \hat{P}_{kk'}^{j} | \Phi_{k''} \rangle}. \tag{4.15} \]

A self-consistent solution is achieved when

\[ G_{ph}^l = 0 \quad \forall \quad l, p, h. \tag{4.16} \]

This implies that the RES HF wavefunction is stationary with respect to hole-particle mixings of any of the determinants in the expansion.
4.4 Application to molecular systems

The **phfmol** program first described in the previous chapter is capable of optimizing multi-configuration symmetry-projected states, both with the FED and RES approaches. Our FED implementation re-uses overlap and Hamiltonian matrix elements and thus scales as $O(n)$ with the number of symmetry-projected configurations.

One of the most important issues regarding a practical implementation of the FED and RES approaches is to prepare an initial guess of the underlying HF transformations in the symmetry-projected configuration expansion. This was discussed in some detail by Koch and Dalgaard [62]. Our approach is currently simplistic: we prepare an initial guess of the HF transformations in the FED approach as random unitary rotations of the orbitals corresponding to the HF solution, in the form $\exp(i\lambda K)$, with $\lambda \approx 0.01$ and $K$ being a Hermitian matrix. This mixing is done in a way that breaks all the symmetries that the HF solution may possess. Our initial guess for RES calculations is the converged FED expansion with the same number of determinants. Given that the symmetry-projected FED or RES equations will reach a stationary point depending on the initial guess provided, a smarter scheme to prepare the initial guess is desirable. Nevertheless, it is difficult to anticipate *a priori* the structure of generally non-orthogonal determinants that will interact the most through the Hamiltonian with the set of previously obtained determinants.

4.4.1 Ground-state energy of $N_2$

We start by considering the ground state energy of the nitrogen molecule, both at the equilibrium geometry ($r_{eq}$) and at $1.5 r_{eq}$. We show in Fig. 4.1 the evolution of the
FED energy with the number of transformations \( n \) added for a series of (symmetry-projected) methods. Calculations were performed using the Cartesian \( \text{cc-pVDZ} \) basis set. We compare our results with CCSD [full] and CCSD(T) [full]\(^\ddagger\) reference energies (obtained with the \textsc{gaussian} suite). For spin projected methods, projection to the singlet state was carried out; for methods involving spatial symmetry projection, projection was done to the totally symmetric irreducible representation.

We observe from the results in Fig. 4.1 that the rule stating that the last added determinant should bring less correlation than the previously added one is satisfied in most cases. In those cases where it is not, this is because we have failed to converge to the global minimum in the potential energy landscape. Several other features deserve further discussion:

- At equilibrium, spatial symmetry projection (with the \( D_{2h} \) group) brings significantly more correlation than spin projection with the same number of symmetry-projected configurations. This is not too obvious at \( 1.5 \, r_{eq} \), yet \( D_{2h} \)-UHF remains competitive with SGHF while being significantly cheaper.

- The use of broken spin-symmetry determinants (UHF-type) brings significantly more correlation than the use of RHF determinants at \( 1.5 \, r_{eq} \). This remains true even when several configurations have been added; it takes roughly 4 RHF configurations to obtain the same energy as a single UHF configuration.

- When both spin and spatial symmetry are restored, a small number of configurations seems to be sufficient to obtain energies of comparable quality to CCSD

\(^\ddagger\)Here, CCSD stands for coupled-cluster singles and doubles [53]. CCSD(T) includes perturbative triples corrections to the former. The “full” keyword denotes the fact that the full set of orbitals was correlated in the coupled-cluster approach.
Figure 4.1: Ground-state energy of the N$_2$ molecule predicted by a variety of FED approaches at $r = r_{eq}$ (top panel) and $r = 1.5r_{eq}$ (bottom panel) as a function of the number $n$ of symmetry-projected configurations. Here, $r_{eq} = 1.09768$ Å [56]; a Cartesian cc-pVDZ basis set is used. The straight lines in each panel mark the CCSD [full] and CCSD(T) [full] reference energies.
or CCSD(T). At $1.5 r_{eq} \approx 16 D_{2h} S$-UHF configurations bring more correlation than CCSD(T). This is remarkable considering the ease of interpretation associated with such wavefunction.

Unfortunately, we were unable to produce such a detailed plot using the RES approach, as it becomes significantly more difficult to converge than the corresponding FED expansion. We show, nonetheless, in Table 4.1 a comparison of ground-state energies, evaluated at $r_{eq}$, predicted with FED S-UHF and RES S-UHF as a function of the number of transformations $n$.

It is evident from the results in Table 4.1 that the RES approach yields significantly lower energies than the FED approach for a fixed number of transformations. However, the FED approach allows one to include many more configurations than in the RES approach as the optimization is cheaper and typically takes much fewer iterations with our gradient-based optimization. For instance, Fig. 4.1 includes results with up to 32 FED SUHF configurations. This makes the FED approach much more convenient for practical applications.

4.4.2 Dissociation profiles

Let us now consider the full dissociation profile of the $N_2$ molecule. Dissociation curves predicted with a FED $D_{2h} S$-UHF approach are shown in Fig. 4.2, along with the dissociation profile computed with a single symmetry-projected configuration using $D_{2h} S$-GHF. The calculations use the Cartesian cc-pVDZ basis set. We compare our curves with the FCI profile from Ref. [68]. Nevertheless, we stress that the FCI results are not directly comparable: they were obtained with the spherical cc-pVDZ
Table 4.1: Ground-state energy of the nitrogen molecule (at $r = r_{eq}$) predicted with the FED S-UHF and RES S-UHF approaches as a function of the number of transformations $n$. The Cartesian cc-pVDZ basis set was used.

<table>
<thead>
<tr>
<th>$n$</th>
<th>FED S-UHF</th>
<th>RES S-UHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-109.0267</td>
<td>-109.0267</td>
</tr>
<tr>
<td>2</td>
<td>-109.0749</td>
<td>-109.1210</td>
</tr>
<tr>
<td>3</td>
<td>-109.1170</td>
<td>-109.1530</td>
</tr>
<tr>
<td>4</td>
<td>-109.1360</td>
<td>-109.1728</td>
</tr>
<tr>
<td>5</td>
<td>-109.1617</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-109.1720</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-109.1845</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>-109.1922</td>
<td></td>
</tr>
</tbody>
</table>

basis and freezing the 1s core orbital of the N atoms. Both of these effects would contribute to underestimate the FCI energy.\(^5\) The FCI results were included as a reference for the correct shape of the dissociation curve.

The results in Fig. 4.2 show that $D_{2h}$S-UHF yields a very decent dissociation curve even with a single symmetry-projected configuration. Inclusion of 8 symmetry-projected configurations (using the FED approach) results in a curve fairly parallel to the reference FCI curve. The energy improvement due to the additional configurations is seen across the potential energy surface. Interestingly, 2 symmetry-projected configurations with the $D_{2h}$S-UHF method match the results from $D_{2h}$S-GHF with a single configuration. We finally point out that, as the FED approach becomes exact

\(^5\)Near $r_{eq}$, CCSD yields a 12.3 mhartree energy difference once both effects are accounted for.
Figure 4.2: Dissociation profile for the ground state of the N$_2$ molecule obtained with a FED $D_{2h}$S-UHF approach as a function of the number of HF transformations. The single-configuration $D_{2h}$S-GHF profile is included for comparison, as well as the FCI results from Ref. [68], even though they are not strictly comparable (see text).
in the limit of a large number of configurations, the size-consistency error associated with projected Hartree–Fock approaches necessarily disappears.

We consider in Fig. 4.3 the symmetric dissociation profile of the H$_2$O molecule, as predicted with a variety of multi-configuration symmetry-projected approaches. The Cartesian cc-pVDZ basis set was used in our calculations, whereas the FCI results from Ref. [69] were obtained with the spherical cc-pVDZ basis set. The restored quantum numbers in symmetry-projected calculations are $s = 0$ for spin and the $A_1$ irreducible representation of the $C_{2v}$ group.

Results from Fig. 4.3 show a similar scenario as that observed in the N$_2$ dissociation. The $C_{2v}$ S-UHF dissociation profile is already fairly parallel to the FCI solution. It accounts for significantly more correlations near equilibrium than towards dissociation with respect to the UHF solution. With 9 symmetry-projected configurations, the FED $C_{2v}$ S-UHF curve is only a few mhartree off from the FCI curve across the entire potential energy surface.

We have been able to compute the entire dissociation profile using a 3-configuration RES approach based on $C_{2v}$ S-UHF. Interestingly, it yields similar results as a 6-configuration FED approach near equilibrium, but becomes more accurate towards dissociation, rivaling the 9-configuration FED approach. This is a result of the increased flexibility in the resonating HF ansatz. Finally, Fig. 4.3 also shows the dissociation profile predicted with the $C_{2v}$ S-GHF method, using a single configuration. Quite disappointingly, the results are only comparable to a two-configuration $C_{2v}$ S-UHF wavefunction, even though the former is almost two orders of magnitude more expensive to evaluate.

$^*$At $r_{eq}$, CCSD is 3.5 mhartree lower in the Cartesian basis set.
Figure 4.3: Symmetric dissociation profile of the water molecule as predicted with a variety of multi-configuration symmetry-projected approaches. A Cartesian cc-pVDZ basis set was used. FCI results from Ref. [69] are included for comparison, even though they are not strictly comparable (see text).

4.4.3 The copper oxide $[\text{Cu}_2\text{O}_2]^{2+}$ core

We have recently applied the projected Hartree–Fock method [70] to the theoretical study of the copper oxide cores, in particular, the interconversion profile between the \(\mu - \eta^2 : \eta^2\)-peroxodicopper(II) (A) and the bis(\(\mu\)-oxo)-dicopper(II) (B) forms.
The interconversion profile of the bare \([\text{Cu}_2\text{O}_2]^{2+}\) core has been recently studied theoretically by Cramer et al. \([71]\), Malmqvist et al. \([72]\), and Yanai et al. \([73]\) with a variety of highly sophisticated ab initio methods. This system has proven tremendously challenging due to the expected multi-reference character in \(A\) and the large active space that one has to include in traditional multi-reference approaches (a reasonable active space for this system would involve 30 electrons in 28 orbitals).

It should be pointed out that recently Liakos and Neese \([74]\) have shown that the multi-reference character in the copper oxide core is very limited. They examined the influence of ligands as well as relativistic and solvent effects and concluded that the single-reference based local-pair natural orbital coupled-cluster method in fact provides very reliable profiles for this system. Their assessment is likely valid in the presence of ligands and solvent, and is hence relevant for comparison with experimental results. On the other hand, we can still treat the bare copper oxide core as a toy system for which different highly sophisticated theoretical methods yield inconsistent results.

In Ref. \([70]\) we assessed the ability of single-reference symmetry-projected methods to accurately describe the interconversion profile of the bare copper oxide core. Understanding that the RASPT2 (restricted active-space second order perturbation theory) \([72]\), CR-CC (completely renormalized coupled-cluster) \([71]\), and DMRG-SC-CTSD (density-matrix renormalization group with strongly contracted canonical transformation including only single and double excitations) \([73]\) methods provide the likely correct profile for this system, we ranked the S-UHF, S-GHF, KS-UHF, and KS-GHF methods according to how close they came to the former methods. We observed that the more symmetries restored the closer the profile got to the reference methods. We show, in the lower panel of Fig. 4.4, a summary of the results presented in Ref. \([70]\).
We have revisited our results for the interconversion profile of the copper oxide core with our multi-reference FED approaches. We have employed the same basis set as our previous work, save for the fact that our phfmol program cannot currently handle spherical basis sets. The effect of the change of basis is expected to be very small and should not affect the conclusions of our work. The totally symmetric irrep of the $D_{2h}$ group was restored in our calculations.

The upper panel of Fig. 4.4 shows the interconversion profiles obtained by our FED $D_{2h}$S-UHF approach as a function of the number of transformations included. We note that the restoration of spatial symmetry makes a huge difference even when a single configuration is included. A single-determinant $D_{2h}$S-UHF approach predicts A to be $\approx 38$ kcal/mol higher in energy than B, and the profile closely resembles those that we have deemed as accurate. Increasing the number of transformations further raises the energy of A relative to B. Our interconversion profile seems to converge with 6 symmetry-projected configurations to a relative energy of $\approx 50$ kcal/mol, significantly higher than the RASPT2, CR-CC, and DMRG-SC-CTSD curves. Because our results show a relatively smooth convergence with the number of configurations, we believe our results could be more accurate than the ones just quoted.

4.5 Concluding remarks

In this chapter we have described an approach to account for the correlations missing in the symmetry-projected ansatz for the ground state of a molecular system. The

$\text{\footnotesize\textsuperscript{II}}$ The use of Cartesian basis functions lowers the UHF energy at $f = 100$ by 3.2 mhartree. The relative change in energies between the A and B isomers is minimal at the UHF level as observed from Fig. 4.4.
ground state description is improved by making a linear combination of symmetry-projected configuration constructed from a set of (generally non-orthogonal) deformed Slater determinants. Two different optimization procedures were described: a FED approach where only the last-added determinant is optimized (along with the full set of linear variational coefficients), and a RES approach where all the determinants are optimized at once.

Our work has shown that for molecular systems a FED approach tends to be more efficient than a RES approach in building ground state correlations, even if the latter yields a more elegant wavefunction. This is because convergence is easier and the optimization problem can be implemented with a linear computational cost in the number of transformations.

In the cases described in this chapter we observed that a few symmetry-projected configurations are sufficient to account for most of the correlations (both weak and strong) in simple molecular systems, such as the nitrogen and the water molecule. Near equilibrium, we can even obtain variational energies (in small basis sets) that are near the coupled-cluster ones.

Lastly, we revisited the copper oxide cores that we had considered in a previous work. By using a FED expansion in terms of symmetry-projected configurations with good spatial and spin symmetries we were able to improve our results yielding a linear isomerization path that is of comparable quality as those previously reported with RASPT2, CR-CC, or DMRG-SC-CTSD.

An interesting question that results from this work is to determine the most efficient prescription to account for these correlations. We have observed, for instance, that
two S-UHF configurations tend to give energies that are of similar quality as a single S-GHF configuration, while the latter involves a computational effort that is roughly two orders of magnitude larger. Given a determinantal expansion of a fixed size, letting all the determinants be independent will always afford the best description. Nevertheless, by constructing a same-size expansion in terms of the superposition of the Goldstone manifolds of fewer broken-symmetry states one may obtain a wavefunction that is near in quality to the former one. The latter has the virtues of respecting all symmetries of the Hamiltonian and being defined by a smaller number of computational parameters, thus becoming easier to optimize. Identifying those “efficient symmetries” is certainly of paramount importance for practical applications.
Figure 4.4: Relative total energy of $[\text{Cu}_2\text{O}_2]^{2+}$ along a linear isomerization path from B ($f = 0$) to A ($f = 100$). A variety of single symmetry-projected configuration methods are shown in the bottom panel, while a multi-reference FED approach based on $D_{2h}\text{S-UHF}$ is shown in the top panel. CR-CC data was extracted from Ref. [71], while DMRG data was taken from Ref. [73]. Calculations in the upper (lower) panel use Cartesian (spherical) Gaussian functions (see text).
Chapter 5

Excited states

In Chapter 3 we showed how a single symmetry-projected Slater determinant can be used as an ansatz for the ground state of a molecular system with a given set of quantum numbers. Then, in Chapter 4, we showed how such an ansatz can be improved by considering linear combinations of symmetry-projected states, optimized in chains of variational calculations.

In this chapter, we turn our attention to the description of the excited states of a system. It should be obvious that if the excited state has a different symmetry than the ground state, the approach described in the previous chapters can still be used. In other words, one can use the formalism described in Chapter 3 to obtain the ground state corresponding to any given set of quantum numbers.

It is less trivial to describe an excited state of the same symmetry as the ground state. The ansatz used must satisfy orthogonality with respect to the ground state wavefunction in order to provide an accurate description of an excited state. An unrestricted minimization of the symmetry-projected energy functional will most likely collapse to the solution already found.

One can propose two variational strategies to obtain an excited state in terms of (symmetry-projected) configurations:

- Enforce the orthogonality to the ground state by performing a constrained min-
imization. This is accomplished by minimizing a Lagrangian with a multiplier \( \lambda \) that enforces the orthogonality constraint

\[
L[\Psi] = E[\Psi] - \lambda \langle \Psi | \Psi_0 \rangle,
\]  

where \( | \Psi_0 \rangle \) is the ground state already available.

- Use an ansatz that is, by construction, explicitly orthogonal to the ground state.

We prefer the latter approach as it leads to an unconstrained minimization problem, which is typically easier to handle than a constrained minimization one. In the next section we discuss the excited VAMP strategy used to describe the excited states of a system using symmetry-projected HF configurations.

### 5.1 The excited VAMP strategy

Schmid and co-workers [8] introduced the excited VAMP (Variation After Mean Field Projection) strategy to describe the excited states of a nuclei in terms of symmetry projected configurations. This strategy has been successfully used in the nuclear physics community to interpret the spectroscopic features of complex nuclei [75, 6]. We have used this approach, which we proceed to describe in detail, in molecular calculations.

Let us assume that the symmetry-projected HF ground state, for a given set of quantum numbers \( j \), has already been obtained. This we write as

\[
| \Psi_0^{j,m} \rangle = | \psi_0^{j,m} \rangle = \sum_k \hat{P}_{mk} f_k^0 | \Phi_0 \rangle,
\]  

(5.2)
where the index 0 is used to denote that it corresponds to the ground state. $|\Phi_0\rangle$ corresponds to the broken symmetry Slater determinant used to construct $|\Psi_0^{j,m}\rangle$. The choice of notation will become clear shortly.

For the first excited state, we use the ansatz

$$
|\Psi_1^{j,m}\rangle = \left(1 - \hat{S}_1\right) |\psi_1^{j,m}\rangle = \left(1 - \hat{S}_1\right) \sum_k \hat{P}_{jk} f_1^k |\Phi_1\rangle
$$

in terms of the symmetry broken Slater determinant $|\Phi_1\rangle$ and the set of linear variational coefficients $f_1^k$. Here, the index 1 is used to emphasize that the first excited state is being considered. The projection operator

$$
\hat{S}_1 = |\psi_0^{j,m}\rangle \left(\langle \psi_0^{j,m}| \psi_0^{j,m}\rangle\right)^{-1} \langle \psi_0^{j,m}|
$$

is used to guarantee orthogonality with respect to the ground state (Eq. 5.2). Note that the ansatz used for the excited state is not a single symmetry-projected determinant, but rather is a linear combination of determinants. Nevertheless, the flexibility in the ansatz rests solely on the single symmetry-projected determinant $|\Phi_1\rangle$ and the coefficients $f_1^k$, both of them to be determined variationally.

This approach can be used for higher excited states. Let us suppose that we want to describe the $q$-th excited state after having constructed $q-1$ excited states in addition to the ground state. Our ansatz for the $q$-th excited state would be

$$
|\Psi_q^{j,m}\rangle = \left(1 - \hat{S}_q\right) |\psi_q^{j,m}\rangle = \left(1 - \hat{S}_q\right) \sum_k \hat{P}_{mk}^q f_q^k |\Phi_q\rangle,
$$

(5.5)
with the Slater determinant $|\Phi_q\rangle$ and the coefficients $f^q_k$ as variational parameters. Here,

$$\hat{S}_q = \sum_{r,s=0}^{q-1} |\psi^j_r^{,m}\rangle (A^{-1})_{rs} \langle \psi^j_s^{,m}|,$$

$$A_{rs} = \langle \psi^j_r^{,m}|\psi^j_s^{,m}\rangle. \tag{5.7}$$

Let us consider the variational optimization of the $q$-th excited state defined by the ansatz 5.5. The energy functional becomes

$$E^{j,m}[\Phi_q, \{f^q\}] = \frac{\langle \psi^j_q^{,m}| \left(1 - \hat{S}_q\right) \hat{H} \left(1 - \hat{S}_q\right) |\psi^j_q^{,m}\rangle}{\langle \psi^j_q^{,m}| \left(1 - \hat{S}_q\right) |\psi^j_q^{,m}\rangle}. \tag{5.8}$$

The variation with respect to the coefficients $f^q_k^*$ leads to the generalized eigenvalue problem

$$(H^q - E^q N^q) f^q = 0, \tag{5.9}$$

subject to the constraint

$$(f^q)^\dagger N^q f^q = 1_d, \tag{5.10}$$

where $d$ is the dimension of the corresponding irreducible representation. Here, the matrices $H^q$ and $N^q$ are given by

$$H^q_{kk'} = \langle \Phi_q |\hat{P}^j_{km} \left(1 - \hat{S}_q\right) \hat{H} \left(1 - \hat{S}_q\right) \hat{P}^j_{mk'}|\Phi_q\rangle, \tag{5.11}$$

$$N^q_{kk'} = \langle \Phi_q |\hat{P}^j_{km} \left(1 - \hat{S}_q\right) \hat{P}^j_{mk'}|\Phi_q\rangle. \tag{5.12}$$

We note that all matrix elements, though it would seem otherwise, can still be evaluated with a single projection operator. For instance, the overlap matrix elements can
be written as
\[
\mathcal{N}^{q}_{kk'} = \langle \Phi_{q} | \hat{P}_{km} \left( 1 - \hat{S}_{q} \right) \hat{P}_{mk'} | \Phi_{q} \rangle \\
= \langle \Phi_{q} | \hat{P}_{km} \hat{P}_{mk'} | \Phi_{q} \rangle \\
- \sum_{rs} \sum_{k_{1}k_{2}} \langle \Phi_{q} | \hat{P}_{km} \hat{P}_{mk_{2}} | \Phi_{r} \rangle (A^{-1})_{rs} \langle \Phi_{s} | \hat{P}_{k_{1}m} \hat{P}_{mk'} | \Phi_{q} \rangle f_{k_{2}}^{r} f_{k_{1}}^{s*} \\
= \langle \Phi_{q} | \hat{P}_{kk'} | \Phi_{q} \rangle - \sum_{rs} \sum_{k_{1}k_{2}} \langle \Phi_{q} | \hat{P}_{kk_{2}} | \Phi_{r} \rangle (A^{-1})_{rs} \langle \Phi_{s} | \hat{P}_{k_{1}k'} | \Phi_{q} \rangle f_{k_{2}}^{r} f_{k_{1}}^{s*}.
\]

The variational optimization with respect to the underlying HF transformation \(| \Phi_{q} \rangle\) can be done using a Thouless parametrization, as it was done in Section 3.5 for the standard symmetry projected HF state. The local gradient takes the form
\[
G_{ph} = \frac{\sum_{kk'} f_{k}^{q*} f_{k'}^{q} \langle \Phi_{q} | b_{k}^{l} b_{k'}^{l'} | \hat{H} | \psi_{j,m}^{l} \rangle - E_{t} \langle \psi_{j,m}^{l} | \psi_{j,m}^{l} \rangle}{\sum_{kk'} f_{k}^{q*} f_{k'}^{q} \langle \Phi_{q} | \hat{P}_{km} \left( 1 - \hat{S}_{q} \right) \hat{P}_{mk'} | \Phi_{q} \rangle}.
\]

All elements appearing in the above expression can also be evaluated with single projection operators. A self-consistent solution is achieved when the local gradient vanishes for all particle and hole indices.

Even though the states \(| \Psi_{l}^{j,m} \rangle | l = 0, \ldots, q \rangle\) obtained by the excited VAMP strategy are orthogonal amongst each other, they are not necessarily orthogonal through the Hamiltonian. One can, nevertheless, diagonalize the Hamiltonian in such a basis, or equivalently, in the basis of \(| \psi_{l}^{j,m} \rangle\) configurations. This leads to the generalized eigenvalue problem
\[
\sum_{r=0}^{m} \left[ \langle \psi_{r}^{j,m} | \hat{H} | \psi_{r}^{j,m} \rangle - E_{t} \langle \psi_{r}^{j,m} | \psi_{l}^{j,m} \rangle \right] g_{rt} = 0
\]
subject to the constraint
\[
g^\dagger \hat{N} g = 1_{q+1}.
\]
where $\tilde{N}$ is the overlap matrix among the $|\psi_{t}^{j,m}\rangle$ configurations and $E_t$ is the energy of the $t$-th state.

The wavefunctions thus obtained, with the form

$$|\eta_{t}^{j,m}\rangle = \sum_{r=0}^{m} |\psi_{r}^{j,m}\rangle g_{rt}$$

(5.16)

can account for additional correlations in the ground state wavefunction. As we shall see later on, the interaction may be strong in regions of the potential energy surface where, due to an avoided crossing, the ground state wavefunction changes character.

## 5.2 Correlations in excited states

When a one-determinant description of the ground state and each excited state is not sufficiently accurate, one can combine the FED or RES approaches described in Chapter 4 with the excited approach [5]. In this way, each state can be formally described by a linear combination of symmetry-projected configurations based on non-orthogonal HF transformations.

Just as for the ground state, the variational optimization with respect to the set of $n_q$ determinants describing the $q$-th excited state can be carried out all at once (RES) or one-at-a-time (FED). We will only consider the RES approach for simplicity; the FED approach can be also trivially constructed.

The variational ansatz for the $q$-th excited state in terms of $n_q$ symmetry-projected configurations is given by

$$|\Psi_{j,m}^{q}\rangle = \left(1 - \hat{S}_q\right) |\psi_{q,n_q}^{j,m}\rangle$$

$$= \left(1 - \hat{S}_q\right) \sum_{k} \sum_{l=1}^{n_q} \hat{P}_{mk}^{j} f_{lk}^{q} |\Phi_{l}^{q}\rangle,$$

(5.17)
where $|\Phi_q^l\rangle$ corresponds to the $l$-th configuration used to describe the $q$-th excited state. Here,
\begin{equation}
\hat{S}_q = \sum_{r,s=0}^{q-1} |\psi^{j,m}_{r,s}\rangle (A^{-1})_{rs} \langle \psi^{j,m}_{s,n_s}|,
\end{equation}
\begin{equation}
A_{rs} = \langle \psi^{j,m}_{r,n_r}| \psi^{j,m}_{s,n_s}\rangle.
\end{equation}

The energy functional for the $q$-th excited state becomes
\begin{equation}
E^j[\{\Phi_q\}, \{f^q\}] = \frac{\langle \psi^{j,m}_{q,n_q}| (1 - \hat{S}_q) \hat{H} (1 - \hat{S}_q) |\psi^{j,m}_{q,n_q}\rangle}{\langle \psi^{j,m}_{q,n_q}| 1 - \hat{S}_q |\psi^{j,m}_{q,n_q}\rangle}.
\end{equation}

The variation with respect to the coefficients $f_{lk}^{q*}$ leads to the generalized eigenvalue problem
\begin{equation}
(\mathcal{H}^q - E^q \mathcal{N}^q) f^q = 0,
\end{equation}
subject to the constraint
\begin{equation}
(f^q)^\dagger \mathcal{N}^q f^q = 1_h,
\end{equation}
where $h \leq n_q d$ is the number of linearly independent states obtained from the diagonalization of $\mathcal{N}^q$ and $d$ is the dimension of the irreducible representation associated with the symmetry projection. Here, the matrices $\mathcal{H}^q$ and $\mathcal{N}^q$ are given by
\begin{equation}
\mathcal{H}^q_{kl,k' l'} = \langle \Phi_q^l | \hat{P}^j_{km} \left(1 - \hat{S}_q\right) \hat{H} \left(1 - \hat{S}_q\right) \hat{P}^j_{mk'} |\Phi_q^{l'}\rangle,
\end{equation}
\begin{equation}
\mathcal{N}^q_{kl,k' l'} = \langle \Phi_q^l | \hat{P}^j_{km} \left(1 - \hat{S}_q\right) \hat{P}^j_{mk'} |\Phi_q^{l'}\rangle.
\end{equation}

The variational optimization with respect to the set of underlying HF transformations $\{|\Phi_q\rangle\}$ can be done using a Thouless-based parametrization. The local gradient with respect to the $l$-th determinant in the expansion takes the form
\begin{equation}
G_{ph}^l = -\frac{\sum_{k,k',l' k''} f_{lk}^{q*} f_{l' k'}^{q} \langle \Phi_q^l | \hat{b}^j_{h} b_p \hat{P}^j_{km} \left(1 - \hat{S}_q\right) \hat{H} \left(1 - \hat{S}_q\right) \hat{P}^j_{mk'} |\Phi_q^{l'}\rangle}{\sum_{k',l' k''} f_{l' k'}^{q*} f_{lk}^{q} \langle \Phi_q^{l''} | \hat{P}^j_{km} \left(1 - \hat{S}_q\right) \hat{P}^j_{mk'} |\Phi_q^{l''}\rangle}.
\end{equation}
A self-consistent solution is achieved when the local gradient vanishes for all particle and hole indices of all HF-type transformations.

We close this section by noting that a diagonalization of the Hamiltonian among the $q+1$ states obtained by an excited FED/RES strategy can be carried out in a similar fashion as that discussed for the excited VAMP strategy.

5.3 Applications to molecular systems

We have implemented the excited symmetry-projected HF approach described previously as part of our phfmol program. If a single symmetry-projected configuration is used to describe each state, the method scales linearly with the order of the state described. That is, the optimization of the first excited state is twice as expensive as that of the ground state.

We discuss the application of the method to two different systems: the dissociation profile of the carbon dimer and the vertical excitation spectrum of formaldehyde. In order to showcase the excited approach, we have to apply it to systems for which excited states of the same symmetry as the ground state are known. Unfortunately, we have not implemented the capability of evaluating oscillator strengths of the excited states, but it is straightforward to do so.

5.3.1 Dissociation profile of the carbon dimer

We consider the dissociation profile of the carbon dimer in the 6-31G(d) basis. Exact answers are available for this system from Ref. [76]. The dissociation of the carbon dimer is very challenging from a theoretical point of view: not only is a double-bond
being dissociated, but there is a low-lying excited state of the same-symmetry ($^1\Sigma_g^+$) as the ground state nearby in energy. In fact, an avoided crossing occurs at $\approx 1.7 \text{ Å}$, where the character of the two states is interchanged. In addition, there is also a low-lying $^1\Delta_g$ state that in fact becomes the ground state at large interatomic separation. Note that within the $D_{2h}$ subgroup available in most quantum chemical packages, the $^1\Sigma_g^+$ and the $^1\Delta_g$ states have the same symmetry: $^1A_g$.

An assessment of the ability of several sophisticated quantum chemical methods to describe the dissociation profile was presented in Refs. [76] and [77]. Most coupled-cluster approaches fail to provide even a qualitatively correct description of the dissociation profile of the ground state, with its characteristic non-Morse-like behavior due to the avoided crossing. Only multi-reference approaches such as CASPT2 (complete active-space second-order perturbation theory) or MRCI (multi-reference configuration interaction) can accurately describe the dissociation profile of all three states considered.

The dissociation profile of four low-lying singlet states of $C_2$ as predicted with the excited $D_{4h}$ S-UHF method is shown in Fig. 5.1. The use of the $D_{4h}$ subgroup allows us to distinguish between the $^1\Sigma_g^+$ and the $^1\Delta_g$ irreducible representations of the $D_{\infty h}$ group: the former becomes $A_{1g}$ while the latter has a $B_{1g}$ character. For the $^1A_{1g}$ states we show the profiles obtained before (top panel) and after (bottom panel) they are allowed to interact in the final diagonalization of Eq. 5.14.

Several features of the exact dissociation profile are displayed by our $D_{4h}$ S-UHF approximation. In particular, we observe that the $B_{1g}$ state is correctly predicted to be the lowest energy state for $r_{C-C} > 1.6 \text{ Å}$. The avoided crossing observed in the full CI profile appears after the final diagonalization of Eq. 5.14 is performed and the
symmetry-projected configurations are allowed to interact. Hence, the dissociation profile predicted for the lowest-lying $^1A_{1g}$ state correctly displays the characteristic non-Morse-like behavior. One should note, however, that the carbon-carbon distance of closest approach between the two $^1A_{1g}$ states is slightly larger than in the FCI solution. We finally point out that the curves obtained for the three states for which the FCI solution is available are fairly parallel to the latter. This validates our description of the ground and excited states of $C_2$ in terms of a few symmetry-projected configurations.

5.3.2 Vertical excitation spectrum of formaldehyde

Formaldehyde is the simplest of the carbonyl compounds and as such is ubiquitous in nature. The presence of a $\pi$-system and the lone pairs of oxygen permit $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ valence transitions, hence allowing formaldehyde to participate in photochemical reactions. Because of its small size, formaldehyde has been widely studied both experimentally and theoretically.

Some vertical excitation* transitions of formaldehyde have been experimentally determined (see Refs [78] and [79]). The vertical excitation spectrum of formaldehyde has been studied by several authors, both to help in the assignment of the spectrum, as well as to test different theoretical approaches. We refer the reader to the work by Hadad et al. [80], Pitarch-Ruiz et al. [81], and references therein. Recently, Schreiber et al. [82] have provided best-theoretical estimates for some low-energy valence and Rydberg transitions of formaldehyde.

---

* A vertical excitation corresponds to an electronic transition occurring at the ground state geometry, without a further geometry relaxation in the excited state.
Our focus here is to test whether our approach can provide reasonable excitation energies. In particular, we focus on the vertical excitation spectrum as we currently lack the ability to optimize the geometries of ground and excited states. We use the ground state $C_{2v} \text{ geometry from Ref. [80]}$ (optimized with MP2/6-31G(d), where MP2 corresponds to the many-body second-order perturbation theory). The basis set 6-311(2+,2+)G(d,p) we use was also obtained from the same work. This basis set should prove sufficiently accurate for an initial assessment of the quality of our method in describing both valence and Rydberg transitions.

In Fig. 5.2 we show how six different singlet $A_1$ states are obtained by the chain of variational calculations defined in the excited approach. Observe that the states are not necessarily obtained in a strict increasing-energy order. The right-most column shows the resulting set of states after the final diagonalization of Eq. 5.14 is carried out. In this particular case, the ground state gains almost no additional correlations as it is well separated from other states energetically. On the other hand, several of the states interact strongly as evidenced by the large differences observed from column 6 to the column labeled as “final”.

We show, in Fig. 5.3 the full low-lying singlet and triplet vertical spectrum of formaldehyde predicted with the $C_{2v}$S-UHF approach. A comparison with experimental results from Refs. [78] and [79] is also provided. As we have used a limited basis set and our treatment of electron correlation is only approximate, we cannot expect perfect agreement with experimental numbers.

The agreement between our $C_{2v}$S-UHF and the experimental results is remarkable, as each of the states depicted in Fig. 5.3 is described by essentially a single symmetry-projected configuration. By this we mean that, for a given symmetry, we have de-
scribed as many states as the number of symmetry-projected configurations used. There is no a priori reason to expect that all states should be well approximated by such a small number of configurations, or that the quality obtained for different symmetries should be the same. Nevertheless, the agreement with the experimental excitation energies is quite good, with maximum deviations of \( \approx 1 \) eV for both singlet and triplet states.

5.4 Concluding remarks

The spectrum of a molecular system constitutes the fingerprint of its quantum mechanical character. Characterization of the low-lying excited states of a system is of paramount importance in order to understand photochemical and photophysical processes occurring in nature. The ground state formalism discussed in previous chapters can be used to obtain the lowest-lying state of the system for each possible set of quantum numbers. On the other hand, accessing an excited state of the same symmetry as the ground state has always been challenging for variational strategies. This is because, if the optimization is carried out using the same formalism as that used for the ground state, a variational collapse is almost inevitable. In the formalism discussed in this chapter we circumvented this collapse by using an ansatz that is explicitly orthogonal to states of the same symmetry previously obtained.

In a nutshell, our formalism uses chain of variational calculations to characterize the low-lying excited states of a system with a given set of quantum numbers in terms of symmetry-projected configurations. The use of the latter implies that the wavefunctions thus obtained have a well defined set of quantum numbers. We have also described how one may go about building correlations in the excited states if
a single symmetry-projected configuration proves insufficient to account for all the correlations in a given state.

We have applied the excited VAMP formalism to describe the dissociation profile of the $\text{C}_2$ molecule and to characterize the low-lying spectrum of formaldehyde. Several features of the potential energy curve of the carbon dimer were correctly reproduced; in particular, the non-Morse shape of the lowest lying $A_1$ state is obtained after the two symmetry-projected configurations are allowed to interact. This constitutes the avoided crossing also observed with other multi-configurational methods such as MRCI or CASPT2. The low-lying singlet and triplet spectrum of formaldehyde was characterized and compared with available experimental adiabatic excitation energies. We observed a good agreement between our computed spectrum and the experimental one (all excitation energies are correct within a $\approx 1 \text{ eV}$ window). This is remarkable given that we have not accounted for thermal or zero-point energy corrections and that each state was essentially described by a single-symmetry projected configuration.

The methodology here considered can be applied to larger systems as it has mean-field cost. It may well prove superior to other methods that can describe excited states of large systems such as CIS (configuration interaction singles), TD-HF (time-dependent HF), or TD-DFT (time-dependent density functional theory). This is because each state can go beyond the singly-excited, particle-hole character assumed by these other methods.
Figure 5.1: Dissociation profiles for low-lying singlet states of the $C_2$ molecule computed with the $D_{4h}$S-UHF / 6-31G(d) method. A comparison with FCI curves from Ref. [76] is shown. The $D_{4h}$S-UHF profiles for the two $^1A_{1g}$ states as obtained before (top panel) and after (bottom panel) the diagonalization of Eq. 5.14 are displayed. The avoided crossing is correctly described by $D_{4h}$S-UHF in the bottom panel.
Figure 5.2: Evolution of the $^1A_1$ spectrum of formaldehyde as computed with the excited $C_{2v}$-S-UHF method with increasing number of symmetry-projected configurations. The last column shows the spectrum obtained after the final diagonalization of Eq. 5.14 is performed.
Figure 5.3: Low-lying singlet and triplet states of the formaldehyde molecule predicted with the $C_2v$-S-UHF method. The 6-311(2+,2+)G(d,p) basis was used in the calculations. Experimental excitation energies from Refs. [78] and [79] are shown as red and blue triangles for singlet and triplet states, respectively.
Chapter 6

The one-dimensional Hubbard model

In previous chapters we have discussed approximations to the ground and excited states of molecular systems in terms of symmetry-projected configurations. In this chapter, we apply the same machinery to a simpler Hamiltonian, the periodic one-dimensional Hubbard Hamiltonian introduced in Section 2.4. We work on this simpler model Hamiltonian in order to shed light on certain aspects of the symmetry-projected approximation that are easier to handle with simpler Hamiltonians such as the Hubbard model. Even though we will make some contact with the physics of the 1D Hubbard, the reader should keep in mind that it is not the purpose of this chapter to investigate the physics of the Hubbard model. Instead, we use the Hubbard model, for which the exact solution is known [10], in order to investigate the accuracy of the symmetry-projected approximation.

Some of the features that will be discussed are summarized next:

- The size-extensivity problem of symmetry-projected HF.

- Spin-spin correlations in the Hubbard model.

- The structure of the underlying determinants in symmetry-projected configurations is not arbitrary, but shows localized defects that can be associated to the quantum fluctuations in the system.

- The quality of the full low-lying spectrum for a small lattice.
6.1 The symmetries of the Hubbard Hamiltonian

Before applying the symmetry-projected machinery, we need to establish the symmetries of the model Hamiltonian of Eq. 2.10.

The Hubbard Hamiltonian is spin-independent and can thus be shown easily to commute with the square of the total spin-operator $\hat{S}^2$, as well as with any of its projections ($\hat{S}_x, \hat{S}_y, \hat{S}_z$). This allows us to use the full spin projection in the same way we used it for the molecular Hamiltonian.

The periodic one-dimensional lattice with $L$ sites has the same symmetry as an $L$-vertex polygon. That is, the spatial symmetry group of the Hamiltonian is the $D_L$ dihedral group. Calculations that restore the full dihedral group will use the acronym SG (SG = space group) attached to the name.

We note that there is an additional pseudo-spin symmetry [83, 9] in the case of half-filling (when there is one-electron per site). We have not considered the pseudo-spin symmetry or the full SO(4) group obtained by the product of the SU(2) spin group with the pseudo-spin group in our calculations. The pseudo-spin group is not independent of the particle number symmetry. It can only be broken, at the mean field level, by using Hartree–Fock–Bogoliubov states, which lies beyond the scope of the present work.

6.2 Size-extensivity and symmetry-projected HF

An approximate many-body method is considered size extensive if the energy is predicted to be extensive with respect to system size. That is, as the system size is
increased, the energy per volume should tend to a constant. Note that this is related with the size-consistency problem discussed before, but they are not the same as size-consistency involves non-interacting fragments. We note that HF can be shown to be size-extensive (as discussed below).

In order to explore the size-extensivity of symmetry-projected HF, we have performed calculations on a series of periodic Hubbard 1D lattices of increasing size, at half-filling (one-electron per site) and $U/t = 4$. The results are shown in Fig. 6.1.

In Fig. 6.1 we have considered the effects of spin projection (S), space-group projection (SG) and the combination of both (SGS). The top panel shows that as the lattice size is increased, the energy per site recovered by the symmetry-projected schemes increases, ultimately yielding the same energy per site as HF in the thermodynamic limit ($L \to \infty$). For small lattice sizes, symmetry projection recovers a large amount of the total correlation energy, here defined as

$$E_{\text{corr}} = E - E_{\text{UHF}}, \quad (6.1)$$

where $E$ is the energy predicted by a given method.

Interestingly, the energy per site in S-UHF increases linearly with system size for sufficiently large systems. This behavior was observed before in calculations on molecular Hamiltonians (see, e.g., Ref. [4]). The bottom panel provides another interesting look at the same data. The correlation energy in S-UHF tends to a constant, regardless of whether the calculation is done in a PAV or VAP framework. Once space-group projection is introduced, the correlation energy decreases with system size, but it does so at a less than linear ratio, which is why the total energy per site is eventually going back to HF.
Figure 6.1: Energy per site (top) and total correlation energy (Eq. 6.1) with respect to UHF (bottom) predicted by a variety of symmetry-projected HF methods on Hubbard lattices of increasing size $L$. Calculations were done at half-filling and $U/t=4$. The quantum numbers recovered are $S=0$ and $k=\pi$, with the state being symmetric under reflections of the lattice axis. The filled diamonds in S-UHF correspond to PAV results, while the open ones correspond to VAP results. The exact energies were obtained by solving the Lieb-Wu equations of Ref. [10].
The behavior just described for the symmetry-projected schemes is a reflection of the size-inextensivity of the methods: whereas the top panel of Fig. 6.1 shows that the HF and exact energies-per-site tend to a constant, the same figure shows that symmetry-projected schemes predict an increasing energy-per-site as the system size is enlarged.

One may wonder what happens if a multi-reference ground state is considered. We show in Fig. 6.2 the energy predicted in a FED SG-UHF approach for lattices of increasing size, when 1 and up to 4 determinants are used in the expansion. From the figure, it is evident that the multi-reference approach recovers more correlation than the single-reference. Nevertheless, if the system size is increased while keeping the number of determinants in the expansion constant, the method is not size-extensive. In other words, in order to maintain the quality of the wavefunction one needs a larger number of configurations for systems of increasing size. It would be interesting to know, at least in a simple case, how many configurations are needed in order to keep the energy per site constant. This, however, we are not in a position to answer at this time.

It is evident from Fig. 6.1 that space-group projection and spin projection provide a very different description of the ground state of the Hubbard model. In order to understand where this difference arises, one can look in the overlap among the states in the Goldstone manifold. That is, we consider

$$\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle$$

as a function of the group elements $\vartheta$ sampled in each of the different projections. For collinear spin projection, the Euler angle $\beta$ is used in the integration manifold,
Figure 6.2: Energy per site predicted by FED SG-UHF expansions for Hubbard lattices of increasing size $L$. The exact energies were obtained by solving the Lieb-Wu equations of Ref. [10].
whereas in the case of space group projection the group elements are generated by the allowed translations and reflections among the lattice sites.

We present in Fig. 6.3 the behavior of the overlap as a function of the group elements sampled in S-UHF. Fig 6.4 reports the corresponding behavior with SG-UHF. (The behavior of the Hamiltonian overlaps, not shown, is very similar to that of the overlaps, as the former are proportional to the latter [see Eq. B.18].) From Fig. 6.3, we see that as the system gets larger, the volume of $\beta$ actually contributing to the full overlap integral in the spin-projected method is reduced. This explains the size-inextensivity of S-UHF: as the system gets larger, the interaction between the states in the Goldstone manifold is reduced, eventually vanishing in the thermodynamic limit.

A different picture emerges if one considers the translations in space-group projection. We see that almost all translations contribute to the integral with equal weight (save for $T^0 = I$). As the lattice size increases, the overlap $\langle \Phi | \hat{T}^j | \Phi \rangle$ gets smaller, but the integration volume increases, reflecting the fact that there is a larger amount of allowed symmetry operations. This observed difference in behavior among states in the Goldstone manifolds defined by spin and space-group projection can be used to rationalize the qualitative differences observed in the correlation energy.

### 6.3 Spin-spin correlation function

Having described the behavior of the energy predicted by symmetry-projected methods for the one-dimensional Hubbard model, we now turn to other observables. Specifically, we intend to address whether other physical observables also suffer from the size extensivity problem discussed in the previous section.
Figure 6.3: Absolute value of the overlap among states in the Goldstone manifold defined by spin projection (S-UHF) for Hubbard lattices of increasing size. The overlap is plotted as a function of the Euler angle $\beta$. The calculation was carried out at half-filling and $U/t = 4$. Notice that as the lattice gets larger, the profile becomes more and more sharply peaked.
Figure 6.4: Absolute value of the overlap among states in the Goldstone manifold defined by space-group projection (SG-UHF) for Hubbard lattices of increasing size. Only translations by even-sites are used in the plot, as translations by odd-sites have a negligible overlap with the reference determinant. The calculation was performed at half-filling and $U/t = 4$. Notice that except for the singularity at $j/L = 0$ and $j/L = 1$, the profile is almost constant.
We consider in this section the magnetic structure factor $S(q)$ at $q = \pi$, defined as

$$S(q = \pi) = \sum_j (-)^j \langle \vec{S}_0 \cdot \vec{S}_j \rangle,$$

(6.2)

where $\vec{S}_i$ is a spin operator acting on site $i$ of the lattice.

It is known that the spin-spin correlation function in real-space, for a half-filled system, behaves as $\approx (\log j)^\sigma / j$ (with an anti-ferromagnetic structure) [84]. This implies that, as a function of lattice size, the magnetic structure factor $S(q = \pi)$ should behave as $(\log L)^{1+\sigma}$. Here, $\sigma$ is a logarithmic correction that can be obtained by studying sufficiently large lattices, and which we will be ignored in our discussion. In Fig. 6.5 we show the magnetic structure factor computed with UHF and a series of symmetry-projected HF methods. The “exact” results from the figure were obtained from a linear fit to DMRG (density-matrix renormalization group) calculations, carried out with the publicly available ALPS [85] code, for lattices of sizes 14, 18, 22, 26, and 30.

We observe that S-UHF follows closely the behavior of UHF, where the magnetic structure factor plotted as a function of $\log L$ diverges with a power $\alpha > 1$. (The exponent $\alpha \approx 6.5$ can be determined from the slope, for sufficiently large lattices, in the log-log plot shown as an inset.) On the other hand, space-group projection yields, for sufficiently small systems, an approximately linear behavior. For larger systems, nevertheless, SG-UHF and SGS-UHF start to track the UHF behavior. This is a reflection that the quality of the wavefunction deteriorates as the system size increases.
Figure 6.5: Magnetic structure factor ($S(q = \pi)$) computed with a variety of symmetry-projected HF methods on Hubbard lattices of increasing size $L$. The calculations were done at half-filling and $U/t = 4$. It is known that the magnetic structure factor should behave as $(\log L)^{1+\sigma}$, where $\sigma$ is a small correction. For sufficiently small lattices, SG-SUHF displays a quasi-linear behavior, but then it follows UHF (just as S-UHF and SG-UHF do) and diverges. The “exact” behavior was obtained by fitting DMRG data for small lattices. The inset shows a log-log plot of the UHF data from the full figure.


6.4 Structure of the reference determinants

As we have described before, the (single-configuration) symmetry-projected HF states are fully characterized by the underlying broken symmetry Slater determinant $|\Phi\rangle$. The symmetry-projected HF approach has therefore not lost all the connection with the single-particle picture that allows one to easily grasp the physics in the wavefunction. In this section, we compare the structure of the intrinsic determinant obtained from symmetry-projected HF approximations with the standard HF approach. In particular, we are interested in detecting whether there is any physical meaning behind the structure of the deformed determinant.

In Fig. 6.6 we show a comparison of the structure of the deformed determinants for calculations on an $L = 128$ Hubbard lattice at half-filling and $U/t = 4$. The structure of the HF state is almost fully governed by an anti-ferromagnetic alignment of localized spins at each site. We have exploited this structure in order to produce an easy-to-read plot. Here, the dot product between the spin at site $j$ and that at site 1 is plotted as a function of the site index $j$. We have removed an overall anti-ferromagnetic factor in order to render the curves smoother. HF (UHF) predicts a spin-density wave of amplitude $\approx 0.15$. S-UHF predicts almost the same structure for the reference determinant. Once space-group projection is introduced, the determinant obtained from a VAP approach displays well localized solitonic defects in the spin-density wave. These are not present in the PAV description, as the reference determinant is identical to the HF one. The position of the defect is unimportant, as the space-group projection operator will make it travel around in order to restore the translational invariance of the symmetry-projected wavefunction. The localized defects introduced once the optimization is carried out in the presence of the projec-
Figure 6.6: Structure of the underlying deformed determinant obtained from a variety of symmetry-projected HF methods for a Hubbard lattice of $L = 128$ sites at half-filling and $U/t = 4$. Here, the dot product of the spin expectation value between site $j$ and site 1 is plotted as a function of the lattice site. An overall antiferromagnetic factor $(-1)^j$ is included in order to render the curves smoother. The UHF and S-UHF curves are almost indistinguishable. Notice the localized sharp defects in the spin-density wave introduced by the space-group projection.

6.5 Low-lying spectrum of small lattices

For sufficiently small Hubbard lattices, one can carry out an exact diagonalization of the Hubbard Hamiltonian in order to obtain the full low-lying spectrum. This is
useful as it provides a direct comparison with the quality of the spectrum predicted by symmetry-projected HF methods. Moreover, in both cases all the states can be characterized by their full set of quantum numbers.

We have performed an exact diagonalization, using an in-house code, for a 10-site Hubbard lattice at half-filling and $U/t = 4$. Similarly, we have obtained the lowest-lying singlet and triplet states (two singlets and two triplets) for each allowed irreducible representation with the SGS-GHF method. We have used a single SGS-GHF configuration to describe each state. A comparison of the results is shown in Fig. 6.7, where the states are ordered according to their momentum eigenvalue. The right panel shows the deviations between the SGS-GHF and the exact diagonalization energies. Except for a single outlier, all other states are correct to within $0.02 \, t$, which demonstrates the quality of the predicted spectrum.

### 6.6 Concluding remarks

In this chapter, we have applied the symmetry-projected approach to a model Hamiltonian, namely the one-dimensional periodic Hubbard Hamiltonian. Due to its simplicity, this allowed us to explore certain aspects of the symmetry-projected approach that would have been more difficult even in simple molecular systems.

We showed that the energy predicted by symmetry-projected HF is not size-extensive. That is, whereas the percentage of the correlation energy recovered by a symmetry-projected ansatz can be quite large for small systems, it decays to zero in the thermodynamic limit even for ordered systems: the same energy-per-site is obtained as in the symmetry-broken HF approach. This fact can be understood by looking at
Figure 6.7: Low-lying spectrum of a 10-site Hubbard lattice at half-filling and $U/t = 4$ as predicted with SG-SGHF (left) and deviations from the exact diagonalization energies (right). Two states of each irreducible representation have been obtained with the excited VAMP approach. The $+$, $-$ signs displayed for states with $k = 0, \pi$ denote the character of the state under reflections of the lattice axis. The exact diagonalization spectrum would overlap almost exactly on top of the SG-SGHF one as evidenced by the magnitude of the deviations shown in the right panel.
the overlap among the different determinants in the Goldstone manifold. As the system size increases, the overlap among those determinants tends to vanish. We observed, nevertheless, that spin projection and spatial-symmetry (space-group) projection yield very different behavior. The differences can again be understood by looking at the structure of the associated Goldstone manifolds. Interestingly, we do obtain a decreasing correlation energy with space-group projection as the system size increases, yet it does not scale linearly with system size as would be required for the method to be size extensive. A multi-configuration approach can be used to fix the size-extensivity problem, but an increasingly larger number of configurations is required as the system is enlarged.

We then considered the magnetic structure factor as an example of an observable that reflects the physics of the one-dimensional Hubbard chain. As the system size increases, the quality of the predicted magnetic structure factor deteriorates in the same way as the energy, eventually tracking the behavior of the Hartree-Fock.

The real-space structure of the deformed determinants was explored. When space-group projection is carried out in a variation-after-projection framework, a characteristic solitonic structure appears. Thus the symmetry-projected wavefunction is composed of determinants with local quantum fluctuations (which break the spin-density wave character of the HF solution) superposed in such a way as to recover the symmetry of the Hamiltonian.

Lastly, we have considered the full low-lying spectrum of a 10-site one-dimensional Hubbard chain. In this case, we obtained through an excited formalism constructed in terms of single symmetry-projected configurations, a low-lying spectrum in excellent quantitative agreement with that obtained from an exact diagonalization.
Chapter 7

Conclusions and outlook

The molecular Hamiltonian possesses certain symmetries that are useful in classifying its eigenstates, both from the theoretical and the experimental point of view. When approximate wavefunctions are used, in particular the HF method, imposing the symmetries of the Hamiltonian introduces constraints that can only raise the energy. In molecular systems that develop strong correlation, HF typically yields a lower energy when symmetry-breaking is permitted. This symmetry breaking allows the mean-field approximation to capture some of the strong correlations associated with the appearance of exact or near degeneracies. On the other hand, the symmetry-broken state becomes unphysical and displays incorrect qualitative features.

Since 1955, Löwdin suggested the use of a symmetry-projected HF ansatz for the ground state of a molecular system. This ansatz can capture the strong correlations captured by the symmetry-broken mean field while at the same time cleaning up the wavefunction in order to obtain the correct quantum numbers. In doing so, often even more correlations are captured. The symmetry-projected HF wavefunction remains, however, easy to grasp as it is completely determined by the structure of the underlying broken-symmetry determinant. All these reasons make this ansatz particularly appealing.

After decades of work in the quantum chemistry community, the spin-projected HF method was mostly discarded due to the difficulty of evaluating the associated ener-
gies and the realization that the method does not yield size-consistent results, even when carried out self-consistently. In addition, the speculation by Löwdin that a symmetry-projected approach could capture $\approx 95\%$ of the correlation energy in molecular systems near equilibrium turned out to be incorrect. We emphasize that the self-consistent optimization is crucial in cases where the system does not spontaneously breaks symmetry or it does not develop strong deformations. In such cases, the results obtained from a projection-after-variation and variation-after-projection formalisms can be quite different.

In this work, we have presented an efficient scheme to carry out symmetry-projected HF calculations in molecular systems using robust numerical methods first introduced in the nuclear physics community. The structure of the projection operators used, simpler than those introduced by Löwdin and long used in quantum chemistry, is crucial in rendering the method efficient. We have presented self-consistent calculations on molecular systems using spin, point-group, and complex conjugation projection. All the symmetries (except for particle number) have been broken and restored in a projection-after-variation formalism. Our results are consistent with previous results which showed that symmetry-projected HF can account for a large fraction of the correlation in sufficiently small systems. The method, is however, neither size-consistent nor size-extensive.

In a subsequent chapter, we have considered two approaches that build ground-state correlations beyond those capture by the symmetry-projected ansatz. In essence, a multi-configurational approach based on symmetry-projected configurations can quickly capture the strong and dynamical correlations in molecular systems, as shown in several examples. As the system size increases, more configurations are needed in order to maintain the quality of the wavefunction. We want to emphasize that both
of the approaches considered, a FED and a RES expansion, are exact in the limit where the number of configurations is sufficient to sample the entire Hilbert space of the problem. We discussed how the methods could become practical workhorses in quantum chemistry if the “efficient symmetries” are identified and good guesses can be prepared for the multi-configurational ansatz.

Even though an accurate ground-state formalism is always welcomed, a quantum mechanical system is characterized by its discrete spectrum. We have discussed an efficient approach to describe excited states of the same-symmetry as the ground state. This approach uses chains of variational calculations based on symmetry-projected configurations. Our results suggest that this approach can yield an accurate representation of the low-lying spectrum of molecular systems, even in situations where the excitations do not have a particle-hole character. Furthermore, one can introduce correlations both in the ground- and excited states by using a multi-configurational approach.

Following the above strategy, the ground state and low-lying states are approximated in terms of a few symmetry-projected configurations defined in terms of broken symmetry Slater determinants. An interesting question to address is whether there is any physics behind the structure of the broken symmetry determinants optimized self-consistently. We have observed hints of it by applying the method to the one-dimensional Hubbard model. If spatial symmetry-projection is carried out, localized solitonic defects are observed in an otherwise antiferromagnetic spin-density wave obtained by HF. These defects can be regarded as basic units of quantum fluctuations.

We believe that the methods described in this work deserve further consideration in the quantum chemistry community. With them, one can obtain the full low-lying
spectrum of a given system where each state has well-defined quantum numbers. Because it is a true wavefunction, variational approach, all properties can be evaluated straightforwardly. The methods can be used in situations where strong correlations are dominant or when there are competing strong and weak correlations. In this sense, they may be complementary to other common techniques among quantum chemists.
Appendix A

Thouless’ theorem

In this appendix, we provide a proof of the theorem due to Thouless [86] relating two non-orthogonal \(N\)-particle Slater determinants. This is used in the derivation of the expressions for matrix elements between non-orthogonal Slater determinants (see Appendix B) and in the optimization of (symmetry projected) HF states (see section 3.5). Our proof of Thouless’ theorem closely follows that provided by Ring and Schuck [18] for quasi-particle (Hartree–Fock–Bogoliubov) states.

Consider an \(N\)-particle Slater determinant \(\ket{\Phi}\) which is a vacuum to the operators \(\{b_h^\dagger \mid h = 1, \ldots, N\}\) and \(\{b_p^\dagger \mid p = N + 1, \ldots, M\}\). It may be represented as

\[
\ket{\Phi} = \prod_{h=1}^{N} b_h^\dagger \ket{-},
\]

where \(\ket{-}\) is the bare fermion vacuum.

**Theorem.** Any \(N\)-particle Slater determinant \(\ket{\Phi_0}\) which is not orthogonal to \(\ket{\Phi}\) may be written as

\[
\ket{\Phi_0} = \mathcal{N} \exp \left( \sum_{p=N+1}^{M} \sum_{h=1}^{N} Z_{ph} b_p^\dagger b_h \right) \ket{\Phi},
\]

where the coefficients \(Z_{ph}\) are unique. Conversely, any wave function given by A.2, with \(\ket{\Phi}\) given by A.1, is an \(N\)-particle Slater determinant. Here, \(\mathcal{N} = \bra{\Phi} \Phi_0 \rangle\) is a normalization constant.
In order to prove the theorem, we start from the condition that both $|\Phi\rangle$ and $|\Phi_0\rangle$ are $N$-particle Slater determinants. $|\Phi_0\rangle$ is constructed as a vacuum to the operators $\{b_0^0 | h = 1, \ldots, N\}$ and $\{b_p^0 | p = N + 1, \ldots, M\}$. Both sets of operators ($\{b_h^\dagger, b_p\}$, $\{b_h^0, b_p^0\}$) satisfy the anti-commutation rules defined by Eq. 2.13. These operators are related to the elementary fermion operators according to

\begin{align}
  b_0^\dagger &= \sum_j D_{j0}^* c_j^\dagger, \quad (A.3a) \\
  b_0^0 &= \sum_j D_{j0} c_j^\dagger, \quad (A.3b)
\end{align}

where we have used the index $q$ to generically refer to hole or particle states.

We can now relate $\{b_h^0, b_p^0\}$ to $\{b_h^\dagger, b_p\}$ by using the inverse HF transformation (Eq. 2.15). This leads to

\begin{align}
  b_h^0 &= \sum_{h'} L_{h'h}^* b_{h'}^\dagger + \sum_p Y_{ph}^* b_p^\dagger, \quad (A.4a) \\
  b_p^0 &= \sum_{p'} M_{p'p} b_{p'}^\dagger + \sum_h \tilde{Y}_{hp} b_h, \quad (A.4b)
\end{align}

where we have set

\begin{align}
  L_{h'h} &= (D^\dagger D^0)_{h'h}, \quad (A.5a) \\
  M_{p'p} &= (D^\dagger D^0)_{p'p}, \quad (A.5b) \\
  Y_{ph} &= (D^\dagger D^0)_{ph}, \quad (A.5c) \\
  \tilde{Y}_{hp} &= (D^\dagger D^0)_{hp}. \quad (A.5d)
\end{align}

We will now assume that the $N \times N$ matrix $L$ is invertible, which is only true if $\langle \Phi | \Phi_0 \rangle \neq 0$ (see Appendix B). We will see below that if $L$ is invertible, $M$ too must
be invertible. We now introduce the operators

\[
\tilde{b}_h^0 = \sum_{h'} (L^{s-1})_{h'h} b_{h'}^0, \quad \text{(A.6a)}
\]

\[
\tilde{b}_p^0 = \sum_{p'} (M^{-1})_{p'p} b_{p'}^0. \quad \text{(A.6b)}
\]

Substituting Eq. A.4 into Eq. A.6, we arrive at

\[
\tilde{b}_h^0 = b_h^0 + \sum_{p} Z_{ph} b_{p}^\dagger, \quad \text{(A.7a)}
\]

\[
\tilde{b}_p^0 = b_p + \sum_{h} W_{ph} b_{h}, \quad \text{(A.7b)}
\]

where we have set

\[
Z_{ph} = \sum_{h'} Y_{ph'}^* (L^{s-1})_{h'h}, \quad \text{(A.8a)}
\]

\[
W_{ph} = \sum_{p'} \tilde{Y}_{hp'} (M^{-1})_{p'p}. \quad \text{(A.8b)}
\]

By explicit computation of the anti-commutation rules among the operators \{\tilde{b}_h^0, \tilde{b}_p^0\}, one can readily conclude that \(W = -Z\). This also implies that if \(L\) is invertible, so is \(M\). The transformed operators become

\[
\tilde{b}_h^0 = b_h^0 + \sum_{p} Z_{ph} b_{p}^\dagger, \quad \text{(A.9a)}
\]

\[
\tilde{b}_p^0 = b_p - \sum_{h} Z_{ph} b_{h}, \quad \text{(A.9b)}
\]

We are now in a position to investigate whether the transformed operators, defined by Eq. A.9, annihilate the state defined by the r.h.s. of Eq. A.2. Before attempting to do so, we evaluate the commutators

\[
\left[ b_{h}, \exp \left( \sum_{p' h'} Z_{p'h'} b_{p'}^\dagger b_{h'} \right) \right] = \left( -\sum_{p} Z_{ph} b_{p}^\dagger \right) \exp \left( \sum_{p' h'} Z_{p'h'} b_{p'}^\dagger b_{h'} \right), \quad \text{(A.10a)}
\]

\[
\left[ b_{p}, \exp \left( \sum_{p' h'} Z_{p'h'} b_{p'}^\dagger b_{h'} \right) \right] = \left( +\sum_{h} Z_{ph} b_{h} \right) \exp \left( \sum_{p' h'} Z_{p'h'} b_{p'}^\dagger b_{h'} \right). \quad \text{(A.10b)}
\]
We can now evaluate the action of the operators from Eq. A.9 on the state from the r.h.s. of Eq. A.2

\[
\tilde{b}^{\dagger}_{h} \exp \left( \sum_{ph} Z_{ph} b^{\dagger}_{p} b_{h} \right) |\Phi\rangle = \left( - \sum_{p} Z_{ph} b^{\dagger}_{p} + \sum_{p} Z_{ph} b^{\dagger}_{p} \right) \exp \left( \sum_{p',h'} Z_{p'h'} b^{\dagger}_{p'} b_{h'} \right) |\Phi\rangle = 0, \quad (A.11a)
\]

\[
\tilde{b}_{p} \exp \left( \sum_{ph} Z_{ph} b^{\dagger}_{p} b_{h} \right) |\Phi\rangle = \left( + \sum_{h} Z_{ph} b_{h} - \sum_{h} Z_{ph} b_{h} \right) \exp \left( \sum_{p',h'} Z_{p'h'} b^{\dagger}_{p'} b_{h'} \right) |\Phi\rangle = 0. \quad (A.11b)
\]

This essentially completes the proof. \( \{\tilde{b}^{\dagger}_{h}, \tilde{b}_{p}\} \) annihilate the r.h.s. of Eq. A.2. The operators \( \{b^{\dagger}_{h}, b_{p}\} \) that kill the state \( |\Phi_{0}\rangle \) on the l.h.s. of Eq. A.2 are simple linear combinations of \( \{\tilde{b}^{\dagger}_{h}, \tilde{b}_{p}\} \); N-particle Slater determinants built from either sets of operators are the same up to a normalization factor.
Appendix B

Matrix elements between non-orthogonal Slater determinants

This appendix discusses the evaluation of matrix elements between non-orthogonal Slater determinants. The expressions derived are used in the evaluation of expectation values with symmetry-projected states, as well as in all types of configuration mixing approaches. Our derivation of the expressions for matrix elements follows that provided by Ring and Schuck [18]. We point the interested reader to the work by Balian and Brezin [87], which used non-unitary canonical transformations to evaluate matrix elements between non-orthogonal quasi-particle (Hartree–Fock–Bogoliubov) states.

The most important result discussed in this appendix is the fact that Wick’s theorem [11] can be used to evaluate matrix elements between non-orthogonal determinants, as shown by the work of Balian and Brezin [87]. This non-intuitive condition permits the evaluation of arbitrarily complicated matrix elements solely in terms of a transition density matrix, simplifying greatly the task at hand.

We consider two non-orthogonal \(N\)-particle Slater determinants, \(\{\Phi_i\} | i = 1, 2\), each of them a vacuum to the operators \(\{b_h^{\dagger} | h = 1, \ldots, N\}\) and \(\{b_p | p = N + 1, \ldots, M\}\). The Slater determinants may be represented as

\[
|\Phi_i\rangle = \prod_{h=1}^{N} b_h^{\dagger} |\rangle - \rangle, \tag{B.1}
\]
where $|−\rangle$ is the bare fermion vacuum. The operators just referred to are expressed as linear combinations of the elementary fermion operators. That is,

$$b_q^\dagger = \sum_j D_{jq}^* c_j^\dagger,$$

(B.2)

where we have used the index $q$ to generically refer to hole or particle states. In what follows, we assume that the operators $\{c_j \mid j = 1, \ldots, M\}$ obey standard fermion anti-commutation rules.

## B.1 Norm overlap

The overlap between two $N$-particle Slater determinants can be obtained by application of Wick’s theorem on the bare fermion vacuum. That is,

$$\langle \Phi_1|\Phi_2 \rangle = \langle |−\rangle | b_N^\dagger b_{N-1}^\dagger \cdots b_1^\dagger |\rangle = \det M,

(B.3)$$

where $M_{ij} = \sqrt{\langle b_i^\dagger b_j^\dagger \rangle}$, with other possible contractions vanishing. Matrix elements of $M$ can be easily evaluated as

$$\sqrt{\langle b_i^\dagger b_j^\dagger \rangle} = \sum_{m_1 m_2} D_{m_1 i}^1 D_{m_2 j}^{2*} \sqrt{\langle c_{m_1}^\dagger c_{m_2}^\dagger \rangle}

= \sum_{m_1 m_2} D_{m_1 i}^1 D_{m_2 j}^{2*} \langle |c_{m_1} c_{m_2}^\dagger |\rangle

= \sum_m D_{m_1}^1 D_{m_2}^{2*}.

(B.4)$$

Our final expression for the overlap between $N$-particle Slater determinants is

$$\langle \Phi_1|\Phi_2 \rangle = \det_N (D^1^\text{T} D^{2*}),$$

(B.5)
where $D^1$ and $D^2$ are $M \times N$ matrices (of occupied orbitals) and therefore the determinant is evaluated over an $N \times N$ matrix. We have emphasized this with the notation $\det_N$.

**B.2 Operator matrix elements**

Consider now the expectation value

$$\langle \Phi_1 | c_{l_1}^{\dagger} \cdots c_{l_p}^{\dagger} c_{k_1} \cdots c_{k_p} | \Phi_2 \rangle$$

(B.6)

between the non-orthogonal Slater determinants $\{ | \Phi_i \rangle | i = 1,2 \}$. Trivially, the number of creation and annihilation operators in the string of field operators has to be the same in order for the matrix element not to vanish.

Because the states $\{ | \Phi_i \rangle | i = 1,2 \}$ are not orthogonal, we can use Thouless’ theorem (see Appendix A) to write $| \Phi_2 \rangle$ as

$$| \Phi_2 \rangle = \exp(\hat{Z}) | \Phi_1 \rangle \langle \Phi_1 | \Phi_2 \rangle,$$

(B.7)

$$\hat{Z} = \sum_{ph} \mathcal{Z}_{ph} b_p^{\dagger} b_p^1.$$  

(B.8)

Similarly, making use of the vacuum properties of the operators $\{ b_p^1 \}$, we can express $\langle \Phi_1 |$ as

$$\langle \Phi_1 | = \langle \Phi_1 | \exp(-\hat{Z}).$$

(B.9)

It follows that the matrix element from Eq. B.6 can be evaluated as

$$\langle \Phi_1 | c_{l_1}^{\dagger} \cdots c_{l_p}^{\dagger} c_{k_1} \cdots c_{k_p} | \Phi_2 \rangle$$

$$= \langle \Phi_1 | \Phi_2 \rangle \langle \Phi_1 | \exp(-\hat{Z}) c_{l_1}^{\dagger} \cdots c_{l_p}^{\dagger} c_{k_1} \cdots c_{k_p} \exp(\hat{Z}) | \Phi_1 \rangle$$

$$= \langle \Phi_1 | \Phi_2 \rangle \langle \Phi_1 | d_{l_1} \cdots d_{l_p} d_{k_1} \cdots d_{k_p} | \Phi_1 \rangle,$$

(B.10)
where we have introduced the operators

\[ \tilde{d}_l = \exp(-\hat{Z}) c_l^\dagger \exp(\hat{Z}), \quad (B.11a) \]
\[ d_k = \exp(-\hat{Z}) c_k \exp(\hat{Z}), \quad (B.11b) \]

Using the inverse of the HF transformation (Eq. 2.15), we express the operators \{\tilde{d}_l\} and \{d_k\} in terms of the operators \{b_{1h}^{\dagger}\} and \{b_{1p}^{\dagger}\} that annihilate the state \|\Phi_1\rangle:

\[ \tilde{d}_l = \exp(-\hat{Z}) c_l^\dagger \exp(\hat{Z}) = c_l^\dagger - [\hat{Z}, c_l^\dagger] \]
\[ \quad = \sum_h D^{1\dagger}_{ih} b_h^{\dagger} + \sum_p \left( D_{ip}^{1\dagger} - \sum_h Z_{ph} D_{ih}^{1\dagger} \right) b_p^{\dagger}, \quad (B.12a) \]
\[ d_k = \exp(-\hat{Z}) c_k \exp(\hat{Z}) = c_k - [\hat{Z}, c_k] \]
\[ \quad = \sum_h \left( D_{kh}^{1\dagger} + \sum_p Z_{ph} D_{kp}^{1\dagger} \right) b_h^{\dagger} + \sum_p D_{kp}^{1\dagger} b_p^{\dagger}. \quad (B.12b) \]

Because \{\tilde{d}_l, d_k\} are given as linear combinations of \{b_{1h}^{\dagger}, b_{1p}^{\dagger}\} which annihilate \|\Phi_1\rangle, Wick’s theorem [11] can be used to evaluate the corresponding matrix elements. The non-vanishing contractions among the operators \{b_{1h}^{\dagger}, b_{1p}^{\dagger}\} are easily found to be

\[ \overline{b_h^{\dagger} b_{h'}^{\dagger}} = \delta_{hh'}, \quad (B.13a) \]
\[ \overline{b_p^{\dagger} b_{p'}^{\dagger}} = \delta_{pp'}. \quad (B.13b) \]

It follows that the non-vanishing contractions among the operators \{\tilde{d}_l, d_k\} are of the
form

\[ \tilde{d}_l \tilde{d}_k = \sum_{hh'} D_{lh} \left( D_{kh'}^{1*} + \sum_p Z_{p,h'} D_{kp}^{1*} \right) \delta_{hh'} \]

\[ = \sum_h D_{lh} D_{kh}^{1*} + \sum_{ph} D_{lh} Z_{ph} D_{kp}^{1*}, \tag{B.14a} \]

\[ \tilde{d}_l d_k = \sum_{pp'} D_{lp}^{1*} \left( D_{kp'}^{1} - \sum_h Z_{p',h} D_{kh}^{1} \right) \delta_{pp'} \]

\[ = \sum_p D_{lp}^{1*} D_{kp}^{1} - \sum_{ph} D_{lp}^{1*} Z_{ph} D_{kh}^{1}. \tag{B.14b} \]

All matrix elements of the form of Eq. B.6 can be evaluated in terms of the transition density matrix \( \rho_{12} \) given by

\[ \rho_{kl}^{12} = \frac{\langle \Phi_1 | c_i^† c_k | \Phi_2 \rangle}{\langle \Phi_1 | \Phi_2 \rangle} = \langle \Phi_1 | \exp(-\hat{Z}) c_i^† c_k \exp(\hat{Z}) | \Phi_1 \rangle \]

\[ = \sum_h D_{lh} D_{kh}^{1*} + \sum_{ph} D_{lh} Z_{ph} D_{kp}^{1*}, \tag{B.15} \]

where

\[ Z_{ph} = \sum_{h'} (D_{1T} D_{2}^{2*})_{ph'} (\mathcal{L}^{s-1})_{h'h}, \tag{B.16a} \]

\[ \mathcal{L}_{h'h} = (D_{1T} D_{2})_{h'h}. \tag{B.16b} \]

Here, we have used Eqs. A.5 and A.8a to provide the explicit forms of \( Z \) and \( \mathcal{L} \).

**Hamiltonian expectation value**

As an example of the application of the above equations, let us now consider the Hamiltonian expectation value among two non-orthogonal Slater determinants |\( \Phi_1 \rangle \) and |\( \Phi_2 \rangle \). Given a two-body Hamiltonian in the usual second-quantized form

\[ \hat{H} = \sum_{ik} \langle i|\hat{h}|k \rangle c_i^† c_k + \frac{1}{4} \sum_{ijkl} \langle ij|\hat{v}|kl \rangle c_i^† c_j^† c_l c_k, \tag{B.17} \]
the Hamiltonian matrix element can be evaluated as

\[
\frac{\langle \Phi_1 | \hat{H} | \Phi_2 \rangle}{\langle \Phi_1 | \Phi_2 \rangle} = \sum_{ik} h_{ik} \rho^{12}_{ki} + \frac{1}{2} \sum_{ijkl} \langle ij | \hat{v} | kl \rangle \rho^{12}_{ki} \rho^{12}_{lj} 
\]

\[= \text{Tr} \left( h \rho^{12} + \frac{1}{2} \Gamma^{12} \rho^{12} \right), \quad (B.18)\]

where

\[\Gamma^{12}_{ik} = \sum_{jl} \langle ij | \hat{v} | kl \rangle \rho^{12}_{lj}. \quad (B.19)\]

Here, \(\rho^{12}\) has the form provided in Eq. B.15.
Appendix C

Stability condition for symmetry-projected HF solutions

In this appendix, we consider the stability matrix (Hessian matrix) for symmetry-projected HF states with respect to variations of the underlying symmetry-broken HF state. For standard Hartree–Fock states, the stability problem was first considered by Thouless [86].

We note that, in minimizing the energy expression, we guarantee that we arrive at a stationary point in the multi-dimensional space defined by the orbital rotation parameters. It is, nevertheless, convenient to establish that it is indeed a local minimum. A positive definite Hessian matrix, or second derivative matrix, is a necessary and sufficient condition for the solution to be a local minimum.

In order to derive the form of the Hessian matrix, we consider the form of the symmetry-projected energy described in Sec. 3.5, that is, the one given by Eq. 3.33.

The Hessian matrix takes the form

\[ H = \begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}, \tag{C.1} \]

where

\[ A_{ai,bj} = \frac{\partial^2}{\partial Z_{ai} \partial Z_{bj}} E^j[Z] \bigg|_{Z=0}, \tag{C.2} \]

\[ B_{ai,bj} = \frac{\partial^2}{\partial Z_{ai}^* \partial Z_{bj}^*} E^j[Z] \bigg|_{Z=0}, \tag{C.3} \]
where we have used $a, b$ for particle indices and $i, j$ for hole indices.

The matrix elements of $A$ and $B$ are given by

$$A_{ai,bj} = K_{ai,bj} - E_j N_{ai,bj} - K_{ai,0} N_{bj,0}^* - N_{ai,0} K_{bj,0}^* + 2 E_j N_{ai,0} N_{bj,0}^*.$$  \hspace{1cm} (C.4)  

$$B_{ai,bj} = K_{ai,bj} - E_j N_{ai,bj} - K_{ai,0} N_{bj,0} - N_{ai,0} K_{bj,0} + 2 E_j N_{ai,0} N_{bj,0}.$$  \hspace{1cm} (C.5)

Here, we have used the definitions

$$N_{ai,0} = \frac{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{b}_{i}^\dagger b_{a} \hat{P}_{kk'}^{j} | \Phi \rangle}{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{P}_{kk'}^{j} | \Phi \rangle},$$  \hspace{1cm} (C.6)  

$$K_{ai,0} = \frac{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{b}_{i}^\dagger b_{a} \hat{H} \hat{P}_{kk'}^{j} | \Phi \rangle}{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{P}_{kk'}^{j} | \Phi \rangle},$$  \hspace{1cm} (C.7)  

$$N_{ai,bj} = \frac{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{b}_{i}^\dagger b_{a} \hat{P}_{kk'}^{j} \hat{b}_{j}^\dagger b_{b} | \Phi \rangle}{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{P}_{kk'}^{j} | \Phi \rangle},$$  \hspace{1cm} (C.8)  

$$K_{ai,bj} = \frac{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{b}_{i}^\dagger b_{a} \hat{H} \hat{P}_{kk'}^{j} \hat{b}_{j}^\dagger b_{b} | \Phi \rangle}{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{P}_{kk'}^{j} | \Phi \rangle},$$  \hspace{1cm} (C.9)  

$$N_{ai,bj,0} = \frac{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{b}_{i}^\dagger b_{a} \hat{P}_{kk'}^{j} | \Phi \rangle}{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{P}_{kk'}^{j} | \Phi \rangle},$$  \hspace{1cm} (C.10)  

$$K_{ai,bj,0} = \frac{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{b}_{i}^\dagger b_{a} \hat{H} \hat{P}_{kk'}^{j} | \Phi \rangle}{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{P}_{kk'}^{j} | \Phi \rangle}. $$  \hspace{1cm} (C.11)

Each of the quantities above can be evaluated as an integration over transition matrix elements. For instance,

$$N_{ai,0} = \frac{1}{\sum_{kk'} f_{k}^* f_{k'} \langle \Phi | \hat{P}_{kk'}^{j} | \Phi \rangle} \sum_{kk'} f_{k}^* f_{k'} \int d\vartheta w_{kk'}(\vartheta) n(\vartheta) N_{ai,0}(\vartheta),$$  \hspace{1cm} (C.12)

where $n(\vartheta) = \langle \Phi | \hat{R}(\vartheta) | \Phi \rangle$ and

$$N_{ai,0}(\vartheta) \equiv \frac{\langle \Phi | \hat{b}_{i}^\dagger b_{a} \hat{R}(\vartheta) | \Phi \rangle}{\langle \Phi | \hat{R}(\vartheta) | \Phi \rangle}. $$  \hspace{1cm} (C.13)  

Matrix elements such as the one obtained above can be evaluated using Wick’s theorem in the way described in Appendix B. We here collect all expressions; in writing
them, we will drop the $\vartheta$ label in the transition density matrix and its contractions
$[\rho \equiv \rho(\vartheta), \Gamma \equiv \Gamma(\vartheta)]$ to improve readability. Additionally, $h(\vartheta)$ is defined by Eq. 3.28b.

\[
N_{ai,0}(\vartheta) = \sum_{mn} D^*_{mi} D_{na} \rho_{nm} \tag{C.14}
\]

\[
N_{ai,bj}(\vartheta) = \sum_{mnpq} D^*_{mi} D_{na} (R(\vartheta) D^*)_{pb} (R^*(\vartheta) D)_{qj} [\rho_{nm} \rho_{qp} + \rho_{qm} (1 - \rho)_{np}] \tag{C.15}
\]

\[
N_{ai,bj,0}(\vartheta) = \sum_{mnpq} D^*_{mi} D^*_{pj} D_{qb} [\rho_{nm} \rho_{qp} + \rho_{qm} (1 - \rho)_{np}] \tag{C.16}
\]

\[
K_{ai,0}(\vartheta) = \sum_{mn} D^*_{mi} D_{na} \times
\left\{ \begin{array}{l}
h(\vartheta) \rho_{nm} + [(1 - \rho) (h + \Gamma) \rho]_{nm} \\
+ \rho_{nm} [\rho (h + \Gamma) (1 - \rho)]_{qp} + \rho_{qp} [(1 - \rho) (h + \Gamma) \rho]_{nm} \\
+ \rho_{qm} [(1 - \rho) (h + \Gamma) (1 - \rho)]_{np} - (1 - \rho)_{np} [\rho (h + \Gamma) \rho]_{qm} \\
+ \sum_{wxyz} \langle wx|\hat{v}|yz\rangle \rho_{qw} (1 - \rho)_{nx} (1 - \rho)_{yp} \rho_{zm} \end{array} \right\} \tag{C.17}
\]

\[
K_{ai,bj}(\vartheta) = \sum_{mnpq} D^*_{mi} D_{na} (R(\vartheta) D^*)_{pb} (R^*(\vartheta) D)_{qj} \times
\left\{ \begin{array}{l}
h(\vartheta) [\rho_{nm} \rho_{qp} + \rho_{qm} (1 - \rho)_{np}] \\
+ \rho_{nm} [\rho (h + \Gamma) (1 - \rho)]_{qp} + \rho_{qp} [(1 - \rho) (h + \Gamma) \rho]_{nm} \\
+ \rho_{qm} [(1 - \rho) (h + \Gamma) (1 - \rho)]_{np} - (1 - \rho)_{np} [\rho (h + \Gamma) \rho]_{qm} \\
+ \sum_{wxyz} \langle wx|\hat{v}|yz\rangle \rho_{qw} (1 - \rho)_{nx} (1 - \rho)_{yp} \rho_{zm} \end{array} \right\} \tag{C.18}
\]

\[
K_{ai,bj,0}(\vartheta) = \sum_{mnpq} D^*_{mi} D_{na} D^*_{pj} D_{qb} \times
\left\{ \begin{array}{l}
h(\vartheta) [\rho_{nm} \rho_{qp} + \rho_{qm} (1 - \rho)_{np}] \\
+ \rho_{nm} [\rho (h + \Gamma) (1 - \rho)]_{qp} + \rho_{qp} [(1 - \rho) (h + \Gamma) \rho]_{nm} \\
- \rho_{qm} [\rho (h + \Gamma) (1 - \rho)]_{np} + (1 - \rho)_{np} [\rho (h + \Gamma) (1 - \rho)]_{qm} \\
+ \sum_{wxyz} \langle wx|\hat{v}|yz\rangle \rho_{qw} \rho_{nx} (1 - \rho)_{yp} (1 - \rho)_{zm} \end{array} \right\} \tag{C.19}
\]
Appendix D

Reduced density matrices of spin-projected states

In this appendix, we discuss how to evaluate expectation values of arbitrary operators between spin-projected states. Because an arbitrary string of field operators does not commute with the spin projection operator, it would seem that one is forced to carry out a projection of the bra and ket states in evaluating such matrix elements, which would become too expensive. We discuss how this is avoided by decomposing the string of field operators into irreducible tensor components. This is closely related to the well-known Wigner–Eckart theorem [26].

Consider the evaluation of the expectation value of an arbitrary operator $\hat{O}$ between spin-projected states. That is, we aim to compute

$$\langle j_1 m_1 | \hat{O} | j_2 m_2 \rangle,$$

where $j$ and $m$ characterize the spin quantum numbers of the projected states. In general, we evaluate this expectation value as

$$\langle j_1 m_1 | \hat{O} | j_2 m_2 \rangle = \sum_{k_1 k_2} f^*_k f_k \langle \Phi_1 | \hat{P}_{j_1, m_1} \hat{O} \hat{P}_{j_2, m_2, k_2} | \Phi_2 \rangle,$$

where $|\Phi_1\rangle$ and $|\Phi_2\rangle$ are broken-symmetry reference determinants and $\hat{P}_{j, m, k}$ is the usual spin-projection operator. In order to simplify the evaluation of this matrix element, we note that an arbitrary operator $\hat{O}$ can always be written as a linear combination of tensor components $\hat{T}_{\lambda, \mu}$ that satisfy

$$\hat{R}(\Omega) \hat{T}_{\lambda, \mu} \hat{R}^{-1}(\Omega) = \sum_{\nu} \hat{T}_{\lambda, \nu} D_{\nu, \mu}^{\lambda}(\Omega),$$

where $\hat{R}(\Omega)$ is a rotation operator.
where $\Omega = (\alpha, \beta, \gamma)$ is the set of Euler angles, $\hat{R}(\Omega)$ is the spin-rotation operator, and $D_{\nu,\mu}^\lambda(\Omega)$ is Wigner’s $D$-matrix.

Using the definition of the spin-projection operator, it is not difficult to show [88] that

$$\hat{P}_{k_1,m_1}^{j_1} \hat{T}^{\lambda,\mu} \hat{P}_{m_2,k_2}^{j_2} = \langle j_1 \, m_1 \, \lambda - \mu | j_2 \, m_2 \rangle \times$$

$$\sum_{\mu'} (-1)^{\mu' - \mu} \langle j_1 \, k_1 \, \lambda - \mu' | j_2 \, k_1 - \mu' \rangle \hat{T}^{\lambda,\mu'} \hat{P}_{k_1 - \mu',k_2}^{j_2}, \quad (D.4)$$

where we have used the following properties [89] of Wigner’s $D$-matrix:

$$D_{m',m}^j(\Omega) = (-1)^{m'-m} D_{-m',-m}^j(\Omega) \quad (D.5)$$

$$D_{\mu',\mu}^\omega(\Omega) D_{m',m}^j(\Omega) = \sum_{J=|j-\omega|}^{j+\omega} \langle \omega \, \mu' \, j \, m' | J \, m' + \mu' \rangle \times$$

$$\langle \omega \, \mu \, j \, m | J \, m + \mu \rangle D_{m'+\mu',m+\mu}^j(\Omega). \quad (D.6)$$

One can use the above expression to evaluate expectation values of arbitrary operators efficiently. If the expectation value is evaluated between states with the same spin quantum numbers this simplifies to

$$\hat{P}_{k_1,m}^{j_1} \hat{T}^{\lambda,\mu} \hat{P}_{m,k_2}^{j_2} = \delta_{\mu,0} \langle j \, m \, \lambda \, 0 | j \, m \rangle \times$$

$$\sum_{\mu'} (-1)^{\mu'} \langle j \, k_1 \, \lambda - \mu' | j \, k_1 - \mu' \rangle \hat{T}^{\lambda,\mu'} \hat{P}_{k_1 - \mu',k_2}^{j_2}, \quad (D.7)$$

As expectation values of arbitrary operators can be evaluated in terms of appropriate traces of (transition) density matrices, we concentrate on the tensorial character of reduced density operators in the remaining part of this appendix.
D.1 Tensorial character of individual fermion operators

In this section we discuss the tensorial character of elementary fermion creation and annihilation operators. The spin-rotation operator $\hat{R}(\Omega)$ transforms the fermion operators according to

$$
\hat{R}(\Omega)\hat{C}_{p,\uparrow} \hat{R}^{-1}(\Omega) = e^{-i(\alpha+\gamma)/2} \cos(\beta/2) \hat{C}_{p,\uparrow} + e^{+i(\alpha-\gamma)/2} \sin(\beta/2) \hat{C}_{p,\downarrow}, \tag{D.8a}
$$

$$
\hat{R}(\Omega)\hat{C}_{p,\downarrow} \hat{R}^{-1}(\Omega) = e^{+i(\alpha+\gamma)/2} \cos(\beta/2) \hat{C}_{p,\downarrow} - e^{-i(\alpha-\gamma)/2} \sin(\beta/2) \hat{C}_{p,\uparrow}, \tag{D.8b}
$$

$$
\hat{R}(\Omega)\hat{C}^{\dagger}_{p,\uparrow} \hat{R}^{-1}(\Omega) = e^{+i(\alpha+\gamma)/2} \cos(\beta/2) \hat{C}^{\dagger}_{p,\uparrow} + e^{-i(\alpha-\gamma)/2} \sin(\beta/2) \hat{C}^{\dagger}_{p,\downarrow}, \tag{D.8c}
$$

$$
\hat{R}(\Omega)\hat{C}^{\dagger}_{p,\downarrow} \hat{R}^{-1}(\Omega) = e^{-i(\alpha+\gamma)/2} \cos(\beta/2) \hat{C}^{\dagger}_{p,\downarrow} - e^{+i(\alpha-\gamma)/2} \sin(\beta/2) \hat{C}^{\dagger}_{p,\uparrow}. \tag{D.8d}
$$

These equations can be rewritten as

$$
\hat{R}(\Omega)\hat{C}_{p,\uparrow} \hat{R}^{-1}(\Omega) = \sum_\sigma \hat{C}_{p,\sigma} \hat{D}_{\sigma,\frac{1}{2}}^{\frac{3}{2}}(\Omega), \tag{D.9a}
$$

$$
\hat{R}(\Omega)\hat{C}_{p,\downarrow} \hat{R}^{-1}(\Omega) = \sum_\sigma \hat{C}_{p,\sigma} \hat{D}_{\sigma,\frac{1}{2}}^{\frac{3}{2}}(\Omega), \tag{D.9b}
$$

$$
\hat{R}(\Omega)\hat{C}^{\dagger}_{p,\uparrow} \hat{R}^{-1}(\Omega) = \sum_\sigma \hat{C}_{p,\sigma} \hat{D}_{\sigma,\frac{1}{2}}^{\frac{3}{2} \ast}(\Omega), \tag{D.9c}
$$

$$
\hat{R}(\Omega)\hat{C}^{\dagger}_{p,\downarrow} \hat{R}^{-1}(\Omega) = \sum_\sigma \hat{C}_{p,\sigma} \hat{D}_{\sigma,\frac{1}{2}}^{\frac{3}{2} \ast}(\Omega), \tag{D.9d}
$$

where the tensorial character of the fermion operators is explicit.

D.2 One-particle density operators $\hat{\Gamma}_{k}^i = c_{i}^{\dagger} c_k$

We can use the transformation properties of the individual fermion operators to find the transformation properties of one-particle density operators $\hat{\Gamma}_{k}^i = c_{i}^{\dagger} c_k$. We arrive
at
\[
\hat{R}(\Omega) c_{i,\sigma_i}^\dagger c_{k,\sigma_k} \hat{R}^{-1}(\Omega) = \sum_{\mu,\nu} c_{i,\mu}^\dagger c_{k,\nu} D_{\mu,\sigma} \frac{1}{2} \hat{\Gamma}_{\mu,\sigma} (\Omega) D_{\nu,\sigma} \frac{1}{2}^* (\Omega)
\]
\[
= \sum_{J=0}^{\infty} \left( \frac{1}{2} \sigma_i \frac{1}{2} - \sigma_k \right) J \sigma_i - \sigma_k \right) \times\]
\[
\sum_{\mu,\nu} (-1)^{\sigma_k - \nu} \left( J_{\mu} \frac{1}{2} - \nu \right) \times\]
\[
c_{i,\mu}^\dagger c_{k,\nu} D_{J,\nu,\sigma} \frac{1}{2} \hat{\Gamma}_{\mu,\sigma} (\Omega).
\] (D.10)

From the above expression, the form of the irreducible tensor components \( \hat{T}_{\lambda,\mu} \) corresponding to one-particle density operators is easily derived. These are provided in Table D.1.

Table D.1 : Irreducible tensor components from one-particle density operators \( \hat{\Gamma}_{i} \).

\[
\begin{array}{ll}
\hat{T}_{k_i}^{0,0} & \frac{1}{\sqrt{2}} \left[ \hat{\Gamma}^{k_i,\uparrow}_{i,\uparrow} + \hat{\Gamma}^{k_i,\downarrow}_{i,\downarrow} \right] \\
\hat{T}_{k_i}^{1,0} & \frac{1}{\sqrt{2}} \left[ \hat{\Gamma}^{k_i,\uparrow}_{i,\uparrow} - \hat{\Gamma}^{k_i,\downarrow}_{i,\downarrow} \right] \\
\hat{T}_{k_i}^{1,1} & -\hat{\Gamma}^{k_i,\downarrow}_{i,\uparrow} \\
\hat{T}_{k_i}^{1,-1} & +\hat{\Gamma}^{k_i,\uparrow}_{i,\downarrow}
\end{array}
\]

The form of the spin-blocks written as linear combinations of the different irreducible tensor components \( \hat{T}_{\mu}^{\lambda} \) can now be easily worked out. These are given in Table D.2.

D.3 Two-particle density operators \( \hat{\Gamma}_{i}^k \hat{\Gamma}_{j}^l = c_{i}^\dagger c_{k} c_{j}^\dagger c_{l} \)

The irreducible representations for operators of the form \( \hat{\Gamma}_{i}^k \hat{\Gamma}_{j}^l = c_{i}^\dagger c_{k} c_{j}^\dagger c_{l} \) can be easily found in terms of the irreducible representations for one-particle density operators.
Table D.2: Spin-blocks of one-particle density operators \( \hat{\Gamma}_i^k \) as linear combinations of irreducible tensor components from Table D.1.

\[
\begin{align*}
\hat{\Gamma}^k_{i,\uparrow} & \quad \frac{\sqrt{2}}{2} \left( \hat{T}_{ki}^{0,0} + \hat{T}_{ki}^{1,0} \right) \\
\hat{\Gamma}^k_{i,\downarrow} & \quad \frac{\sqrt{2}}{2} \left( \hat{T}_{ki}^{0,0} - \hat{T}_{ki}^{1,0} \right) \\
\hat{\Gamma}^k_{i,\uparrow} & \quad -\hat{T}_{ki}^{1,+1} \\
\hat{\Gamma}^k_{i,\downarrow} & \quad +\hat{T}_{ki}^{1,-1}
\end{align*}
\]

Namely, the following relation can be used:

\[
\hat{R}(\Omega) \hat{T}^{\lambda,\mu} \hat{T}^{\lambda',\mu'} \hat{R}^{-1}(\Omega) = \sum_{\nu,\nu'} \hat{T}^{\lambda,\nu} \hat{T}^{\lambda',\nu'} D^{\lambda} \nu,\mu(\Omega) D^{\lambda'} \nu',\mu'(\Omega) \\
= \sum_{J=|\lambda-\lambda'|}^{\lambda+\lambda'} \langle \lambda \mu \lambda' \mu' | J \mu + \mu' \rangle \times \\
\sum_{\nu,\nu'} \langle \lambda \nu \lambda' \nu' | J \nu + \nu' \rangle \hat{T}^{\lambda,\nu} \hat{T}^{\lambda',\nu'} D^J \nu+\nu',\mu+\mu'(\Omega).
\]

(D.11)

Using the above equation, we have worked out the irreducible tensor components for the two-particle density operators of the form \( \hat{\Gamma}_i^k \hat{\Gamma}_j^l = c_i^\dagger c_k c_j^\dagger c_l \) in Table D.3. These tensor components satisfy

\[
\begin{align*}
\hat{R}(\Omega)^{0\times0} \hat{T}^{0,0} \hat{R}^{-1}(\Omega) & = \hat{T}^{0,0} D^0_{0,0}(\Omega), \quad \text{(D.12a)} \\
\hat{R}(\Omega)^{1\times0} \hat{T}^{1,\mu} \hat{R}^{-1}(\Omega) & = \sum_{\mu} \hat{T}^{1,\nu} D^1_{\nu,\mu}(\Omega), \quad \text{(D.12b)} \\
\hat{R}(\Omega)^{0\times1} \hat{T}^{1,\mu} \hat{R}^{-1}(\Omega) & = \sum_{\mu} \hat{T}^{1,\nu} D^1_{\nu,\mu}(\Omega), \quad \text{(D.12c)} \\
\hat{R}(\Omega)^{1\times1} \hat{T}^{\lambda,\mu} \hat{R}^{-1}(\Omega) & = \sum_{\mu} \hat{T}^{\lambda,\nu} D^1_{\nu,\mu}(\Omega). \quad \text{(D.12d)}
\end{align*}
\]
The left-superscript that we have attached to the $\hat{T}$ operators denote the type of direct product among the irreducible tensors of the elements of the one-particle density matrix.

The form of the spin-blocks written as linear combinations of the different irreducible tensor components $\hat{T}^{\lambda,\mu}$ can now be easily worked out. These are given in Table D.4.

### D.4 Density matrix elements for $m = 0$ states

As an example of the application of the above formulas, we here provide the explicit expressions appropriate for the computation of the one- and two-particle density matrix elements for states with $m = 0$. In such a case, Eq. D.7 further simplifies to

$$\hat{P}^j_{k_1,0} \hat{T}^{\lambda,\mu} \hat{P}^j_{0,k_2} = \delta_{\mu,0} \langle j 0 \lambda 0 | j 0 \rangle \times$$

$$\sum_{\mu'} (-1)^{\mu'} \langle j k_1 | \mu' \rangle \langle j k_1 - \mu' | \hat{T}^{\lambda,\mu'} \rangle \hat{P}^j_{k_1-\mu',k_2}. \quad (D.13)$$

Observe also that tensor components of the form $T^{\lambda,\mu}$ do not contribute for $\mu \neq 0$. This simply reflects that such a tensor component changes the value of $m$ of the ket (or bra) state and hence has no contribution to density matrix elements.

Elements of the one-particle density matrix can be evaluated as

$$\langle \hat{\hat{P}}^j_{k_1,0} \hat{\hat{\hat{P}}}^{k,\uparrow}_{i,\uparrow} \hat{\hat{P}}^j_{0,k_2} \rangle = \langle \hat{\hat{P}}^j_{k_1,0} \hat{\hat{\hat{P}}}^{k,\downarrow}_{i,\downarrow} \hat{\hat{P}}^j_{0,k_2} \rangle$$

$$= \frac{\sqrt{2}}{2} \langle \hat{\hat{P}}^{0,0}_{k_1,k_2} \rangle = \frac{1}{2} \left( \langle \hat{\hat{\hat{P}}}^{k,\uparrow}_{i,\uparrow} \rangle + \langle \hat{\hat{\hat{P}}}^{k,\downarrow}_{i,\downarrow} \rangle \right) \hat{P}^j_{k_1,k_2}. \quad (D.14a)$$

$$\langle \hat{\hat{P}}^j_{k_1,0} \hat{\hat{\hat{P}}}^{k,\downarrow}_{i,\uparrow} \hat{\hat{P}}^j_{0,k_2} \rangle = \langle \hat{\hat{P}}^j_{k_1,0} \hat{\hat{\hat{P}}}^{k,\uparrow}_{i,\downarrow} \hat{\hat{P}}^j_{0,k_2} \rangle = 0 \quad (D.14b)$$
Elements of the two-particle density matrix can be evaluated as

\[
\langle \hat{P}_j^{i} \hat{\Gamma}^{k,\uparrow}_{i,\uparrow} \hat{\Gamma}^{l,\downarrow}_{j,\downarrow} \hat{P}_0^{j}_{k_2} \rangle = \langle \hat{P}_j^{i} \hat{\Gamma}^{k,\uparrow}_{i,\uparrow} \hat{\Gamma}^{l,\downarrow}_{j,\downarrow} \hat{P}_0^{j}_{k_2} \rangle
\]

\[
\begin{align*}
&= + \frac{1}{2} \langle 0 \times 0 \hat{T}^{0,0}_{k_1,k_2} \rangle - \frac{\sqrt{3}}{4} \langle 1 \times 1 \hat{T}^{0,0}_{k_1,k_2} \rangle \\
&\quad + \frac{\sqrt{3}}{4\sqrt{2}} \langle j \ 0 \ 0 \ 0 | j \ 0 \ 0 \rangle \times \\
&\quad \sum_{\mu'} \left( -1 \right)^{\mu'} \langle j \ 1 \ 0 \ 2 - \mu' | j \ 0 \ 1 \ 2 \rangle \right) \times \\
&\quad \hat{T}^{2,\mu'}_{k_1,k_2} \hat{P}_0^{j}_{k_2} \ (D.15a)
\end{align*}
\]

\[
\langle \hat{P}_j^{i} \hat{\Gamma}^{k,\uparrow}_{i,\downarrow} \hat{\Gamma}^{l,\downarrow}_{j,\uparrow} \hat{P}_0^{j}_{k_2} \rangle = \langle \hat{P}_j^{i} \hat{\Gamma}^{k,\uparrow}_{i,\downarrow} \hat{\Gamma}^{l,\downarrow}_{j,\uparrow} \hat{P}_0^{j}_{k_2} \rangle
\]

\[
\begin{align*}
&= + \frac{1}{2} \langle 0 \times 0 \hat{T}^{0,0}_{k_1,k_2} \rangle + \frac{\sqrt{3}}{4} \langle 1 \times 1 \hat{T}^{0,0}_{k_1,k_2} \rangle \\
&\quad - \frac{\sqrt{3}}{4\sqrt{2}} \langle j \ 0 \ 0 \ 0 | j \ 0 \ 0 \rangle \times \\
&\quad \sum_{\mu'} \left( -1 \right)^{\mu'} \langle j \ 1 \ 0 \ 2 - \mu' | j \ 0 \ 1 \ 2 \rangle \right) \times \\
&\quad \hat{T}^{2,\mu'}_{k_1,k_2} \hat{P}_0^{j}_{k_2} \ (D.15b)
\end{align*}
\]

\[
\langle \hat{P}_j^{i} \hat{\Gamma}^{k,\uparrow}_{i,\downarrow} \hat{\Gamma}^{l,\uparrow}_{j,\downarrow} \hat{P}_0^{j}_{k_2} \rangle = \langle \hat{P}_j^{i} \hat{\Gamma}^{k,\uparrow}_{i,\downarrow} \hat{\Gamma}^{l,\uparrow}_{j,\downarrow} \hat{P}_0^{j}_{k_2} \rangle
\]

\[
\begin{align*}
&= - \frac{1}{\sqrt{3}} \langle 1 \times 1 \hat{T}^{0,0}_{k_1,k_2} \rangle \\
&\quad - \frac{1}{\sqrt{6}} \langle j \ 0 \ 2 \ 0 | j \ 0 \ 0 \rangle \times \\
&\quad \sum_{\mu'} \left( -1 \right)^{\mu'} \langle j \ 1 \ 2 \ 0 - \mu' | j \ 0 \ 1 \ 2 \rangle \right) \times \\
&\quad \hat{T}^{2,\mu'}_{k_1,k_2} \hat{P}_0^{j}_{k_2} \ (D.15c)
\end{align*}
\]

All other spin-blocks of the two-particle density matrix identically vanish. Note that for singlet states \((j = 0)\) the evaluation is further simplified due to the fact that

\[
\langle 0 \ 0 \ 2 \ 0 | 0 \ 0 \rangle = 0.
\]
Table D.3: Irreducible tensor components from two-particle density operators $\hat{\Gamma}_i^k \hat{\Gamma}_j^l$.

\[
\begin{array}{ll}
0 \times 0 \hat{T}_{ki,lj}^{0,0} & \frac{1}{2} \left[ +\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\downarrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\uparrow}^l - \hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\downarrow}^l \right] \\
1 \times 0 \hat{T}_{ki,lj}^{1,0} & \frac{1}{2} \left[ +\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\downarrow}^l - \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\downarrow}^l \right] \\
1 \times 0 \hat{T}_{ki,lj}^{1,-1} & \frac{1}{2} \left[ -\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\downarrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\uparrow}^l - \hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\downarrow}^l \right] \\
0 \times 1 \hat{T}_{ki,lj}^{1,0} & \frac{1}{2} \left[ +\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\downarrow}^l - \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\downarrow}^l \right] \\
0 \times 1 \hat{T}_{ki,lj}^{1,-1} & \frac{1}{2} \left[ -\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\downarrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\uparrow}^l - \hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\downarrow}^l \right] \\
1 \times 1 \hat{T}_{ki,lj}^{1,0} & \frac{1}{2} \left[ -\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\downarrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\uparrow}^l - \hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\downarrow}^l \right] \\
1 \times 1 \hat{T}_{ki,lj}^{1,+1} & \frac{1}{2} \left[ +\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\downarrow}^l - \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\downarrow}^l \right] \\
1 \times 1 \hat{T}_{ki,lj}^{1,-1} & \frac{1}{2} \left[ -\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\downarrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\uparrow}^l - \hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\downarrow}^l \right] \\
1 \times 1 \hat{T}_{ki,lj}^{2,0} & \frac{1}{6} \left[ +\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l - \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\downarrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\uparrow}^l - \hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\downarrow}^l \right] \\
1 \times 1 \hat{T}_{ki,lj}^{2,+1} & \frac{1}{6} \left[ -\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\downarrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\uparrow}^l - \hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\downarrow}^l \right] \\
1 \times 1 \hat{T}_{ki,lj}^{2,-1} & \frac{1}{6} \left[ +\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l - \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\downarrow}^l + \hat{\Gamma}_{i,\downarrow}^k \hat{\Gamma}_{j,\uparrow}^l - \hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\downarrow}^l \right] \\
1 \times 1 \hat{T}_{ki,lj}^{2,+2} & +\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l \\
1 \times 1 \hat{T}_{ki,lj}^{2,-2} & +\hat{\Gamma}_{i,\uparrow}^k \hat{\Gamma}_{j,\uparrow}^l 
\end{array}
\]
Table D.4: Spin-blocks of two-particle density operators $\hat{\Gamma}_i^k \hat{\Gamma}_j^l$ as linear combinations of irreducible tensor components from Table D.3.

<table>
<thead>
<tr>
<th>$\hat{\Gamma}_i^{\uparrow} \hat{\Gamma}_j^{\uparrow}$</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hat{\Gamma}_i^{\uparrow} \hat{\Gamma}_j^{\uparrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\downarrow} \hat{\Gamma}_j^{\downarrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\downarrow} \hat{\Gamma}_j^{\downarrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\downarrow} \hat{\Gamma}_j^{\downarrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\uparrow} \hat{\Gamma}_j^{\uparrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\downarrow} \hat{\Gamma}_j^{\downarrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\downarrow} \hat{\Gamma}_j^{\downarrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\uparrow} \hat{\Gamma}_j^{\uparrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\downarrow} \hat{\Gamma}_j^{\downarrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\downarrow} \hat{\Gamma}_j^{\downarrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\uparrow} \hat{\Gamma}_j^{\uparrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\downarrow} \hat{\Gamma}_j^{\downarrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\downarrow} \hat{\Gamma}_j^{\downarrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
<tr>
<td>$\hat{\Gamma}_i^{\uparrow} \hat{\Gamma}_j^{\uparrow}$</td>
<td>$+ \frac{1}{2} \left( 0 \times 0 \hat{T}<em>{ki,ij}^{0,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}<em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}</em>{ki,ij}^{1,0} + \frac{1}{2} \times 1 \hat{T}_{ki,ij}^{2,0} \right)$</td>
</tr>
</tbody>
</table>
Bibliography


