The Stochastic Gradient Approximation: an application to Li nanoclusters

by

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ABSTRACT OF DISSERTATION

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Abstract

The Stochastic Gradient Approximation (SGA) is the natural extension of Quantum Monte Carlo (QMC) methods to the variational optimization of quantum wave function parameters. While many deterministic applications impose stochasticity, the SGA fruitfully takes advantage of the natural stochasticity already present in QMC in order to utilize a small number of QMC samples and approach the minimum more quickly by averaging out the random noise in the samples. The increasing efficiency of the method for systems with larger numbers of particles, and its nearly ideal scaling when running on parallelized processors, is evidence that the SGA is well suited for the study of nanoclusters. In this thesis, I discuss the SGA algorithm in detail. I also describe its application to both quantum dots, and to the Resonating Valence Bond wave function (RVB). The RVB is a sophisticated model of electronic systems that captures electronic correlation effects directly and that improves the nodal structure of quantum wave functions. The RVB is receiving renewed attention in the study of nanoclusters due to the fact that calculations of RVB wave functions have become feasible with recent advances in computer hardware and software.
Dedication

I dedicate this thesis to the hope that in the future physics will be used for the betterment of humankind and not to its detriment, and I dedicate it also to both my mother and my father, without whom my sensibilities regarding this hope would not be so strong.
Acknowledgments

I'd gratefully like to acknowledge the support I've received over these years of work from my advisor, Prof. Arun Bansil, as well as the others in our group who have encouraged my incessant asking of questions. Seppo Sahraakorpi shared with me a love of the details of computer programming. Prof. Robert Markiewicz reliably contributed valuable comments when necessary and did an outstanding job of editing this thesis word-for-word through revision after revision, for which I am especially grateful.

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My work here was fundamentally influenced by the QMcBeaver code, and specifically the work of Michael Feldmann and Chip Kent, as well as the others who have contributed to, and continue to develop, the QMcBeaver code. This code carries QMC methodologies into the modern programming era with its careful attention to open-source, object-oriented development, and it is both a pleasure and an inspiration to be a part of such work. As a final point, the cold fact of the matter is, as only those with intimate familiarity with the QMcBeaver code will fully understand: Chip and Mike are cool.

In addition, the modern, object-oriented Zori code is equally deserving of acknowledgment.

My understanding of variational optimization in QMC deepened when I had the opportunity to work with Leonardo Spanu, who graciously provided the Turbopair code and introduced me to the RVB wave function in the context of this well-developed VMC and DMC package. We co-authored a paper together. I'd also like to acknowledge his advisor during part of the time we worked together, and another co-author, Claudio Attaccalite.

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List of abbreviations

AGP - Antisymmetrized Geminal Product (wave function)
BCC - Body-centered cubic
CC - Coupled Cluster (wave function)
CI - Configuration Interaction (wave function)
DDDA - Dynamic Distributable Decorrelation Algorithm
DFT - Density Functional Theory
DMC - Diffusion (Quantum) Monte Carlo
DQMC (D-QMC) - Diffusion Quantum Monte Carlo
EFP - Effective Fluctuation Potential variational quantum monte carlo method
EMD - electron momentum density
eV - electron volts
FS - Fermi Surface
GUI - Graphical User Interface
Ha - Hartrees
HDF - Heirarchical Data Format
HDF5 - Heirarchical Data Format, version 5
HF - Hartree-Fock (wave function)
HL - Heitler-London
JAGP (J-AGP) - Jastrow Antisymmetrized Geminal Product (wave function)
JS - Jastrow-Slater (wave function)
JS-HF Jastrow-Slater Hartree-Fock (wave function)
JS-LDA Jastrow-Slater Local Density Approximation (wave function)
JS-V0 Jastrow-Slater wave function with virtual orbitals set to zero
LCAO - Linear Combination of Atomic Orbitals
LDA - Local Density Approximation
LRDMC - Lattice Regularized Diffusion (Quantum) Monte Carlo
LSF - Least-squares fit
meV - milli-electron volts
NaN - Not a number
QD - Quantum Dot
QMC - Quantum Monte Carlo
RVB - Resonating Valence Bond (wave function)
SGA - Stochastic Gradient Approximation
SR - Stochastic Reconfiguration
STO - Slater-type Orbitals
VB - Valence Bond (wave function)
VMC - Variational (Quantum) Monte Carlo
VQMC (V-QMC) - Variational Quantum Monte Carlo
WF - wave function
XML - eXtensible Markup Language
Chapter 1

Motivation

This is a work about a study of quantum dots, $\text{H}_2\text{O}$ clusters, and Li clusters using the Stochastic Gradient Approximation (SGA), a new methodology that improves upon variational quantum Monte Carlo (V-QMC, or VMC) methods by more efficiently utilizing statistical information obtained during computer simulations. It works by taking advantage of randomness, in the same spirit as QMC itself takes advantage of randomness (as the name *Monte Carlo* implies). In this way, the SGA is the natural extension of QMC into variational methods.

We begin with a short motivation.

1.1 Nanoclusters

The search for more efficient computer simulation methods finds its origin in the need to develop ways for Quantum Monte Carlo (QMC) to move beyond its limited use in the study of small molecular systems and simple periodic structures. Even after 30 years, QMC methods are hardly able to study molecules more complicated than methane ($\text{CH}_4$), and breakthrough studies continue to reflect this limitation; for example, a recent important study involved the carbon dimer, $\text{C}_2$ [1]. On the one hand, this speaks to the accuracy with which QMC methods are able to study nanophysical systems. Nobody is surprised by the fact that even very small systems show immense complexity when studied in the greatest
possible detail, and therefore nobody expects that the most accurate ab-initio methods will simultaneously be able to study large systems. On the other hand, it also speaks to its weakness. Most research of experimental value on the nanoscopic scale involves clusters larger than those that can be studied with QMC methods.

QMC continues to show promise in becoming more sophisticated and efficient. This thesis will provide a thorough background, and then discuss the SGA, as well as our applications of the SGA to systems of current experimental interest. In addition, we’ll place our work in the context of recent developments in Appendix A.

1.2 Magnetization in Quantum Dots

Quantum Dots (QD) are nanoscopic regions of isolated charge and may have important applications in different fields, notably computer technology and photovoltaics. The magnetic properties of quantum dots exhibit interesting and important shell-like behavior. We performed a detailed QMC calculation of the magnetization properties of two-dimensional quantum dots. We discuss our results in Ch. 5.

1.3 The RVB wave function

The Resonating Valence Bond (RVB) wave function allows us to capture the most important electron-electron correlation effects within a Hilbert subspace of two-body basis functions, rather than single-body. Typical Jastrow-Slater (JS) methods require an expansion into many determinants in order to capture these electronic correlation effects. The computational resources required to simulate these multi-determinant expansions grow exponentially with cluster size and become infeasible for anything but the smallest clusters. By capturing correlation effects within a set of natural two-body orbitals, the RVB allows an efficient representation of the wave function within a single determinant even for large cluster sizes and represents a major advance for QMC methods. We provide a detailed RVB study of Li clusters in Ch. 6. Our calculations help explain experimental results that deviate from the standard Jastrow-Slater model that has typically been used to represent these clusters.
1.4 The SGA

The SGA is a method designed to work in the regime of large nanoclusters which have been difficult to study with other QMC methods. In this regime, calculations of the many-body QMC wave function or its derivatives dominate the time needed for the calculation, and severely limit the number of samples that can be obtained to calculate desired quantities (Eq. 4.4). Therefore, it is increasingly important to guarantee that all statistical information obtained from the QMC calculation is being utilized as efficiently as possible. For 50 years, methods to increase the efficiency of basic QMC calculations have been extensively developed, notably beginning with the work of Metropolis, et al. [2] in 1953. However, very little effort has gone into increasing the efficiency of specifically variational QMC calculations (VMC), which add a new level of complexity to QMC calculations by allowing variation of the QMC wave function within a parameterized landscape. The SGA consequently extends the benefits of the Monte Carlo nature of QMC calculations into the more complicated level of VMC. Here, the SGA takes advantage of the Monte Carlo randomness by exact analogy to QMC. It employs statistical methods to allow for highly noisy calculations at each point in the variational landscape, while nonetheless providing accurate results, and it can do so more efficiently than the deterministic VMC methods that have been employed since the inception of QMC.

1.5 Large nanoclusters

The SGA overcomes central difficulties inherent in the application of VMC methods to the study of large nanoclusters. Previous methods generally involve careful, hands-on trial runs in order to prepare a successful computation. These trial runs typically involve an intensive use of computer resources. For large nanoclusters in which available resources are at an absolute premium, this hands-on overhead is a serious feasibility concern. The SGA is designed to run in a way that is automatically the most efficient. Preparing an SGA computation involves only very small trial runs on a single processor. Therefore, the SGA is an excellent candidate for VMC calculations of large, computationally intensive
nanoclusters.

In addition, in our work we have overcome another technical challenge that arises in QMC studies of large nanoclusters - the diverging QMC decorrelation length. This difficulty makes direct QMC statistical analysis impossible. The problem can be overcome, however, by scaling the integrated autocorrelation time.

We discuss these topics in Chs. 7 and 8.

1.6 Parallelization

During the past 10 years, as improvements have been introduced into the world of QMC, engineers and computer scientists have continued to develop hardware platforms and software design methods that are a generation ahead of what QMC scientists have typically utilized. QMC codes have not been scaled to thousands of processors, and as parallel hardware and internet software infrastructure becomes more sophisticated, QMC will highly benefit from template-based, XML- or HDF-data-based, web-enabled and object-oriented design methodologies.

One of the fundamental motivations for the development of the SGA is its applicability to parallel processing. The SGA has been designed from the ground up to be able to take advantage of massively parallelized computing systems. In fact, the SGA possesses distinct features which make it particularly suited for parallel processing.

Effective parallel algorithms must strike an essential balance between serial processing and interprocessor communication. Parallel codes on one extreme of this balance - embarrassingly parallel codes that are exclusively serial-based codes running simultaneously on many processors with no interprocessor communication except at the beginning and the end - scale perfectly with the number of processors, but completely fail to allow different processors to take advantage of information from other processors to intelligently guide their own computations. On the other extreme of the balance - highly intensive parallel codes that constantly exchange information between processors so that all processors benefit from the information available on all other processors on a continuous basis - the algorithms allow an ideal use of parallel processing, but completely fail to scale well with the number
of processors, because interprocessor communication dominates use of the processor time. The ideal balance for parallel processing is one in which each processor is able to benefit extensively from information available on other processors, and yet one in which this highly beneficial interprocessor communication is limited so that it consumes an optimum fraction of processing time. The SGA is ideally suited to obtaining this balance. Individual processor steps within the SGA algorithm are, by the nature of the algorithm, fundamentally constructed as bite-sized chunks large enough to minimize interprocessor communication time, and small enough to allow all processors to benefit from the information available on all other processors.

We discuss these issues in Ch. 8.
Chapter 2

Overview

The purpose of this chapter is to provide an overview that covers all of the material in this thesis without much use of mathematical formulas, although a thorough background in mathematics and physics is assumed.

This thesis will consider in detail the theoretical basis and computational implementation of a computer simulation method known as stochastic optimization. In our application of stochastic optimization to QMC, we give it the name Stochastic Gradient Approximation (SGA), to distinguish the stochasticity from the natural stochasticity that appears in any QMC calculation.

2.1 Stochastic optimization in QMC

Stochastic optimization has applications in a wide range of computational methods and applications. The field achieved a rigorous foundation with a seminal paper by Robbins and Monro in 1951 [3] detailing the first proof of stochastic convergence. In the past ten years, however, the field has seen a huge upsurge of interest due to its importance in the area of computer simulations [4]. Over this time a new and rich rigorous formal mathematics has emerged detailing convergence and convergence rates.

However, when considering the many and varied applications of stochastic optimization to research across broad fields, it is a stark fact that Quantum Monte Carlo methods are
not among its current applications. This, despite the fact that Monte Carlo methods are known to be very well suited to stochastic optimization methods for the obvious reason that QMC is itself a stochastic method.

The method was first introduced to QMC in 1997 [5]. Since then, it has been employed in a limited number of applications. However, importantly, the method has not yet been rigorously placed into the context of stochastic optimization theory, and key implementation details have not been properly utilized. In Ch. 8, we discuss five essential points required for effective use of the method. In Appendix C, we discuss the possibility of including statistical error bars with variational parameters, something not yet accomplished with VMC.

2.2 The waste of statistical information in VMC

A motivating force behind this work is the realization that statistical information is typically wasted in implementations of variational QMC. Specifically, despite tremendous work in improving the statistical efficiency of QMC methods along a variety of fronts, most current VMC methods nonetheless update the variational parameters based only on the immediately preceeding value of the parameter, in a purely deterministic fashion. Therefore, all information from the history of the optimization is completely lost.

Therefore, at each variational step, current methods must use a relatively large number of samples in order to evaluate the energy integral. A quote from James C. Spall, an expert in the area of stochastic optimization, is included in order to clarify the point:

Recalling the basic steepest descent algorithm...a significant innovation of Robbins and Monro (1951) was the recognition that this is a wasteful use of the measurements. Recall that the energy is merely an intermediate calculation towards the ultimate goal of trying to find a [minimum]. There is little interest in the energy per se. So, the main innovation in stochastic approximation is to do a form of averaging across iterations. At first thought, this type of averaging may seem dubious, since the underlying evaluation point is changing across iterations. But, as suggested by Robbins and Monro, this across-iteration aver-
Figure 2-1: A comparison between stochastic and deterministic optimization. The two axes represent two variational parameters in the wave function ansatz. Gradient lines for the energy appear in each plot. (A) Initial guess of the variational parameters that minimize the energy. (B) A stochastic method requires many steps to move recklessly through the landscape, but each step takes a very short time. For clarity, the first three steps are labeled. The noisy errors eventually cancel out, and the path leads to the minimum. (C) A deterministic optimization requires only 10 steps, but each step requires a long calculation. In this case, the time that is taken for these long calculations is time that is somewhat wasted. Despite the much larger number of iterations, the stochastic optimization ran about 50 times faster and resulted in a better estimate of the minimum. Note: the data shown is taken from an H\textsubscript{2} optimization.

...aging can lead to a more effective use of the input information than expending a large amount of resources in getting accurate estimates for the energy at each iteration. ([6], p. 97)

(The italics appear in the original. We have inserted energy in place of the objective function, which is the name given to the function being minimized.)

The distinction between stochastic and deterministic methods can be stated in the form of an analogy between a large cargo ship and a small, agile speedboat; see Fig. 2-1.\textsuperscript{1} The cargo ship weathers storms and moves straight to its destination. The speedboat, on the other hand, is more prone to being blown off target, but can race past the cargo ship and sometimes arrive at its destination more quickly.

The analogy, though a good one, fails to consider the dimensionality of the underlying problem. As the number of particles in the system increases, stochastic methods can do better and better in contrast to their deterministic counterparts.

\textsuperscript{1}The example of the Hydrogen molecule energy grid and SGA optimization that appears in Fig. 2-1 and in Ch. 8 is adapted from the following talk. D. Nissenbaum, B. Barbiellini, and A Bansil, Simple geometry optimization with Variational Quantum Monte Carlo method, American Physical Society, APS March Meeting, March 21-25, 2005, abstract A32.00009.
Stating the matter in a different way, instead of trying to minimize the number of variational steps, stochastic optimization attempts to maximize it, and the effort of the method goes into minimizing the time per step, rather than minimizing the number of steps. Stochastic optimization is a fundamentally statistical approach in a different sense than QMC - it is a statistical approach with respect to variation of the parameters, not with respect to calculation of a quantity at a single parameter.

In stochastic optimization, the source of the noise is irrelevant. The noise can come from any source - experimental measurement error, inherently random physical processes influencing the data, incomplete data that is modeled as randomness, high-temperature effects, etc. In the case of QMC based stochastic optimization, the noise is a direct result of the QMC stochasticity, but the QMC origin of the noise is irrelevant. The QMC statistical error simply behaves as a random variable that is added to an otherwise deterministic result at each variational step.

2.3 Overview of physical systems under study

2.3.1 Nanoclusters

Miniaturization of engineered systems has had a great influence upon the technology of human civilization in a number of areas, notably computer hardware and materials technology such as plastics - to name just two. Miniaturization has reached the point where both the needs and the capabilities point to a new realm of physical systems, one in which the bulk properties of the materials no longer adequately describe the behavior, and instead the systems have become small enough that surface effects become non-negligible - i.e. the physical systems describe nanoscopic particles or regions. It is theorized, for example, that within about a decade miniaturization of solid-state systems in the creation of computer chips using improvements upon current techniques will reach its theoretical limit, and will need to be replaced by significantly nanoscopic methods such as single electron transistors, or, in a different and new realm of computation, quantum computers. As another example, already pharmaceutical development involves manipulation at the molecular level in some
cases. The immediate applications are too varied to go into detail here, but the interested reader can refer to references [7, 8, 9] for a general overview.

There is, therefore, a need for a better understanding of the physics of these systems. In the case of the work described here - quantum dots, H$_2$O clusters, and Li clusters - there are various applications, which we discuss here.

### 2.3.2 Quantum dots

Quantum dots are of fundamental importance in applied nanophysics. Their importance lies in two broad areas. First, as a controlled localized region of electrons, quantum dots form the simplest possible test bed in which to understand the behavior of individual electrons in a controlled nanoscopic environment, the results of which are often directly relevant to the study of other nanoscopic systems. Second, quantum dots themselves have the potential for influential applications as single- or few-electron transistors, or other applications in computing [10, 11, 12, 13], biology [14, 15], and photovoltaics (solar power) [16, 17, 18, 19], among a variety of other possible applications.

Our study of quantum dots reveals a new and interesting understanding of the spin states of these systems. In particular, we confirm Hund’s rule that nanoscopic systems have a tendency to spontaneously magnetize. In addition, we are able to quantitatively measure the extent to which the competing phase due to Coulomb repulsion between opposite-spin electrons plays a role.

### 2.3.3 Lithium

Li is a good candidate with which to develop more sophisticated theories that model nanoclusters, for essentially two reasons. First, Compton scattering experiments involving Li have revealed a phase diagram that is theoretically incompatible with standard current Fermi liquid models [20, 21]. An understanding of Li, therefore, may help us develop models that go beyond the standard Fermi liquid picture. Second, Li is a low-Z atom (Z=3) and so complexities due to more complicated higher-level atomic wave functions (3s, 3p, etc.) do not - at our level of study - play a significant role. This, combined with the small
number of electrons in each atom, allows us to study the scaling of properties of both this material and the simulation method itself (the SGA) as the number of atoms increases.

Also, Li materials are an active area of research today due to the potential of Li-based materials to act as a medium for on-board hydrogen storage [22, 23] - i.e., as a material to store and release H$_2$ for use as a motor vehicle fuel, in the context of humanity’s urgent challenge to replace fossil fuels.

2.3.4 The RVB wave function  

In order to develop a model that might account for the complicated phase diagram of Li, we employ the RVB wave function in the study of Li clusters. To do this, we utilized a recently developed VMC method, Stochastic Reconfiguration (SR). We also utilized another recent QMC development, the Lattice Regularized Diffusion Monte Carlo (LRDMC) method. We compare our results to SGA-optimized standard Jastrow-Slater (JS) wave functions, to see if the Fermi liquid anomalies might be described by the RVB. Our results reveal that the RVB is consistent with the observed anomalies and is a promising candidate for further research along these lines. In addition, the RVB has the potential to help understand the physics of nanoclusters at a deeper level than the JS by including higher-level (virtual) molecular orbitals in a natural way.

2.3.5 H$_2$O clusters  

As common and well-studied a molecule as H$_2$O, the highly polarizable nature of this molecule, and the related importance of van der Waals interactions in materials in solution, still flaunt our best attempts at understanding such systems as LiH$_2$ in solution, a candidate material for hydrogen storage. In such systems, relatively small changes in the physical model of H$_2$O lead to very different results regarding predictions of the practicality of using the material in technological applications.

Unlike Li, H$_2$O contains the O atom (Z=8), in which 3s and 3p levels may play a significant role. In this work we do not study this aspect in detail. However, we found an anomaly in our study of H$_2$O that we did not attempt to resolve (see Fig. 7-9), which is
likely due to the higher-$Z$ nature of this molecule.

### 2.4 Large clusters and stochastic optimization

In the course of applying the SGA to QMC methods, the power and efficiency of stochastic optimization methods revealed itself as we tackled cluster sizes that are larger than those that have typically been studied with QMC methods. In combination with massively parallel computing infrastructures, the SGA allows QMC calculations to be performed on clusters that were previously inaccessible with QMC methods.

In order to gain the benefits of stochastic optimization for large clusters, a fundamental challenge emerged regarding correlations between QMC samples. We discuss this technical issue in detail in Ch. 7.

### 2.5 Outline of thesis

An outline of the thesis is as follows. In Ch. 3, we provide a background of many-body physics. In Ch. 4, we provide a background of the QMC method. In Chapter 5, we discuss our study of quantum dots, including a determination of the spin-resolved pair correlation function and its application to the study of the magnetization of the dot. In Chapter 6 we describe the RVB wave function and proceed to describe our study comparing the RVB wave function with the standard JS wave function in Li clusters. In Chapter 7, we discuss in greater detail the autocorrelation time in QMC calculations and its relevance to sample size, cluster size, and parallelization of QMC code. In Chapter 8 we discuss the SGA in technical detail, including its utility for parallel computing and large nanoclusters.

The thesis also contains a number of appendices that we hope will prove useful. In Appendix A we discuss recent major advances in VMC. In Appendix B we describe challenges involved with the error analysis of a key quantity discussed in this thesis, the analytical gradient of the energy. In Appendix C we discuss the exciting possibility of associating a statistical error bar with the variational parameters in an SGA calculation - something that would be new in the field and, we believe, an asset. In addition, we discuss the necessary
stochastic formulas that need to be solved in order to achieve this goal. In Appendix D we develop the concept of a *region of convergence* for an SGA calculation in order to simplify discussion and analysis of the SGA. In Appendix E we introduce the concept of an *efficiency parameter* that might be used as a simple universal measure with which to compare different variational schemes. In Appendix F we discuss issues regarding the normalization of the quantum wave function in QMC. In Appendix G we discuss the technical issue, still a subject of debate in the QMC community, of the difference between single-electron and all-electron moves in the Metropolis-like stage of a QMC computation. In Appendix H we discuss different formulations of the electron pair correlation function. In Appendix I we provide a unique and detailed derivation of the standard Slater determinant used in QMC calculations. Finally, in Appendix J we derive the standard formulas for the statistical accuracy of a QMC calculation.
Chapter 3

Many-body theory in a nutshell

3.1 Wave functions

In the formulation of quantum mechanics describing systems in which the number of particles $M$ is fixed in time, every physical system is represented by a wave function $\Psi_s(\{\vec{r}\}, \{s\}, t)$ existing in a potential energy landscape described by the function $V(\{\vec{r}\}, t)$ (which may in addition be non-local; i.e. dependent on $\Psi$), with a corresponding complete set of observables represented by possibly non-local mathematical operators $\{\hat{O}(\{\vec{r}\}, t)\}$ from which can be obtained all possible information about the system at any point of time, so long as the given functions are completely known at any particular time and the operators at all times. Here, $\{\vec{r}\}$ and $\{s\}$ represent the full set of position and spin coordinates of all particles in the system, and $t$ represents the time. For this thesis we assume that $V$ and $\hat{O}$ are independent of spin. Of course, a suitable set of self-consistent units need to be chosen to represent these and all other non-unitless quantities that appear in the mathematical formalism. For this thesis, we employ atomic units, in which position coordinates are measured in bohr radii $a_o$ (given by the expectation value of the distance between the nucleus and the electron of the H atom in the Born-Oppenheimer approximation), time is measured in seconds $s$, and energy is measured in Hartrees $Ha$. For the other quantities in the system of atomic units, including derived quantities, the reader can refer to a standard textbook about quantum mechanics. In this thesis, for convenience we sometimes describe
quantities using other unit systems; because the unit is always included as part of the indicated quantity, it is always clear from context when this is the case. A frequent example of this is energy, which is often described in electron volts eV in this thesis.

In the case of the nanoclusters discussed in this thesis, the physical systems are composed entirely of electrons and atomic nuclei. In the general case, the spatial and spin coordinates of all particles - electrons and nuclei - are represented by the set \( \{ \vec{r} \} \) and \( \{ s \} \), with \( \vec{r} \) equal to the coordinate of an individual particle in 3-dimensional space and \( s \) its spin coordinate. However, the fact that the masses of the nuclei dwarf the mass of the electron by 3 or more orders of magnitude, implies that electronic transitions and other observable effects that can be traced primarily to electronic behavior can often reasonably be approximated as though they reside in a fixed potential landscape described by the Coulomb charge associated with the nuclei as though the nuclei are unmoving - merely parameters of the model, and not particles within the system being modeled. The \( M \) particles are then typically the electrons in the system, and from here forward we consider only this case. This is the Born-Oppenheimer approximation. It is an adiabatic approximation; that is, the nuclei are nonetheless allowed to move. However, their motion is described classically and the electronic state of the system is determined to respond quickly enough that during the response the nuclei do not move sufficiently to influence the results of the model. The quantum behavior is therefore entirely determined by the electrons, except for any quantum behavior imposed upon the classical model of the nuclei. The reader is again referred to an introductory text about quantum mechanics for a more thorough discussion of the Born-Oppenheimer approximation [24]. Throughout the work described in this thesis, we exclusively use the Born-Oppenheimer approximation in our models.

In this work, we also exclusively use the non-relativistic description of quantum mechanics, and we do not allow the number of electrons \( M \) to vary. To go beyond either of these assumptions would require significant and non-trivial modifications of the mathematical formalism, with an entirely different analysis and method of computer calculation; it would be a very different work. In many physical systems, the more sophisticated mathematical formulations and the physics they represent are necessary, particularly to describe systems
at high temperature. However, it has generally been shown that in the study of ground states or low-energy excited states of nanoclusters, both of these approximations are quite safe and the resulting simplification of the model is highly desirable [25]. We will therefore not discuss these issues, or the accuracy of these approximation, any further. However, the interested reader may refer to refs. [26, 27] for a good overview.

The state of a system described by the wave function $\Psi_s(\{\vec{r}\}, \{s\}, t)$ is sometimes represented in the Dirac ket notation as $|\Psi_s(\{\vec{r}\}, \{s\}, t)\rangle$. We will use this notation where it is convenient, and switch back and forth between the notational conventions for readability. As in the case of the wave function formalism, the ket formalism is a useful, complete and consistent notation describing all of the quantum mechanical objects and their precise mathematical relationships, and we will not review either of the notations here. The reader unfamiliar with the use of wave function notation is referred to most any introductory text on quantum mechanics. The reader unfamiliar with the use of ket notation, and its formal relationship with the notation employing the wave function $\Psi_s$, is directed to one of a variety of introductory texts; for example, ref. [28].

3.2 Observables

The time-dependent Schrodinger equation is the foundation of non-relativistic quantum mechanics and its solution determines the wave function $\Psi_s(\{\vec{r}\}, \{s\}, t)$ at any time. In turn, any observable represented by the operator $\hat{O}(\{\vec{r}\}, t)$ (assumed spin-independent throughout this thesis) is calculated at any time as the expectation value of the state:

$$\hat{O}(\{\vec{r}\}, t) = \langle \Psi_s(\{\vec{r}\}, \{s\}, t) | \hat{O}(\{\vec{r}\}, t) | \Psi_s(\{\vec{r}\}, \{s\}, t) \rangle.$$

In the work described in this thesis, the time-dependent Schrodinger equation is not solved except indirectly using a Wick transformation and utilizing the diffusion Monte Carlo (DMC) method, which is discussed in the next chapter. In our work we are not directly interested in the time development of $\Psi_s$. (The time development of $\Psi_s$ is indirectly involved when discussing single-particle excited states, equilibration time, and correlation time; how-
ever, we won’t discuss these issues.) Instead, this work focuses primarily on determining some of the time-independent ground state properties of a time-independent set of observables \( \{ \hat{O}(\{ \vec{r} \}) \} \) - properties at zero absolute temperature. Chief among these observables is the energy, whose value is given by the expectation value of the Hamiltonian operator \( \hat{H} \) for the correct ground state.

The ultimate goal of the research involved in our work is to determine the correct ground states of the systems we study, and to calculate the expectation value of the Hamiltonian and other desired quantities of interest for this state, such as the cohesive energy. In solving for the ground state, a fundamental problem encountered by any physicist is the complexity implied by the Schrodinger equation with any but the simplest potential surfaces \( V \). In fact, for almost every system currently known and virtually every system of experimental interest, the Schrodinger equation is simply unsolvable. For example, the equation can be solved in the case of hydrogenic atoms (atoms with a single electron or positron, and a nucleus of charge \( Z \)) and in many simplified 1-dimensional cases. However, even the simple \( \text{H}_2 \) molecule, with its two electrons and two nuclei, is analytically unsolvable. Certainly, the challenge becomes even more difficult in molecules whose geometric complexity increases and whose constituent atoms have a larger nuclear charge \( Z \) with a correspondingly larger number of electrons.

3.3 Ab Initio methods

Therefore, approximation methods need to be employed to solve the Schrodinger equation. Noting that these are many-body systems - systems with typically many electrons in the set \( \{ \vec{r} \} \) and \( \{ s \} \) - one of the most powerful and significant approximations that has been developed in the past 50 years is Density Functional Theory (DFT), which describes any physical system of electrons and nuclei in any external potential by a mathematical function of only one electron coordinate \( \vec{r} \) (we will not discuss spin in DFT here), in particular by describing the system entirely in terms of the overall electron density \( \rho(\vec{r}) \). We will not include a review of DFT here, but will say one important fact about DFT: the DFT mathematical formalism (i.e., its equations) include a term, the exchange-correlation term,
which if known ahead of time (i.e., before attempting to solve the equations) would provide the exact solution to the many-body problem if the equations could then be solved. However, this term is rarely known ahead of time. Therefore, iterative methods are employed to estimate the exchange-correlation term and solve the DFT equations. Because the exchange-correlation term is not known \textit{a priori}, the DFT equations are, in practice, not capable of providing the exact \textit{ab initio} result for observable quantities of interest for any realistic system under study. DFT is the most common \textit{ab initio} method used to solve for observable quantities of quantum-mechanical systems, because it runs remarkably quickly - many orders of magnitude more quickly than QMC - and it gives outstandingly accurate results for a very wide variety of systems. The reader interested in learning about DFT is referred to any introductory textbook on computational solid-state theory; for example, ref. [29].

The Quantum Monte Carlo method (QMC), the method that underlies the work described in this thesis, is another \textit{ab initio} technique. By \textit{ab initio} is implied a technique whose purpose is to directly solve Schrodinger’s equation. However, like every other \textit{ab initio} method, QMC is incapable of solving Schrodinger’s equation. Therefore, QMC, as well as DFT, must make an underlying approximation. In the case of QMC, unlike DFT, the many-body nature of the wave function is strictly maintained. Instead of a simplification to a one-particle density $\rho(\vec{r})$, in QMC a wave function \textit{ansatz}, or \textit{trial wave function}, is employed to represent the exact many-body wave function; i.e. a wave function of a particular intelligently chosen functional form, parameterized by various constants, is assumed to be the correct solution of the Schrodinger equation. A choice of this \textit{ansatz}, though a significant part of the effort, nonetheless once made bypasses entirely the need to solve the Schrodinger equation, instead leaving only the second part of the research task: namely, solving for the expectation value of any desired observable. Because QMC utilizes a many-body wave function, rather than a single-particle density, it is usually considered to be a “more accurate” method than DFT. However, because QMC is simply another approximation method, the phrase “more accurate” must be gauged on its merits. In fact, sometimes DFT provides more accurate results than QMC.

The QMC method is precisely a technique that can be used to determine the expectation
value of an observable, given a known many-body wave function. QMC is a broad method that has specific variants. One such variant is the diffusion quantum Monte Carlo method (DMC), which is able to improve upon the initial wave function ansatz by filtering out higher-energy components of the wave function. By higher energy is meant eigenstates of the energy with energies exceeding the ground state energy. However, DMC is limited to improvements that filter from the initial wave function ansatz only the projections in Hilbert space of the higher-level energy eigenstates onto the subspace of functions that share the nodal structure of the wave function ansatz. This limitation is due to the fermion sign problem, and it will be briefly discussed when the DMC formalism is presented later in this chapter. If the fermion sign problem is ever completely solved, then DMC will be a method capable of solving exactly for the ground-state energy of any non-relativistic many-body quantum mechanical system with fixed electron number $M$. However, it would take an infinite amount of computational time to solve the problem even in this case. In a finite amount of time, the limit of the exact energy can only be approached, but in general the accuracy can be determined by extrapolation and very good accuracies can be obtained.

It is impossible to use the DMC method to calculate anything directly except for the expectation value of the ground state energy within the fixed nodal structure. Even the analytical form of the wave function is lost. For this reason, it is also useful to use the less exact, vanilla QMC method (also described later in this chapter), which maintains the analytical form of the wave function during the calculation, and which allows calculations of any observable quantity, as well as excited states. Because the analytical form of the wave function is maintained, it is possible to optimize the parameters that appear in the wave function ansatz, until a minimum value of the energy (or an improved value of any other observable quantity) is determined. The process of optimizing the parameters using the vanilla QMC method is called the variational quantum Monte Carlo method (VMC). Even if the goal is to run the more accurate DMC calculation, it is essential to begin with the best possible guess for the nodal structure of the wave function ansatz. It is essential because DMC calculations take a long time to run, typically much longer than vanilla QMC calculations with fixed parameters, and the better the initial guess of the nodal structure,
the faster the DMC calculation. The nodal structure can be modified by performing a VMC calculation. Therefore, both VMC and DMC play important roles in QMC research. VMC calculations allow the researcher more information about the physics of the system because of the analytical form; DMC calculations utilize the best VMC calculations as their starting point and typically result in the most accurate calculations that QMC can provide.

Another useful ab-initio method that we refer to during this thesis is the Configuration Interaction (CI) method. CI is exactly correct in the sense that if there were an infinite amount of computation time available, it would provide exact results. However, the computations are generally more tedious and take longer than DMC calculations. CI involves a multi-determinant expansion of the many-body wave function, and we will not discuss it here. (The interested reader is referred to, for example, ref. [30] for more details.) Because an infinite amount of computation time is never available, CI methods must limit the basis set used and must curtail the number of determinants in the expansion, both of which limit the accuracy in practice. When well applied on small systems, the method is essentially exact. When pushing the limit, however, CI results must be considered carefully to gauge their accuracy, and only in this context used as part of a methodical study of the system. For example, in the case of Li clusters, some older published CI calculations are likely less accurate than modern-day DFT calculations (see Chapter 6).

3.4 The Hartree-Fock method

Hartree-Fock (HF) methods form a “baseline”, or workaday reference point, for many physical systems. They form a baseline in the important sense that the correlation energy is defined as the difference between the exact energy of the system and the energy calculated using the HF method. HF wave functions can be analytically determined in almost every case, and typically do not take very long to solve even for the most complex physical systems studied today. HF methods are a useful baseline with which to define correlation energy, because HF includes the Pauli exchange behavior of the electrons in the many-body wavefunction, but includes the Coulomb repulsion only in the mean field sense - namely, as though the wave function were only a single-electron wave function, with that single
electron residing in a potential landscape with a Coulomb contribution from the other electrons that is simply constructed as the total average density of the electrons described by the wave function. Any energetic effects that result from the Coulomb repulsion between two individual electrons that cannot be modeled in this mean field sense is defined to be a contribution to the correlation energy. Explicit calculation of the total correlation energy - which provides the exact energy - requires a many-body wave function more sophisticated than HF. In general, these more sophisticated wave functions cannot be solved analytically; QMC is therefore the primary method used today to calculate observables of such many-body wave functions. The fraction of the correlation energy obtained is a simple gauge that is routinely used to describe the accuracy of any particular result, and therefore the quality of a given QMC wave function ansatz.

The HF formulation provides an algorithm involving a set of formulas that need to be solved in order to construct the HF solution. Different HF solutions exist depending on restrictions placed upon the wave function. For all cases studied in this thesis, there are three restrictions. First, the number of spin-up and spin-down electrons must be the same. Second, the spin-up and spin-down electrons behave identically. Third, the systems are assumed to exist in the many-body spin singlet state. With these restrictions in place, a set of equations known as the Roothaan equations must be solved, and given a specific (non-orthogonal) basis of atomic orbitals in Hilbert space (which forms a subspace of the true, infinite-dimensional Hilbert space), the HF wave function is uniquely defined as the solution to these equations. The HF solutions are guaranteed to provide the lowest uncorrelated energy for the system under consideration. We will not go into technical details about the HF method here. The interested reader is referred to ref. [30] for an outstanding introduction to the HF method.

There are other computational methods that we mention in passing to provide a taste of the complexity of the field of ab-initio calculations. Coupled-Cluster methods (CC) are a more sophisticated version of HF methods that introduce electron correlations [31]. The Multi-Configuration HF method is an important improvement upon the HF method that can be considered an intermediate between CI and HF methods [32]. Various perturbation
methods exist in different forms [30]. These methods have been extensively studied, sometimes overlap, and are sometimes combined (for a discussion and example, see ref. [33]). We will not go into any details here. This is far from an exhaustive list of current *ab-initio* methods.

Another important point must be fully considered when attempting to understand the applicability of any QMC model of electron correlations. Although the wave function might not incorporate electron correlations, the *Hamiltonian* typically imposes some features that might conceptually be considered correlations between electrons, due to the potential energy term given by $\frac{1}{r}$ in the case of two electrons separated by a distance $r$. In fact, if it were not for this Coulomb repulsion term within the Hamiltonian to account for many-body effects, a wave function (WF) of the HF form would be all but worthless. Despite the fact that Coulomb repulsion is incorporated into the model, even for uncorrelated wave functions, the HF wave function and its solutions are, nonetheless, described as *uncorrelated*. Sometimes, the potential terms in the Hamiltonian that describe Coulomb repulsion are described as introducing correlations. It should be understood in this context that even an *uncorrelated* wave function such as the HF has basic Coulomb repulsion (correlation) incorporated in the overall model in this fashion; context should dictate what is meant by the word *correlation*.

In order to extend beyond the HF approximation - to take a plunge into the realm of electron correlations in many-body wave functions - it is necessary to introduce wave functions that are more complicated than a determinant of single-particle wave functions (introduced in the next section). In a sense, the HF determinant can be considered merely the natural extension of single-particle wave functions into a many-body wave function. A ‘true’ many-body wave function would have terms that cannot be decomposed into the product or sum of single-particle functions. Such a wave function would be a truly correlated one. In the next section, we introduce such a wave function: the Jastrow-Slater, which has been the bread and butter of QMC for many years. In Ch. 6 we introduce a more sophisticated correlated wave function, the RVB. First, though, we introduce the representation of the HF wave function as a simple Slater determinant.
3.5 The Jastrow-Slater wave function

QMC calculations will be discussed in detail in the next chapter, but at this point it is convenient to introduce a typical wave function that models many-body fermionic systems, the one that has been employed in QMC calculations since the inception of the field. First we introduce the Slater determinant, which is a representation of the HF wave function discussed in the previous section. We then proceed to discuss the most commonly used correlated wave function, the Jastrow-Slater.

3.5.1 Slater determinants

A wave function consisting of a determinant of single-particle functions - a Slater determinant - automatically satisfies the Pauli exclusion principal that derives from the fact that for fermionic systems, the wave function must be antisymmetric with respect to a complete exchange of coordinates (spatial and spin) of any two fermionic particles represented by the wave function. Indeed, let us suppose that we have a set of single-particle spatio-spin basis functions \( \{ \phi(\vec{r})\xi(s) \} \). Here, \( \{ \phi(\vec{r}) \} \) are a set of purely spatial single-particle basis functions.

The spin formulation for the Slater determinant is subtle. Because it is rather difficult to find derivations regarding the formulation, and because it is valuable to contrast the formulation with the newer RVB wave function discussed in Ch. 6, we include a full discussion of the spin formulation here. For our purposes, we utilize the formulation of ref. [34], which develops upon the notation used in ref. [28].

Before presenting the full Slater determinant within our desired spin formulation, we’ll present an example in the case \( M = 2 \) and employ bra/ket notation. Consider the spatio-spin state \( |\Psi\rangle \) of a two-particle system, a single-particle normalized position basis state \( |\phi\rangle \), and a set of two single-particle orthonormal spin basis states \( |\xi_\uparrow\rangle \) and \( |\xi_\downarrow\rangle \), and suppose

\[
|\Psi\rangle = \frac{1}{\sqrt{2}} \left( |\phi^{(1)}\rangle \otimes |\xi_\uparrow^{(1)}\rangle \otimes |\phi^{(2)}\rangle \otimes |\xi_\downarrow^{(2)}\rangle - |\phi^{(1)}\rangle \otimes |\xi_\downarrow^{(1)}\rangle \otimes |\phi^{(2)}\rangle \otimes |\xi_\uparrow^{(2)}\rangle \right) \tag{3.1}
\]

\[
= \frac{1}{\sqrt{2}} \left( |\phi^{(1)}\xi_\uparrow^{(1)}\phi^{(2)}\xi_\downarrow^{(2)}\rangle - |\phi^{(1)}\xi_\downarrow^{(1)}\phi^{(2)}\xi_\uparrow^{(2)}\rangle \right) \tag{3.2}
\]
where the superscripts keep track of which subspace the ket refers to, and where the ket notation has been shortened in the second line. It can easily be confirmed that this state is normalized.

Let us now define a continuous dummy spin dimension \( s \), such that a ket in spin space can be defined as a function of \( s \). Such a ket is labeled \( |js_i\rangle \). Further, among the possible values of \( s \) are the two values \( \uparrow \) and \( \downarrow \). When \( s = \uparrow \), \( |s\rangle = |\xi_\uparrow\rangle \), and when \( s = \downarrow \), \( |s\rangle = |\xi_\downarrow\rangle \).

By taking the inner product of \( |\Psi\rangle \) with the bra \( \langle \bar{r}^{(1)}s^{(1)}\bar{r}^{(2)}s^{(2)}| \), we find that

\[
\Psi(\bar{r}_1, \bar{r}_2, s_1, s_2) = \frac{1}{\sqrt{2}} \left[ \langle \bar{r}^{(1)}| \phi^{(1)} \rangle \langle \bar{r}^{(1)}| \xi^{(1)}_\uparrow \rangle \langle \bar{r}^{(2)}| \phi^{(2)} \rangle \langle \bar{r}^{(2)}| \xi^{(2)}_\downarrow \rangle \right] (3.3)
- \left[ \langle \bar{r}^{(1)}| \phi^{(1)} \rangle \langle \bar{r}^{(1)}| \xi^{(1)}_\downarrow \rangle \langle \bar{r}^{(2)}| \phi^{(2)} \rangle \langle \bar{r}^{(2)}| \xi^{(2)}_\uparrow \rangle \right] (3.4)
\]

where we have written all inner products using function notation, and the particle indices have been shifted to subscripts. We can see that the two functions \( \xi^{(1)}_\uparrow(s) \) and \( \xi^{(1)}_\downarrow(s) \) are then defined to be identically equal to 0 except when \( s \) takes the value of the spin subscript. The unity expansion operator in spin space is

\[
1 = \int |s\rangle \langle s| ds. \quad (3.5)
\]

Inserting this within a spin inner product \( \langle \xi_n| \xi_m \rangle \) yields

\[
\int \langle \xi_n| s \rangle \langle s| \xi_m \rangle ds = \int \langle s| \xi_n^* \rangle \langle s| \xi_m \rangle ds = \int \xi_n^*(s)\xi_m(s)ds = \delta_{mn} \quad (3.6)
\]

In two dimensions of spin and space, the unity operator becomes

\[
1 = \int |\bar{r}_1s_1\bar{r}_2s_2\rangle \langle \bar{r}_1s_1\bar{r}_2s_2| d\bar{r}_1ds_1d\bar{r}_2ds_2 = \int |\bar{r}_1s_1\bar{r}_2s_2\rangle \langle \bar{r}_1s_1\bar{r}_2s_2| d\bar{r} ds, \quad (3.7)
\]

where the ket \( |\bar{r}_1s_1\bar{r}_2s_2\rangle \equiv |\bar{r}_1\rangle \otimes |s_1\rangle \otimes |\bar{r}_2\rangle \otimes |s_2\rangle \) and where \( d\bar{r} ds \equiv d\bar{r}_1ds_1d\bar{r}_2ds_2 \). The extension to \( M \) particles is straightforward.
The final expression of Eq. 3.3 can be written

$$\Psi = \frac{1}{\sqrt{2}} \det \begin{vmatrix} \phi(\vec{r}_1)\xi_1(s_1) & \phi(\vec{r}_1)\xi_1(s_1) \\ \phi(\vec{r}_2)\xi_1(s_2) & \phi(\vec{r}_2)\xi_1(s_2) \end{vmatrix}$$.

(3.8)

We find that

$$\Psi = \frac{1}{\sqrt{2}} \phi(\vec{r}_1)\phi(\vec{r}_2) \det \begin{vmatrix} \xi_1(s_1) & \xi_1(s_1) \\ \xi_1(s_2) & \xi_1(s_2) \end{vmatrix}$$

(3.9)

$$= \frac{1}{\sqrt{2}} \phi(\vec{r}_1)\phi(\vec{r}_2)[\xi_1(s_1)\xi_1(s_2) - \xi_1(s_2)\xi_1(s_1)]$$

(3.10)

which shows that in this formulation, the \( \text{H}_2 \) molecule with its opposite-spin electrons exists in the spin singlet state.

It can also be seen that the wave function of Eq. 3.9 is in the spin singlet state by operating on it with the spin operator \( S^2 \), where \( S = S_1 + S_2 \), the sum of the individual angular momentum operators; the wave function is an eigenstate of \( S^2 \) with eigenvalue 0. (The fact that the wave function is also an eigenstate of \( S_z \) with eigenvalue 0 is straightforwardly due to the fact that the number of spin-up and the number of spin-down electrons is the same.)

We will now eliminate the spin variables in the case of an operator that does not depend on the spin state of the wave function, a condition which applies to every operator in this thesis, except where noted. We give the derivation in great detail for \( \text{H}_2 \), so that the extension to \( M \) particles will be straightforward. For any spin-free operator, we have, for the expectation value:

$$\langle \Psi | \hat{O} | \Psi \rangle = \langle \Psi | \int |\vec{r}_1 s_1 \vec{r}_2 s_2 \rangle \langle \vec{r}_1 s_1 \vec{r}_2 s_2 | d\vec{r} ds \hat{O} | \Psi \rangle$$

(3.11)

$$= \int \langle \Psi | \vec{r}_1 s_1 \vec{r}_2 s_2 \rangle \langle \vec{r}_1 s_1 \vec{r}_2 s_2 | \hat{O} | \Psi \rangle d\vec{r} ds$$
where the factor of $\frac{1}{2}$ results from the normalization constant of Eq. 3.8, and where we write $O$, rather than $\hat{O}$, to indicate that the quantity $\hat{O} |\Psi\rangle$ is represented in the spatio-spin coordinate basis. Continuing, we have

\begin{align*}
    \langle \Psi| \hat{O} |\Psi\rangle &= \frac{1}{2} \int \left( \phi(\vec{r}_1)\phi(\vec{r}_2)\xi_1^+(s_1)\xi_1^+(s_2) - \phi(\vec{r}_1)\phi(\vec{r}_2)\xi_1^+(s_1)\xi_1^+(s_2) \right) \\
        &\quad \cdot O \left[ (\phi(\vec{r}_1)\xi_1^+(s_1)\phi(\vec{r}_2)\xi_1^+(s_2) - \phi(\vec{r}_1)\xi_1^+(s_1)\phi(\vec{r}_2)\xi_1^+(s_2)) \right] d\vec{r} \, ds 
\end{align*}

and finally

\begin{align*}
    \langle \Psi| \hat{O} |\Psi\rangle &= \frac{1}{2} \int \phi(\vec{r}_1)\phi(\vec{r}_2)O[\phi(\vec{r}_1)\phi(\vec{r}_2)] d\vec{r} \\
        &\quad \left\{ \int \xi_1^+(s_1)\xi_1^+(s_2)\xi_1^+(s_1)\xi_1^+(s_2) ds - \int \xi_1^+(s_1)\xi_1^+(s_2)\xi_1^+(s_1)\xi_1^+(s_2) ds \right\} \\
        &\quad - \int \xi_1^+(s_1)\xi_1^+(s_2)\xi_1^+(s_1)\xi_1^+(s_2) ds + \int \xi_1^+(s_1)\xi_1^+(s_2)\xi_1^+(s_1)\xi_1^+(s_2) ds 
\end{align*}

Utilizing Eq. 3.6 and the discussion preceding it, we find that

\begin{align*}
    \langle \Psi| \hat{O} |\Psi\rangle &= \int \phi(\vec{r}_1)\phi(\vec{r}_2)O[\phi(\vec{r}_1)\phi(\vec{r}_2)] d\vec{r}. \quad (3.17)
\end{align*}

Next, let us consider a different formulation for $H_2$ that leads to identical results when the spin terms are integrated out in the case of spin-free operators. In this formulation,
let us construct the same state as described in Eq. 3.1, and after constructing the state, obtain the value of the wave function when the spin coordinates are assumed to be $s_1 = \uparrow$ and $s_2 = \downarrow$; i.e. when electron 1 is spin-up and electron 2 is spin-down. Note that in this formulation, Eq. 3.8 is not a good description of the wave function, because certain matrix elements are precisely zero; the factor of $\frac{1}{2}$ is nonetheless present (from Eq. 3.1).

The integration of Eq. 3.5 simplifies to the single quantity $j s_i h s_j$. We find that

$$
\langle \Psi | \hat{O} | \Psi \rangle = \frac{1}{2} \int \phi(\vec{r}_1)\phi(\vec{r}_2)O[\phi(\vec{r}_1)\phi(\vec{r}_2)] d\vec{r}, \quad (3.18)
$$

which is identical to Eq. 3.17 except for the factor of $\frac{1}{2}$. This constant factor appears because the other non-zero spin contribution (which, in the previous case, was present from Eq. 3.16) is missing. Referring to Eq. 3.16, we see that fixing the spin state of the particles affects only the numerical constant in front of the integration. Therefore, in order to derive a spatial wave function that yields equivalent results, we are free to fix the spin state of Eq. 3.8, as long as we modify the normalization constant appropriately.

This simple example is a specific case of a general principle. The formulation involving Eq. 3.18 is less appealing than the formulation leading to Eq. 3.17. However, this formulation will prove to be far more convenient when we consider the general case of $M$ electrons.

In Appendix I we extend the method by providing a full derivation of the standard Hartree-Fock result in the case of the full $M$-body wave function. The result for the Hartree-Fock wave function is a product of a spin-up and a spin-down determinant,

$$
\Psi = \frac{1}{(M/2)!} D^\uparrow D^\downarrow, \quad (3.19)
$$
where the normalization constant $\frac{1}{(M/2)!}$ is also derived in the appendix, and where

$$D^\dagger = \det \begin{vmatrix} \phi_1 (\vec{r}_1) & \phi_2 (\vec{r}_1) & \ldots & \phi_{M/2} (\vec{r}_1) \\ \phi_1 (\vec{r}_3) & \phi_2 (\vec{r}_3) & \ldots & \phi_{M/2} (\vec{r}_3) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_1 (\vec{r}_{M-1}) & \phi_2 (\vec{r}_{M-1}) & \ldots & \phi_{M/2} (\vec{r}_{M-1}) \end{vmatrix}$$

(3.20)

and

$$D_\downarrow = \det \begin{vmatrix} \phi_1 (\vec{r}_2) & \phi_2 (\vec{r}_2) & \ldots & \phi_{M/2} (\vec{r}_2) \\ \phi_1 (\vec{r}_4) & \phi_2 (\vec{r}_4) & \ldots & \phi_{M/2} (\vec{r}_4) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_1 (\vec{r}_M) & \phi_2 (\vec{r}_M) & \ldots & \phi_{M/2} (\vec{r}_M) \end{vmatrix}$$

(3.21)

are the spin-up and spin down Slater determinants.

Eq. 3.19 is the basic equation of computational quantum Monte Carlo. (Note that QMC integrations can usually ignore normalization - if they are performed properly - because the normalization constant cancels in the standard integration; see Eqs. 4.1 and 4.2.) In a computer algorithm, a choice must be made as to the relative spin states of each electron, and so Eq. 1.2 in Appendix I cannot be employed directly. However, from the appendix we see that Eq. 3.19 (Eq. I.22 in Appendix I) can be used instead - a product of determinants of fixed spin-up and fixed spin-down electrons.

Let us now discuss the antisymmetry of the wave function. This issue is worth discussing because it is tempting to assume that Eq. 3.19 is the true many-body wave function, and not a wave function with the spin states imposed. In fact, the antisymmetry of the wave function cannot be deduced from Eq. 3.19. As chance would have it, the wave function of Eq. 3.19 is antisymmetric with respect to the exchange of any two electrons "known" to be of same spin in this spin-imposed state. This is straightforwardly due to the fact that such an exchange is equivalent to the exchange of two rows of one of the determinants. However, the fact that exchange of same-spin electrons leads to the proper antisymmetric property of the function in Eq. 3.19 is misleading. Because of electron indistinguishability, we cannot impose ahead of time the spin states of the electrons; as we’ve said, Eq. 3.19 is
an *evaluation* of the wave function of Eq. I.2 for a specific value of the spin coordinates \(\{s\}\), and nothing more. Therefore, to test for antisymmetry of the wave function we cannot “choose” two electrons that have the same spin. Instead, we must refer directly to Eq. I.2 to deduce that a swapping of the position and spin coordinates of *any* two electrons, regardless of spin state, leads to the proper antisymmetric property.

The same statements apply to an exchange of electrons “known” to be of opposite spin. In this case it is particularly relevant and important to discuss the matter carefully, because the naive approach - swapping the position coordinates of a pair of opposite-spin electrons in Eq. 3.19 - does not lead to the expected antisymmetric result. Antisymmetry of the wave function with respect to “opposite-spin” electrons *cannot* be deduced from Eq. 3.19. Eq. I.2 *must* be used.

It is particularly important to notice the unintuitive result that an exchange of a pair of opposite-spin electrons leaves both of the determinants in the spatial part of the wave function *completely unchanged* in Eq. 3.19. This can only be understood in terms of Eqs. I.3 and I.4.

The Slater determinant of Eq. 3.19 is a basic form used to model many-body wave functions in QMC. By a proper choice of the single-particle spatial functions \(\{\phi\}\), the HF solution discussed in Section 3.4 has exactly the form of Eq. 3.19. As noted in Section 3.4, however, this wave function cannot describe electron correlations. Also, because the HF solutions can be analytically calculated, there is no possibility that VMC calculations can improve upon wave functions of this form.

It is also important to note that sometimes, any wave function of the form in Eq. 3.19 is referred to as a *HF* wave function, even though the HF wave function is one that includes only the single-particle spatial functions \(\{\phi\}\) which are the solution of the relevant HF equations (such as the Roothaan equations in the restricted closed-shell formulation [30]).

We have not discussed, or even defined, other possible HF formulations, such as the open-shell restricted case, the closed-shell unrestricted case, or the full open-shell unrestricted case. The spin formulation in these cases is more involved.
3.5.2 Jastrow factors

The spatial wave function ansatz is typically improved by incorporating electron correlations in the form of a multiplicative factor known as a Jastrow factor $J$. We therefore introduce a new wave function $\Psi$,

$$\Psi = JD^\dagger D^\dagger,$$  \hspace{1cm} (3.22)

with $J$ defined as an exponential function of distances between the particles of the system, including possibly the nuclei. The wave function described by Eq. 3.22 is called a Jastrow-Slater wave function.

Because normalization of the wave function with a Jastrow factor cannot be determined without a QMC calculation, we leave off the factor $\frac{1}{(M/2)!}$ and understand that the wave function in Eq. 3.22 is not normalized. Also, in all cases the Jastrow factor is symmetric with respect to the exchange of any two electron coordinates so that it does not affect the antisymmetry of the wave function. Deriving the wave function in the form of Eq. 3.22 from a tensor product formulation including spin (Eq. 3.1) requires an infinite expansion and will not be considered.

The Jastrow factor can take different forms. It can include the so-called single-body term, which is exclusively an exponential function of the distance between electrons and nuclei. It can include a two-body term, which is an exponential function of the distance between different electrons. Finally, it can include a three-body term, which is an exponential function of the distance between different electrons, dependent also on the distance of the electron pair from a nucleus.

As an example of a Jastrow term, consider the common Pade-Jastrow function for which we place into the exponent a ratio of two polynomials in the electron distance. We have

$$J_{\text{two-body}} = \prod_{i,j>i} e^{\frac{a_1 r_{ij} + a_2 r_{ij}^2 + \ldots}{1+b_1 r_{ij} + b_2 r_{ij}^2 + \ldots}}.$$ \hspace{1cm} (3.23)

Because the Jastrow term introduces correlations between electrons, it is most important at close electron distances, and therefore the leading terms of the polynomials dominate.
Figure 3-1: An example of a typical Pade-Jastrow factor $e^{ \frac{x}{1+\beta}}$ describing two electrons (shown normalized in the figure). The Jastrow factor approaches a constant except when the electrons come near one another. In this way, the Jastrow factor models electron correlations, which cannot be modeled by a Hartree-Fock (HF) wave functions. The strength of the correlations (roughly associated with the correlation length) can be tuned by the variational parameter. The curve on the left, with $\beta = 1$, corresponding to a longer correlation length than the curve on the right, $\beta = 2$.

Note that the Jastrow factor approaches a constant value except when the electrons come near one another. See Fig. 3-1. It is exactly for this reason that the Jastrow factors are able to model electron correlations so effectively - they capture the physics of electrons correlations directly. Without a Jastrow factor, many terms in a CI expansion are necessary to model the correlated behavior of nearby electrons.

A significant problem with the HF wave function is that it is unphysical when two electrons approach one another. The local energy (discussed in the next section) of the true ground state (or excited state) wave function must be the same - at any point in configuration space. This includes all points at which two electrons of opposite spin come into direct contact, a situation which is perfectly allowed within a quantum mechanical system. For a continuous and finite wave function ansatz such as the Jastrow-Slater, with a singularity in the potential energy $V$ at such a point, the first derivative of the wave function must exhibit a discontinuity in order that the second derivative exhibits a singularity from the kinetic energy term that exactly cancels the singularity in the potential. The discontinuity in the first derivative is a cusp, and any requirement imposed upon the wave function that the two singularities cancel is known as a cusp condition. Satisfying the cusp condition is essential in order to avoid destroying the accuracy of the numerical calculation for the same
reasons discussed in conjunction with the Hellman-Feynman force in Section 4.12.1.

3.5.3 Cusp conditions

The electron-electron cusp conditions for a wave function of the form described in Eq. 3.22 can be obtained by considering two electrons in close approach and writing the Hamiltonian and the wave function in terms of their center-of-mass coordinates, and leaving the remaining electron coordinates unchanged. Before rewriting in terms of the new coordinates, the Hamiltonian is given by

\[ H = \frac{-1}{2} \nabla_{\{\bar{r}\}_e}^2 + V (\{\bar{r}\}) \]

where \(\{\bar{r}\}_e\) are the electron coordinates, and \(\{\bar{r}\}\) are all coordinates, including nuclear coordinates, of the system. After rewriting, the Hamiltonian becomes

\[ H = -\left( \nabla_r^2 + \frac{1}{4} \nabla_R^2 \right) - \frac{1}{2} \nabla_{\{\bar{r}\}_{e-others}}^2 + V (\{\bar{r}\}) \]

where \(\mathbf{r}\) is the displacement vector between the two electrons under consideration, \(\mathbf{R}\) represents their center-of-mass position, and the gradient \(\nabla_{\{\bar{r}\}_{e-others}}^2\) is with respect to all other electron coordinates. Considering only those terms that diverge in the local energy, we must impose the following cusp condition requirement:

\[ \lim_{\mathbf{r} \to 0} \left\{ \frac{1}{JD^jD^k} \left( -\nabla_r^2 + \frac{1}{\mathbf{r}} \right) JD^jD^k \right\} < \infty, \quad (3.24) \]

where \(\mathbf{r} = |\mathbf{r}|\) and we have utilized the form \(\frac{1}{\mathbf{r}}\) of the divergence of the potential function \(V\) at close range. Only one factor in the product formulation of \(J\) in Eq. 3.23 affects the cusp condition; let us write this factor as \(e^{f(r)}\) and then expand Eq. 3.24, yielding

\[ \lim_{\mathbf{r} \to 0} \left\{ \frac{1}{JD^jD^k} \left\{ \frac{2f}{r} + fn - \left( f\bar{n} \right)^2 + \frac{1}{r} \right\} JD^jD^k \right\} < \infty, \quad (3.25) \]

where the prime represents differentiation with respect to \(r\).

Interestingly, Eq. 3.25 indicates different close-range behavior for anti-parallel spin than
for parallel spin electron pairs due to the quantity $D^\dagger D^\dagger$. For electrons with anti-parallel spin in contact, in general $D^\dagger D^\dagger \neq 0$; however, for electrons with parallel spin in contact, Eqs. 3.20 and 3.21 indicate that $D^\dagger D^\dagger$ is precisely zero because two rows in one of the determinants are the same.

Considering first the anti-parallel spin case and considering only the divergent $\frac{1}{r}$ terms in Eq. 3.25, we find that

$$\lim_{r \to 0} \left\{ \frac{2f^l + 1}{r} \right\} < \infty,$$

or that

$$\frac{df}{dr} \bigg|_{r=0} = -\frac{1}{2} \quad \text{(anti-parallel spin cusp condition).}$$

(3.26)

Considering now the case of parallel spin electrons, we expand $D^\dagger D^\dagger$ around $r = 0$ in a very general form and utilize the fact that $D^\dagger D^\dagger \to 0$, and we find that $D^\dagger D^\dagger \approx b \cdot r + O \left( r^3 \right)$ for some undetermined vector $b$, and hence that $\nabla_r (D^\dagger D^\dagger) \bigg|_{r=0} = b$ and $\nabla^2_r (D^\dagger D^\dagger) \bigg|_{r=0} = 0$. Inserting these results into Eq. 3.25 and considering only the divergent $\frac{1}{r}$ terms, we find that

$$\lim_{r \to 0} \left\{ \frac{4f^l + 1}{r} \right\} < \infty,$$

and hence that

$$\frac{df}{dr} \bigg|_{r=0} = -\frac{1}{4} \quad \text{(parallel spin cusp condition).}$$

(3.27)

The cusp conditions therefore require that, for the quantity $a_1$ that appears in Eq. 3.23, we have $a_1 = -\frac{1}{2}$ in the case that the Jastrow factor represents anti-parallel spin electrons, and we have $a_1 = -\frac{1}{4}$ in the case of parallel-spin electrons. A similar derivation shows that $a_1 = Z$ (the atomic number) in the case of the electron-nucleus Jastrow factor.

### 3.5.4 Linear Combination of Atomic Orbitals (LCAO)

In order to complete the introduction to many-body wave functions, it is necessary to discuss the choice of single-particle functions $\{ \phi (\vec{r}) \}$ that comprise the Slater determinant. As mentioned previously, solutions to the HF problem can provide these functions. In general, these functions are constructed from a set of single-particle basis functions, often
taken to be the union of the individual hydrogenic atomic orbitals associated with the atoms of the system, a *linear combination of atomic orbitals* (LCAO). We then have

\[ \phi_k(\mathbf{r}) = \sum_{B,i} c_{B,i,k} \varphi_{B,i}(\mathbf{r}), \]

where \( B \) runs over all nuclei, \( i \) runs over all hydrogenic orbitals (\( s, p, d, \ldots \)), \( \varphi_{B,i} \) is the hydrogenic orbital, and \( c_{B,i,k} \) is the coefficient in the case of the function \( \phi_k \).

The hydrogenic orbitals \( \{ \varphi \} \) are necessarily non-orthogonal, as adjacent atoms can be separated by any distance, and so the construction of the functions \( \{ \phi \} \) becomes merely a question of the choice of coefficients \( c \). In the case of the HF solution, the single-particle solutions \( \{ \phi \} \) are guaranteed to be orthogonal in the appropriate Hilbert space, due to a proper choice of coefficients. In general they are not orthogonal. In addition, the exponents within the hydrogenic orbitals are sometimes modified to make the hydrogenic orbitals more or less diffuse (noting that the orbital exponent determines how rapidly the radial function decays), because there is no reason to suppose that the optimum choice of exponents for the many-body wave function should be the same as for the single hydrogenic atom.

### 3.5.5 Slater-type orbitals (STO) and contractions of Gaussian primitives

For the sake of significantly improving the computational efficiency of the QMC calculation, the hydrogenic orbitals - called *Slater-type orbitals* (STO’s) - are often approximated by a sum of Gaussian functions, called *Gaussian orbitals* (with the word “orbital” being used loosely). The hydrogenic (STO) orbitals in radial coordinates are

\[ \varphi_{n,l,m} = C \left( \sum_{q=0}^{n-1} g_q (Zr)^q \right) e^{-\tilde{z}r} Y_l^m(\theta, \varphi), \]

where \( n, l, \) and \( m \) are the quantum numbers resulting from the solution of the Schrödinger equation for a hydrogenic atom, \( Z \) is the nuclear charge, \( \tilde{z} \) is a constant numerical value (typically \( Z/n \)), \( Y_l^m \) are the spherical harmonics, \( C \) is the normalization constant, \( g_q \) are constants, and the function is centered on the given atomic nucleus. For \( n = 1 \), the sum
over $q$ is ignored.

It can be deduced from Eq. 3.19 that as the number of nuclei and electrons increases, the number of integrals that are products of multiple STO’s increases exponentially. Unfortunately, these integrals are much more computationally intensive than integrals with multiple Gaussian factors, the latter of which can be simplified and easily calculated [30]. Therefore, Gaussian orbitals allow for much faster integrations during numerical simulations. Gaussian orbitals take the form

$$\varphi = C x^a y^b z^c e^{-\tilde{z}r^2}$$

(3.30)

where $a + b + c = l$, the quantity $x^a y^b z^c$ roughly represents the angular function $Y_l^m$, and the Gaussian $e^{-\tilde{z}r^2}$ roughly represents the quantity $e^{-\tilde{z}r}$. It is sometimes said that the sum over powers in $r$ is “dropped”. The combination $(a, b, c)$ is chosen to represent the angular function in the sense that, for example, the $p_x$ orbital has $a = 1$, $b = 0$, and $c = 0$.

The obvious differences in functional form between the Gaussian and the Slater orbitals require that a sum, or contraction, of these Gaussian functions (primitives), represent any given STO. In this case, we have

$$\varphi_i = \sum_{j=1}^{d} C_{j,i} x^{a_{j,i}} y^{b_{j,i}} z^{c_{j,i}} e^{-\tilde{z}_{j,i}r^2},$$

where each function $\varphi_i$ in Eq. 3.28 (the index $B$ is left off, because the origin is assumed to be at the given nucleus) is written as a contraction of $d$ Gaussian primitives. The coefficients and exponents of the contraction are held fixed for all nuclei in the sum in Eq. 3.28. Tremendous effort has gone into determining the optimum choice and number of Gaussian primitives which must be used to model the STO’s in contracted form for the best approximation of either atoms or molecules. The end result for the single-particle molecular orbitals used in the Slater determinants of Eq. 3.19, in terms of the Gaussian primitives, is

$$\phi_k(\vec{r}) = \sum_{B,i,k} c_{B,i,k} \sum_{j=1}^{d} C_{j,i} x_{B}^{a_{j,i}} y_{B}^{b_{j,i}} z_{B}^{c_{j,i}} e^{-\tilde{z}_{j,i}r^2_M},$$

(3.31)

where the Gaussian functions are taken to be centered at the nucleus with index $B$, as
indicated by the subscripts.

It is also possible to use a long list of uncontracted Gaussian primitives in the expansion of Eq. 3.28, avoiding the double sum in Eq. 3.31, and allowing the Gaussian coefficients and exponents to vary from atom to atom. However, time and experience have shown that the best approach is usually to use the contracted form, in which the Gaussian exponents remain fixed and only the coefficients $c_{B,i,k}$ vary from molecular orbital to molecular orbital. The coefficients $c_{B,i,k}$ are known as molecular orbital coefficients. The Gaussian primitive coefficients and exponents are collectively known as the zeta coefficients.

An additional common improvement upon this scheme is to double the number of Gaussian primitives, splitting each into a nearly equivalent pair, one with a slightly increased exponent and the other with a slightly decreased exponent. This is called a double-zeta contraction, which proves to be an effective way to add flexibility into the wave function.

Various labeling schemes are employed to represent different basis sets using Gaussian contractions. A simple example is STO-3G, implying that Slater-type orbitals are each approximated with a contraction of 3 Gaussians. A more sophisticated (and realistic) example is a STO—(9s5p)/[3s2p] which implies that 9 s-type Gaussian primitives will be contracted into 3 s-type Slater orbital basis functions, and similarly 15 p-type Gaussian primitives (5 each of $p_x$, $p_y$, and $p_z$) will be contracted into 6 p-type Slater orbital basis functions (2 each of $p_x$, $p_y$, and $p_z$). Note that only s-type primitives are used in contractions for s-type Slater orbitals, and similarly for p-, d-, etc. types. Sometimes, hybrid orbitals are used, which combine (for example) s- and p- primitives into a single contraction. See ref. [35] or [36] for a good introduction. Hybrid orbitals are a fundamental concept that do not require Gaussian contraction, but Gaussian contraction is one way to represent them. Hybrid orbitals are typically employed in a valence bond approach, discussed in Chapter 6.

For future reference, let us now consider writing the Slater determinant of Eq. 3.20 or Eq. 3.21 explicitly in terms of the fully antisymmetric Levi-Civita symbol $\epsilon_{k_1 k_2 \ldots k_M}$ as

$$D^\dagger = \epsilon_{k_1 k_2 \ldots k_M} \prod_p \phi_{k_p} (\vec{r}_p) = \epsilon_{k_1 k_2 \ldots k_M} \prod_p \sum_{B,i} c_{B,i,k_p} \varphi_{M,i} (\vec{r}_p) \quad (3.32)$$
where Einstein summation is used for sums over $k_1, k_2, \ldots, k_B$, each sum ranges from 1 to $B$, and the product over $p$ ranging from 1 to $B$. (See a standard mathematical physics text for more details on this representation.)

The product

$$\phi_{\text{hp}} \equiv \prod_p \phi_{kp}(\vec{r}_p)$$

(3.33)

for any non-zero Levi-Civita value is known as a Hartree product; it represents one possible product of functions designated by a unique combination of molecular orbital/electron index pairings. The total Slater determinant is the sum of all such possible products. See ref. [30] for more details on the Hartree product.

The wave function of the form in Eq. 3.22 can be extended by including, in the place of the product $D^\dagger D^{\dagger}$, instead a sum of such products. In this sum, each determinant is constructed from a matrix with a different set of single-particle basis functions. Typically, these include atomic excited states that were not included in the simple, single-determinant Jastrow-Slater wave function of Eq. 3.22. Such a sum of Slater determinants (without the Jastrow factor) is the CI or CI-like wave function mentioned previously. In fact, it can be shown that an infinite expansion in Slater determinants with the atomic orbitals of the system always describes the exact many-body wave function [30]. Multideterminant wave functions with a Jastrow factor included are also employed in QMC calculations [37, 38]. Issues regarding multiple determinant wave functions will be discussed briefly at the beginning of Chapter 6.

This completes the introduction to the many-body theory used in this thesis. In the next chapter we will present the mathematical formalism of the QMC method, and its application to the VMC method and the SGA.
Chapter 4

The Quantum Monte Carlo method and variational optimization

This chapter provides a general background of QMC methods.

4.1 The QMC integral

Given a many-body wave function ansatz $\Psi$ for the solution to the ground state (and/or possibly one or more excited states) of the time-independent Schrodinger’s equation for a system of electrons and/or nuclei in an external potential $V$ in the non-relativistic Born-Oppenheimer approximation with fixed particle count $M$, the expectation value of a time-independent observable $\hat{O}$ is given by $\langle \Psi | \hat{O} | \Psi \rangle = \int \Psi^* \hat{O} \Psi d\mathbf{r}$, where $\mathbf{r} \equiv \{ \mathbf{r}_e \}$ (from the previous chapter) for convenience. Here, $\Psi$ and $\hat{O}$ are functions of the coordinates of the electrons in the system (with $\Psi$ assumed to be normalized), and because we are working in the Born-Oppenheimer approximation for these systems composed entirely of electrons and nuclei, the number of particles $M$ will be taken to be the number of electrons. The integration takes place over the $3M$-dimensional configuration space of the many-body electron wave function and the $3M$-dimensional differential element is represented by $d\{ \mathbf{r} \}$. $\Psi^*$ is
the complex conjugate of $\Psi$. Noting that for solutions of the time-independent Schrödinger equation, observable quantities remain unchanged when $\Psi$ is multiplied by an overall complex phase factor, and since the time-independent Hamiltonian has no explicitly imaginary elements, we are free to perform this gauge transformation such that $\Psi$ becomes entirely real, $\Psi(\mathbf{r}) \in \mathbb{R}$ for all $\mathbf{r}$. For the remainder of this thesis, $\Psi$ will therefore be assumed to be real. Defining $\langle \hat{O} \rangle \equiv \langle \Psi | \hat{O} | \Psi \rangle$, we therefore have

$$\langle \hat{O} \rangle = \int \Psi \hat{O} \Psi d\mathbf{r} = \int |\Psi|^2 \frac{\hat{O} \Psi}{\Psi} d\mathbf{r} = \int |\Psi|^2 \hat{O}_L d\mathbf{r}, \quad (4.1)$$

where the quantity

$$\hat{O}_L \equiv \frac{\hat{O} \Psi}{\Psi} \quad (4.2)$$

is referred to as the “local value of the operator $\hat{O}$”, or informally, the “local value of the observable” represented by that operator. The quantity $\hat{O}_L$ is not an operator, but rather a scalar quantity. It is nonetheless sometimes referred to colloquially as an “operator” as a simple way of referring to the operator that it contains. Typically, $\hat{O}$ is the Hamiltonian operator representing the total energy of the system, and $\hat{O}_L = \frac{H \Psi}{\Psi}$ is the local energy, a function of the electron coordinates. However, $\hat{O}_L$ need not even represent an operator corresponding to an observable; any well-defined quantity whose integral weighted according to $|\Psi|^2$ is desired, can appear in the integrand. The QMC method is simply a method to solve the integral of Eq. 4.1.

Alternatively to Eq. 4.1, we here provide for future reference the definition $\langle \hat{O} \rangle$ in the case of a non-normalized wave function $\Psi$. In this case, we still define $\langle \Psi | \hat{O} | \Psi \rangle$ as $\int \Psi \hat{O} \Psi d\mathbf{r}$. However, in this case we define

$$\langle \hat{O} \rangle \equiv \frac{\int \Psi \hat{O} \Psi d\mathbf{r}}{\int |\Psi|^2 d\mathbf{r}} = \frac{\int |\Psi|^2 \hat{O}_L d\mathbf{r}}{\int |\Psi|^2 d\mathbf{r}} \quad \text{(non-normalized $\Psi$)}. \quad (4.3)$$

Because $\Psi$ is an approximation to an eigenstate, $\hat{O}_L$ is, in general, not always equal to $\langle \hat{O} \rangle$, as it would be if $\Psi$ were an eigenstate. Instead, $\hat{O}_L$ has some non-zero variance $\sigma_{\hat{O}_L}^2$ throughout configuration space, with this variance approaching a lower limit of 0
as the variational ansatz approaches the eigenstate during variational optimization of the parameters.

Because that the rightmost integral in Eq. 4.1 is an integral over $\hat{O}_L$ weighted according to the normalized quantity $|\Psi|^2$, we see that it can be approximated by a finite sum of $N$ calculations of $\hat{O}_L$ at configuration points selected randomly from a distribution described exactly by the function $|\Psi|^2$. We have

$$m_t = \frac{1}{N} \sum_{i(\in |\Psi|^2)}^{N} \hat{O}_L (\vec{r}_i) = \frac{1}{N} \sum_{i(\in |\Psi|^2)}^{N} \frac{\hat{O}\Psi}{\Psi}, \quad (4.4)$$

understanding that the samples used for the sum are to be randomly selected from the distribution $P = |\Psi|^2$, as indicated by $i(\in |\Psi|^2)$ appearing as part of the summation index description.

If $|\Psi|^2$ is not normalized, Eq. 4.3 must be used in order to normalize it; however, the sum of Eq. 4.4 remains unchanged because the normalization constant cancels in the fraction. In the unusual case in which it is not desired for $|\Psi|^2$ to be normalized in Eq. 4.1, then Eq. 4.4 must be multiplied by the factor $\int |\Psi|^2 \, d\vec{r}$.

The method of approximation utilizing Eq. 4.4 is the Quantum Monte Carlo technique, so named in reference to Monte Carlo’s gambling casinos, where ostensibly one increases one’s chances of beating the house (or other players) by an intelligent understanding of the statistics to better one’s odds, even though in the end it’s just the luck of the draw that decides the winners and losers. In the case of the QMC method (and Monte Carlo methods in general) it is the randomness of the draws from configuration space that inspires the analogy. Every QMC calculation gives a different result, and statistical laws must be employed to determine their standard deviation. Sadly to say, in casinos one usually does not beat the house even with good knowledge of the statistics, but in QMC calculations, a good knowledge of the statistics is certain to guarantee success.

The larger the number of samples points $N$, the more accurate the estimate in Eq. 4.4. We have

$$\langle \hat{O} \rangle = m = \lim_{N \to \infty} m_t = \lim_{N \to \infty} \frac{1}{N} \sum_{i(\in |\Psi|^2)}^{N} \hat{O}_L (\vec{r}_i). \quad (4.5)$$
In Appendix J we derive the statistical accuracy in the case of finite $N$.

### 4.2 The curse of dimensionality

Before deriving these statistical formulas, it is worth mentioning that the QMC method is by no means the only method available to solve integrals such as those of Eq. 4.1. In fact, QMC itself is used to refer to any method that employs random sampling to select a set of evaluation points in the domain of integration, not just the method described above. Given that there are both many non-QMC methods, and other QMC methods than the one described above, it is necessary to understand why, and under what circumstances, the current QMC method should be employed.

Standard numerical integration techniques all rely on a grid, or some intelligent, possibly dynamically weighted grid, in order to select evaluation points in the domain of integration. In the simplest case - that of a simple, homogeneous, $3M$-dimensional rectangular grid properly covering the relevant domain - the curse of dimensionality straightforwardly arises from the fact that the number of sample points required to solve the integral to a particular degree of accuracy scales as $x^{3M}$, where $x$ is the density of grid points along any dimension. Even for unrealistically small $x$ (for example, $x = 2$) and for a relatively small many-body system, such as $M = 10$ electrons, we find (in this example) that approximately $N = 10^9$ sample evaluations are required, which is already about the maximum used in modern QMC simulations. However, current calculations frequently simulate systems with $M = 100$ or more electrons, and of course $x = 2$ is unrealistically small. Clearly, the grid method is completely out of the question for many-body integrals. Even with the most intelligent modifications, the grid method is nonetheless only capable of improving either $x$ by making $x$ become some function of the coordinates, or of improving the coefficient that precedes the $x^{3M}$ term. The scaling for all standard numerical integration techniques remains as $x^{3M}$.

In practice, the number of particles that can be solved using standard numerical integration methods is limited to about $M = 10$. Essentially, were this the whole story, many-body integrals would be unsolvable, even computationally, for physicists today.
Figure 4-1: Example of an arbitrary function and a set of grid points (dotted vertical purple lines) that might be used as sample evaluation points to calculate the integral of the function over the domain shown.

Figure 4-2: The same arbitrary function as Fig. 4-1, this time with the sample evaluation points selected randomly. Remarkably, choosing the sample points randomly allows for exponentially faster convergence of the integral than using a grid, as the dimension of the integral becomes larger.

However, by selecting evaluation points randomly, a fascinating transition in the nature of the problem takes place due to the fact of the strong law of large numbers and the central limit theorem. Before deriving the new scaling law, a simple conceptual picture is in order.

Fig. 4-1 shows an arbitrary function and 10 sample points distributed on a grid with which to evaluate the function. As the grid density increases, the mean value \( m_t \) of the evaluations will tend to the mean value \( m \) of the function. In this 1-dimensional example, the result converges more quickly than using the method of Fig. 4-2, in which an identical number of sample points have been chosen, but this time randomly.

However, as the dimensionality of the integral increases, the method employing random samples quickly becomes more efficient. In fact, the strong law of large numbers guarantees convergence (assuming the function has finite variance), and the central limit theorem states the rate of convergence quite concisely. We have

\[
\sqrt{N} (m_t - m) \sim \text{Normal}(0, \sigma_{\text{raw}}^2), \tag{4.6}
\]

the normal distribution centered at 0 of variance \( \sigma_{\text{raw}}^2 \), where \( \sigma_{\text{raw}}^2 \) is the variance of \( \hat{O}_L \).
throughout the space. The proportionality symbol represents the fact that the statistical 
*spread* of results on the left-hand side assumes this distribution. The equation is valid for 
any $N$. When the quantity $\sigma_{raw}^2$ is *estimated* from the set of $N$ samples, $\sqrt{N}$ is sometimes 
replaced with $\sqrt{N - 1}$ for a slight improvement in accuracy.

The convergence of Eq. 4.6 is explicitly independent of the number of dimensions $M$, 
in sharp contrast to the grid method with its $x^{3M}$ scaling, a most remarkable and entirely 
unintuitive result. In the case of high-dimensional integrals, the conceptual “order” repre-

sing by a grid fails, and randomness is the only practical way to solve the problem, 
resulting in the phrase “Monte Carlo” to describe these methods. The remarkable trans-
formation allowed by a random selection of sample points opens the world of Monte Carlo 
simulations for high-dimensional many-body simulations.

The dimensionality, however, can appear implicitly in the problem in the variance term 
$\sigma_{raw}^2$. There is no simple form to represent the dependence of $\sigma_{raw}^2$ on $M$; it varies from case 
to case. It has been an unceasing effort throughout the 50-year history of QMC simulations 
to find methods to reduce the variance $\sigma_{raw}^2$, either by choosing a different observable with 
which to optimize the wave function, or by incorporating computational tricks that do 
not change the value of the integral in Eq. 4.1, but do decrease the integrand’s variance. 
Also, improvements in the wave function itself are driven by the attempt to decrease its 
variance, as not only does this decrease the number of required samples, but it also suggests 
convergence towards the true wave function, the variance of $\hat{O}_L$ being precisely 0 in this case. 
The method of variance minimization, in fact, has dominated the physics QMC community 
for nearly 20 years, only recently giving way to direct energy minimization as a result of 
further recent advances, which we discuss in Section 8.7.2 and in Appendix A.

In Appendix J we derive Eq. 4.6. For convenience, we write the basic equations here. 
For the variance $\sigma_m^2$ representing the spread of results obtained in a QMC calculation of 
the integral in Eq. 4.1 utilizing $N$ independently selected samples, we have 

$$\sigma_m^2 = \left\langle \hat{O}_L^2 \right\rangle - \left\langle \hat{O}_L \right\rangle^2 = \frac{\sigma_{raw}^2}{N},$$  \hspace{1cm} (4.7)
which is identically equal to $1/N$ times the raw variance of $\hat{O}_L$. By "raw variance," we mean the square of the true spread (standard deviation) of the local values $\hat{O}_L$, independent of the number of sample points $N$. Using the usual notation to describe such a statistical spread of results, we have

$$\langle \hat{O}_L \rangle \approx m \pm \frac{\sigma_{\text{raw}}}{\sqrt{N}},$$

(4.8)

where $\sigma_{\text{raw}} = \sqrt{\langle \sigma_{\text{raw}}^2 \rangle}$ is the standard deviation of the values $\hat{O}_L$ throughout the space.

### 4.3 QMC reweighting and bias

It is relevant to the work in this thesis to discuss the merits of the QMC method using sample points selected from the distribution $P \equiv |\Psi|^2$, rather than from a uniform, or some other, distribution. QMC methods can use other distributions $Q$ from which to randomly select samples, and in these cases the integrand in Eq. 4.1 or Eq. 4.3 must be multiplied by the weighting factor

$$w = \frac{P}{Q}.$$  

(4.9)

In the case of either Eq. 4.1 or Eq. 4.3, in the place of Eq. 4.4, we have

$$m_t = \frac{1}{N} \sum_{i(\in Q)}^N \frac{P}{Q} \hat{O}_L = \frac{1}{N} \sum_{i(\in Q)}^N w \hat{O}_L.$$  

(4.10)

Multiplying by a weight introduces weighting error which typically decreases the accuracy of the calculation.

It is also useful to note that in Eq. 4.10, for an infinite number of samples we have

$$\frac{1}{N} \sum_{i(\in Q)}^N w = \int Q w = \int Q^P = \int P = 1.$$  

Therefore,

$$\sum_{i(\in Q)}^N w = N.$$  

As a result, we can replace $N$ in Eq. 4.10 by the sum of the weights.

The simplest approach to QMC does blanket sampling without any distribution at all ($Q$
is a constant, the uniform distribution, and \( w = P \). In the case of Eq. 4.1, this is equivalent to selecting sample points at random from the domain, not weighted according to \( |\Psi|^2 \), and calculating \( \Psi \hat{O} \Psi \) directly. Any other choice of sampling distribution \( Q \) is called importance sampling, because the sample points indicate a preference for certain regions over others - the more important regions.

It is possible to utilize a set of sample points, very near in distribution to the desired distribution \( P \), that were obtained from a calculation of a very slightly different wave function than the wave function associated with \( P \). In this case, the weights \( w \) will typically be close to unity, and one can suppose that the estimation \( m_t \) might be a very good one, despite the weighting error. The word reweighting is used to describe this special case of importance sampling.

### 4.4 Importance sampling

The blanket approach \((Q = 1)\), though exponentially more efficient for large numbers of particles than standard numerical integration, is nonetheless typically exponentially less efficient than the use of even the most simple methods that employ some reasonable choice of importance sampling. Further, the choice \( Q = P = |\Psi|^2 \) is far from the optimum choice. The ideal choice for an importance sampling distribution is, straightforwardly for the case represented by Eq. 4.1, the quantity \( \Psi \hat{O} \Psi \) itself, for which the evaluation of the sample points in Eq. 4.10 is trivial - each evaluation resulting in the same constant value, namely 1. However, in this case, because we must not normalize \( \Psi \hat{O} \Psi \), the sum in Eq. 4.4 must be multiplied by the “normalization constant” \( \int \Psi \hat{O} \Psi \), as discussed in Section 4.1, and we must therefore know the answer to the problem ahead of time, which makes this choice of importance sampling unrealistic.

The differences between a blanket approach \((Q = 1)\), a non-optimum but nonetheless non-constant choice of \( Q \), and the unrealistic optimum choice of \( Q \), are shown by way of a trivial example in Fig. 4-3.

In the case of Eq. 4.1, the best choice known today is to construct \( Q \) as a non-optimum probability distribution \( Q = P = |\Psi|^2 \), utilizing an ansatz for the wave function \( \Psi \). It is
important to reiterate, however, that this choice of importance sampling is not optimum. As more becomes known about the general functional form of $\hat{O}_L = \frac{\hat{O}}{\Psi}$, an ansatz of some sort for the local value of the observable - or some related quantity - might be constructed, rather than an ansatz for $\Psi$, to improve efficiency. The newest energy minimization methods (Appendix A) are a step in this direction.

It is enlightening to demonstrate the impact that importance sampling has on the statistical accuracy of a QMC calculation. Using Eq. 4.8, let us demonstrate the statistical accuracy in the case of uniform sampling ($Q = cst$). We have, using the energy as an example,

$$\int \left( \frac{H \Psi}{\Psi} \right) |\Psi|^2 d\mathbf{r} = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{H \Psi}{\Psi} \right) |\Psi|^2 \pm \frac{\sigma_{\text{random}}}{\sqrt{N}} \quad \text{(random sampling)},$$  \hspace{1cm} (4.11)

where in this case

$$\sigma_{\text{random}} = \sqrt{\left\langle \left( \frac{H \Psi}{\Psi} |\Psi|^2 \right)^2 \right\rangle - \left\langle \left( \frac{H \Psi}{\Psi} \right) |\Psi|^2 \right\rangle^2}.$$  \hspace{1cm} (4.12)
On the other hand, using the standard QMC distribution \( P = |\Psi|^2 \), we have

\[
\int \left( \frac{H\Psi}{\bar{\Psi}} \right) |\Psi|^2 d\mathbf{r} = \frac{1}{N} \sum_{i(\in |\Psi|^2)}^N \left( \frac{H\Psi}{\bar{\Psi}} \right) \pm \frac{\sigma_{\text{weighted}}}{\sqrt{N}} \quad \text{(sampling weighted acc. to } |\Psi|^2),
\]

with

\[
\sigma_{\text{weighted}} = \sqrt{\left< \left( \frac{H\Psi}{\bar{\Psi}} \right)^2 \right> - \left< \frac{H\Psi}{\bar{\Psi}} \right>^2}. \tag{4.13}
\]

It is clear from Eqs. 4.12 and 4.13 that the error terms are very different, and in fact the value \( |\Psi|^2 \) typically has a spread that is vastly larger than the spread of \( \frac{H\Psi}{\bar{\Psi}} \). The spread of \( |\Psi|^2 \) (per particle) increases exponentially with the number of particles for the wave functions employed in this thesis, whereas the spread of local energies \( \frac{H\Psi}{\bar{\Psi}} \) (per particle) is typically, to a first order of approximation, constant.

It should now be clear that obtaining sample points distributed according to \( P = |\Psi|^2 \) is essential for the efficient use of QMC. Until now the assumption has been that we have available such a set of sample points, without any question as to how the sample points may be obtained. We now discuss the important matter of how these sample points are obtained.

### 4.5 Markov Chain Monte Carlo

Calculation of the integral of Eq. 4.1 requires a set of random sample points distributed according to \( P = |\Psi|^2 \). It is the Metropolis algorithm (and significant modern-day improvements) that are used to obtain this set of sample points.

Even if the analytical function \( |\Psi|^2 \) were analytically tractable in the sense that any desired integrals could easily be performed, it is still in general mathematically impossible to construct a method capable of selecting a single random sample directly from a distribution. Only very special functions are amenable to such methods.

The method that must be employed in the general case is to begin with an arbitrary coordinate \( \{ \mathbf{r} \}_0 \) that is not selected from the distribution, and through a sequence of steps modify the coordinate (or “walk”) until, eventually, the sequence of coordinates (or “walker”) “fol-
lows” the distribution. Therefore, an infinite number of sequential positions of this walker will be in accordance with the distribution. Convergence to the distribution - gauged by minimizing the number of sequential steps that must be taken by the walker in order to match the target distribution according to some given criteria - will occur more quickly if the walker is allowed to equilibrate for some number of steps before positions are sampled, as evidently walkers do not begin distributed correctly. Equilibration is non-trivial and will be discussed in greater detail in Chs. 7 and 8. (Note that each individual coordinate, or position, during the walk, is in fact a $3M$-dimensional vector describing a possible arrangement of electrons in the system.)

Such a sequence of steps is, in its simplest form, a Markov chain, for which each step of the walk depends only on the current value of the coordinate (as well as the wave function $\Psi$). Although more sophisticated methods that consider the history of the walker’s steps have been developed, such as reptation QMC, we will not discuss them in this thesis, nor have they been employed in our calculations.

### 4.5.1 Transition rule and detailed balance

The theory of Markov chains and their convergence is well-developed and very active. The variety of possible distributions makes for many entirely different classes of problems, and there is no single best transition rule that determines each step of the walk. Clearly, in order to obtain random samples, the transition rule must incorporate an element of randomness. Given a transition rule $\tilde{A}(\mathbf{r}, \mathbf{s})$ that defines each step that moves the walker from its current position $\mathbf{r}$ to a random, unknown new position $\mathbf{s}$ (not to be confused with the spin coordinates $\{s\}$ from the preceding chapter), we can define a transition function $A(\mathbf{r}, \mathbf{s})$ that is the normalized distribution resulting from an appropriately complete infinite number of applications of $\tilde{A}(\mathbf{r}, \mathbf{s})$. For a properly-selected $\tilde{A}(\mathbf{r}, \mathbf{s})$, $A(\mathbf{r}, \mathbf{s})$ must be a well-defined function, by construction. There is a simple way to describe the condition that must be satisfied by $A(\mathbf{r}, \mathbf{s})$ in order that the long-time-average distribution of the walker’s positions be identical to a target distribution $Q(\mathbf{r})$ (typically $|\Psi|^2$ in the case of QMC).
We must, have, for $A$,

$$
\int Q(\vec{r}) A(\vec{r}, \vec{s}) \, d\vec{r} = Q(\vec{s}). \tag{4.14}
$$

A more restrictive condition is detailed balance,

$$
Q(\vec{r}) A(\vec{r}, \vec{s}) = Q(\vec{s}) A(\vec{s}, \vec{r}), \tag{4.15}
$$

otherwise known as reversibility. Evidently, inserting 4.15 into 4.14,

$$
\int Q(\vec{r}) A(\vec{r}, \vec{s}) \, d\vec{r} = \int Q(\vec{s}) A(\vec{s}, \vec{r}) \, d\vec{r} = Q(\vec{s}) \int A(\vec{s}, \vec{r}) \, d\vec{r} = Q(\vec{s}),
$$

we find that the condition of Eq. 4.14 is satisfied. In general, the condition of detailed balance is simpler to prove for a given transition rule.

### 4.5.2 The Metropolis algorithm

A very successful and well-known transition rule, still frequently used in simple QMC computations today, is the Metropolis algorithm, developed in 1953 by Metropolis, et. al. [2]. The Metropolis algorithm defines the transition rule $\tilde{A}(\vec{r}, \vec{s})$ as follows. Starting at $\vec{r}$, choose a random new coordinate $\vec{t}$ according to some symmetric distribution $T(\vec{r}, \vec{t})$. Of course, for the algorithm to be practical, it must be possible to conveniently and efficiently choose a random value from the distribution $T$, unlike from $|\Psi|^2$. By fiat, $T(\vec{r}, \vec{t}) = T(\vec{t}, \vec{r})$. Generate a random number $b$ uniformly in the range $[0, 1]$. If $b \leq \frac{Q(\vec{r})}{Q(\vec{t})}$, then $\vec{s} = \vec{t}$ and the move is said to be accepted. Otherwise, $\vec{s} = \vec{r}$ and the move is said to be rejected.

Evidently, the probability of accepting a move from $\vec{r}$ to a given $\vec{t}$ in the Metropolis algorithm is $\min\left\{1, \frac{Q(\vec{t}) T(\vec{t}, \vec{r})}{Q(\vec{r}) T(\vec{r}, \vec{t})}\right\}$. The probability of making a move from $\vec{r}$ to $\vec{t}$ is therefore $T(\vec{r}, \vec{t}) \min\left\{1, \frac{Q(\vec{t}) T(\vec{t}, \vec{r})}{Q(\vec{r}) T(\vec{r}, \vec{t})}\right\}$. However, this is the same as the probability of making a move from $\vec{r}$ to $\vec{s}$. Therefore, $\tilde{A}(\vec{r}, \vec{s})$ can be constructed for the Metropolis algorithm as $\tilde{A}(\vec{r}, \vec{s}) = T(\vec{r}, \vec{s}) \min\left\{1, \frac{Q(\vec{s}) T(\vec{s}, \vec{r})}{Q(\vec{r}) T(\vec{r}, \vec{s})}\right\}$. (It is assumed that $\vec{r} \neq \vec{s}$.)
Therefore,

\[ Q(\vec{r}) A(\vec{r}, \vec{s}) = Q(\vec{r}) T(\vec{r}, \vec{s}) \min \left\{ 1, \frac{Q(\vec{s}) T(\vec{s}, \vec{r})}{Q(\vec{r}) T(\vec{r}, \vec{s})} \right\} \]

\[ = \min \{ Q(\vec{r}) T(\vec{r}, \vec{s}), Q(\vec{s}) T(\vec{s}, \vec{r}) \}, \]

which is a symmetric function in \( \vec{r} \) and \( \vec{s} \). Thus, the detailed balance condition (Eq. 4.15) is satisfied for the Metropolis algorithm.

The choice of transition function \( T(\vec{r}, \vec{s}) \) is critical for efficiency in the Metropolis algorithm. Typically, a random coordinate within a \( 3M \)-dimensional sphere centered on \( \vec{r} \), of radius

\[ \Delta r \propto \sqrt{\Delta \tau}, \tag{4.16} \]

is chosen as the transition rule, where \( \Delta \tau \) is some interval representing time in the DMC equation (Section 4.15); see ref. [39] (pp. 39-43) for a good discussion of the relationship between \( \Delta r \) and \( \Delta \tau \) in QMC, and why the condition of Eq. 4.16 applies in the case of VMC as well as DMC. Also note that the related quantity \( \tau \) from Ch. 7.13 is rescaled to represent the number of integer steps in the Metropolis (or Metropolis-like) algorithm, and is therefore untied in that chapter from the atomic units represented here.

However, many more intelligent choices than the simple transition function of Eq. 4.16 exist. Some such choices, such as the Langevin algorithm, go beyond the Metropolis algorithm in that the transition function \( T \) is not symmetric. In such cases, detailed balance must be proven. One of the most common transition functions used today in QMC is a modified version of the Langevin algorithm, introduced by Umrigar, et. al., in 1993 [40]. It is the one used in all calculations described in this thesis, unless otherwise noted. We will not discuss the details of the transition rule for the Langevin or the modified Langevin algorithm in this thesis; however, note that the relationship described in Eq. 4.16 holds even in the case of the modified Langevin algorithm in a generalized sense; see ref. [41].

We will now discuss complications to Eq. 4.8 that result from the necessity of using a Markov chain to supply random samples, rather than being able to provide random samples directly from the distribution \( P \). Clearly, because each position except the first in
the Markov chain depends on the previous, adjacent positions cannot both be randomly selected from the target distribution, but instead each position depends on the previous position in some way. This non-randomness is a correlation between adjacent, and also nearby, positions in the Markov chain. Evidently, because over a long period of time the positions of the walker are described by the target distribution, the correlation between any two points decreases as the distance (in Markov chain steps) increases between the points. The autocorrelation function is a measure of this correlation, and a global measure of the significance of correlation in the chain as a whole, independent of step separation, is given by the integral of the autocorrelation function in the form of a single autocorrelation time $\tau$. The nature and extent of this correlation has played a central role in the development of the SGA and will be discussed in detail in Chs. 7 and 8. If the autocorrelation time $\tau$ is known, the correction to Eq. 4.8 is given simply as

$$\left\langle \hat{O}_L \right\rangle \approx m \pm \frac{\sigma_{\text{raw}}}{\sqrt{N}} \quad (4.17)$$

a result we derive in Ch. 7.

The primary issues involved in the calculation of the fundamental QMC integral of Eq. 4.1 have now been addressed. In summary, using as an example a calculation of the total energy of the system, the local energy $\tilde{H}_L$ is sampled $N$ times to calculate the sum of Eq. 4.4, as an approximation of the total energy. The accuracy of the approximation is given by Eq. 4.17. Sample points are selected by use of a Markov chain with an appropriately chosen transition function, such as a Metropolis algorithm or a modified Langevin algorithm. The effort to increase the efficiency of the computation - i.e. its speed and accuracy - must be directed towards an improvement either of the variance $\sigma_{\text{raw}}^2$ of the local energy, or an improvement in the transition rule in the Markov chain that leads to a decrease in correlations in the chain as indicated by the autocorrelation time $\tau$.

See ref. [42] for an excellent introduction to the Metropolis algorithm, as well as QMC methods in general.
4.6 Local variance of the energy

In fact, another quantity - not the energy - has been extensively used for QMC calculations during the past 20 years (as mentioned previously) due to its improved variance. It is the local variance of the operator \( \hat{O} \), defined as

\[
\text{local variance} = \hat{O}_L^2 - \left( \langle \hat{O}_L \rangle \right)^2.
\]

Almost always, the operator \( \hat{O} \) employed for a local variance calculation is the energy; we will discuss this shortly in the context of variance minimization.

Eq. 4.18 can be simply derived from the definition of the expectation value of the variance

\[
\left\langle \left( \hat{O}_L - \langle \hat{O}_L \rangle \right)^2 \right\rangle = \langle \hat{O}_L^2 \rangle - \left( \langle \hat{O}_L \rangle \right)^2,
\]

for which the correct approximation is obtained by selecting the local quantity as defined in Eq. 4.18.

In the case of the variance, \( \langle \hat{O}_L \rangle \) cannot, of course, be determined at each individual sample point, because it is by definition an average over an infinite number of sample points. Two approaches are used to deal with this difficulty. For the first approach, notice that the summation in Eq. 4.4 to obtain the right-hand side of Eq. 4.19 must be accumulated over all steps taken by the walker before the division by \( N \) can take place. Therefore, both the summation for \( \langle \hat{O}_L^2 \rangle \) and the summation for \( \langle \hat{O}_L \rangle \) can be performed simultaneously and only after \( N \) steps do they need to be combined. However, due to the fact that the very purpose of variance minimization is typically to avoid a more accurate calculation of \( \langle \hat{O}_L \rangle \), the value \( \langle \hat{O}_L \rangle \) obtained with this approach may not be as accurate as an estimate for the quantity \( \langle \hat{O}_L \rangle \) that is imposed by the researcher ahead of time, such as the calculated HF energy. The second approach, therefore, is to impose an estimate of the quantity \( \langle \hat{O}_L \rangle \), labeled \( E_{\text{guess}} \) in the case of the energy, instead of calculating an approximation for \( \langle \hat{O}_L \rangle \). Strictly speaking, the second approach is not an approximation of the local variance, but is instead an approximation of a related quantity (the second moment of the local operator.
with respect to a reference value. A linear combination of the local variance and the second moment is sometimes used.

In this context, it is useful to point out that, in general, higher moments are related to the statistical error of lower moments; we will not discuss or derive the relations here.

Using $E_{\text{guess}}$, Eq. 4.18 becomes

$$\text{local variance} = \hat{O}_L^2 - E_{\text{guess}}^2.$$  \hspace{1cm} (4.20)

### 4.7 The Variational theorem and variational optimization

The issues so far discussed involve a direct calculation of the integral of Eq. 4.1 for a fixed wave function \textit{ansatz}. If this were the only use of QMC calculations, QMC would be far less prevalent. An entirely new set of issues arises when QMC is used not only to perform the calculation of Eq. 4.1, but also to optimize the variational parameters that appear in the wave function \textit{ansatz}. This is the task of variational Monte Carlo - VMC. Much effort has gone into improving variational methods. This chapter lays the foundation for a detailed discussion of modern-day VMC methods, including the SGA.

The \textit{variational theorem} is the simple but powerful theorem that underlies VMC. Variational optimization is one of the most useful applications of QMC, and is almost always used as the starting point for more accurate DMC calculations.

The variational theorem can be simply stated. Any wave function \textit{ansatz} for a many-body physical system is guaranteed to have as the expectation value of its energy a value that is greater than, or equal to, the true energy of the ground state of the system. Equality holds only when the wave function \textit{ansatz} is proportional to the exact ground state wave function (i.e. when it is the ground state). The proof of the variational theorem is simple, and we do not provide it here. See ref. [43] for a proof. Without giving a formal derivation, the explanation for the variational theorem is that any wave function \textit{ansatz} is a linear combination of the exact ground state and the exact excited states. Excited states all contribute an energy equal to or higher than the ground state energy, and so can only have the effect of raising the energy above the ground state energy.
According to the variational theorem, we have \( \langle H \rangle_{\text{ansatz}} \geq \langle H \rangle_{\text{exact}} \), or, equivalently,

\[
E_{\text{ansatz}} \geq E_{\text{exact}}
\]

for any set of variational parameters within any acceptable wave function ansatz. Therefore, \( E_{\text{ansatz}} \) is an upper bound on the exact ground state energy of the system.

In the QMC community, we speak of lowering the energy, as though we have some kind of control over the energy. Of course we do not. Instead, we are making use of the variational theorem, which guarantees that the known upper bound of the exact energy has, in fact, been lowered. The goal is to approach the exact energy of the system from above, as though cranking a vice more and more tightly.

**HF theory and correlation energy**

A remark is in order that revisits HF theory in this context (see Section 3.4). Because HF calculations are generally simple to perform, and define a baseline of zero correlation for the calculation of the energy, it is typical for QMC researchers to perform the HF calculation, and then attempt to retrieve larger and larger fractions of the correlation energy by use of VMC or DMC simulations. Sometimes, the exact energy is known ahead of time, either from an exact experiment, or from a very detailed ab-initio calculation. In this case, the final closing position of the vice is known ahead of time, and we know how much “juice” there remains to be squeezed out by the vice. Different QMC methods frequently utilize such benchmark systems in order to compare the fraction of the correlation energy they are able to retrieve. As a rule of thumb, DMC is usually able to retrieve better than 90% of the correlation energy for most systems.

Note that although the variational theorem states that the exact energy is always lower than the energy calculated using variational QMC (what is typically described as the “variational energy”, \( E_{\text{ansatz}} \)), it is still possible for QMC calculations to provide a result that is lower than \( E_{\text{exact}} \). This is due to the fact that results obtained using QMC for finite \( N \) are not equal to \( E_{\text{ansatz}} \), but instead are distributed with a standard deviation given by
Eq. 4.17 due to the statistical error inherent in the QMC calculation. It is important, in addition, to recall that about 1/3 of calculated results lie outside the range $E_{\text{ansatz}} \pm \frac{\sigma_{\text{raw}}}{\sqrt{2}}$, the standard deviation giving only a measure of the width of a Normal distribution. Like most statistical distributions, there are long tails on the distribution of $m_{t}$, so there are occasional calculations that result in a value many standard deviations from the mean.

4.7.1 The variational landscape

In order to obtain the best possible wave function, researchers typically include one or more variational parameters within the wave function ansatz. These parameters are allowed to assume different values in order to best capture the relevant physics for a particular system. We can consider the parameters that appear in the wave function (from here forward, $\tilde{\beta}$), along with the corresponding exact energies of the trial wave functions associated with these varying parameters, to form a variational landscape. There is an exact energy associated with every point in the landscape. However, only the global minimum of the energy in the landscape corresponds to what is typically described as the energy of the wave function. And of course, this energy is not the exact ground state energy, but is typically higher, in accordance with the variational theorem.

The “energy of the wave function” frequently appears in reports on QMC calculations, and in such cases it is assumed that the variational parameters have been properly optimized so that it is the lowest energy of the wave function associated with the optimum parameters that is implied.

4.7.2 Reweighting revisited

In order to navigate the variational landscape during a VMC computation, typically many points in the landscape need to be sampled. At each point, the calculation of Eq. 4.4 must be performed, with the possible inclusion of a weighting function $w$ (discussed in Section 4.4) associated with an incorrect distribution $Q = P_{0}$, where $P_{0}$ is the correct distribution at a previous point in the variational search. This latter reveals the fundamental importance of reweighting within VMC. Not only is reweighting usually necessary in order to obtain a
smooth energy curve with a well-defined minimum - raw QMC calculations would otherwise show a statistical scatter that wipes out the location of the minimum - but reweighting also provides a dramatic efficiency improvement, because the Metropolis-like algorithm does not need to be performed at every variational step. However, it also introduces reweighting bias. Naturally, the bias due to reweighting typically increases the further away is the point of the search in the variational landscape from the point associated with $P_0$.

4.8 Variance minimization

Because many calculations of the form of Eq. 4.4 are involved in a variational calculation, one at each different set of variational parameters, and because establishing the most efficient path through the variational landscape is non-trivial, it takes far longer to perform a variational calculation than it does to perform a single calculation of the energy. It is for this reason that variance minimization is often employed - that is, $\hat{O}_L$ in Eq. 4.1 is chosen to be the local variance, rather than the local energy.

When discussing the variance of the local energy, it is useful to recognize that the local energies appearing in Eq. 4.4 are clustered around their mean value and form a distribution. An example distribution is plotted in Fig. 4-4 for Li$_2$ modeled with the all-electron HF wave function. As the figure reveals, the local energies form a roughly Gaussian, or normal, distribution. The width of this distribution is the (square root of the) variance of the local energy. The variance of the local variance, on the other hand, when calculated with a Gaussian distribution, is significantly less than the width of the Gaussian itself; from Eq. 4.8 or Eq. 4.17, with $\sigma_{\text{raw}}$ the (square root of the) variance of the local variance throughout the space, it can be seen that, in general, this might indicate a more promising QMC calculation that requires a smaller number of sample points.

In fact, higher-level moments of the energy (the variance being the second moment) have correspondingly smaller variances. It might seem that QMC calculations become infinitely more robust for infinitely higher orders of the energy. However, this is not the case. Each moment of the energy requires, as a reference value, a guess as to the exact value of the preceding order ($E_{\text{guess}}$ in the case of the first order in Eq. 4.20). The errors introduced
by incorrect higher-order guesses quickly destroy the accuracy of the QMC calculation. In fact, if the first-order guess appearing in Eq. 4.20, the energy itself, were known exactly, there would be no need to perform the QMC calculation at all!

Variance minimization does not always provide the benefits discussed here. See ref. [44] for an example.

It has been extensively empirically observed that - if reweighting is used (more on this below) along with an estimate \( E_{\text{guess}} \) - far fewer sample points are sometimes required for variance minimization than for energy minimization for equally accurate results, and in these cases variance minimization proceeds far more quickly than energy minimization. This empirical observation was first introduced into the QMC community in 1988 with a seminal paper by C. Umrigar [45].

4.8.1 The variance as a least-squares fit to data

It is revealing to understand one reason why the variance minimization method works well for a small number of sample points. This issue is discussed in greater depth in ref. [46].
Consider the form of the variance \( \left( \hat{\mathcal{O}}_L - O_{\text{guess}} \right)^2 \) of the quantity which is minimized over a set of fixed sample points. This is exactly the form of a least-squares fit to a set of data. It has a minimum of zero, and furthermore the exact desired result for each sampling of \( \hat{\mathcal{O}}_L^2 \) is known. Therefore, if the exact wave function could be represented by a choice of the variational parameters (with, of course, an incorrect guess \( O_{\text{guess}} \)), the fit would be exact, assuming there are at least as many sample points as variational parameters. This is an indication of the ability of the method to achieve excellent accuracy for a fixed set of sample points.

This beneficial circumstance is only the case because of the least-squares form of the variance. It does not apply to an energy calculation, for which a much larger number of sample points need to be used even with correlated sampling. In the case of reweighting with energy minimization, because the form is not a least-squares-fit with a known lower bound for each term in the sum, outlier terms in the sum of Eq. 4.4 have a tendency to dominate the sum (an unfortunate issue that is in addition to the weighting error of Eq. 4.10). It is therefore common to increase the value of the energy, rather than decrease it, at the new point in the variational landscape with reweighting. The lower bound in the least-squares-fit for the variance minimizes this effect [47].

For all of the reasons discussed above, variance minimization is typically more efficient than straightforward energy minimization.

Although little physics is obtained by employing the local variance, the purpose of the variational method is not to calculate the expectation value of the energy at the intermediate variational steps, but rather simply to locate the global (or local) minimum in the variational landscape, and then to calculate the energy with a relatively lengthy calculation at the optimized point.

However, there is no variational theorem that applies to the method of variance minimization - only to energy minimization. Even if there were, the variance is not the energy; therefore, the minimum of the variance would seem to be unrelated to the minimum of the energy.

However, two straightforward facts immediately indicate that the variance method might
be reliable nonetheless. First, the expectation value of the variance is bounded from below by the known lower bound of zero. Second, the exact ground state wave function has an expectation value for its variance that is precisely zero (which is easy to confirm because the ground state wave function is an eigenfunction of the energy).

Certainly, if the variational wave function ansatz had precisely the same mathematical form as the exact wave function, then the point in the variational landscape that minimizes the energy - the exact ground state - would also have a variance of zero, as can easily be observed from the fact that $\frac{\mathbf{H} \psi}{\psi} = E$ for all samples. In this case, if the point were a distinct minimum in the variance landscape, variance minimization would give exactly the correct result for the energy. However, because the wave function ansatz rarely has exactly the correct form, the minimum of the variance will, in general, not occur at the same point at which the minimum of the energy occurs.

The benefits of a small value of $\sigma_{\text{raw}}$ corresponding to the local variance of Eq. 4.20 are clear; however, there is a flip side to the story. The small value of $\sigma_{\text{raw}}$ carries with it a disadvantage. As the variance optimization proceeds, changes in the variance tend to be small because $\sigma_{\text{raw}}$ itself is small; therefore, more sample points are necessary to distinguish these small differences. Fundamentally, the reason that variance minimization is so effective is not simply the small value of $\sigma_{\text{raw}}$, but in conjunction, it is the use of reweighting (introduced previously) which allows small differences to be revealed and which allows the least-squares form of the variance to provide a benefit.

4.9 Reweighting and finite difference methods

It is important to distinguish two different common uses of reweighting in QMC calculations. First, in calculations of numerical derivatives, two very close points in the variational landscape must be employed, and reweighting can be used in this unique case to obtain an energy difference $\Delta E$ that is very small. Second, in variational QMC, reweighting may be used during the variational optimization at points that are macroscopically separated.

The essence of reweighting is the following. Although the QMC statistical error may be large, if the sample points from the set $P$ in Eq. 4.4 are reused as the points $Q$ in
some following calculation with shifted variational parameters \( \tilde{\beta} \) utilizing Eq. 4.10, then the statistical error in the two calculations is highly \textit{correlated}, and this overall error term cancels in such a way that energy \textit{differences} can be measured quite accurately, even when the energy \textit{values} themselves would otherwise be subject to a noise that would swamp out the differences.

Energy difference methods in this context are more generally known as \textit{finite difference} methods. These methods imply that two very close adjacent points in the variational landscape must be selected in order to calculate the energy difference. (We define one of these distributions as the \( Q \) of Eq. 4.10.) To perform this calculation without reweighting, an unrealistically huge number of sample points would need to be employed in order to distinguish the energies of these two very close points. Numerical differentiation is an ideal use of reweighting because the distributions \( P \) and \( Q \) are so similar that the weightings \( w \) are very close to unity. In the limit that the two distributions become the same, the reweighting bias goes to zero. Therefore, QMC researchers have typically used numerical differentiation with reweighting without any trouble.

However, there does remain some inaccuracy due to the statistical noise. This reweighting bias becomes relevant only when a small number of sample points is used in Eq. 4.10, as in the SGA. For stochastic optimization, numerical derivatives are not nearly as accurate as analytical derivatives, and in fact a very different body of mathematical theory is used to study convergence in the two cases. See ref. \[6\] for a detailed comparison of numerical and analytical derivatives in stochastic optimization.

Because reweighting must always be used when calculating a numerical derivative, the phrase “reweighting” is typically reserved only for the case when reweighting is used during an honest-to-goodness variational optimization, which may or may not employ numerical derivatives. In this case, the distribution \( P \) must be recalculated every once in a while until self-consistency is obtained. Typically, this takes only a handful of iterations; this construes the basic VMC approach.

Note that the reweighting bias can be conceptually understood by a simple special case, that of two wave functions which have a region of zero overlap. Clearly, in such a case the
region of zero overlap is never sampled, and therefore provides a bias to the reweighted results regardless of the number of sample points that are utilized.

The bias of reweighting is extremely difficult to measure, and it can easily destroy a calculation if care is not taken, an issue we discuss now.

The theory of convergence in the case of reweighting is complicated enough that in general QMC researchers do not employ analytical formulas to determine the reweighting bias. Instead, they use a rule of thumb which is sufficient to provide a red flag if the bias is becoming large. Specifically, the minimization must be monitored to ensure that the weights \( w \) do not deviate far from unity. If the weights \( w \) in Eq. 4.10 do become much smaller or larger than 1, it is a sign that reweighting bias is destroying the desired accuracy.

4.10 Resurgence of energy minimization methods

In recent years great attention has again been focused on energy, and related, minimization methods, rather than variance minimization. Different reasons combine to explain the renewed interest.

1. Increased computational power has enabled QMC to be used to perform calculations of systems of experimental interest using the less efficient energy minimization method.

2. Techniques that modify the local energy or its derivatives by reducing its variance without modifying its expectation value have been developed.

3. More efficient optimization methods have been developed. The SGA lies in this category.

4. Improved wave functions have been discovered, with decreased variance.

5. The coordinates of the nuclei cannot be optimized using variance minimization.

The reason for (5) can be described as follows. Every set of nuclear coordinates corresponds to some ground state wave function, with an associated variance of zero. Because variance minimization attempts to locate a distinct zero of the variance, the method fails.
This prohibits QMC researchers from studying the structure of molecular systems using variance minimization.

Variance minimization still plays a role, but the heyday of variance minimization is arguably giving way as more and more researchers return to energy minimization-related methods.

4.11 Energy and force

One of the basic applications of energy minimization-related methods is in the calculation of forces (or generalized forces, defined below), for which, in the Born-Oppenheimer approximation, a simple approach is to determine the gradient of the energy with respect to the nuclear coordinates. Note that in the Born-Oppenheimer approximation, the nuclei are considered instantaneously fixed for calculations of the force, and provide no kinetic energy contribution; therefore, the derivative of the total energy is the same as the derivative of the potential energy.

However, direct application of the basic relationship $\nabla_R E_{\text{total}}$ to calculate the force is subject to the severe drawback discussed in Section 4.8.1; namely, the inevitable outlier points weaken the accuracy of the calculation. The other simple approach - utilizing the Hellman-Feynman theorem (discussed in the following section) - itself has a severe drawback. Because both simple available methods have severe drawbacks, calculations of force and structural optimization have not been accomplished in QMC until recently, with the development of more sophisticated methods. A discussion of these more sophisticated methods appears in Ch. 8 and in Appendix A.

4.12 The Hellman-Feynman theorem

There is an alternative method to calculate forces in QMC that utilizes the Hellman-Feynman theorem. Unfortunately, this method is subject to a severe drawback, which has resulted in the method never being employed with any success until developments that appeared during the past decade. The Hellman-Feynman theorem transforms the problem
from a “brute-force” calculation of the energy at many different points in the variational landscape using Eq. 4.4, with $\hat{O}_L$ equal to the local energy, into a problem in which $\hat{O}_L$ is replaced by a quantum-mechanical operator representing the classical force in the Born-Oppenheimer approximation.

It was R. Feynman in 1939 (for whom the Hellman-Feynman theorem is partially named) who first pointed out that in quantum mechanics, “force” is a muddy concept due to the fact that two different equally valid definitions of the force can give different calculated results in some physical systems [48]. They are:

\begin{equation}
\vec{F} = \vec{\nabla}_\vec{R} \langle H \rangle \quad (4.21)
\end{equation}

and

\begin{equation}
\vec{F} = \langle \vec{\nabla}_\vec{R} H \rangle, \quad (4.22)
\end{equation}

where $\vec{R}$ can be taken to be the full set of nuclear coordinates (see remark that follows), or if $\vec{F}$ is considered to be a generalized force, then $\vec{R}$ can be taken to be the complete set of variational parameters (or any desired subset), and $\vec{F}$ is then defined as in Eq. 4.21. Note that $\vec{F}$ and $\vec{R}$ are not written in boldface because all components of any particle coordinates that may appear in these vector spaces are taken to be represented by the arrow. (For example, if $\vec{R}$ represents 5 nuclear coordinates each in 3-dimensional space, then $\vec{R}$ is a 15-dimensional vector. For 5 electrons $\vec{F}$, the arrow represents a 5-dimensional space, each dimension of which has three components represented by the boldface.) If $\vec{R}$ correspond to $S$ nuclear coordinates which are in turn the variational parameters, then $\vec{\beta} = \vec{R}$.

Evidently, regarding Eq. 4.21, when $|\Psi\rangle$ is an eigenstate corresponding to energy $E_M$, we have

\begin{equation}
\vec{\nabla}_\vec{R} \langle H \rangle = \vec{\nabla}_\vec{R} \langle \Psi | H | \Psi \rangle = \langle \vec{\nabla}_\vec{R} \Psi | H | \Psi \rangle + \langle \Psi | \vec{\nabla}_\vec{R} H | \Psi \rangle + \langle \Psi | H | \vec{\nabla}_\vec{R} \Psi \rangle, \quad (4.23)
\end{equation}
and since $H$ is Hermitian and $|\Psi\rangle$ is an eigenstate with energy $E_M$, we then have

$$\hat{\nabla}_R \langle H \rangle = E_M \langle \hat{\nabla}_R \Psi | \Psi \rangle + \langle \Psi | \hat{\nabla}_R H | \Psi \rangle + E_M \langle \Psi | \hat{\nabla}_R \Psi \rangle$$

(4.24)

$$= E_M \left( \langle \hat{\nabla}_R \Psi | \Psi \rangle + \langle \Psi | \hat{\nabla}_R \Psi \rangle \right) + \langle \Psi | \hat{\nabla}_R H | \Psi \rangle,$$

(4.25)

and since $\langle \Psi | \Psi \rangle = 1$ so that

$$\hat{\nabla}_R \langle \Psi | \Psi \rangle = 0 = \langle \hat{\nabla}_R \Psi | \Psi \rangle + \langle \Psi | \hat{\nabla}_R \Psi \rangle,$$

(4.26)

we have

$$\vec{F} = \hat{\nabla}_R \langle H \rangle = \langle \Psi | \hat{\nabla}_R H | \Psi \rangle \equiv \left\langle \hat{\nabla}_R H \right\rangle$$

(4.27)

and the Hellman-Feynman theorem is proved.

The Hellman-Feynman theorem states that in the Born-Oppenheimer approximation, the forces on nuclei in molecules or solids are those which would arise electrostatically if the electron probability density were treated as a static distribution of negative electric charge, because if $\tilde{R}$ represents the coordinates of the nuclei, then $\hat{\nabla}_R H = \hat{\nabla}_R V$ which, when evaluated inside the integral at a particular value of the dummy integration variable, is the force experienced by the nuclei due to the infinitesimal electron charge distribution at that point. We then have

$$\vec{F} = \left\langle \hat{\nabla}_R V \right\rangle.$$  

(4.28)

As Feynman noted, the theorem provides a useful conceptual basis to understand bonding. For bonding orbitals, the electron density is peaked between two nuclei. According to the Hellman-Feynman theorem, both nuclei will then on average be drawn towards this electron density peak as can be deduced from a straightforward application of classical electrostatic principles, resulting in bonding between the nuclei.
4.12.1 Failure of the Hellman-Feynman theorem

Normalization of the wave function is required for application of the Hellman-Feynman theorem. In the step of the Hellman-Feynman derivation given by Eq. 4.26, the wave function ansatz is assumed to be normalized. However, as we shall see, in practice it is usually impossible to determine this normalization constant. Therefore, in practice the wave function ansatz is almost never normalized.

Revisiting Eq. 4.4, it is clear that in practice, to carry out the calculation, normalization of the wave function ansatz is not required even though the wave function is assumed to be normalized, because by design the normalization term cancels in the fraction. In the Hellman-Feynman theorem, however, no such cancellation occurs in the step indicated by Eq. 4.26. Therefore, the Hellman-Feynman theorem does not rigorously apply, in practice, in QMC calculations; rather, it becomes an approximation.

Furthermore, because the wave function ansatz is not an exact eigenfunction, the step indicated by Eq. 4.24, in which $H |\Psi\rangle$ is replaced by $E_M |\Psi\rangle$, also does not rigorously hold in practice in QMC calculations. Both of these inaccuracies introduce bias into Hellman-Feynman calculations of the force in QMC.

The above biases are evidently difficult to quantify. Nonetheless, considerations of these biases have not been undertaken in detail, because the Hellman-Feynman force is subject to the more severe drawback that the variance of $\nabla_{\hat{R}} H$ is infinite, and therefore so is the error of any QMC calculation of this quantity. The infinite variance in this case can be easily observed by the fact that

$$\nabla_{\hat{R}} H = \nabla_{\hat{R}} V.$$  

With $V$ for a particular electron and nucleus with coordinates $\hat{r}$ and $\hat{R}$, respectively, given by $\frac{-1}{|\hat{r} - \hat{R}|}$, we have $\nabla_{\hat{R}} V = \frac{(\hat{r} - \hat{R})}{|\hat{r} - \hat{R}|^3}$, which grows infinitely large in magnitude as the electron approaches the nucleus. The extension to multiple electrons and nuclei is straightforward. The variance of $\nabla_{\hat{R}} H$, given as $\langle \Psi | (\nabla_{\hat{R}} V - \langle \nabla_{\hat{R}} V \rangle)^2 |\Psi\rangle$, is therefore infinite. Note that in Section 3.5.3, we discussed the similar infinite term appearing in the potential $V$ that is part of the Hamiltonian calculation $\langle \Psi | H |\Psi\rangle$. However, in the latter case the inclusion
of the Jastrow factor provides a contribution that exactly cancels the divergence. No such cancellation appears in the former case, and the Hellman-Feynman theorem, as it stands, cannot be utilized to calculate forces in QMC.

However, variance-reduction methods within Monte Carlo allow for a reduction in the variance of a Monte Carlo integrand (Eq. 4.1), without changing the value of the integral itself. Such sophisticated methods have only recently been applied within QMC to obtain forces using the Hellman-Feynman theorem [49, 50].

4.13 Analytical gradients and generalized forces

In practice, QMC calculations do not have at their disposal an exact eigenfunction of the energy. Therefore, the Hellman-Feynman theorem is only a useful approximation - even if it could be utilized. A better approach is to recognize that in VMC, it is a wave function ansatz that is being minimized, not the true eigenfunction. As a practical matter, it is therefore better to perform analytical energy gradients directly on the quantities involving the wave function ansatz than it is to employ the Hellman-Feynman theorem. Like the Hellman-Feynman theorem, analytical gradients are, fortunately, able to transform gradients of the Hamiltonian into gradients of quantities involving only the wave function and the potential, which can then easily be obtained in a QMC calculation.

Analytical energy gradients can be taken with respect to any variational parameters, not just nuclear coordinates. Such gradients are therefore considered to be generalized forces that drive the system towards its lowest energy state, whether involving the electronic structure or the geometry of the atomic nuclei.

Given $\langle H \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$ in the place of the left-hand side of Eq. 4.23 to account for the non-normalized wave function that we utilize in practice (see Eq. 4.3), we then have

$$\frac{\partial \langle H \rangle}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} =$$

$$\frac{1}{\langle \Psi | \Psi \rangle} \left( \frac{\partial}{\partial \beta} \langle \Psi | H | \Psi \rangle + \langle \Psi | H \frac{\partial \Psi}{\partial \beta} \rangle + \langle \Psi | \left( \frac{\partial H}{\partial \beta} \right) | \Psi \rangle \right)$$

$$\quad - \left( \frac{1}{\langle \Psi | \Psi \rangle} \right)^2 \langle \Psi | H | \Psi \rangle \left( 2 \langle \Psi | \frac{\partial \Psi}{\partial \beta} \rangle \right).$$
Because $H$ is Hermitian, we have
$$\langle \Psi | H \frac{\partial \Psi}{\partial \beta} \rangle = \left\langle \frac{\partial \Psi}{\partial \beta} \right| H | \Psi \rangle = \int \Psi \frac{\partial \Psi}{\partial \beta} \psi H d \mathbf{r} = \int \Psi^2 \frac{\partial \Psi}{\partial \beta} \psi H d \mathbf{r} = \partial \langle H \rangle / \partial \beta;$$
also, $\langle \Psi | \frac{\partial \Psi}{\partial \beta} \rangle = \int \Psi \frac{\partial \Psi}{\partial \beta} d \mathbf{r} = \int \Psi^2 \frac{\partial \Psi}{\partial \beta} d \mathbf{r}$, and since $\frac{\partial H}{\partial \beta}$ appears in parentheses (meaning that the differentiation takes place before the operator acts), the kinetic energy term vanishes for the Hamiltonians considered in this thesis, leaving $\frac{\partial H}{\partial \beta} = \frac{\partial V}{\partial \beta}$. We therefore have
$$\frac{\partial \langle H \rangle}{\partial \beta} = 2 \left\langle E_{\text{local}} \frac{\partial \ln \Psi}{\partial \beta} \right\rangle + \left\langle \frac{\partial V}{\partial \beta} \right\rangle - 2 \langle H \rangle \left\langle \frac{\partial \ln \Psi}{\partial \beta} \right\rangle. \quad (4.29)$$

Unfortunately, the term $\left\langle \frac{\partial V}{\partial \beta} \right\rangle$ with diverging variance when $\beta$ are the nuclear coordinates still appears, so the force between nuclei still cannot be calculated using analytical gradients. However, if the potential energy $V$ is independent of the variational parameters, $\frac{\partial V}{\partial \beta}$ is considered a generalized force. A QMC calculation can then be performed to obtain the generalized force, which cannot be the force on nuclei.

In particular, the quantities that appear in Eq. 4.29 themselves have a QMC statistical error associated with them given by Eq. 4.17, and as we discuss below, this statistical accuracy may be wildly different from that of the original quantity.

In the special case that the variational parameters are not present in the expression for $V$ (i.e. we are not performing a geometric optimization), we then have
$$\frac{\partial \langle H \rangle}{\partial \beta} = 2 \left\langle E_{\text{local}} \frac{\partial \ln \Psi}{\partial \beta} \right\rangle - 2 \langle H \rangle \left\langle \frac{\partial \ln \Psi}{\partial \beta} \right\rangle \quad \text{(no geometric optimization).} \quad (4.30)$$

A similar calculation can provide the Hessian matrix of second derivatives
$$\nabla_{\beta}^2 \langle H \rangle \equiv \frac{\partial^2}{\partial \beta_i \partial \beta_j} \langle H \rangle \quad (4.31)$$
which appears in Ch. 8. This derivation can be found in, for example, ref. [51].

### 4.14 Analytical vs. numerical gradients

It has previously been suggested that analytical gradients are superior to a finite difference approach (numerical gradients), because finite difference methods add a bias. Assuming
incorrectly that the accuracy of the calculation of a quantity and its derivative are equivalent for the same number of sample points, finite difference methods do indeed impose a bias. However, as Section 4.12.1 showed, a QMC simulation that calculates the *analytical expression* of the force between nuclei is guaranteed to *fail* because its statistical accuracy is not the same as that of the energy for a fixed number of sample points.

A finite difference approach, whose accuracy is determined by the statistical noise associated with a calculation of the energy, not its derivative, is perfectly fair game, however. Finite difference method are not subject to the infinite variance failure condition of the analytical gradient methods in the case of forces between nuclei.

These considerations should make clear the importance of recognizing and determining the statistical accuracy of the objective function appearing in Eq. 4.4 - in particular, its variance. As this discussion has shown, such a simple-seeming quantity as the analytical gradient of a well-behaved quantity can itself be completely intractable in QMC, in which case finite difference methods must be employed.

### 4.15 Diffusion Quantum Monte Carlo (DMC)

Diffusion Quantum Monte Carlo (DQMC, or simply DMC) is part of the bread and butter of the QMC workbench. VMC is able to establish the best possible wave function within the variational landscape. DMC, on the other hand, provides the most accurate calculations. VMC is the springboard; DMC is the high jump.

Because this thesis is primarily focused on improved VMC methods, we will not discuss DMC in the same technical detail as VMC methods. However, it is important to understand the close relationship between the two methods.

Consider the time-dependent Schrodinger equation (with $\hbar = 1$, $m_e = 1$, and only electrons described by the wave function in the Born-Oppenheimer approximation),

$$i \frac{\partial}{\partial t} \Psi = \left( -\frac{1}{2} \nabla^2 + V \right) \Psi,$$

where the $\nabla^2$ operator is taken over all electrons coordinates. Performing the substitution
\( \tau = it \), known as a Wick rotation in time, we can completely eliminate \( i \) from the equation for the real wave functions discussed in this thesis. This leaves

\[
\frac{\partial}{\partial t} \Psi = \left( \frac{1}{2} \nabla^2 - V \right) \Psi.
\]

Performing a shift in the energy scale by an amount \( E_R \) changes the energies \( \{ E \} \) of all eigenstates and leads to the energy-shifted equation

\[
\frac{\partial}{\partial \tau} \Psi = \left( \frac{1}{2} \nabla^2 - (V - E_R) \right) \Psi. \tag{4.32}
\]

The bounded solutions to Eq. 4.32 (i.e. the solutions that go to zero as the particles move infinitely far away) can be expanded over the set of eigenfunctions \( \{ \varphi \} \) of the time-independent Schrödinger equation as

\[
\Psi = \sum_{M = 0}^{\infty} c_M \varphi_M(\mathbf{r}) \, e^{-(E_M - E_R)\tau},
\]

with \( c_M \) the expansion coefficients. Evidently, the choice of energy shift \( E_R \) has a profound effect on the long-time behavior. For \( E_R \) too large or small, the wave function diverges or decays exponentially fast. When \( E_R = E_0 \), where \( E_0 \) is the unshifted ground state energy, then \( \Psi \) converges to the ground state wave function, up to a constant. (If there is zero overlap with the ground state, then \( \Psi \) converges to the lowest-energy excited state/s with non-zero overlap.)

This remarkable result would allow an exact determination of the ground state energy, if Eq. 4.32 could be solved numerically. Regarding its solution, notice that if the \( (V - E_R) \) term is removed from Eq. 4.32, it becomes the standard diffusion equation. A numerical solution to the diffusion equation is implemented most efficiently by the proper choice of a random walk through the configuration space [52]. In order to solve the equation numerically, it is required that \( \Psi \) have the same sign everywhere (it is to be interpreted as a population density). Considering now the case in which the \( \nabla^2 \) term were removed, Eq. 4.32 would be the standard birth or decay rate equation that models, for example, population growth.
or radioactive decay. Such rate equations are solved numerically by performing random branching processes that increase or decrease the population based on the current density of the population (see ref. [53] or [39] (pp. 39-43)).

Therefore, Eq. 4.32 is numerically solved by including both the branching process and the diffusion process. Unfortunately, the ground-state wave functions for many-body fermion systems always have at least one node and therefore change sign. It is only possible to solve Eq. 4.32 within each nodal region, prohibiting diffusion of members of the population over the nodal boundaries. Therefore, DMC calculations are able to solve for the ground state energy \( E_0 \) exactly only within the fixed nodal structure of the trial wave function \( \Psi \).

The paper which first introduced DMC methods to the QMC community [52] seemed unconcerned about this shortcoming, stating that “this approximation may be removed” and that “releasing the [fixed-node] constraint will be the subject of a subsequent paper”. However, that paper was never written, and in the intervening 26 years the problem has not been solved. It stands as arguably the single most important impediment preventing progress in QMC today.

Much important work has been done by L. Mitas to understand the nature of the nodal structure in many-body fermionic wave functions [54]; for example, Mitas showed that there are at least two nodal regions for every many-body fermionic system. Mitas has also made significant progress helping to understand the contribution of the nodal structure to the error in QMC calculations.

In order for the method to converge to a stable solution, \( E_R \) must be modified as the algorithm progresses. Intelligent use of a Green’s function provides a mechanism to properly update \( E_R \) and prevent exponential divergence or decay, as well as vastly improve the convergence rate by eliminating heavily weighted walkers. We will not discuss the DMC algorithm in any more detail. A seminal paper by Umrigar [52] not only introduced the method, but provides an outstanding description of it as well.

Having provided the relevant background regarding DMC, we are now in a position to precisely state the close relationship between VMC and DMC. Current efforts to improve,
develop and apply VMC now revolve around the following two points.

1. VMC optimization methods now have as one of their primary purposes an improvement in the nodal structure of the wave function, in addition to a minimization of the energy. In this way, DMC calculations that utilize the optimized VMC wave function as the trial function will give more accurate results.

2. New wave functions with different parameterizations are being developed with the hope that a VMC optimization will supply a trial function for a DMC calculation with an improved nodal structure.

These two points are related. The first focuses more on the VMC algorithm itself, whereas the second focuses more on the wave function ansatz.

The standard theory of many-body wave functions, and the standard QMC optimization methods, have been discussed in these introductory chapters. We now proceed to discuss our studies of quantum dots, Li and H$_2$O clusters, and the RVB wave function.
Chapter 5

Two-dimensional Quantum Dots

5.1 Quantum Dots

A quantum dot is the generic name given to a nanoscopic region of controlled localized charge. The term is applied both to localized nanoscopic semiconductor systems with an unknown number of electrons, and to systems with a countable number of electrons. We consider in this chapter only the latter. Because the charge is confined, motion of the electrons is considered fixed in a time-independent quantum state; therefore, these are considered zero-dimensional objects. (We do not consider transitions between quantum dot states.) Molecules might also be considered zero-dimensional for the same reason. In the case of quantum dots, the electrons are free charged particles under the additional constraint of an effective bounding potential surface - in other words, particles in a box. Often the complicated form of the bounding potential is relevant to the problem, but often the bounding potential is approximated in its very simplest form, as a square well. Even with this very simple approximation, the constrained homogeneous electron gas - a term that is used even for a countable number of electrons - exhibits immense complexity. Without atomic nuclei, a shell structure is nonetheless observed in quantum dots, just as in atoms and molecules. In the case of molecules, the atomic nuclei form the potential surface in which a shell structure develops. In the case of the quantum dot, the shell structure is determined by the dimensions of the square well and parameters associated with the substrate material.
Even for the square well, the electronic behavior is highly dependent on the radius of the dot due to the non-trivial electron-electron interactions.

Quantum dots are of fundamental importance in applied nanophysics. Their importance lies in two broad areas. First, as a controlled localized region of electrons, quantum dots form the simplest possible test bed in which to understand the behavior of individual electrons in a controlled nanoscopic environment, the results of which are often directly relevant to the study of other nanoscopic systems. Second, quantum dots themselves have the potential for influential applications in computing [10, 11, 12, 13], biology [14, 15], and photovoltaics (solar power) ([16, 17, 18, 19], among a variety of other possible applications.

This chapter describes a study of magnetization in 2-dimensional quantum dots (QDs) as a function of the dot radius\(^1\).

When studying a QD, the region of localized charge nonetheless has a dimensionality associated with it. QDs are often modeled in two dimensions because the regions of localized charge are generally created by experimentalists as a surface layer on some material. In the case of this work, the material is GaAs, which has shown promise as a material for useful QD fabrication and which is an active area of research [55, 56, 57]. Interesting behavior results from the interplay between containment effects of the bounded 2-dimensional region, and the effects of correlation between the electrons. As such, QMC simulations are well suited for the study of quantum dots, because QMC is able to model electron correlations directly.

The resulting behavior helps determine the magnetic behavior of the quantum dots, a subject of key interest to experimentalists who work with QDs [58, 59, 60, 61].

This chapter begins with a motivating discussion of the Pauli and Coulomb hole. It continues by introducing an exactly-solvable Hamiltonian, the solution of which is a wave function with the single-Slater-determinant HF form of Eq. 3.19 (a product of up- and down-spin Slater determinants). It also introduces some results that have been obtained with this simple HF solution that describe magnetization properties of QDs in the HF limit,

\(^{1}\)The material in this chapter is adapted from the following paper and talk.
of interest to experimentalists. It then discusses a QMC calculation of a correlated Jastrow-Slater wave function, extending beyond the HF limit of the exactly-solvable Hamiltonian, which provides a measure of the extent to which the correlations might impact the results that were obtained using the simple model Hamiltonian with its HF solution.

5.2 Hund’s rule; the Pauli and Coulomb hole

Hund’s rule states that quantum systems have a tendency to spontaneously magnetize. The difference between same-spin and opposite-spin electrons suffices to describe this phenomena in a conceptual way. Same-spin electrons cannot occupy the same point in space (see Section 3.5; in particular, Eq. 3.5.3). Because the electron density is continuous, there is therefore a Pauli hole associated with same-spin electrons - a region in which two same-spin electrons are less likely to coexist. Because the Pauli hole prevents same-spin electrons from approaching, it provides an overall decrease in energy of the system, because the energy increases when electrons approach one another due to the Coulomb repulsion between electrons. It is therefore energetically favorable for electrons to exist in a same-spin state, which results in a tendency for these systems to spontaneously magnetize.

There is also a Coulomb hole associated with electrons of any spin relationship due to Coulomb repulsion. The Coulomb hole results in non-mean-field behavior of the QD and is therefore directly responsible for electron correlations (see Section 3.4). The greater the effect of the Coulomb hole in comparison to the Pauli hole, the less the system would exhibit a tendency to spontaneously magnetize.

There are many factors involved in magnetization in materials; Hund’s rule describes a tendency, but, as the example of the Coulomb hole indicates, this tendency does not always dominate the overall behavior of the electrons.

The chief work we accomplished with quantum dots using the SGA was to determine the relative strength of the Coulomb hole in comparison to the Pauli hole.
5.3 An exactly solvable Hamiltonian

Our QMC work with the 2-dimensional QD is motivated by the fact that some important experimental predictions can be obtained by use of a simple model Hamiltonian in three dimensions whose solution is of the HF form of Eq. 3.19. This section briefly reviews those results.\(^1\)

The model Hamiltonian \([62]\) we employ to model the QD is given in so-called second-quantized form by

\[\hat{H} = \sum_{\nu\sigma} \epsilon_{\nu\sigma}^0 a_{\nu\sigma}^{\dagger} a_{\nu\sigma} + \frac{1}{2} U \sum_{\nu\nu',\sigma} a_{\nu\sigma}^{\dagger} a_{\nu'}^{\dagger} a_{\nu'-\sigma} a_{\nu\sigma}, \tag{5.1}\]

where \(a_{\nu\sigma}^{\dagger}\) and \(a_{\nu\sigma}\), respectively, are the creation and annihilation operators for the single-particle state \(\phi_{\nu\sigma}\) with eigenvalue \(\epsilon_{\nu\sigma}^0\). The index \(\sigma\) indicates the spin of the electron (up or down), and the index \(\nu\) indicates the single-particle state. The first term (\(\hat{H}_0 = \sum_{\nu\sigma} \epsilon_{\nu\sigma}^0 a_{\nu\sigma}^{\dagger} a_{\nu\sigma}\)) describes the system as a simple sum of the lowest energy single-particle states as though each electron existed in that state without any influence by the other electrons. As we shall see, the single-particle states are determined under the same assumption. Therefore, \(\hat{H}_0\) represents the uncorrelated part of the Hamiltonian. This term represents the kinetic energy of the electrons, because as we shall see the values \(\epsilon_{\nu\sigma}^0\) are obtained by solving Schrodinger’s equation with a Hamiltonian for a single particle without any interaction potential, which is equivalent to one with only a kinetic energy term. The remaining part of the Hamiltonian after \(\hat{H}_0\) describes electron correlations due to the Coulomb repulsion between electrons. (This is not to be confused with a correlated vs. an uncorrelated wave function; see Section 3.4.) The interaction in the second term is, clearly, restricted to electron pairs of opposite spin. Before describing the correlated part of the Hamiltonian further, let us discuss this assumption. Under this assumption, opposite-spin electrons dominate the energetics in the sense that they are the only electron pairs that significantly modify \(\hat{H}_0\). This is equivalent to the statement that the Pauli hole dominates the Coulomb

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\(^1\)Section 5.3 and Section 5.4 present background material that is not the work of the author, adapted from the following paper.
hole; i.e. that the Pauli hole separating same-spin electrons is so large in comparison to the Coulomb hole separating opposite-spin electrons that the energy of the total system is relatively unchanged by ignoring the same-spin electrons.

This key assumption needs to be validated in order for any results of the model to be trustworthy. After these introductory remarks, the remainder of the chapter is devoted to a discussion of our QMC calculations that have validated this assumption.

The parameter $U$ in the correlated part of the Hamiltonian can be viewed as an average energy penalty for two electrons of opposite spin to be in the QD. After all, any improvement in the Hamiltonian upon $\hat{H}_0$ can only be one that increases the total energy due to the Coulomb repulsion between electrons, there being no nuclei in the dot to decrease the energy. If $U$ were zero, there would be no penalty for the electrons to have opposite spin and our assumption that opposite-spin electrons dominate the energetics would clearly be violated. The fact that $U$ is greater than zero describes the tendency of electrons to exist in same-spin states. If $U$ were infinitely large, than it would only be possible for electrons to exist in the system in same-spin states. The quantity $U$ is therefore a measure of the relative strength of the Coulomb and Pauli electron holes. Of course, $U$ could also be negative, describing an anti-Hund’s rule in which it is energetically favorable for electrons to approach one another; this is clearly unphysical and is not considered.

The value of $U$ must be estimated and is therefore the key parameter in this problem. Our current study is motivated by the work of Saniz [62], who estimated the value of $U$ as employed in the case of an uncorrelated system (discussed shortly), which implies that the Coulomb hole does not exist in the resulting wave function solution, the Coulomb hole being represented only by the appearance of $U$ in the Hamiltonian. Note that electron correlations in the homogeneous electron gas and, in particular, in QDs are not well understood, and our QMC study is an attempt to improve upon the work of Saniz, et al., by performing a QMC calculation to estimate $U$ in a correlated system.

With an estimate of $U$ in hand, Saniz, et al., have shown that the Hamiltonian in Eq. 5.1 can be solved exactly. As it turns out, the wave function corresponding to this Hamiltonian takes the form of an uncorrelated wave function of the HF form of Eq. 3.19 (in this case,
an unrestricted HF solution; see Section 3.4), with the uncorrelated single-particle solutions as elements in the spin-up and spin-down matrices. We do not review this solution or derive the corresponding energies here. Instead, the remainder of this section will present various results, without derivation, in order to motivate our own work. The chief result is a signature for spontaneous magnetization within QDs that can be directly measured by experimentalists using momentum-resolved spectrosopies. By spontaneous is meant that the magnetization is dominated by Hund’s rule.

The total energy of the QD described by this Hamiltonian is given by

\[ E = \sum_{\nu \sigma} \left( e^0_{\nu} + \frac{1}{2} U M_{\sigma} \right) f_{\nu \sigma}, \]  

(5.2)

where \( f_{\nu \sigma} \) denotes the Fermi occupation function. Using this expression for the energy, we can determine the population \( M^\uparrow \) of spin-up and \( M^\downarrow \) of spin-down electrons that minimize the energy, given a fixed number of total electrons \( M \). Minimization of Eq. 5.2 yields a symmetrical set of nonlinear equations for these populations \( M^\uparrow \) and \( M^\downarrow \) which can be solved (see ref. [62]).

Choosing the solution where \( M^\uparrow > M^\downarrow \), the average polarization per electron \( \zeta \) is given by

\[ \zeta = (M^\uparrow - M^\downarrow)/M, \]  

(5.3)

or equivalently that the average total polarization is simply \( M^\uparrow - M^\downarrow \). These expressions measure polarization as simply the number of unpaired electrons in a given spin direction, which corresponds to magnetization of the QD.

It is now important to provide a typical example of the application of this methodology to a real quantum dot. We obtain a model for the example, and all of the numerical constants of the model, including the important parameter \( U \), from Saniz et al. [62].

The example involves a three-dimensional QD. The noninteracting part of the Hamiltonian is a spherical square well in 3D; \( V(r) = -8.62 \text{ eV} \) for \( r \leq R \), and \( V(r) = 0 \) otherwise. The mean interelectronic spacing \( r_s \) was set to 5 (in atomic units) and the average density \( M_d \) was fixed by the condition \( M_d(4\pi r_s^3/3) = 1 \). Therefore, the dot radius \( R \) and the num-
ber $M$ of electrons were related by the formula $M = (R/r_s)^3$. The value $r_s = 5$ gives a relatively low density, enabling the authors to consider a wide range of dot radii.

The choice of the parameter $U$ was obtained by the authors by utilizing the single-particle functions $\{\phi\}$ appearing in the Slater determinant - representing the uncorrelated system - which, as mentioned previously, can be calculated ahead of time. To construct $U$, the authors consider the interaction matrix element $\int d\vec{r} d\vec{r}' |\phi_\mu(\vec{r})|^2 v(|\vec{r} - \vec{r}'|) |\phi_\mu(\vec{r}')|^2$, averaged over all occupied states, with $v(r) = e^2 \exp(-r/l)/r$, where $l = \sqrt{r_s}/1.4$ is a screening length that corresponds to the authors’ best guess of the energy penalty from the opposite-spin Coulomb hole represented by $U$. Recall that the Coulomb hole is represented within the Hamiltonian by way of $U$, even though it is not represented by the form of the resulting wave function. For a 12.11 Å radius QD, for which $M = 96$, the value $U = 27.13$ meV was obtained.

Employing this model, adjusting the radius of the quantum dot incrementally, and then solving the nonlinear equations for $M_\uparrow$ and $M_\downarrow$ in order to obtain the polarization from Eq. 5.3, results in the plot shown in Fig. 5-1. (These calculations are not provided here; see ref. [62].) The average polarization $\zeta$ (solid curve) is shown as a function of the dot radius $R$ for a fixed value of the electron density $M_\sigma$. Shown for comparison is the limiting case with no Coulomb correlation represented in the Hamiltonian, $U \to 0$ (dashed curve). As $R$ is increased or as electrons are added, spin polarization $\zeta$ reaches a peak each time a shell is half filled with up-spin electrons and falls to zero when the shell is completed with down-spin electrons, yielding a sequence of “magic numbers”, i.e., $M$ values for which the dot magnetization vanishes. In the high $R$ limit, we have a homogeneous electron gas - a paramagnetic system which does not spontaneously magnetize. The spin polarization oscillations are therefore damped when the size of the system increases; spontaneous magnetization of quantum dots is a truly nanoscopic effect that depends on the containment effects.

It is important to note that the peaks in Fig. 5-1 result from the filling of degenerate single-particle orbitals in 3 dimensions according to Hund’s rule. Therefore, in quantum dots with high symmetry according to this model, we expect to see the strongest spontaneous
Figure 5-1: Using a very simple, exactly solvable Hamiltonian to model a three-dimensional quantum dot, and employing a set of simple numerical parameters to encapsulate correlation and containment effects (see discussion), the solid curve shows the average spin polarization (per electron) as a function of the radius of the quantum dot. The dashed curve shows the limiting case in which Coulomb electronic correlations are set to 0. It can be observed that the magnetization of the quantum dot is highly dependent upon the radius of the quantum dot. (Adapted from ref. [62].)
Figure 5-2: Typical EMD in a QD, $n(p)$, and the magnitude of its first derivative, $|n'(p)|$. The position of the peak in $|n'(p)|$ defines the QD “Fermi momentum”, while its full-width-at-half-maximum defines $\Delta p$. (Adapted from ref. [62].)
Figure 5-3: Electron momentum $p$ in reduced units of $p_f$ (solid curve), and spin polarization (dashed) vs. QD radius R. Simulations are based on the model Hamiltonian of Eq. 1, using parameters discussed in the text. (Adapted from ref. [62].)
magnetization, because these symmetries result in degenerate single-particle states across dimensions. Disorder and symmetry breaking effects will tend to lift these degeneracies and reduce the tendency for the system to spontaneously magnetize.

5.4 Momentum resolved signature of magnetization

In order to make the connection between the predicted polarization from Fig. 5-1 and experimental momentum spectroscopies, we discuss next the electron momentum density (EMD) with the intention of identifying signatures of spin polarization in a quantum dot. The EMD is defined by

\[
n(p) = (2\pi)^{-1} \int_{-\infty}^{\infty} d\omega f(\omega) A(p, \omega),
\]  

(5.4)

where \( f \) is the Fermi function, and \( A \) is the spectral function defined by

\[
A(p, \omega) = -2\text{Im}G^R(p, \omega).
\]  

(5.5)

The one particle Green’s function \( G^R(p, \omega) \) and its imaginary part can be evaluated exactly for the model Hamiltonian of Eq. 5.1. We do not reproduce this work here. Please see ref. [62].

The authors calculated the value \( n(p) \) and average over all momenta to obtain \( n(p) \), with \( p \equiv |p| \), as an experimentalist would obtain in a momentum spectroscopy. The averaged behavior of the EMD and its derivative is shown in Fig. 5-2. The region of rapid decrease in \( n(p) \) can be characterized via the position, \( p_F \), of the peak in \( |n'(p)| \) and the associated full-width-at-half-maximum, \( \Delta p \). In this finite system there is rigorously no such thing as a Fermi momentum, but we may nevertheless refer to \( p_F \) loosely as the quantum dot “Fermi momentum” for simplicity. The quantity \( \Delta p \) can be measured in an experiment by performing momentum spectroscopies using Compton scattering positron annihilation.

In turn, the authors have calculated the quantity \( \Delta p \) as a function of the quantum dot radius \( R \). Fig 5-3 shows this plot (solid line in main graph, left scale) at a fixed electron
density. $\Delta p$ is seen to display peaks. It happens that these peaks are well correlated with those in the magnetization $\zeta$, whose calculation is described in the previous section. In fact, $\Delta p$ can be parameterized as

$$\frac{\Delta p}{p_F} = \Delta p_0/p_F + c\Delta(\zeta - \zeta_0) R,$$

(5.6)

where $\zeta_0$ is the spin polarization in the weakly interacting case ($U \to 0$), where $\Delta(\zeta - \zeta_0)$ represents the full-width-at-half-maximum of the quantity $\zeta - \zeta_0$, and where $c$ is a fitting constant, which depends on various dot parameters. Again, see ref. [62] for details.

Utilizing Eq. 5.6, the polarization $\zeta$ can therefore be extracted from the measured value $\Delta p/p_F$ from an EMD experiment. On a conceptual level, the reason for this correlation between $\Delta p$ and $\zeta$ is that in the polarized system, in effect, there are two separate momentum distributions - one for the up, and one for the down spin electrons. The two associated “Fermi” momenta then give rise to two different peaks in $|n'(p)|$. However, the momentum density spectroscopy is unable to distinguish between these two peaks, and the two peaks instead appear as increased broadening of the overall $\overline{p}$-averaged single peak $\Delta p$ in the total momentum density of the interacting system.

This section has provided a motivation for the importance of a QMC calculation to evaluate the quality of the estimation of the parameter $U$, which is the key parameter describing electron correlations in the Hamiltonian of Eq. 5.1. In the next section we discuss a QMC calculation that we performed to obtain an estimate of $U$.

### 5.5 QMC calculation of the effective interaction

As discussed in Section 3.5.2, a more realistic wave function is obtained by inclusion of a Jastrow factor in combination with a product of Slater determinants. Although this new wave function will not be a solution of the Hamiltonian in Eq. 5.1, we nonetheless expect it to be a better wave function ansatz for a quantum dot than the solution that was evaluated in the previous section, because that model Hamiltonian is a fairly simple one. However, our intention is not to perform the calculations of the last section with such
a wave function, because this cannot be done due to the mathematical complexity of the Jastrow factor. Instead, because this wave function ansatz includes electron correlations, it is a good candidate with which to evaluate the important quantity $U$ in the last section, representing the strength of the opposite-spin Coulomb hole in relation to the same-spin Pauli hole, which was estimated without a direct calculation, to confirm the validity of the results of the previous section.

To do so we will perform a direct QMC calculation of the quantity $U$ ([63]), except that we will do it in the case of a 2-dimensional quantum dot, rather than a 3-dimensional one. The same methods could be employed to perform the calculation on a 3-dimensional dot, and this would be a useful extension of our work to determine if this change in dimensionality has a significant effect.

In the remainder of this chapter, we discuss in detail the approach we used to calculate $U$ with a QMC calculation of a correlated many-body wave function ansatz for a 2-dimensional quantum dot.

In our case we employ for the Jastrow factor the simplest possible form of a Pade-Jastrow function (see Section 3.5.2). We have, for the exponent that appears in Eq. 3.23,

$$u(r) = \frac{r}{1 + \beta r},$$

where $u(r)$ is the exponent, the subscripts are left off for convenience, and $\beta$ is a single variational parameter. Notice that this exponent properly satisfies the cusp conditions, as discussed in Section 3.5.3, but in the case of a 2-dimensional system, rather than a 3-dimensional system. When $J = 1$ or $\beta \to \infty$, $\Psi$ reduces to the form of an unrestricted Hartree-Fock wave function, as expected.

The basis of our calculation is the spin-resolved pair correlation function $g(\vec{r})$, which is essentially a spin-resolved histogram of distances between electron pairs. In Section 5.6.3, we show that an integral over the pair correlation function can be used to determine the quantity $U$, and we provide our result. However, the derivation of the constant prefactor that must be used in the computation of $g(\vec{r})$ from QMC data is surprisingly subtle. The
5.6 Energy calculations utilizing $g(\vec{r})$

5.6.1 The pair correlation function $g(\vec{r})$

In this section and the relevant sections that follow, we use a different notation than that used in the other chapters of this thesis. Here, it is assumed that $\vec{r}$ is a dummy position of a single electron, rather than representing the combined positions of all electrons in the system, as we do in the other chapters. Instead, in this section we use $\vec{r}$ to refer to the set of electron coordinates that appear in the wave function (a single “sample”), rather than using it to refer to a full set of Monte Carlo samples as we do in the other chapters. Also, we assume that we have a two-dimensional problem – i.e. that “volumes” are really areas, and that $d\vec{r} = rdrd\theta$.

For the wave function ansatz $\Psi$ describing $M$ electrons, the expectation value of the potential energy $\langle V \rangle$ is given by

$$\sum_{i<j} \int \frac{1}{r_{ij}} |\Psi(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_j, \ldots, \vec{r}_M)|^2 d\vec{r},$$  \hspace{1cm} (5.8)

where the sums here (and in what follows for the derivations of $g(\vec{r})$) run over the $M$ electrons of the system. In the case of the wave function we have chosen to employ for the quantum dot, given as

$$\Psi = \prod_{i<j} e^{\frac{r_{ij}}{\alpha+\beta r_{ij}}} D_1 D_\perp,$$  \hspace{1cm} (5.9)

we see that Eq. 5.8 breaks into three integrals – one for $i$ and $j$ spin up, one for $i$ and $j$ spin down, and one for $i$ and $j$ having opposite spin. If $M_\uparrow$ and $M_\perp$ are the number of spin-up
and spin-down electrons in the system, respectively, we then have

\[
\langle V \rangle = \sum_{i<j} \int \frac{1}{r_{ij}} |\Psi(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_j, \ldots, \vec{r}_M)^2| d\vec{r}
\]

(a)

\[
= \frac{M_i(M_i-1)}{2} \int \frac{1}{r_{\uparrow\downarrow}} |\Psi|^2 d\vec{r}
\]

(b)

\[
+ \frac{M_i(M_i-1)}{2} \int \frac{1}{r_{\uparrow\downarrow}} |\Psi|^2 d\vec{r}
\]

(c)

\[
+ M_i M_j \int \frac{1}{r_{\uparrow\downarrow}} |\Psi|^2 d\vec{r}
\]

(d)  

(5.10)

where \(r_{\uparrow\downarrow}, r_{\downarrow\uparrow}, \) and \(r_{\uparrow\downarrow}\) refer to pairs of electrons with the given relative spin, and where the integrals in (b), (c), and (d) are to be taken over any such pair of electrons due to the antisymmetry of \(\Psi\).

Next, we introduce the following functions \(g_{\sigma\sigma'}(\vec{r})\) of a single dummy coordinate \(\vec{r}\):

\[
g_{\uparrow\uparrow}(\vec{r}) = \frac{1}{M} \sum_{i<j} \delta_{\uparrow,\sigma_i}\delta_{\uparrow,\sigma_j} \int \delta(|\vec{r}|-r_{ij}) |\Psi|^2 d\vec{r}
\]

(5.11)

\[
g_{\downarrow\downarrow}(\vec{r}) = \frac{1}{M} \sum_{i<j} \delta_{\downarrow,\sigma_i}\delta_{\downarrow,\sigma_j} \int \delta(|\vec{r}|-r_{ij}) |\Psi|^2 d\vec{r}
\]

(5.12)

and

\[
g_{\uparrow\downarrow}(\vec{r}) = \frac{1}{M} \sum_{i,j} \delta_{\uparrow,\sigma_i}(1 - \delta_{\uparrow,\sigma_j}) \int \delta(|\vec{r}|-r_{ij}) |\Psi|^2 d\vec{r},
\]

(5.13)

Note that the subscripts on any position quantity \(\vec{r}_i\) or displacement quantity \(r_{ij}\) indicate that these are positions or displacements of the electrons appearing as arguments to the wave function; in contrast, the quantity \(\vec{F}\) and \(r\) (without subscripts) refer to the dummy variable. Also, note that the variable of integration, \(d\vec{r}\), is not in the same space as the dummy variable \(\vec{r}\). Finally, in the equation, \(M\) is the electron density in the dot, appearing so that \(g_{\sigma\sigma'}(\vec{r})\) remain unitless.

The integrals in each of these functions pull out the value of \(|\Psi|^2\) at each point where \(|\vec{r}| = r_{ij}\), and the sum specifies the proper spin relationship. Notice that although \(g_{\sigma\sigma'}(\vec{r})\) depends only on \(|\vec{r}|\), we nonetheless write \(g_{\sigma\sigma'}(\vec{r})\), rather than \(g_{\sigma\sigma'}(|\vec{r}|)\), to emphasize the fact that the \(\delta\)-function inside each integral assumes a value through the entirety of an identical two-dimensional space as \(r_{ij} = |\vec{r}_i - \vec{r}_j|\).
In order to understand the utility of the functions $g_{\sigma \sigma'}(\vec{r})$, consider the following integral over $g_{\uparrow \downarrow}(\vec{r})$:

\[
\int d\vec{r}^{2n_{\uparrow \downarrow}(\vec{r})} \sum_{i,j} \delta_{\uparrow,\sigma_i} \left( 1 - \delta_{\uparrow,\sigma_j} \right) \int d\vec{r} \delta(|\vec{r} - r_{ij}|) |\Psi|^2 = M_{\uparrow} M_{\downarrow} \int d\vec{r} |\Psi|^2 \left( \int d\vec{r} \delta(|\vec{r} - r_{\uparrow \downarrow}|) \right) (5.14)
\]

which equals Eq. 5.10(d). Therefore, by performing an integral over $g_{\uparrow \downarrow}(\vec{r})$, we are able to obtain the contribution to the potential energy of the system that results from the opposite-spin electron pairs. Notice that $|\Psi|^2$ in Eq. 5.14(d) does not depend on $|\vec{r}|$, but only on $r_{\uparrow \downarrow}$, allowing a switch of the order of integration.

A similar derivation applies for the same-spin cases, so that Eq. 5.10 for the total potential energy of the system becomes

\[
\langle V \rangle = \int \frac{ng_{\uparrow \uparrow}(\vec{r})}{|\vec{r}|} d\vec{r} + \int \frac{ng_{\downarrow \downarrow}(\vec{r})}{|\vec{r}|} d\vec{r} + \int \frac{ng_{\uparrow \downarrow}(\vec{r})}{|\vec{r}|} d\vec{r}.
\]

The quantity $g_{\sigma \sigma'}(\vec{r})$ is the spin resolved radial pair correlation function.

### 5.6.2 Normalization of $g(\vec{r})$ from sample data

We would now like to obtain the value of $g_{\sigma \sigma'}(\vec{r})$ via a QMC simulation; namely, by accumulating a series of sample points from a Metropolis-like algorithm and creating a histogram from these points. In order to do so, the prefactor that multiplies the histogram to obtain the true value of $g_{\sigma \sigma'}(\vec{r})$ is essential; unfortunately, $g_{\sigma \sigma'}(\vec{r})$ is not normalized to 1 when it is obtained as a histogram from a QMC computation. To obtain the constant, let us start
with Eq. 5.13. We find

\[ g_{\uparrow \downarrow} (\bar{r}) = \frac{1}{M} \sum_{i,j} \delta_{\uparrow, \sigma_i} \left( 1 - \delta_{\downarrow, \sigma_j} \right) \int \delta (|\bar{r}| - r_{ij}) |\Psi|^2 \, d\bar{r} \]

\[ = \frac{1}{M} \sum_{\uparrow \downarrow} \int \delta (|\bar{r}| - r_{ij}) |\Psi|^2 \, d\bar{r} \]

(5.16)

where the sum over \( \uparrow \downarrow \) here and in what follows is taken to mean a sum over all opposite-spin pairs. (Similarly, sums over \( \uparrow \uparrow \) and \( \downarrow \downarrow \) are taken to be sums over all spin-up and all spin-down pairs, respectively.

In a computer algorithm, let the width of the histogram bin in \( r \)-space be \( \Delta r \); \( \delta (|\bar{r}| - r_{ij}) \)
averaged within this bin becomes

\[ \delta (|\bar{r}| - r_{ij}) = \begin{cases} \frac{1}{2\pi |\bar{r}| \Delta r} & (|\bar{r}| - \frac{\Delta r}{2} < r_{ij} < |\bar{r}| + \frac{\Delta r}{2}) \\ 0 & \text{(otherwise)} \end{cases} \]  

(5.17)

which preserves the normalization

\[ \int \delta (|\bar{r}| - r_{ij}) \, d\bar{r} = 1 \]  

(5.18)

as required in going from Eq. 5.14(d) to Eq. 5.14(e). Note, for future reference, that this \( \delta \)-function is integrated over the entire 2-dimensional space of \( \bar{r} \) (and also note that this is the same reason \( g_{\sigma \sigma'} (\bar{r}) \) is defined as such, rather than \( g_{\sigma \sigma'} (|\bar{r}|) \)).

We now convert the integral in Eq. 5.16 into a numerical sum that will be amenable for calculation with a computer algorithm. Eq. 5.16 becomes

\[ g_{\uparrow \downarrow} (\bar{r}) = \frac{1}{M} \sum_{\uparrow \downarrow} \left\{ \int \delta (|\bar{r}| - r_{ij}) |\Psi|^2 \, d\bar{r} \right\} \]  

(5.19)

(a)

\[ = \frac{1}{M} \sum_{\uparrow \downarrow} \left\{ \frac{1}{M} \sum_{\bar{r} \in \{ \bar{r} \}} \delta (|\bar{r}| - r_{ij}) \right\} \]  

(b)

\[ = \frac{1}{nN} \sum_{\bar{r} \in \{ \bar{r} \}} \sum_{\uparrow \downarrow} \delta (|\bar{r}| - r_{ij}) \]  

(c)

where we have converted the integral into a standard Monte Carlo summation over a set of
representative configuration points \( \{ \overline{r} \} \) weighted according to \(|\Psi|^2\), and \( N \) is the number of Monte Carlo points in the representative set. This, then, is the function \( g_{\uparrow\uparrow} (\overline{r}) \), treated from a computational point of view.

Similarly, we have

\[
g_{\uparrow\uparrow} (\overline{r}) = \frac{1}{N} \sum_{\overline{r} \in \{ \overline{r} \}} \frac{1}{M} \sum_{ij} \delta (|\overline{r}| - r_{ij}) |\Psi|^2 d\overline{r} \quad (a)
\]

\[
= \frac{1}{M} \sum_{\overline{r} \in \{ \overline{r} \}} \left( \frac{1}{N} \sum_{\overline{r} \in \{ \overline{r} \}} \delta (|\overline{r}| - r_{ij}) \right) \quad (b)
\]

\[
= \frac{1}{nN} \sum_{\overline{r} \in \{ \overline{r} \}} \sum_{ij} \delta (|\overline{r}| - r_{ij}) \quad (c)
\]

and

\[
g_{\downarrow\downarrow} (\overline{r}) = \frac{1}{N} \sum_{\overline{r} \in \{ \overline{r} \}} \frac{1}{M} \sum_{ij} \delta (|\overline{r}| - r_{ij}) |\Psi|^2 d\overline{r} \quad (a)
\]

\[
= \frac{1}{M} \sum_{\overline{r} \in \{ \overline{r} \}} \left( \frac{1}{N} \sum_{\overline{r} \in \{ \overline{r} \}} \delta (|\overline{r}| - r_{ij}) \right) \quad (b)
\]

\[
= \frac{1}{nN} \sum_{\overline{r} \in \{ \overline{r} \}} \sum_{ij} \delta (|\overline{r}| - r_{ij}) \quad (c)
\]

Recalling the value of the \( \delta \)-function from Eq. 5.17, and noting that Eqs. 5.19, 5.20, and 5.21 each represent a histogram, we can see that the height of the histogram in every bin of width \( \Delta r \) at point \(|\overline{r}| \) is given by

\[
g_{\uparrow\uparrow} (\overline{r}) = \frac{1}{2\pi nN |\overline{r}| \Delta r} (\text{total # \uparrow\uparrow pairs separated by } |\overline{r}|) \quad (5.22)
\]

\[
g_{\downarrow\downarrow} (\overline{r}) = \frac{1}{2\pi nN |\overline{r}| \Delta r} (\text{total # \downarrow\downarrow pairs separated by } |\overline{r}|) \quad (5.23)
\]

and

\[
g_{\downarrow\uparrow} (\overline{r}) = \frac{1}{2\pi nN |\overline{r}| \Delta r} (\text{total # \downarrow\uparrow pairs separated by } |\overline{r}|) . \quad (5.24)
\]

The prefactor has now been determined, and these equations can be directly utilized by a computer algorithm with the normalization constant given by Eqs. 5.23 and 5.24.

There are other, equally valid constructions for the pair correlation function with dif-
different normalization constants and it is easy to become confused. In Appendix H we have spelled out all the nit-picky details of the different possible choices, which can be used instead of the formulation presented here.

### 5.6.3 Calculation of $U$ using $g(\mathbf{r})$

Now that we have derived the prefactor for the histogram calculation of $g_{\sigma\sigma'}(\mathbf{r})$, we are in a position to use $g_{\sigma\sigma'}(\mathbf{r})$ to calculate the average repulsion energy between two electrons. (We could just as well have used $\tilde{g}_{\sigma\sigma'}(\mathbf{r})$, $P_{\sigma\sigma'}(r)$, or $\tilde{P}_{\sigma\sigma'}(r)$ from Appendix H.) In this section, we show how to accomplish this.

The average repulsion energy can be expressed as an integral of the spin resolved radial pair correlation function. The pair interaction energy between two electrons of like spin is simply the average potential energy contribution per same-spin pair. We can divide the total potential energy due to same-spin electrons (Eq. 5.15) by the number of same-spin electron pairs, yielding

$$V_{\sigma,\sigma} = \frac{2}{M_{\sigma}(M_{\sigma} - 1)} \int \frac{ng_{\sigma,\sigma}(r)}{r} d\mathbf{r}$$

for the average repulsion energy for same-spin electrons. For electrons of opposite spin, we have

$$V_{\sigma,-\sigma} = \frac{1}{M_{\sigma}M_{-\sigma}} \int \frac{ng_{\sigma,-\sigma}(r)}{r} d\mathbf{r}.$$  \hspace{1cm} (5.26)

The energy penalty $U$ for having a pair of electrons with opposite spin is given by the difference between the average energy for same-spin electron pairs, and the average energy for opposite-spin electrons. We need to allow for the fact that we have same-spin pairs that are both spin-up, and spin-down. The following expression for $U$ is the correct one:

$$U = \frac{1}{2} \sum_{\sigma} (V_{\sigma,-\sigma} - V_{\sigma,\sigma}).$$  \hspace{1cm} (5.27)

This is the general form for the energy penalty $U$ that appears in Eq. 5.1. Of course, the formula could be easily modified to allow for resolution between spin-up and spin-down...
pairs.

We now proceed to apply this general formula for $U$ in a specific calculation of a quantum dot, in order to test the validity of the estimation of $U$ that appears in the first part of this chapter.

5.7 Application to two-dimensional QD

These results can be applied to a 2D quantum dot in order to obtain a numerical value of $U$. Let us consider a QD consisting of 12 electrons enclosed in a 2D square well of size $l = \pi a_B^*$ [64]. Previous authors have already determined that to best represent this quantum dot in GaAs, the renormalized atomic units $a_B^*$ for length and $\text{Ha}^*$ for energy should be used. These renormalized units are obtained from the electron band mass $m^*$ and from the dielectric constant of the material $\varepsilon$. For instance, for GaAs, $m^* = 0.067 m_e$ and $\varepsilon = 12.4$; therefore the modified energy unit is $\text{Ha}^* = 11.8572 \text{ meV}$ and the corresponding modified unit of length is $a_B^* = 9.79 \text{ nm}$. In other materials, these units change significantly. The single-electron states in this simple square QD are

$$\phi_{n_x,n_y,\sigma}(x,y) = \frac{2}{\pi} \sin(n_x x) \sin(n_y y).$$ (5.28)

$M = 12$ electrons give a closed shell system ($M_z = M_\parallel$), with 4 degenerate electrons per shell (two spin-up and two spin-down, with one function in the $x$-direction and one function in the $y$-direction for each spin state).

For the wave function, we employ the Jastrow-Slater form discussed in Ch. 3 utilizing the Jastrow factor of Eq. 5.7, and perform the QMC calculation as discussed in the introductory chapters.

In the HF limit, $\beta \to \infty$ and we do not perform a variational optimization. The result of the Monte Carlo run gives a total energy of $107.785 \pm 0.002 \text{ Ha}^*$.

To determine $U$, we utilize the SGA to optimize the parameter $\beta$. We find that the optimal value of $\beta$ is $\beta = 1.53$, and we find that the total energy is $103.237 \pm 0.001 \text{ Ha}^*$.

Using this fixed value of $\beta$, we ran the Metropolis algorithm to yield a distribution of
configuration points. From this we can create the relatively noiseless histograms $g_{\sigma\sigma'}$, as derived in the previous section. These spin-resolved histograms are shown in Fig. 5-4.

We discuss the figure and perform the calculation of $U$ in the following section.

5.8 Spin Resolved pair interaction energy $U$

The Pauli hole for same-spin electrons can be observed as the dashed curve in Fig. 5-4. We see that the probability of observing a same-spin pair close together drops to zero at zero separation, as expected. The Coulomb hole can most easily be observed in the case of the opposite-spin electrons, where the Pauli principle plays no role. Fig. 5-4 shows that the
Coulomb hole is significantly smaller in appearance than the Pauli hole. The decrease of \( g_{\sigma \sigma'} \) after \( r \approx 1 \ a_B^* \) is a geometrical effect due to the finite size of the QD.

Performing the relevant calculations using the derivations from the previous section, we find that the radial pair correlation functions yields \( V_{\uparrow \uparrow} = 1.039 \text{ Ha}^* \), \( V_{\uparrow \downarrow} = 0.760 \text{ Ha}^* \), and finally that

\[
U = 0.279 \text{ Ha}^*.
\]

In the Hartree-Fock limit, \( V_{\uparrow \uparrow} = 1.176 \text{ Ha}^* \), \( V_{\uparrow \downarrow} = 0.848 \text{ Ha}^* \), and

\[
U_{HF} = 0.329 \text{ Ha}^*.
\]

We have arrived at the main result of this chapter, which is a direct calculation of the energy penalty \( U \) that appears in Eq. 5.1. In order to determine the validity of the selection of \( U \) that was made in the first half of this chapter, we note that the calculation of \( U \) is dependent on the specifics of the quantum dot (its material, dimensions, bounding potential, etc.). Therefore, the relevant comparison for our result \( U = 0.279 \) is with the HF value for the same system in order to determine the extent to which the inclusion of electron correlations in the wave function, and the corresponding appearance of the Coulomb hole, impacts the value of \( U \). In our case, the HF value is \( U_{HF} = 0.329 \text{ Ha}^* \), while the value including electron correlations is \( U = 0.279 \text{ Ha}^* \). Therefore, with a Jastrow term representing electron correlations, the penalty in energy for opposite-spin pairs decreases by 15%.

From this simple example of an application of VMC, we can see the effect of electron correlations in the wave function directly - correlations which were neglected in the solution of Eq. 5.1. Our results indicate that such correlations do not appear to considerably affect the qualitative features of the broadening in \( \Delta p \) of Fig. 5-3. Note that the broadening of \( \Delta p \) is representative of the domination of Hund’s rule effects, which can also be qualitatively observed in Fig. 5-4.

For a more rigorous indicator that a 15% modification of \( U \) is not sufficient to modify a Hund’s rule domination of the magnetization, the Stoner parameter can be employed, as
5.9 Comparison with the Hartree-Fock limit

Before concluding this chapter, we present another picture that quantifies the difference between the Hartree-Fock uncorrelated limit of the electronic structure of the quantum dot, and the inclusion of an optimized Jastrow factor.

In Fig. 5-5 we present again the plot of Fig. 5-4, this time with the Hartree-Fock uncorrelated limit included for comparison. In the figure, we see the pronounced effect described in refs. [65, 66, 67, 68]. This thesis will not discuss the Stoner parameter.
of the inclusion of correlations on opposite-spin electrons. Without the Jastrow factor - the uncorrelated case - there is no Coulomb hole. With the Jastrow factor, a significant Coulomb hole develops. In the case of the same-spin electrons, the same-spin hole deepens.

Despite the different qualitative behavior of the opposite spin electrons with the introduction of correlations, we nonetheless find that the Pauli hole is much larger than the Coulomb hole in both cases. In fact, the introduction of a Coulomb hole for opposite-spin electrons, though it introduces a qualitatively different feature, nonetheless is counterbalanced by the increase in the same-spin hole, contributing to the fact that the effective energy penalty $U$ discussed in this chapter remains roughly constant. The same-spin hole is dominated by the Pauli exchange contribution, but is increased by a contribution from the Coulomb interaction.

The area between the dotted curve and the solid curve is a good way of measuring the overall shift of the electrons due to the inclusion of electron correlations - the “hole” function. In Fig. 5-6, we plot the hole function in the case of opposite-spin electrons. The baseline of the hole function is taken to be zero at all points in the case of uncorrelated electrons. The figure reveals that opposite-spin electrons avoid the region near one another and shift away. This must correspond to an increase in the hole function at some distance away, which we also observe in the hole function. When scaled by a factor of $r$ (see Fig. 17-1 and the discussion regarding that figure), the area under the hole function is precisely zero.

It is interesting to observe the effect of the hole function with a plot of the electron distribution for the quantum dot. We take full advantage of the fact that this is a two-dimensional quantum dot to plot the full electron density. Fig. 5-7 shows the plot. The nodes of the electron density in the Hartree-Fock case result from the sinusoidal nature of the solution of Schrödinger’s equation in a two-dimensional square well. (These nodes correspond to visual peaks, and are not to be confused with the zeroes of the wave function that are relevant for the nodal structure error in DMC calculations.) Introducing electron correlations causes a noticeable change in the plot. The relationship between the electron correlations and the change in the electron density is non-trivial (otherwise, we would not
Figure 5-6: In this figure, we plot the difference between the pair correlation function $g(r)$ in the case when Coulomb interactions are included via an optimized Jastrow factor, and in the Hartree-Fock limit in which electron correlations are not included. The hole function represents a shift of electrons away from each other, so that the density of nearby electrons decreases, with a corresponding increase of electrons some distance away. When scaled by a factor of $r$, the area under the hole function curve is precisely zero.
Figure 5-7: Shown in the figure is a plot of the full electron density for the 2-dimensional quantum dot studied in this chapter. On the left, we plot the Hartree-Fock (uncorrelated) case. On the right, electron correlations have been introduced with the inclusion of a Jastrow factor. The relationship between the introduction of the Coulomb hole, and the electron density, is non-trivial. However, as the figure shows, it has a noticeable effect on the electron density. The nodes result from the solution of the Schrodinger equation in a square well. The nodes persist even when correlations are included, but the electrons are evidently pushed away from the center of the well. Note that axes are not included, in order to make the figures more appealing. The horizontal axes of each figure are the X- and Y-coordinates. The vertical axis of each figure is the electron density $|\Psi|^2$. 
need to perform a QMC calculation when including a Jastrow factor!), but in the right hand plot of Fig. 5-7 we see that the electrons seem to be pushed away from the center of the QD.

This concludes our discussion of our studies of quantum dots.

In the next chapter, we proceed to another application of the SGA, a study of the RVB wave function representation of Li nanoclusters.
Chapter 6

RVB wavefunction for Li nanoclusters

6.1 Motivation

Before discussing the importance of Li in the next section, we here describe the motivation for advances required in the methods used to model nanoclusters with a many-body approach. In Ch. 3 we discussed the importance of the choice of the wave function ansatz employed in QMC calculations, going into particular detail about the issue of the variance of the local energy of the wave function as well as the nodal structure. We also discussed the Jastrow-Slater wave function, which has been the bread and butter of QMC calculations for decades.

The Jastrow factor, when properly constructed, can directly capture the physics of electron correlations without the added computational cost of additional determinants - none of which captures the physics particularly well. In the decades since the introduction of the Jastrow factor, the Jastrow-Slater form of Eq. 3.22 has dominated the field. The question arises, what is the next stage of development of the wave function ansatz that, unlike the multi-determinant CI expansion, can capture the physics as concisely as the Jastrow factor? It makes sense that work in the past decade along these lines has invoked the concept of inseparable two-body functions within the Slater matrix of Eqs. 3.20 and
3.21, rather than single-body functions \( \{ \phi \} \). Ideally, of course, \( M \)-body functions would be employed (only 1 would be necessary to replace Eq. 3.19!) to obtain the exact solution to the many-body problem, so the concept is simply to approach the \( M \)-body limit by starting with two-body functions.

The purpose of the two-body functions is to capture the electron correlations, but an attempt to do this is not straightforward. There is no general theory to describe electron correlations from an \textit{ab-initio} perspective; the wave function, along with the Hamiltonian, is itself the description of the correlations. As Chs. 3 and 4 discuss, good ways to measure improvements in the wave function revolve around the variance of the local energy, and the nodal structure. Of course, a decrease in the energy will also be observed, according to the variational theorem.

Two related approaches have been taken along these lines. The first is the concept of the \textit{Pfaffian}, which directly assists in a determination of the nodal structure of the wave function [37]. This will not be discussed in this thesis except to say that it is similar to the wave function of this chapter in that it includes inseparable two-body functions in the determinant. The second is the Jastrow Antisymmetrized Geminal Product (JAGP), which we have applied to a study of Li nanoclusters. In addition to studying the JAGP, we utilized one of the simple generalized eigenvalue methods of Fig. 10-1 (the Stochastic Reconfiguration (SR) method), as well as the SGA, for variational optimization. This work, a discussion of which comprises the remainder of this chapter, therefore contributes to a variety of current developments in QMC.

The chapter proceeds with a brief introduction to Li, and continues by introducing the concept of the Resonating Valence Bond wave function, which is modeled in a QMC form by the JAGP. The chapter then goes into detail about the calculations we performed and our results\(^1\).

\(^1\)The material in this chapter is adapted from the following talk. D. Nissenbaum, L. Spanu, C. Attaccalite, B. Barbiellini, and A Bansil, \textit{A DQMC study of cohesion energy of small Li clusters based on an RVB nodal structure}, American Physical Society, APS March Meeting, March 13-17, 2008, abstract W13.00009.
6.2 Lithium

Lithium, like other alkali metals, has typically been modeled as a free-electron like system - namely, an electron gas permeated by ions [69]. In recent years, however, experimental and theoretical investigations of Li have revealed a striking deviation from the free-electron model at high pressure - specifically, Li exhibits a complex phase diagram that includes different, unintuitive structural phase transitions [70]. Experimental and theoretical work in Li is now an active area of research, in particular because such research is expected to reveal new aspects of the physics of other light elements under pressure [71], most notably hydrogen. Lithium Hydride (LiH)-related materials are a promising candidate for on-board motor vehicle hydrogen storage [22, 23] which may be of importance for progress towards a fossil-fuel free energy future.

Even at ambient pressure, recent results from high resolution Compton scattering experiments of bulk Li determining the electron momentum density cannot be adequately explained in terms of the Fermi liquid theory. In these experiments, pronounced Fermi liquid deviations were observed [20, 21]. In addition, fairly recent theoretical studies of the bonding properties of bulk Li have also revealed that Li behaves like a “bad free-electron metal” [72]. Further work has revealed the value of an RVB-like approach to improve upon DFT calculations of the electron momentum density [73].

From a practical standpoint for the theoretician, Li is the ideal material in which to study the transition from clusters to a bulk metallic state, because it is the lowest-Z element which exhibits clearly metallic behavior in the bulk phase. Correspondingly, the physics of electron correlations is dominated by shells no greater than 2p or 3s, and so calculations are simpler to perform than for higher-Z elements. In turn, it is possible to study larger Li clusters from an ab-initio perspective than for higher-Z elements. Studies of scaling with cluster size are also relevant for determining the efficiency of new computer algorithms, such as the SGA.
6.3 The Resonating Valence Bond (RVB) wave function

The concept of a resonating valence bond must be considered in the context of a long history in quantum chemistry dating back to the 1930’s, and indeed in chemistry well back into the 1800’s. In the 1930’s and 1940’s, there was an ongoing and fundamental debate between two conceptual views of chemical bonding - the molecular orbital view and the valence bond view. In 1931 Linus Pauling published the first in a series of what some consider to be one of the most important published works in the history of chemistry, “On the Nature of the Chemical Bond” [74]. In this work, Pauling formulated the valence bond approach rigorously in the framework of quantum mechanics. Pauling’s work developed upon the theories of Lewis, for whom the Lewis structure is named [75]; and on the work of Heitler and London (see ref. [76] for an excellent historical perspective, and ref. [77] for a fascinating and informative exact fascimile of one of his important (hand-written) papers). The valence bond concept starts with the assumption that chemical bonding is due to the overlap between a spin-up electron residing in an atomic orbital centered on one atom, and a spin-down electron residing in an atomic orbital of a nearby atom. If the atoms are close enough, the total electron density of the two electrons is larger in the region of overlap between the two nuclei than it is elsewhere, leading to a chemical bond as the nuclei feel less Coulomb repulsion due to the screening of the electrons, and also feel a Coulomb attraction towards the electrons that lie between them. The valence bond approach to describe bonding in a molecule is a fundamentally two-electron approach. Each bond is considered to be the result of the interaction of two electrons, each on a different atom. Of course, due to the antisymmetry of the wave function with respect to the exchange of any two electrons, the electrons are “shared” between the atoms. The bond is constructed from two-particle functions. The bonds in a molecule described with the valence bond approach can be easily represented by a Lewis structure - a figure in which a molecule is pictured with line segments, each representing a bond that connects two atoms. See either representation of benzene in Fig. 6-1 for an example.

In contrast, the molecular orbital approach, as discussed in Ch. 3, is a fundamentally one-electron approach. The Slater determinant is a trivial but powerful antisymmetrization
In the resonating valence bond approach to quantum chemistry developed by Linus Pauling, the benzene molecule \((\text{C}_6\text{H}_6)\) is modeled as a superposition of two equally compatible valence bond structures.

```latex
\[
\begin{array}{c}
\text{H} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{H} \quad \text{H} \\
\end{array}
```

Figure 6-1: In the resonating valence bond approach to quantum chemistry developed by Linus Pauling, the benzene molecule \((\text{C}_6\text{H}_6)\) is modeled as a superposition of two equally compatible valence bond structures.

to construct the many-body wave function.

In the molecular orbital approach, *individual* molecular orbitals - rather than pairs of electrons - are considered to be either *bonding* single-particle orbitals, or *antibonding* single-particle orbitals. Notice here that the bonding characteristic of the molecule is described in terms of a single-particle function, in contrast to the *two*-particle function of the valence approach. Those molecular orbitals with a node - indicating zero single-electron occupancy - located between two atoms, are antibonding with respect to those atoms. Conversely, a region of increased relative single-particle density between two atoms is a bonding orbital with respect to those atoms. When the molecular orbital description is used, bonding between atoms is not quite as simple to understand as the Lewis structure formulation of the valence bond approach. Bonding must be understood by considering the total occupancy of the molecular orbitals. If bonding and antibonding orbitals (with respect to a given pair of atoms) are each occupied by the same number of electrons, then the effect of the bonding orbitals is canceled by the effect of the antibonding orbitals, and there is no bond between the atoms. Only if the occupancy of the bonding orbitals exceeds the occupancy of the antibonding orbitals is a bond formed between the atoms.

Both the valence bond approach and the molecular orbital approach have weaknesses. The weaknesses of the valence bond approach can be appreciated by considering benzene (see Fig. 6-1). No Lewis structure suffices to represent the symmetry of this molecule.
Therefore, Pauling introduced the concept of the *resonating* valence bond (RVB), which describes molecules as a resonance between Lewis structures. As we shall see, this is more mathematically challenging to represent, and this challenge has inhibited the development of the RVB approach for almost 50 years. The weaknesses of the molecular orbital approach were discussed in a different context in Ch. 3. For \( M \) electrons in a molecule in the ground state, there can only be \( M/2 \) occupied molecular orbitals, represented by the dimension of the Slater determinant. Such a description cannot possibly capture effects from higher-level molecular orbitals without a CI-type expansion.

Fundamental to each valence bond is the fact that there must be an *atomic* orbital available that has a significant overlap with an atomic orbital centered on a nearby nucleus. Consider now a molecule such as methane, CH\(_4\). This molecule has been conclusively shown by experiment to possess 4 perfectly symmetric bonds. The bond angles are all equivalent, the molecule forms a perfect tetrahedral pyramid, and exactly the same energy is required to dissociate any of the 4 hydrogen atoms. If valence bond theory were to be used employing hydrogenic atomic orbitals, we would find that the bonds could not be symmetric, as two of the valence electrons of carbon exist in the single \( s \)-orbital, and two of the electrons exist in two of the three available \( p \)-orbitals. Even a promotion of one of the \( s \)-electrons into the empty \( p \)-orbital does not create 4 degenerate atomic orbitals available for bonding within the valence bond model. Therefore, Pauling introduced *hybridized* orbitals, combinations of hydrogenic orbitals. In the case of methane, the single \( s \)-orbital and the
three \( p \)-orbitals merge into four degenerate new orbitals called \( sp^3 \) orbitals. The bonding structure of methane can be adequately represented in this fashion and represents a success of the valence bond approach.

Nonetheless, the debate between the valence bond approach and the molecular orbital approach slowly shifted in favor of the molecular orbital approach in the 1950’s, and dominated physics for four decades. In large part, the success of the molecular orbital approach is related to the fact that it is easier to write computer programs that utilize the molecular orbital approach than it is to write computer programs that utilize the valence bond approach. Within QMC, this is reflected by the ease with which the HF equations may be solved to construct molecular orbitals. There is no analogous method that can easily solve for the weights of the valence bond configurations in an RVB approach. The RVB optimization is challenging because there is no easily obtainable starting point and all pairing parameters - analogous to the atomic orbital coefficients \( c_{B,i,k} \) of Eq. 3.31 - must be optimized at once. There is no theory, analogous to HF theory, that provides a simple analytical solution.

However, the rapid development of computational capabilities has made the RVB amenable to detailed study within QMC, allowing a full optimization of the pairing parameters. The Jastrow factor can still be included, a point we will discuss shortly. Our work has shown that the RVB wave function, though more computationally challenging, is both more efficient and allows more flexibility than the molecular orbital approach. In fact, using the RVB, we show that it is even possible to construct superior single-particle molecular orbitals than have previously been obtained using HF molecular orbital theory when used with a Jastrow factor, and therefore has the potential to illuminate new physics as well as provide superior energies. The RVB therefore represents a breakthrough that has been made possible by computational advances.

### 6.4 Valence-bond approach applied to \( \text{H}_2 \)

The difference between the valence bond approach and the molecular orbital approach can be depicted by way of an example. In Ch. 3 when we discussed the Slater-Jastrow wave
function, we used the hydrogen molecule $H_2$ to provide a detailed example. We will again use the hydrogen molecule as an example now.

In Ch. 3, we did not discuss the form of the single-particle molecular orbitals. To construct these, it suffices to include only the smallest possible atomic basis set - the 1$s$ orbitals centered on each hydrogen atom. This basis set consequently has two members. The typical way to describe $H_2$ in terms of molecular orbitals is to construct the two orthogonal functions

$$\phi_b(\vec{r}) = \frac{1}{\sqrt{2(1 + S_{AB})}} (\varphi_A(\vec{r}) + \varphi_B(\vec{r})) \tag{6.1}$$

and

$$\phi_a(\vec{r}) = \frac{1}{\sqrt{2(1 - S_{AB})}} (\varphi_A(\vec{r}) - \varphi_B(\vec{r})) \tag{6.2}$$

where $\varphi_A$ represents the 1$s$ orbital on one of the atoms and $\varphi_B$ represents the 1$s$ orbital of the other atom. Note that the two atomic basis functions are not orthogonal, an issue for all polyatomic molecules that the Hartree-Fock method handles elegantly. The molecular orbitals in Eq. 3.19 must be orthogonal in order to utilize Koopman’s theorem [30] and for other reasons (which this thesis does not discuss) in the Jastrow-Slater formulation. The quantity $S_{AB}$ is the overlap integral $\int \phi_a(\vec{r}) \phi_b(\vec{r}) \, d\vec{r}$. In general, $S$ is the symmetric overlap matrix for any number of atomic wavefunctions centered on the atoms of a molecule. Assuming the atomic orbitals $\varphi_A$ and $\varphi_B$ are normalized, then the coefficients $\frac{1}{\sqrt{2(1 \pm S_{AB})}}$ include the overlap term $S_{AB}$ in order that $\varphi_A$ and $\varphi_B$ are normalized.

The first wave function $\phi_b$ is the bonding molecular orbital - this type of orbital is labeled $\sigma_{1s}$. See Fig. 6-3. When the atoms are close enough together, the electron density between the atoms increases and the electron in such a single-particle state spends most of its time between the nuclei, screening the nuclear repulsion and causing the nuclei to feel a force towards the region of negative charge between them. This force is responsible for the bond. The antibonding orbital $\phi_b^*$, labeled $\sigma_{1s}^*$, on the other hand, has a node between the nuclei of zero electron density. The electrons tend to spend more time away from the region between the two nuclei, and therefore screening is limited and the protons tend to feel both a repulsion from each other, and an attraction towards the regions of negative charge which
Figure 6-3: When two 1s hydrogenic atomic orbitals centered on different nearby atoms are added together in the configuration space of a single electron, two possible single-particle molecular orbitals are obtained. The $\sigma_{1s}$ bonding orbital results when the two atomic orbitals are added. The $\sigma^*_{1s}$ antibonding orbital results when they are subtracted. Shown in each figure is an isosurface of the electron density. The gap between the nuclei in the antibonding orbital correctly represents the fact that there is a node of zero electron density midway between the two nuclei.

It turns out that the functions $\phi_b$ and $\phi_a$ are the restricted closed-shell Hartree-Fock solutions, given the limited 1s atomic basis set we have employed. It is straightforward to perform the computation of $\langle \phi | H | \phi \rangle$ to show that the energy of the bonding orbital is, indeed, less than the energy of the antibonding orbital, and this holds true even employing the true HF interpretation of the energy of a single-particle molecular orbital [30], which this thesis has not discussed. This result can also be intuitively understood using the reasoning discussed in the previous paragraph. Note that the bonding orbital is a symmetric function without nodes, while the antibonding orbital is an antisymmetric function with a (single) node, and one expects the function with fewer nodes to have a lower energy, in correspondence with general principles of wave mechanics and quantum mechanics.

In the restricted closed-shell HF solution, electrons will fill the available orbitals in spin-up spin-down pairs from the lowest-energy molecular orbital on up. In the case of H$_2$, the two electrons therefore both fill the bonding orbital. The restricted closed-shell HF solution as presented in Ch. 3 assumes that the number of same-spin electrons is the same as the
number of opposite-spin electrons. The more general unrestricted HF solution, which is not
discussed in this thesis, lifts this restriction; however, even in the unrestricted HF solution,
the electrons turn out to possess opposite spin, except at infinite separation where the two
isolated H atoms possess an unrestricted HF solution that is degenerate with respect to the
relative spin state of the electrons. Therefore, for any HF solution representing the bonded
molecule, the electrons both populate the bonding orbital, and no electrons populate the
antibonding orbital. Therefore, for the molecule as a whole the bonding orbital has double
occupancy and the antibonding orbital has zero occupancy. The resulting bond “count”
in the Lewis structure sense is given in the molecular orbital interpretation by the general
formula \[
\frac{\# \text{ bonding} - \# \text{ antibonding}}{2},
\]
in which either the antibonding orbitals “dominate” and
the atoms repel one another at all distances, the bonding orbitals dominate and they exist
in an attractive well, or neither dominates and the atoms do not interact. For the H\textsubscript{2}
molecule, the bond count is 1, as expected. If this were the He\textsubscript{2} “molecule”, the four
electrons would equally fill the bonding and the antibonding orbitals and the bond count
would be 0, explaining why He atoms typically do not interact.

We can now explicitly construct the wave function in the molecular orbital interpretation. It is constructed from the lowest-level restricted HF molecular orbitals, which are
employed in the Slater determinant formulation of Eq. 3.22. (We will ignore the Jastrow
factor, because it is not a part of the molecular orbital construction.) In the case of H\textsubscript{2}, the
determinants are formed from spin-up and spin-down matrices each with only 1 element,
because there is only 1 spin-up and 1 spin-down electron in the molecule. The molecular
orbital for this element is chosen to be the lower-energy bonding orbital \(\phi_b\). The product
of Slater determinants in Eq. 3.22 is

\[
\Psi_{\text{H}_2-\text{MO}} = \frac{1}{2(1 + S_{AB})} \left( \varphi_A \left( \vec{r}^A \right) + \varphi_B \left( \vec{r}^B \right) \right) \left( \varphi_A \left( \vec{r}^A \right) + \varphi_B \left( \vec{r}^B \right) \right) \quad (6.3)
\]

where the normalization constant from Eq. 3.19 has been included, the wave functions \(\varphi\)
have been labeled as \(A\) or \(B\) to distinguish one nucleus from the other, and the electron
coordinates \(\vec{r}\) have been labeled with their respective spin designations in this spin-imposed
state. Recall from Ch. 3 that calculations are performed on wave functions with the spin states imposed upon the electrons.

Eq. 6.3 is the simple (1s-only), minimal-energy wave function for $\text{H}_2$ using the molecular orbital interpretation via a restricted, closed-shell Hartree-Fock calculation. Expanding the product of single-particle molecular orbitals yields

$$
\Psi_{\text{H}_2-\text{MO}} = \frac{1}{2(1 + S_{AB})} \left( \varphi_A \left( \vec{r}_A \right) \varphi_A \left( \vec{r}_B \right) + \varphi_B \left( \vec{r}_A \right) \varphi_B \left( \vec{r}_B \right) + \varphi_A \left( \vec{r}_A \right) \varphi_B \left( \vec{r}_B \right) + \varphi_B \left( \vec{r}_A \right) \varphi_A \left( \vec{r}_B \right) \right)
$$

(6.4)

We can see from this expansion that both covalent and ionic terms are included. The first two terms are ionic, in which the electrons both reside on one atom, and the other atom has no electrons. The final two terms are covalent, because the electrons reside on different atoms. By expanding Eq. 6.3, we see that all possible configurations are included in the Hartree-Fock approximation. This results directly from the fact that the electrons in the wave function are completely uncorrelated. We could have predicted that the wave function had to have a form such as Eq. 6.4, in which all possible configurations are included, because the HF ansatz does not include correlations. The signs of the individual terms cannot be predicted, only their equal weights. In fact, the antibonding orbital $\phi_a$ has the same form as Eq. 6.4, with equal weights for all configurations, but with different signs and a different normalization constant. The wave function is completely uncorrelated because in an uncorrelated wave function, no electron can exhibit a preference to be located on any particular atom in a way that depends on any other electron; for a molecule of the simple symmetry of $\text{H}_2$, this requires that the weights have equal magnitude.

Note also that the restricted closed-shell HF ground state many-body solution is symmetric with respect to the two electrons, in analogy to the fact that the single-particle lowest-level HF molecular orbital is symmetric with respect to the configuration space of a single electron. It turns out that to describe the bonded $\text{H}_2$ molecule (i.e. when the atoms are at their bonding separation), the restricted HF solution and the more general unre-
stricted HF solution provide the same result for the ground state wave function. Therefore, in general, the fully uncorrelated ground state wave function for \( \text{H}_2 \) has a symmetric spatial function, which corresponds to the antisymmetric spin singlet state. This is in agreement with the discussion of Ch. 3. That chapter also discussed the possibility of a triplet solution.

Although the wave function of Eq. 6.4 is the correct HF solution, it is certainly not the exact solution for the \( \text{H}_2 \) molecule, bonded or otherwise. In addition, the restricted HF solution dramatically fails when the atoms are separated by a large distance. In the case of infinite separation, there is no bonding between the atoms, and the ground state consists of two individual \( \text{H} \) atoms - not the ions \( \text{H}^- \) and \( \text{H}^+ \). However, Eq. 6.4 indicates a non-negligible probability of observing the ionic form - a completely unphysical situation. It is clear that the restricted HF solution, at the very least, fails to describe dissociation of the molecule. (The unrestricted HF solution is far more accurate.)

We now turn to a detailed study of the valence bond (VB) approach to \( \text{H}_2 \), in preparation for our presentation of the full Resonating-Valence-Bond formulation. The valence bond approach is very different than the single-determinant molecular orbital approach in that correlations are imposed upon the wave function and therefore represent a dramatic departure from the Hartree-Fock formulation. Using the valence bond approach in the case of \( \text{H}_2 \), we hand-select the configurations that we suspect might best represent the molecule. Using this approach we impose that because the hydrogen atoms bond, we should exclude ionic configurations. The valence bond approach therefore yields the wave function

\[
\Psi_{\text{H}_2-\text{VB}} = \frac{1}{\sqrt{2(1 + S_{AB}^2)}} \left( \varphi_A \left( \vec{r}_1 \right) \varphi_B \left( \vec{r}_1 \right) + \varphi_B \left( \vec{r}_1 \right) \varphi_A \left( \vec{r}_1 \right) \right). \tag{6.5}
\]

Despite the assumption that ionic configurations do not contribute to the bonding, this wave function actually turns out to be worse than the HF solution, which includes the ionic configurations, when the hydrogen atoms are at their proper bonding separation. However, the wave function works fairly well in the limit of infinite atomic separation, and therefore the VB approach describes dissociation without the catastrophe of the restricted HF solution. It is still far from the best wave function that can be constructed to describe
dissociation, but we will not discuss such improvements here.

This simple valence bond wave function is known as the description in the Heitler-London limit, reflecting the fact that, in general, the Heitler-London approach is a valence bond approach.

Note that the valence-bond many-body wave function is also fully symmetric with respect to the exchange of the two (opposite-spin) electrons. We could have chosen instead the fully antisymmetric form by flipping one of the signs so that the two terms carry opposite sign. Similar reasoning to that of the antibonding single-particle molecular orbital shows that this state, however, will be higher in energy than the symmetric state. Therefore, both in the case of the uncorrelated Hartree-Fock molecular orbital solution, and in the case of the Heitler-London valence bond solution, the lowest-energy wave function is symmetric with respect to the exchange of the electrons, and the opposite-spin electrons therefore typically form the antisymmetric spin singlet state.

Now that we have laid the foundation for the $H_2$ example by contrasting the molecular orbital approach and the valence bond approach, we can proceed to write both solutions in a more rigorous general framework, which lays the groundwork for the construction of the RVB wave function. The example of $H_2$ is a useful one to introduce the framework so that it can be contrasted with the more traditional and, in some ways, simpler molecular orbital framework.

### 6.5 The geminal matrix

Let us introduce the general framework by presenting an example, that of the HF solution in Eq. 6.4. We can write the HF solution as

$$
\Psi_{H_2\cdot HF} = \frac{1}{2(1 + S_{AB})} \left[ \begin{array}{c} \varphi_A (\vec{r}_1) \\ \varphi_B (\vec{r}_1) \\ \varphi_A (\vec{r}_2) \\ \varphi_B (\vec{r}_2) \end{array} \right] \begin{bmatrix}
1 & 1 \\
1 & 1 \\
\varphi_A (\vec{r}_1) & \varphi_A (\vec{r}_2) \\
\varphi_B (\vec{r}_1) & \varphi_B (\vec{r}_2)
\end{bmatrix} \tag{6.6}
$$

where the matrix is called the geminal matrix. All possible atomic orbital pairs of opposite-spin electrons are included in the matrix. Note that we have changed the label of the
wave function from MO to HF because this molecular orbital description is the Hartree-Fock solution. Also note that the formula reflects the fact that it is possible to write the HF solution as a sum of geminal pairs. In the case of \( \text{H}_2 \), the presence of all 1’s in the geminal matrix indicates that all geminal pairs have equal weight and that therefore the wave function is \textit{uncorrelated}, as we expect for the HF solution, as discussed previously.

We already know that the Heitler-London wave function for \( \text{H}_2 \) is correlated. Also, the Heitler-London wave function cannot be described in the molecular orbital approach described by Eq. 3.19, as expected for a strictly valence bond approach. But because we have control over each geminal pair using the geminal matrix approach, we can easily write the Heitler-London valence bond wave function for \( \text{H}_2 \) as

\[
\Psi_{\text{H}_2-\text{VB}} = \frac{1}{\sqrt{2 \left(1 + S_{AB}^2\right)}} \begin{bmatrix} \varphi_A (\vec{r}_1) & \varphi_B (\vec{r}_1) \end{bmatrix} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \varphi_A (\vec{r}_1) \\ \varphi_B (\vec{r}_1) \end{bmatrix}. \quad (6.7)
\]

Note that the diagonal terms in the geminal matrix represent the ionic contributions, and are therefore 0 in a standard valence bond approach. Also note that because we can write both the Hartree-Fock molecular orbital solution, and the Heitler-London valence bond solution, in terms of this framework, we see that the geminal matrix approach allows more flexibility than the molecular orbital approach.

We wish now to discuss the valence bond features of this framework.

As the example of the hydrogen molecule \( \text{H}_2 \) shows, both the molecular orbital approach and the valence bond approach can be expanded as a sum of individual Hartree-like products (Section 3.5.5), where in this case each factor in the Hartree product is an atomic orbital centered on one of the atoms, rather than each factor being a molecular orbital. This type of Hartree product is nonetheless a legitimate Hartree product, because the molecular orbitals for a system can always be chosen to be identical to the atomic orbitals. (Of course, with such a choice of molecular orbitals, the HF solution will not be obtained, and in fact this expansion in the new “molecular orbital” basis occurs only after-the-fact.) We use this form of Hartree product expansion only for convenience.

The expansion in Hartree products extends to molecules with any number of electrons.
Figure 6-4: In the resonating valence bond framework, a molecule is conceptually described as a resonance of Lewis structures. Shown in part A of the figure is a resonance between the two states that appear in the HL wave function for Li$_4$. Shown in part B is the additional resonance made possible in the RVB model. In the RVB wave function, the resonance in part B is damped by the Jastrow factor. The strength of the damping can be determined by a variational QMC calculation.

In all such cases, each of the $M$ electrons appears in a single atomic orbital factor in each Hartree product, for $M$ factors in total for each Hartree product. Different electrons can reside in an orbital on any atom; for example, Hartree products exist in the expansion in which all $M$ electrons reside on a single atom. Of course, the coefficient of this Hartree product will be exceedingly low for $M$ much greater than 2 in the case of an optimized wave function.

This type of Hartree product expansion is useful in showing the strength of the various covalent and ionic terms, as the example of H$_2$ shows. It is also useful for another reason - it relates the molecular orbital picture and the valence bond picture directly. By improving upon the HF molecular orbital picture to include multiple determinants, and likewise by including all atomic orbitals across all atoms in the valence bond picture, we arrive at a full CI expansion which can be expanded in Hartree products in both cases, enabling us to show that the two pictures are equivalent.

The discussion near the beginning of this chapter hopefully made clear the fact that the valence bond approach was initially developed to capture the physics of molecular bonding in a simple way, by including only the relevant valence bonds. Therefore, the “conceptual appeal” of excluding ionic configurations in the valence bond approach corresponds to the
historic need to mathematically simplify the valence bond problem. The geminal matrix is a relatively recent introduction, and according to the spirit of the typical valence bond approach the matrix would roughly specify the geometry of the molecule by containing 1’s for the matrix elements connecting atoms that bond, and 0’s otherwise. However, given modern computational capabilities, it is perfectly reasonable to include ionic configurations within the valence bond approach, as the Hartree-Fock case does, as well as to include core contributions. In fact, Pauling himself proposed such ionic configurations in an RVB approach to Li, as indicated in Fig. 6-4, which is taken directly from Pauling’s paper on the subject [78]. In this paper, Pauling introduces the concept of a metallic orbital to describe conductivity in Li by utilizing a valence bond approach. Also see Pauling’s Nature publication [79] for a discussion of the theory of metallic orbitals. The metallic orbital is an available hybridized orbital that allows valence bonds to form as depicted in part B of the figure, in which one atom carries a net negative charge and another atom carries a net positive charge. According to this model, the resonating valence bonds carry the region of positive and negative charge quickly through the metal, resulting in electrical conductivity.

The concept of the metallic orbital has not taken root within the physics community. However, Pauling did not have at his disposal the methods of Quantum Monte Carlo. Using these QMC methods, we are able to develop an RVB approach without the use of metallic hybridized orbitals, for two reasons. First, using the geminal matrix we can explicitly write the wave function as a sum of any possible pair of atomic orbitals, without adhering to the Pauling rule that each valence bond must correspond to some available atomic orbital (i.e. that only two electrons can exist in the orbital). We can ignore this principle because we are not calculating bond energies via a heuristic approach, but instead we are performing a direct, ab-initio, all-electron calculation of the exact energy integral based on an arbitrary wave function ansatz which can have any sum of Hartree product configurations. The so-called metallic hybridized orbitals therefore can be thought of as the “bonding” of an atom with itself; i.e. a double occupancy of a pair of opposite-spin valence electrons on a single atom, corresponding to a Hartree product representing an ionic configuration. Note that the Hartree product (in its atomic orbital form) in such a case will have multiple
electrons associated with the “self-bonded” atom, and each electron can appear only once in such a Hartree product. Second, we can modulate the strength of any of these “metallic” (ionic) orbitals by inclusion of the Jastrow factor, which represents the Coulomb repulsion between electrons and therefore suppresses double occupancy. It is the interplay between the Jastrow factor and the function representing the pairing of electrons (the geminal function) that represents the full RVB wave function ansatz within the QMC framework.

Armed with this background, we are now ready to present the geminal matrix as utilized by the RVB wave function within QMC. We have, for a general geminal expansion \( \psi_G \) equivalent to Eq. 6.6 or Eq. 6.7,

\[
\psi_G(r^+, r^-) = \sum_{i,j} \sum_{a,b} \lambda_{a,b}^{i,j} \phi_{a,i}(\vec{r}^+) \phi_{b,j}(\vec{r}^-),
\]

where the indices \( i, j \) run over a subset of atomic orbitals centered on nuclei \( a, b \), and the normalization constant is not included. It can be seen that Eq. 6.8 is exactly the mathematical extension of Eq. 6.6 or Eq. 6.7 to any number of atomic orbitals and nuclei, with the matrix given by the coefficients \( \lambda_{i,j}^{a,b} \). The geminal function could just as easily be written as a single sum

\[
\psi_G(\vec{r}^+, \vec{r}^-) = \sum_{i,j} \lambda_{i,j} \phi_i(\vec{r}^+) \phi_j(\vec{r}^-),
\]

where the indices \( i \) and \( j \) both run over all atomic orbitals. The formulation in Eq. 6.9 makes it more clear that the matrix of Eqs. 6.6 and 6.7 is constructed from the coefficients \( \lambda_{i,j} \). The formulation in Eq. 6.9 also makes clear that the basis functions \( \phi \) do not need to be atomic orbitals - they can be any single-particle functions, including molecular orbitals that consist of linear combinations of atomic orbitals (Section 3.5.4). We will, in fact, construct such orbitals in Section 6.9 and Section 6.10.3.

The full geminal function can be written as

\[
\psi_G(r^+, r^-) = \begin{bmatrix}
\phi_1(\vec{r}^+) & \phi_2(\vec{r}^+) & \ldots & \phi_{M/2}(\vec{r}^+)
\end{bmatrix} \begin{bmatrix}
\lambda_{1,1} & \lambda_{1,2} & \ldots & \lambda_{1,M/2} \\
\lambda_{2,1} & \lambda_{2,2} & \ldots & \lambda_{2,M/2} \\
\ldots & \ldots & \ldots & \ldots \\
\lambda_{M/2,1} & \lambda_{M/2,2} & \ldots & \lambda_{M/2,M/2}
\end{bmatrix} \begin{bmatrix}
\phi_1(\vec{r}^-) \\
\phi_2(\vec{r}^-) \\
\ldots \\
\phi_{M/2}(\vec{r}^-)
\end{bmatrix},
\]

(6.10)
which is the generalization of Eqs. 6.6 and 6.7 to \( M/2 \) pairs of opposite-spin electrons. The normalization constant is not included.

Although the geminal function looks like a Slater determinant, the geminal function is a function of only two electrons, and more specifically of two opposite-spin electrons - a spin-up and a spin-down electron. In fact, the geminal function corresponds to the single-particle molecular orbitals in the molecular orbital approach, rather than the Slater determinant, because all of the unique complexity and richness of the wave function is contained in the geminal. In the next section we will antisymmetrize the geminal function, which corresponds to a Slater determinant in the molecular orbital approach.

6.6 Antisymmetrized Geminal Product (AGP)

We now introduce the spin part of the RVB formulation. A comparison with the spin formulation of the Hartree-Fock molecular orbital approach is instructive, and the reader is encouraged to refer to Appendix I for the Hartree-Fock derivation while following the derivation of the RVB here; we will refer to the relevant HF equations as they arise. We follow a similar set of steps as in the HF derivation.

In analogy to the set of molecular orbitals of Hartree-Fock theory, we introduce in this case a single function of two electrons, the spin-resolved geminal function \( \psi_G^s(\mathbf{r}^\alpha, s^\alpha, \mathbf{r}^\beta, s^\beta) \) as

\[
\psi_G^s(\mathbf{r}^\alpha, s^\alpha, \mathbf{r}^\beta, s^\beta) = \psi_G(\mathbf{r}^\alpha, \mathbf{r}^\beta) \xi(s^\alpha, s^\beta),
\]

(6.11)

where \( \alpha \) and \( \beta \) index the electrons, with the constraint that the spins of the electrons are opposite, and where \( \xi(s^\alpha, s^\beta) \) is an as-yet undetermined two-electron spin function.

From the spin-resolved geminal function we construct the full, many-body wave function, in analogy to the Hartree-Fock many-body function of Eq. I.2. For the RVB it will be more convenient to use a different labeling scheme than we use in the case of the HF wave function. In this notation, we index the electrons in opposite-spin pairs with the same
numerical subscript, so that there are $\frac{M}{2}$ such pairs. We have:

$$\Psi_{\text{AGP}}^{s} = \hat{A}\left[\psi_{G}^{s}(r_{1}^{\alpha}, s_{1}^{\beta}, \tau_{1}^{\alpha}, s_{1}^{\beta})\psi_{G}^{s}(r_{2}^{\alpha}, s_{2}^{\beta}, \tau_{2}^{\alpha}, s_{2}^{\beta})...\psi_{G}^{s}(r_{M/2}^{\alpha}, s_{M/2}^{\beta}, \tau_{M/2}^{\alpha}, s_{M/2}^{\beta})\right],$$

(6.12)

where $\hat{A}$ is the antisymmetrizer that guarantees that $\Psi_{\text{AGP}}^{s}$ is fully antisymmetric with respect to the exchange of any two electrons. Note that the full argument to $\hat{A}$ is analogous to a Hartree product of molecular orbitals, and therefore Eq. 6.12 is analogous to the Hartree-Fock function of Eq. I.2. The acronym AGP stands for Antisymmetrized Geminal Product.

(Note: the following derivation is the work of the author and, to the best of this author’s knowledge, unique.)

In the single-particle molecular orbital approach, it is simple to construct the antisymmetrizing wave function as a Slater determinant. Unfortunately, with the two-particle functions, there is no simple mathematical form for the antisymmetrization and we must utilize the symbol $\hat{A}$ to represent it. We find that $\hat{A}$ is a sum of Hartree-like products, each Hartree-like product being a product of two-particle, rather than single-particle, factors:

$$\hat{A} = \sum_{k} \prod_{\{i,j\}_k} \psi_{G}^{s}(r_{i}^{\alpha}, s_{i}^{\beta}, \tau_{j}^{\alpha}, s_{j}^{\beta}),$$

(6.13)

where each term $k$ in the sum corresponds to a different set $\{i,j\}$ defining the product of geminals. This formula is analogous to Eq. I.2, the Slater determinant which antisymmetrizes the single-particle molecular orbitals. At this stage, a determinant of a matrix of geminals - though it possesses the form of Eq. 6.12 - is not yet able to capture the antisymmetry.

Without a way to easily represent the proper choice of sets $\{i,j\}_k$ in Eq. 6.13, the problem becomes more difficult. However, we can simplify the problem by proceeding analogously to the case of the molecular orbital (Hartree-Fock) approach by assuming that the spatial function $\psi_{G}$ is symmetric with respect to the exchange of its two arguments,
and by assuming that the spin function $\xi$ is *antisymmetric* and therefore given by

$$\xi(s^\alpha, s^\beta) = \xi_\delta(s^\alpha, s^\beta) \equiv \xi_\uparrow(s^\alpha)\xi_\downarrow(s^\beta) - \xi_\downarrow(s^\alpha)\xi_\uparrow(s^\beta),$$  \hspace{1cm} (6.14)

the spin singlet state within the subspace of these two electrons.

The assumption that $\psi_G$ is symmetric requires that the $\Lambda \equiv \lambda_{ij}$ matrix of Eq. 6.9 be symmetric. The assumption that pairs of particles form a singlet state within the geminal leads to the fact that the total molecule exists in the spin singlet state; namely, a state in which $S^2 \equiv (S_1 + S_2 + ... + S_M)^2 = 0$ (doing without spin indexing), and in which $S_z$ for the full molecule is also zero. These results for $S^2$ and $S_z$ can be straightforwardly obtained by applying the appropriate many-body angular momentum operators to the wave function of Eq. 6.12 and utilizing the fact that individual pairs of electrons in each term of the $k$-sum in Eq. 6.13 are separable.

For this spin singlet wave function, we consider the expectation value of any spin-free operator, $\hat{O}$, given by $\langle \Psi | \hat{O} | \Psi \rangle$. For simplicity, we use for the geminal the notation

$$\psi^\delta_G(\vec{r}_i^\alpha, s_i^\alpha, \vec{r}_j^\beta, s_j^\beta) \equiv \psi^\delta_G(i, j)$$

for particles $i$ and $j$, where it is understood that the first particle has label $n$ with $\alpha$ spin, and the second has label $m$ with $\beta$ spin.

We have

$$\langle \Psi | \hat{O} | \Psi \rangle = \int \hat{A}[\psi^\delta_G(i, j)]\hat{O}\hat{A}[\psi^\delta_G(\vec{i}, \vec{j})]d\vec{r}ds$$

$$= \int \sum_k \prod \psi^\delta_G(i, j)\hat{O}\sum_k \prod \psi^\delta_G(\vec{i}, \vec{j})d\vec{r}ds,$$

$$= \int \left[ \sum_k \prod \psi_G(i, j)\xi_s(i, j) \right] \hat{O} \left[ \sum_k \prod \psi_G(\vec{i}, \vec{j})\xi_s(\vec{i}, \vec{j}) \right] d\vec{r}ds$$

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\[ I_{k,\tilde{k}} = \int \prod_{\{i,j,i,j\}_{kk}} \psi_G(i,j)\hat{O}\left\{ \psi_G(i,j) \right\} \xi_{s(i)}(s_j) - \xi_{s(i)}(s_j) \right\} d\mathbf{r} ds \]

where the product in \( I_{k,\tilde{k}} \) runs over the appropriate values of \( i, j, \tilde{i}, \tilde{j} \) (labeled with the joint symbol \( kk \)), and where \( d\mathbf{r} \equiv d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_M \) (doing without spin indexing) and \( ds = ds_1 ds_2 \ldots ds_M \). Note that the symbol \( \tilde{k} \) should not be taken to mean the product \( (k) \left( \tilde{k} \right) \).

The integrand of each integral \( I_{k,\tilde{k}} \) contains the product of \( M \) spin singlet functions, with each electron represented in exactly two factors in the product. When expanded, the product of singlet functions result in \( 2^M \) different terms, and we have for the integrand \( I_{k,\tilde{k}} \):

\[ I_{k,\tilde{k}} = \left( \int \prod_{\{i,j,i,j\}_{kk}} \psi_G(i,j)\hat{O}\left\{ \psi_G(i,j) \right\} d\mathbf{r} \right) \] 
\[ \times \left( \sum_{b=1}^{2^M} \prod_{x=1}^{M} (-1)^{a_{x,\tilde{x},\tilde{k}}} \xi_{\nu_{x,\tilde{x},\tilde{k}}}(x) \xi_{a_{x,\tilde{x},\tilde{k}}}(x) ds \right) \]

where the product over all \( M \) particles represented by \( x \) (without using notation with spin
indexing in the product) utilizes spin functions with the proper selection of spin orientations 
\( \mu \) and \( \nu \) resulting from the \( b^{th} \) expansion of the \( M \) spin singlet functions, and \( \mu \) and \( \nu \) depend on \( x, k, \) and \( \tilde{k} \) as well as \( b \). The sign of the spin product in the lower half of Eq. 6.16 is 
\( \pm 1 \), determined by the value \( a_{x,b,\tilde{k}k} \) which can be either 0 or 1. In this product, the spin 
functions appear in pairs - two each for every electron. Therefore, only in the case that each 
and every pair of spin functions possess the same spin orientation will the integral over spin 
be non-zero - and in this case the value of the integral will be 1. Eq. 6.16 then indicates 
that for spin-free operators, the integral \( I_{k,\tilde{k}} \) can be obtained by integrating over the spatial 
function \( \psi_G \) - the spin components integrate out. The \( 2^M \) spin integrals result in an integer 
value that multiplies the spatial integration.

The importance of the choice of the spin singlet function can be seen in Eq. 6.16. The 
value \( a_{x,b,\tilde{k}k} \) is affected by the fact that the spin singlet function was chosen in Eq. 6.11. 
Note that if we had instead chosen one of the same-spin triplet states, there would be no 
expansion of \( 2^M \) spin factors. If the opposite-spin triplet state had been chosen, the sign of 
all spin integrations would be positive and \( a_{x,b,\tilde{k}k} \) would always equal 0.

Choosing the singlet function, in conjunction with a symmetric geminal function \( \psi_G \), 
results in a useful simplification of the expectation value \( \langle \Psi | \hat{O} | \Psi \rangle \). No matter what the 
values of \( k, \tilde{k} \) are, the sum over the \( 2^M \) spin integrals results in either 0, or a constant integer 
value that does not depend on \( k, \tilde{k} \). (We will not derive this result here; the derivation 
is tedious but straightforward and is not, to our knowledge, presented anywhere in the 
literature.) It also turns out that the values of \( k, \tilde{k} \) that are zero are exactly the ones such 
that it becomes possible to write the full many-body AGP wave function of Eq. 6.12 as 
a simple determinant, analogous to the Hartree-Fock Slater determinant, without affecting 
the value of \( \langle \Psi | \hat{O} | \Psi \rangle \). We have

\[
\Psi_{\text{AGP}} = \det \begin{vmatrix}
\psi^s_G(\tilde{r}_1^1, \tilde{r}_1^1) & \psi^s_G(\tilde{r}_1^1, \tilde{r}_2^1) & \cdots & \psi^s_G(\tilde{r}_1^1, \tilde{r}_{M/2}^1) \\
\psi^s_G(\tilde{r}_2^1, \tilde{r}_1^1) & \psi^s_G(\tilde{r}_2^1, \tilde{r}_2^1) & \cdots & \psi^s_G(\tilde{r}_2^1, \tilde{r}_{M/2}^1) \\
\vdots & \vdots & \ddots & \vdots \\
\psi^s_G(\tilde{r}_{M/2}^1, \tilde{r}_1^1) & \psi^s_G(\tilde{r}_{M/2}^1, \tilde{r}_2^1) & \cdots & \psi^s_G(\tilde{r}_{M/2}^1, \tilde{r}_{M/2}^1)
\end{vmatrix}, \quad (6.17)
\]
where the function $\Psi_{\text{AGP}}$ is a purely spatial function, analogous to the spatial Hartree-Fock function of Eq. I.12. Therefore, for the sake of calculating expectation values of spin-free operators, we are free to use Eq. 6.17, rather than Eq. 6.12. Not only are the appearance of zeroes in Eq. 6.16 necessary for Eq. 6.17, but also necessary is the fact that all non-zero integrals in Eq. 6.12 (for each such $k, \tilde{k}$) have the same integer result for the sum over spin integrals. Both of these conditions result from the choice of the singlet wave function in Eq. 6.11.

In both the RVB and the HF cases, we have integrated out the spin component and constructed a simple form for the spatial part of the wave function that yields equivalent results for expectation values. Also, in both cases, within the spatial function we fix the spin values of each electron according to its index within the determinant, a necessity for computer computations, but in seeming violation to the spirit of antisymmetry. Finally, in both cases the resulting many-body wave function is a spin singlet.

As stated, in direct analogy to the Hartree-Fock function of Eq. I.22, considerations of the geminal function of Eq. 6.17 does not allow for an understanding of the antisymmetry of the many-body wave function. Swapping the position and spin of two electrons in Eq. 6.17 does not result in the (negative of the) same wave function. As in the Hartree-Fock case, one needs to return to the spin-included wave function of Eq. 6.12 in order to observe the antisymmetry. For the AGP wave function, we see from Eq. 6.12 that the full many-body wave function is antisymmetric - by definition. Therefore, in both cases we see that the inclusion of spin plays a central role in the antisymmetry of the wave function. Antisymmetry cannot be revealed by looking at the spatial part alone, in either the Hartree-Fock or the RVB formulation.

The non-trivial antisymmetrization nonetheless provides the simple result in Eq. 6.17 - a generic determinant of geminal pairing functions $\psi_G$. All of the complexity in the wave function stems from the geminal itself, rather than from the antisymmetrization determinant. The geminal is the function that determines the valence-bond characteristics of the desired wave function. We now proceed to discuss the construction of the geminal function.

A determination of the proper coefficients in the $\Lambda$ matrix is non-trivial. This is not
simply due to the fact that the physics regarding the proper influence of the ionic contributions is unknown. It also stems from the fact that the full many-body wave function is constructed by taking the determinant of a matrix of opposite-spin geminals, as in Eq. 6.17 - the AGP. A great deal of complicated cancellation of terms takes place in an expansion of this determinant into Hartree products, in an analogous fashion to the cancellation of bonds across molecular orbitals to obtain the Lewis structure in the molecular orbital approach - though the cancellation is intractably more complicated in the case of the RVB, which is not a molecular orbital approach. Due to the determinant of geminals, the relationship between the pairing constants $\lambda_{i,j}$ in Eq. 6.9 and the coefficients of the corresponding Hartree products representing the ionic contributions is non-intuitive and non-trivial. The example of the hydrogen molecule, though useful as a starting point to understand the relationship between the molecular orbital perspective, the valence bond perspective, and the expansion in Hartree products, is nonetheless too simple to provide an understanding of realistic systems.

In this context, we now discuss complexities that appear beyond the simple example of the hydrogen molecule $H_2$.

### 6.7 Variational freedom of the AGP

In the case of $H_2$, the Hartree-Fock solution was easily obtained. This is due to the fact that there are only two (opposite spin) electrons in the system, and therefore no AGP determinant needs to be calculated because the AGP matrix has only a single geminal. However, when there are multiple geminals, construction of the A-matrix as in Eq. 6.6, with all 1’s to represent an equal contribution from ionic and covalent bonds, leads to a many-body wave function when the determinant is expanded that is precisely zero in all cases. Therefore, construction of the Hartree-Fock wave function in the geminal representation is non-trivial. Note that if the Hartree-Fock solution were as simple as Eq. 6.6 seems to indicate, there would be no need for the self-consistent Hartree-Fock equations (such as the Roothaan equations) discussed in Ch. 3; instead, calculation of the HF solution would involve a trivial diagonalization of a simple matrix of 1’s, and a calculation of the
corresponding eigenvectors. (The calculation of the normalization constants would still require the overlap integrals.) If we attempt to obtain the HF solution by a full optimization of the A-matrix, without employing the Hartree-Fock self-consistent field equations, we find ourselves involved in a serious optimization problem without any simple analytical solution. Therefore, in the valence bond approach, obtaining the HF solution is non-trivial. This is one reason that the valence bond approach has been less appealing than the molecular orbital approach over the past 50 years.

Despite these complexities, the RVB wave function can provide greater variational freedom to construct ionic and core contributions than the molecular orbital approach. This can be deduced from the number of variational parameters that appear in the two wave functions. For the sake of counting the variational parameters in this context, let us ignore the Jastrow factor (which can appear in both wave functions). From Eq. 3.19, we see that the restricted closed-shell Hartree-Fock Slater wave function has \( M/2 \) molecular orbitals. Each molecular orbital is a linear combination of atomic orbitals (LCAO); let us assume there are \( P \) such atomic orbitals. The number of variational parameters is therefore \( MP/2 \).

In contrast, in the RVB approach the A-matrix is a symmetric \( P \times P \) matrix, which therefore contains \( P(P + 1)/2 \) variational parameters. The minimum number of atomic orbitals is half the number of electrons, or \( P \geq M/2 \). Although for a limited basis set it is possible for the molecular orbital approach to have more variational freedom, note that \( M \) is fixed but we can always choose to add more atomic orbitals into the basis set for any system to increase \( P \). Therefore, the RVB approach can always be designed to have greater variational freedom than the molecular orbital approach. This translates into greater control over the individual Hartree products representing individual ionic contributions in an expansion of the wave function.

There is a more intuitive way to understand the variational freedom of the VB approach, in contrast with the HF approach. Let us again consider an expansion of each wave function in Hartree products. However, for the HF wave function, let us return to the true molecular orbital Hartree product, as defined in Ch. 3. We can see, quite straightforwardly from an expansion of the determinant in Eq. 3.19 in molecular orbital Hartree products, that
each such Hartree product has a coefficient of 1. A further expansion into Hartree products of atomic orbitals yields coefficients that appear arbitrary and do not seem to reveal any particular pattern. However, when enough atomic orbitals are included in the VB basis, these coefficients nonetheless span only a limited subspace of the space spanned by the full VB approach. The VB approach therefore allows more freedom to exclude (or include) ionic terms.

6.8 Jastrow + AGP (JAGP) ansatz for the RVB

Including or excluding ionic terms in a valence-bond description of molecules is subject to the challenges discussed in Section 6.3; namely, there is no general formulation to construct the coefficients of the Hartree products, the connection between the expansion in Hartree products and the A matrix is non-trivial, and we expect ionic contributions such as Pauling’s “metallic orbital” (Fig. 6-4) to be small, so that the wave function is highly dependent on small changes in the A matrix. More simply stated, we see that the function $\Psi_{\text{AGP}}$ includes electron correlations, but it nonetheless does so without directly accounting for Coulomb repulsion, and merely provides a more direct description of bonding, as in the Heitler-London formulation and the example of the H$_2$ molecule in Eq. 6.5.

The Coulomb hole (Ch. 5) cannot directly be modeled by the RVB wave function. The RVB is designed to capture bonding in a direct fashion, and through an improved description of bonding, it indirectly describes the Coulomb hole.

Therefore, in order to gain the benefit of the valence-bond approach to account for the resonating structures such as those pictured in Fig. 6-4, while at the same time including the Coulomb hole directly, we include a Jastrow factor, just as we do in the molecular orbital formulation. The Jastrow factor also has the effect of inhibiting double occupancies so that the RVB wave function is not severely dependent on small changes in the $\lambda_{i,j}$ parameters.

The RVB wave function ansatz that we employ can therefore be written as

$$\Psi_{\text{RVB}} \equiv \Psi_{\text{JAGP}} = J\Psi_{\text{AGP}} \quad (6.18)$$
where $J$ is the Jastrow factor. Also see ref. [80] for details on the formulation.

The variational parameters of the RVB wave function include the elements of the $\Lambda$-matrix and the Jastrow parameters, but they can also include the orbital exponents and coefficients in the atomic basis functions (the zeta parameters discussed in Ch. 4).

6.9 Natural orbitals

Once the variational parameters have been optimized, it does not particularly help to study the $\Lambda$-matrix of optimized $\lambda_{i,j}$ coefficients directly, due to the non-trivial relationship between these coefficients and the ionic contributions.

Instead, we utilize the language of molecular orbitals to interpret the physics revealed by the AGP in the RVB model. Once the optimization of the RVB $\lambda$-matrix parameters has been carried out, we can perform a diagonalization involving the $\lambda$-matrix, obtaining a new basis set of natural molecular orbitals which reflect the relevant physics of the system. To deal with the fact that the atomic orbitals are not orthogonal, we must first create the density matrix by multiplying the $\lambda$-matrix by the overlap matrix $S$. Once the proper density matrix $\Lambda S$ is obtained, we diagonalize it to obtain the natural orbitals. The natural orbitals are orthonormal, despite the fact that the atomic basis functions are not orthonormal. Finally, the matrix of orthonormal natural orbitals, in the original atomic basis, is used to create a unitary transformation matrix which acts on the $\lambda$-matrix to reveal the occupancy of the natural orbitals.

Once the $\lambda$-matrix is diagonalized, the vectors that appear in Eq. 6.10 no longer contain atomic orbitals. Instead, each element in these vectors contain a linear combination of atomic orbitals (LCAO) - i.e., a molecular orbital. This reveals that the basis functions in the RVB wave function do not need to be atomic orbitals, and in fact the double sum of Eq. 6.8 is merely a special case of an RVB wave function, used as a starting point for a variational optimization. The general form of the AGP wave function is given by Eq. 6.9. The eigenvalues of the diagonalization of $\Lambda$ represent the relative occupancy of the natural molecular orbitals. We thus see that the valence bond approach and the molecular orbital approach are unified within this RVB prescription.
These natural orbitals can be thought of as an optimized set of molecular orbitals beyond the Hartree-Fock approximation; and more than $M/2$ of them can be included in a single determinant, unlike in the case of the HF wave function. Assuming the eigenvalues are ordered according to the magnitude of occupancy, any orbitals greater than the first $M/2$ are \textit{virtual} orbitals. The exact Hartree-Fock limit is obtained by setting the occupancy of virtual orbitals to zero, and setting the occupancy of the first $M/2$ orbitals to 1 so that all such orbitals have the same occupancy, as required by the HF method.

It is instructive to provide an example of the diagonalization of the $\Lambda$-matrix to obtain both the natural orbitals and the occupancy of the virtual orbitals. The example continues the discussion of $H_2$. Let us diagonalize first the Hartree-Fock solution, Eq. 6.6, and then by way of comparison let us diagonalize the valence bond solution, Eq. 6.7.

A diagonalization of the HF solution for $H_2$, Eq. 6.6, results in the following matrix of natural orbitals:

$$
\tilde{U}_{\text{HF}} = \begin{bmatrix}
1 & -1 \\
1 & 1
\end{bmatrix},
$$

where $\tilde{U}_{\text{HF}}$ is the unnormalized Unitary matrix, whose columns are the natural orbitals expressed in the old atomic orbital basis of Eq. 6.8, which performs the transformation into the basis of natural orbitals in the HF case. We choose not to include normalized eigenvectors in $\tilde{U}_{\text{HF}}$ because including 1’s is more conceptually appealing; the tilda is included to represent that this is an unnormalized unitary matrix. In the basis of natural orbitals, we have for the $\Lambda$-matrix in the HF case,

$$
\Lambda_{\text{nat-HF}} = \begin{bmatrix}
1 & 0 \\
0 & 0
\end{bmatrix},
$$

where the subscript indicates that this $\Lambda$-matrix represents the HF solution expressed in the basis of natural orbitals. In the case of $H_2$ there is only one occupied natural orbital, both electrons occupying this orbital. We know that this orbital is the bonding orbital represented by Eq. 6.1. We therefore expect to see not only a diagonal matrix but also that only the first diagonal element is non-zero in $\Lambda_{\text{nat-HF}}$; in fact this is the case, with the
first diagonal element containing 1. We also expect that the first natural orbital in \( U_{A-HF} \) is the bonding orbital of Eq. 6.1, which has equal occupancy of the 1s orbital on both atoms, with the same sign. In fact this, too, is the case, as we can see from the first column of \( U_{A-HF} \). The virtual orbital is the antibonding orbital of Eq. 6.2, as expected (multiplied by an irrelevant negative sign).

We now move on to the Heitler-London case and diagonalize the \( \Lambda \)-matrix of Eq. 6.7. We find that

\[
\tilde{U}_{A-HL} = \begin{bmatrix}
1 & -1 \\
1 & 1
\end{bmatrix}
\]

and that

\[
\Lambda_{\text{nat-HL}} = \begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix}.
\]

Again, for conceptual clarity the components of these matrices do not reflect the proper normalization. Interestingly, the natural orbitals remain unchanged in the Heitler-London limit, but the occupancy of the natural orbitals carries an equal weight for both the bonding and the antibonding orbital. However, the occupancy of the virtual antibonding orbital is negative. This is a general characteristic of the occupancy of virtual orbitals in an RVB model.

A number of different points are worth highlighting regarding a comparison of the HF and the HL case. First, the HL includes equal weight of the occupancy of the antibonding orbital, which completely cancels the ionic occupation from the bonding orbital, as desired within the Heitler-London approach. Second, the valence bond description moves beyond the Hartree-Fock description by allowing occupancy of the virtual orbitals. Within the Hartree-Fock picture, occupancy of virtual orbitals is impossible. Third, the fact that the natural orbitals are the same in both the Hartree-Fock and the Heitler-London case is a coincidence of the simplistic \( \text{H}_2 \) model. If it were not, as discussed previously, the HF solution could be trivially obtained by a diagonalization of the \( \Lambda \)-matrix. Finally, note that the virtual antibonding orbital possesses an additional node and thereby including occupancy of this orbital modifies the nodal structure. We therefore see how the RVB wave function
is able to directly affect the nodal structure of the wave function in a straightforward way.

Of course, the introduction of the Jastrow factor has a significant effect on the natural orbitals by suppressing double occupancy directly, so that pressure on the valence function to accomplish this task is lifted. We again reiterate that the Jastrow factor describes the Coulomb hole directly. The Coulomb hole cannot easily be captured by the natural orbitals.

We shall now apply a similar approach to model Li clusters. First, we perform an RVB optimization of the A-matrix and the Jastrow parameters, and study the gains in energy that result from the modified nodal structure.

\section{Applications to Li nanoclusters}

The RVB wave function has an interesting history leading up to the formulation as presented in this chapter. Although it was first applied by Pauling to Li, in 1987 P. Anderson proposed the RVB wave function as the natural ground state for the high temperature superconducting materials \cite{Anderson87}. The RVB picture was able to capture most of the aspects of the phase diagram of the cuprates \cite{Anderson82, Anderson83}.

Anderson \cite{Anderson84} has recently clarified that the Pauling RVB idea cannot account for all of the properties of metals that depend on the Fermi Surface (FS). However, since the existence and nature of the FS in bulk Li has been questioned by the high resolution Compton scattering studies performed by Shülke and collaborators \cite{Shülke21}, the RVB paradigm might model the Li ground state.

A number of authors have performed calculations on bulk Li as well as Li nanoclusters \cite{Liu72}, but an implementation of the RVB utilizing QMC simulations has not been attempted. Previous studies include an implementation of the RVB for small Li clusters \cite{Liu85}, but without the accuracy of modern QMC methodologies. Here, we provide our results of QMC calculations beyond the limitations of the standard Jastrow-Slater wave function (WF) for the Fermi liquid ground state \cite{Sorella86} using the JAGP ansatz for the RVB.

The RVB in the form we present has recently been studied by Sorella, \textit{et al.} \cite{Sorella80}, Casula \textit{et al.} \cite{Casula87}, and Sterpone, \textit{et al.} \cite{Sterpone88}. We'd also like to highlight two useful theses: one on the subject of the RVB (ref. \cite{Thesis89}), and one on Li clusters which provides useful benchmarks.
Figure 6-5: Cohesive energies per atom for Liₘ with M = 2, 4 and 8, representing systems of dimension d = 1, 2 and 3, respectively, calculated using the diffusion Quantum Monte Carlo all-electron method. The plot compares the RVB nodal structure against the standard HF nodal structure. The error bars are comparable to the size of the points. The inset shows the difference in cohesive energies between the models.

We have performed Diffusion Monte Carlo (DMC) calculations to obtain precise estimates of the energy, this technique being limited in accuracy only by the nodal structure of the variational ansatz. For all our Li clusters, we obtain a distinct nodal structure improvement of the cohesive energy in comparison to standard JS WFs. In addition, diagonal expansions in the natural orbitals confirm the RVB nature of the ground state.

Atomic orbitals in the JAGP are expanded in a Gaussian basis set. For the all-electron case we use a Gaussian basis set of 8s6p contracted to [3s1p], while in the pseudopotential calculations a 4s4p contracts to [2s1p]. The Jastrow factor \( J = J_1 J_2 J_3 \) is composed of an electron-nuclear (\( J_1 \)), an electron-electron (\( J_2 \)), and an electron-electron-nuclear (\( J_3 \)) term; it guarantees that the cusp conditions are satisfied and it allows the correct charge distribution in the system. The Jastrow parameters, \( \lambda \) parameters, Gaussian (Slater) orbital exponents, and orbital coefficients have been optimized by energy minimization using the method of Stochastic Reconfiguration (SR).

SR is a generalized eigenvalue method (see Ch. 8) developed by Sorella and coworkers.
We will not provide a detailed account of the SR methodology here. However, it is important to highlight the relevance of these state-of-the-art variational methods to help solve for the large number of variational parameters that appear in the $\Lambda$-matrix. Referring to Fig. 10-1 and the discussion that follows, we see that the generalized eigenvalue methods represent a major advance in VMC methods. Previous VMC methods that worked in configuration space - rather than a space of generalized eigenfunctions - were able to improve upon the HF molecular orbital coefficients in Eq. 3.31, but the optimization of these coefficients was made easier by the fact that the HF orbitals are already close to the desired solution, the introduction of the Jastrow parameter allowing a conceptually second-order improvement both in VMC, and even in DMC calculations. The improvement in DMC calculations due to the presence of the Jastrow factor is not very intuitive. Because the Jastrow parameter is positive everywhere, it cannot affect the nodal structure, and thus DMC calculations with and without a Jastrow factor yield identical results for identical AGP functions (although convergence will be slower without the presence of the Jastrow factor). However, the presence of the Jastrow during the VMC calculation influences the VMC result and consequently modifies the nodal structure, and this result is the input to the DMC calculation; therefore, the presence of the Jastrow factor has a significant impact on the DMC result, albeit indirectly.

The optimized parameters of the RVB wave function, on the other hand, are not as close to the HF solution as the optimized parameters of a HF+Jastrow solution. Considering the variational landscape discussed in Section 4.7.1, we can say that the RVB-optimized parameters lie farther away in some sense from the HF parameters in the variational landscape than the HF+Jastrow-optimized parameters do. In practice, it is difficult for standard methods to locate a minimum that is farther away from the starting choice of the variational parameters. The challenge of optimizing the RVB parameters was also discussed in a previous section of this chapter, along similar lines. The newer VMC methods have made optimization of these parameters possible, and we highlight here the necessity of the use of a generalized eigenvalue method to perform the optimization.

We have compared the JAGP WF with three categories of standard single-determinant
JS WFs. First, we have studied the all-electron case, comparing the JAGP with a standard JS WF whose Slater determinant is constructed with Hartree-Fock orbitals (abbreviated JS-HF). We next have considered the case of a pseudopotential replacing the core electrons and Kohn-Sham orbitals for the valence electrons calculated using Density Functional Theory (DFT) with the Local Density Approximation (this WF is abbreviated as JS-LDA). Finally, we have considered a standard JS WF defined as the JAGP WF in its most simplified limit by forcing the occupation of the virtual orbitals to zero (abbreviated JS-V0) - a WF that is identical in form to a standard JS WF, as discussed previously.

6.10.1 Jastrow-Slater HF comparison

For the all-electron JS-HF WF, we studied clusters of 2, 4, and 8 Li atoms modeled with HF orbitals obtained using the software Jaguar [92]. The JS-HF included the $J_1$ and $J_2$ terms, which were optimized using an improved version of the Stochastic Gradient Optimization (SGA) [5] method. Details about the cluster geometries and the HF orbitals for the JS-HF are given in ref. [93]. Our JS-HF DMC results are given in Table 6.1 for the dimer, the planar cluster Li$_4$ and the three dimensional Li$_8$. For all three clusters, we obtain distinct corrections of about 30 meV per atom for the cohesive energy. Fig. 6-5 illustrates the results. The values obtained by the DMC method with JS WFs are already quite successful, because the cohesive energy $E_{coh}$ values compare fairly well with the experimental values given in ref. [94], and because JS DMC calculations are known to retrieve better than 90% of the correlation energy [95]. Also, in both cases we observe the expected increase (see ref. [94]) of the cohesive energy with cluster size, describing the tendency for these clusters to grow in size. However, when we consider the difference $\Delta E = E_{coh}^{JAGP} - E_{coh}^{JS-HF}$, the inset of Fig. 6-5 shows the nodal structure corrections of about 30 meV per atom.

The bonding properties of Li can be described quite accurately by replacing the core electrons with a pseudopotential, because the 1s core states do not participate in the bonding, as we confirm. For example, pseudopotential DMC calculations can successfully predict the small binding energy for the LiPs molecule [96], in accord with the results of more sophisticated DMC all-electron calculations [97]. Also, with the aid of a pseudopotential,
Table 6.1: DMC all-electron calculations comparing the JS-HF and the JAGP wave function for Li clusters. The first two columns present the total energy per atom, in Ha. The next two columns present the cohesive energy per atom, in eV. The final column presents the difference in cohesive energies, in meV.

<table>
<thead>
<tr>
<th>N</th>
<th>$E_{\text{JS-HF}}^{\text{DMC}}$ (Ha)</th>
<th>$E_{\text{JAGP}}^{\text{DMC}}$ (Ha)</th>
<th>$E_{\text{coh}}^{\text{JS-HF}}$ (eV)</th>
<th>$E_{\text{coh}}^{\text{JAGP}}$ (eV)</th>
<th>$\Delta E_{\text{coh}}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-7.49593(8)</td>
<td>-7.4971(1)</td>
<td>0.491(2)</td>
<td>0.522(3)</td>
<td>32(5)</td>
</tr>
<tr>
<td>4</td>
<td>-7.5036(1)</td>
<td>-7.50485(13)</td>
<td>0.699(3)</td>
<td>0.733(4)</td>
<td>34(6)</td>
</tr>
<tr>
<td>8</td>
<td>-7.5130(1)</td>
<td>-7.51440(23)</td>
<td>0.955(3)</td>
<td>0.993(6)</td>
<td>38(9)</td>
</tr>
</tbody>
</table>

Table 6.2: Same as Table 6.1, but for DMC pseudopotential calculations comparing the JS-LDA and the JAGP wave function. This data set includes Li$_{20}$. Note that the results differ from those of Table 6.1, because here a pseudopotential is being employed.

<table>
<thead>
<tr>
<th>N</th>
<th>$E_{\text{JS-LDA}}^{\text{DMC}}$ (Ha)</th>
<th>$E_{\text{JAGP}}^{\text{DMC}}$ (Ha)</th>
<th>$E_{\text{coh}}^{\text{JS-LDA}}$ (eV)</th>
<th>$E_{\text{coh}}^{\text{JAGP}}$ (eV)</th>
<th>$\Delta E_{\text{coh}}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-0.21318(4)</td>
<td>-0.21534(8)</td>
<td>0.45932(7)</td>
<td>0.51625(9)</td>
<td>56.9(2)</td>
</tr>
<tr>
<td>4</td>
<td>-0.22100(3)</td>
<td>-0.22357(5)</td>
<td>0.67212(6)</td>
<td>0.74020(6)</td>
<td>68.1(1)</td>
</tr>
<tr>
<td>8</td>
<td>-0.23152(3)</td>
<td>-0.23225(1)</td>
<td>0.95839(6)</td>
<td>0.97640(2)</td>
<td>18.01(8)</td>
</tr>
<tr>
<td>20</td>
<td>-0.237750(5)</td>
<td>-0.23893(1)</td>
<td>1.12791(4)</td>
<td>1.15817(2)</td>
<td>30.26(6)</td>
</tr>
</tbody>
</table>

the optimization of the JAGP WF can be performed on larger clusters - such as the Li$_{20}$ cluster [72] - within reasonable CPU time. Another advantage of the pseudopotential is the possibility of more easily disentangling the valence characteristics of the $\Lambda = \lambda_{ij}$ matrix in Eq. 6.9 from core contributions, as we shall report. This submatrix will be helpful to identify the RVB signature occupations of the virtual orbitals.

6.10.2 Jastrow-Slater LDA comparison

Next, we have considered the JS-LDA pseudopotential WF for Li clusters containing 2, 4, 8, and 20 atoms, in order to measure the impact of these one-body orbitals on the nodal structure. The inner 1s core electrons were replaced by the norm-conserving pseudopotential provided by Burkatzki et al. [98]. The JS-LDA WF was constructed using Kohn-Sham LDA orbitals obtained with the PWscf code [99]. The LDA calculations used a cubic simulation cell whose sides have length 40 a.u., and a plane-wave cut-off of 70 Ry. The JS-LDA WF included the $J_1$ and $J_2$ terms, optimized using the same method as the JAGP. For the JS-LDA calculations, we used a modified version of the DMC, the Lattice Reguralized Diffusion Monte Carlo (LRDMC) [100], that allows the inclusion of a non-local pseudopotential in a
Table 6.3: VMC calculations of the JS-LDA and the JAGP wave function for Li clusters. The first two columns compare the total energy per atom. The variational JAGP results for Li$_2$ and Li$_4$ are lower than the diffusion JS-LDA results from Table 6.2, indicating superior performance of the wave function even at the variational level for the JAGP than can be obtained at the diffusion level for the JS-LDA. The final two columns show the variance $\sigma^2$ of the local energy, per atom, in eV. The JAGP shows a smaller variance than the JS-LDA.

consistent variational scheme. The JS-LDA DMC results are shown in Table 6.2. In this case, the JAGP also yields the lowest total energies. In addition, the results confirm that in Li clusters, the RVB nodal structure provides a correction, which in this case tends to be more than 20 meV per atom.

6.10.3 Natural orbitals for Li$_4$

We now discuss a study of the natural orbitals of the JAGP model of Li clusters with pseudopotential. We performed the diagonalization of the $\Lambda$-matrix of Eq. 6.9, as discussed earlier in this chapter. We diagonalize the $\Lambda$-matrix and study the natural orbitals in the case of Li$_4$, Li$_8$ and Li$_{20}$.

Fig. 6-6 shows the eigenvalues. In the top of Fig. 6-6 are the positive eigenvalues. In the bottom of the figure, the negatives eigenvalues are shown using an expanded scale. The RVB signature indicates a departure from the standard JS nodal structure - and by extension into the bulk, a departure from the Fermi liquid picture [86]. This departure can be explained as follows. If the generating geminal yields a standard JS ansatz, the occupied orbitals would have equal weights, and the remaining orbitals would not contribute. However, in the case of the RVB, the virtual orbitals have non-zero amplitudes, but with opposite sign. Contrary to the standard JS description, virtual orbitals - i.e., orbitals with index greater than $N/2$ - have a small but finite, negative, occupancy. (Here, negative means that the eigenvalue of a $\Lambda$-matrix diagonalization is negative.) Also, the natural orbitals contain a
Figure 6-6: Eigenvalues of the diagonalized \( \Lambda \) matrix, representing the occupation of the natural geminal orbitals. Top half: eigenvalues for the first \( \frac{M}{2} \) natural orbitals. Bottom half: expanded view of the eigenvalues for the virtual orbitals. Unlike a standard Jastrow-Slater wave function, the JAGP allows occupancy of the higher-level orbitals. A characteristic of the RVB is a sign flip when passing from the primary to the virtual orbitals.

significant \( p \)-character. An important \( 2p - 2p \) \( \pi \)-contribution was observed in ref. [101] in the AGP WF for \( \text{Li}_2 \), and this substantial \( p \)-character causes a departure from the standard JS nodal structure. Recent experiments find that Li impurities in an Al matrix produce an anomalous transfer from \( s \)- to \( p \)-like character and thus constitute another example in which the standard Fermi liquid picture breaks down and properties of the correlated inhomogeneous electron gas must be considered [102].

We also have visualized the first four natural orbitals for \( \text{Li}_4 \), which includes two virtual orbitals. See Fig. 6-7. Obtaining these natural orbitals might be used as the starting point for a more sophisticated understanding of the physics of the wave function. In addition, conceivably we could perform faster optimizations of larger molecules by first obtaining a reasonable set of natural orbitals in a JAGP description, and then performing an expansion of a desired wave function in a basis of these natural orbitals. This would dramatically limit the number of variational parameters, and could help isolate the relevant physics in much the same way as the generalized eigenvalue methods described in Ch. 8, such as SR. It is even possible that improved generalized eigenvalue methods could be developed that use a
Figure 6-7: The first four natural orbitals for Li$_4$, as obtained by a full diagonalization of the $\Lambda$-matrix of Eq. 6.9 using an SR optimization of the JAGP wave function. The first two orbitals are improvements upon the two occupied Hartree-Fock orbitals. The 3$^{rd}$ and 4$^{th}$ orbitals are virtual - they would be unoccupied in a molecular orbital single Slater determinant description. The natural orbitals here have been represented by plotting an isosurface for each orbital. The grey dots represent the atomic nuclei - they are not part of the isosurface.
A detailed study of the natural orbitals of an RVB-optimized wave function has not been performed within QMC. In fact, to our knowledge the natural orbitals themselves have not been visualized, as we have done in Fig. 6-7. We highlight the possibilities of a natural orbital description of the RVB wave function in order to suggest the potential of such an approach.

6.10.4 A Variational Monte Carlo (VMC) comparison

Table 6.3 provides the results of VMC calculations of the JS-LDA and the JAGP wave function for Li clusters. The table confirms the relatively high quality of the JAGP wavefunction at the variational level. By comparing Table 6.3 with Table 6.2, note that our variational results using the JAGP are superior to the diffusion results using the JS-LDA for Li$_2$ and Li$_4$. Table 6.3 also shows the significantly smaller variance of the local energy for the RVB WF, indicating more efficient and less time-consuming calculations [93].

6.10.5 A comparison with suppressed virtual orbitals

Finally, to directly measure nodal structure effects due to the one-body orbitals, and as an additional consistency check within our method, we have utilized the JS-V0 WF. With this WF, we can estimate the energy contribution from occupation of the virtual orbitals by forcing the pairing wave function to possess only the $N/2$ fully occupied orbitals, with zero occupancy of the virtual orbitals. These calculations were performed for Li$_4$, Li$_8$ and Li$_{20}$ with pseudopotential, and in all three cases, for both VMC and DMC calculations, we confirm the DMC results obtained in Table 6.2, an improvement in the cohesive energy of at least 20 meV per atom due to the RVB nodal structure. As stated previously, the definition of JS-V0 assures that the Jastrow factor, basis set, and functional form are identical in the JAGP and in the JS-V0 WFs, so $\Delta E_{RVB} = E_{coh}^{JAGP} - E_{coh}^{JS-V0}$ is a direct calculation of the resonance energy. This confirms that the gain in energy is a direct effect of the RVB, and not the result of a different Jastrow factor or a different single particle basis set.

In conclusion, in our work studying Li clusters with the RVB wave function, we have
performed calculations of various cluster sizes in order to compare standard JS WFs with the RVB WF. Our results show that in Li clusters, the RVB WF is able to recover about 20 meV of correlation energy per atom that is unrecoverable with calculations using standard JS nodal structures. In addition, we observe a distinct RVB signature in an eigenvalue decomposition of the JAGP Λ-matrix. These results lend evidence to an RVB ground state for Li, showing a distinct nodal structure improvement and gain in correlation energy when Li clusters are modeled as an RVB state. This suggests that electron pairing might explain the Fermi liquid deviations observed in recent high resolution Compton scattering experiments of bulk Li. In addition, the RVB WF has a significantly smaller variance than standard JS WFs, allowing for faster computations. In conjunction with rapidly developing methods of parallelization and a developing understanding of the nodal structure properties of many-body WFs, the RVB WF therefore shows promise in providing new insights for correlation effects in Li, as well as improving the computational efficiency with which researchers can perform QMC calculations of progressively larger nanoclusters.
Chapter 7

Equilibration and autocorrelation

The effort to scale Quantum Monte Carlo codes to large molecular clusters has come with some unexpected challenges. Because the time required to perform even a single evaluation of the wave function for very large clusters such as Li\textsubscript{64} is very great (\(\sim 1\) s), minimizing the number of QMC samples for the optimization is of paramount importance. We have developed the SGA in part to be able to handle large clusters. However, we have found that the number of steps required to equilibrate also increases as the cluster size increases, compounding the difficulties. A detailed study of equilibration is therefore important, and we provide such a study in this chapter. Both of these difficulties were anticipated, however. In our work, an unanticipated difficulty arose when applying the SGA to large clusters. In the limit of a small number of Metropolis samples, a calculation of the statistical error using standard binning methods becomes impossible. Instead, the scaling of the autocorrelation time must be employed, an issue that QMC researchers have not encountered before, to our knowledge. To resolve this issue, an understanding of Markov chain correlations becomes essential. We present a full discussion of these issues, and the results we have obtained for Li and H\textsubscript{2}O clusters, in this chapter\textsuperscript{1}.

\textsuperscript{1}The material in this chapter is adapted from the following paper and talks.

D. Nissenbaum, B. Barbiellini, and A Bansil, \textit{Decorrelation of samples in Quantum Monte Carlo calculations and applications to metallic nanoclusters}, American Physical Society, APS March Meeting, March 5-9, 2007, abstract B27.00008.
As we have discussed in Ch. 4, QMC calculations are fundamentally limited by the statistical accuracy that can be obtained in a reasonable amount of computation time. The issue of statistical accuracy looms large, in particular, with the SGA - for clusters of any size - for the reasons to be discussed in Ch. 8; namely, the SGA method takes advantage of noisy measurements during a variational optimization and therefore attempts to minimize, to the extent possible, the number of Metropolis (i.e., Langevin) steps used during each step of the optimization.

In the SGA, the number of Metropolis steps is lowered beneath the threshold of acceptability for other methods, such that the resulting QMC calculation is highly inaccurate. In the SGA, we attempt to find the number of Metropolis steps that is most effective for use with stochastic minimization. The accuracy of each QMC calculation is not determined after-the-fact, as it is for the other methods. Instead, the accuracy of each QMC calculation is a fundamental parameter that is required for an understanding of the SGA convergence.

It isn’t uncommon to find “overkill” used for other QMC optimization methods. By its nature, this approach is inefficient. In the case of the SGA, it is, in fact, difficult even to find a way to perform overkill, because the SGA algorithm fundamentally avoids overkill by working in the limit of a small number of samples and following the variational minimum as closely as possible at any given moment during the computation.

7.1 The autocorrelation time $\tau$

When the number of atoms in a metallic cluster increases, the gap to the excited states shrinks as the electronic states begin to form a band and approach the bulk metallic character. This shrinking gap between the ground state and the excited states induces progressively greater statistical correlations among samples due to the Markovian character of the QMC sampling algorithm. We address this problem through an analysis of the integrated autocorrelation time $\tau$ [103] which has not been considered in previous work on scaling; in particular, Williamson, et al. [104] do not consider this correlation factor in their studies of non-metallic clusters. We demonstrate with the example of Li clusters that the problem of correlations among samples increases rapidly as the system size grows, making it
increasingly difficult to decorrelate samples and determine the statistical error of the QMC calculation. Nevertheless, by invoking the scaling relationship of $\tau$, efficient computations of large clusters become feasible, even in the presence of highly correlated samples.

7.2 Equilibration, autocorrelation and determination of the statistical error bar

Markov Chain correlations (or, more generically, QMC correlations) strictly pertain to the Metropolis (or Metropolis-like) stage of a vanilla QMC calculation - i.e. a single step of the VMC algorithm. See the brown box of Fig. 8-1 in Ch. 8. QMC correlations do not pertain directly to the variation of the parameters in the wave function. The primary way that QMC correlations impact VMC is by the fact that the statistical accuracy, per VMC step, is made worse by correlations. This effect is particularly important for the SGA, for which an understanding of the accuracy for a very small number of QMC samples is helpful. Indirectly, also, QMC correlations impact the variation of the parameters because there are correlations between the set of Metropolis sample points in one VMC iteration and the next. This effect will impact the rates of convergence for the SGA discussed in Ch. 8, and we do not pursue this second-order effect in this thesis.

In Fig. 7-1 we lay out the general theoretical approach to the Metropolis algorithm. In this computationally unrealistic approach, an infinite number of walkers are employed (corresponding to the different rows in the figure). As discussed in Ch. 4, the purpose of the walkers is to obtain a distribution of sample points that matches $P = |\Psi|^2$. At the first step of the Metropolis algorithm, $q = 1$, we must position the walkers at points in configuration space according to some distribution; because the purpose of the Metropolis algorithm is to obtain this distribution over time, we cannot of course position the walkers initially at the desired distribution. Only after a certain number of steps will detailed balance be achieved to the desired degree of accuracy. At this point we declare that equilibration is complete, and we enter the data-taking stage of the Metropolis algorithm. (As shown in Fig. 10-1 of Ch. 8, the Metropolis algorithm runs concurrently with the data-taking stage.) The
Figure 7-1: Schematic of the walkers (Markov chains) used in the QMC Metropolis (or Metropolis-like) algorithm. In the ideal approach shown here, an infinite number of walkers equilibrate for a sufficient number of Metropolis steps, represented by the red dots. After equilibration, the value of the local observable is averaged over all the black dots at $k = 1$, and the calculation is terminated; only the first column of black dots is sampled. In realistic calculations, however, a finite number of walkers is employed, and the value of the local observable is averaged over many columns of black dots.
data-taking stage corresponds to the black dots.

When $k = 1$, the walkers have equilibrated and therefore the infinite number of sample points corresponding to the column at $k = 1$ are distributed according to $|\Psi|^2$. We then perform a single data-taking operation at $k = 1$ by averaging the value of the local observable at this point in the Metropolis algorithm. This provides the result to 100% accuracy (ignoring the error due to any residual equilibration that needs to be performed). The calculation ends and the walkers never move to the point $k = 2$.

In the ideal approach with an infinite number of walkers, QMC correlations do not enter the problem.

In realistic calculations only a finite number of QMC walkers can be used. Therefore, the statistical error discussed in Ch. 4, presented in Eq. 4.8, and derived in Appendix J is introduced into the calculation.

The discussion so far hopefully reveals the benefit of parallel processing in QMC calculations. For vanilla QMC calculations (not necessarily VMC or DMC calculations), the algorithm is embarrassingly parallelizable. Each processor plays the role of a different walker. If a sufficient number of processors are available to obtain the desired degree of accuracy at $k = 1$, the process has been completely parallelized. However, it would still be inefficient due to the equilibration stage that every walker must undergo.

### 7.2.1 Equilibration

Fig. 7-2 shows an example of the equilibration stage with a fairly large number of processors (2,048). We have chosen to show the data for a calculation of the most difficult cluster we studied, Li$_{64}$. For the sake of this calculation, we use the Hartree-Fock wave function ansatz, because it has a known ground state energy. We use here Umrigar’s version of the modified Langevin algorithm discussed in Ch. 4. Each step of the Li$_{64}$ calculation, in which all electrons were moved for every Langevin step, requires on the order of one processor second. The importance of minimizing the number of Metropolis steps (here, Langevin steps) is therefore of the utmost importance for large cluster sizes.

The initial position of the walkers in Fig. 7-2 has been randomly selected in a somewhat
The equilibration stage of a QMC calculation is demonstrated in this figure for the challenging Li\textsubscript{64} cluster. The data show a massively parallel calculation with 2,048 walkers. The walkers begin with a randomly selected reasonable initial distribution with three electrons placed near every atom in the cluster. At each step of the Metropolis-like algorithm (in this case the modified Langevin algorithm), a full energy calculation is performed across all walkers under the assumption that all walkers have previously been equilibrated. The result is plotted as $E - E_o$, where $E_o$ is the known Hartree-Fock ground-state energy for the system. The variational theorem guarantees that the resulting energy will be higher than the ground state energy. The statistical error in each calculation is represented by the error bars. Equilibration is considered complete when the curve crosses some threshold near the ground state energy. We use the Hartree-Fock wave function in this example, in order to provide a known ground-state energy for the demonstration. In this example, only 800 Langevin steps were required to obtain a HF estimated gross accuracy of $\pm 0.2$ Hartrees. As the desired accuracy increases, so does the equilibration time. For this calculation, all electrons were moved in every Langevin step - the total number of required steps for equilibration would have been significantly greater if we had chosen single-electron moves.
intelligent way, by placing three electrons near each nucleus. At each Langevin step, a complete averaging of the energy across all 2,048 processors is performed under the assumption that the walkers have previously been equilibrated. The statistical accuracy is calculated according to Eq. 4.8, and corresponds to the error bars in the figure. The variational theorem guarantees that the mean value during equilibration is greater than the ground state energy. Near the beginning of any equilibration process, the possibility of anomalous points with an exceedingly large variance is greatly increased. A few such anomalous points appear near the beginning of the equilibration shown in the figure - such as the second Langevin step. For aesthetic purposes we have removed the error bars from these anomalous points.

The energy equilibration curve follows a roughly exponential path, although different effects contribute to the equilibration rate with different exponential constants, and only after some time have all but the longest-range exponential factor died away. Due to the exponential decay, the equilibration curve has as its asymptote the true ground state energy, which it approaches exponentially fast, but never touches. Therefore, we must choose a desired energy threshold surrounding the true ground state energy, and when the mean value of the equilibration curve crosses this threshold, we arbitrarily decide that equilibration is complete. Typically this threshold corresponds to the desired accuracy of the calculation.

In the case of Li_{64} it is especially important to understand the smallest number of steps that is acceptable for the equilibration stage of the calculation, because each Langevin step requires on the order of 1 second per processor. The equilibration shown in Fig. 7-2 requires on the order of 30 minutes when run in fully parallelized fashion, and this only equilibrates the walkers to a gross accuracy of 0.2 Ha per atom, which is insufficient for most purposes. For the Li_{64} calculations we present later in this chapter, we found that the accuracy of 0.2 Ha was insufficient. In order to obtain the smooth results we present, we chose to equilibrate the walkers for a full week. We did not desire to perform a detailed study of the minimum possible equilibration time, because our chief interest was in getting smooth and reliable results.

Unfortunately, each and every processor needs to spend this much time in the equilibration stage. Although in our case we need only a single processor for the results of this
The cost of equilibration

Figure 7-3: The cost of equilibration becomes prohibitive for large nanoclusters because the time per step increases. The red dots in the figure show the wasted CPU time for a massively parallel calculation. During the equilibration stage no data is accumulated. A parallelized QMC calculation must strike the proper balance between the number of processors and the total length of the calculation.

Large clusters have typically not been studied in QMC. To our knowledge, Li$_{64}$ is the largest all-electron molecular cluster that has been studied to date. In the case of smaller clusters, overkill has typically been employed to guarantee proper equilibration. In general, overkill is the act of utilizing more sample points than are required, for any stage of the computation. As this discussion reveals, the typical approach of overkill is no longer satisfactory for large clusters. Instead, a more careful analysis needs to be undertaken. Fig. 7-4 shows our determination of the time constant for Li$_{64}$. The figure shows a log plot of the data in Fig. 7-2. The image to the left shows the full range of the data. The transitories can be observed to influence the first part of the equilibration, and then fade away as the
Figure 7-4: Shown in the figure is a determination of the exponential constant for the equilibration curve of Fig. 7-2. As discussed in the text, transitories appear during the initial stage of equilibration. The transitories die away and the equilibration curve is dominated by a single exponential time constant, in this case calculated to be about 10 in atomic units. Leading exponent dominates. The image to the right zooms in on the linear portion of the equilibration. A line fit through the data provides the time constant - here, about 10, in atomic units. Using this time constant, we may extrapolate the curve out to larger times and use this resulting curve to estimate the equilibration that is necessary to obtain the accuracy that we desire before the data sampling stage begins. Using this method revealed that 1 week was sufficient for equilibration for the accuracies we quote in the remainder of this chapter in the case of the challenging Li$_{64}$ cluster.

Note that the scatter in the curve of Fig. 7-4 is minimal near the beginning of equilibration and increases as the energy minimum is approached. This is simply due to the fact that $E - E_0$ becomes very small as equilibration progresses, as indicated by the exponent approaching $-3$. As the equilibration progresses, the line diverges to $-\infty$, as it should.

When a Jastrow factor is included to model electron correlations, the wave function changes and the equilibration time may also change. We suspect the change in equilibration time will tend in our favor and decrease, because the variance of the local energy improves
The preceding discussions reveal that in realistic QMC calculations the ideal scenario of a fully parallelized run is impractical. We therefore introduce the methods of correlated sampling for serial calculations, the subject of the remainder of this chapter. Schematically, the approach is described in Fig. 7-5. In the figure, we see a single walker - running on a single processor - emulating multiple walkers. Because both the decorrelation factor \( \kappa \) and the integrated autocorrelation time \( \tau \) are typically much shorter than the equilibration length, it is highly beneficial to use a single processor to emulate multiple walkers. Therefore, for a massively parallel calculation, the proper balance between the number of processors and the time per processor must be found, in cases where the equilibration stage requires a significant amount of time.

with a Jastrow factor. However, the ground state energy with a Jastrow factor is not known ahead of time, so the method of Fig. 7-4 cannot be employed in this case. We demonstrate here a universal method that can be employed for any system, by utilizing the Hartree-Fock result to determine the equilibration time and then extrapolating the curve as required.
single processor - emulating multiple walkers (compare to Fig. 7-1). As the Langevin steps proceed during the stage of the calculation represented by the black dots, the position of the walker in configuration space slowly changes, and slowly decorrelates from prior positions. After enough Langevin steps have been taken, the position of the walker in configuration space is essentially independent of a given previous position, and therefore corresponds to a new row in the figure, which emulates an additional walker. The decorrelation length (given in Metropolis steps; \( \kappa \) in the figure) is typically much smaller than the equilibration length. Therefore, when the equilibration time is significant, it is more efficient to utilize each walker for many steps in the black stage of Fig. 7-1, even when running a massively parallel calculation. For massively parallel calculations, the proper balance of serial and parallel methodologies is critical for optimum efficiency.

**7.2.2 Autocorrelation and statistical error**

Fig. 7-5 reveals the possibility of performing an average of the objective function (i.e., the energy) over all the black dots, and not just over the decorrelated black dots as represented by the column \( k = 1 \). Because the effective points at \( k = 2, k = 3, \text{etc.} \), also satisfy the probability distribution \( \pi \), there is no reason not to include them in the calculation (Eq. 4.4). However, the error calculation (Eq. 4.8) assumes not only that the points \( \{ s_n \} \) in Eq. 4.4 are distributed according to \( \pi \), but also that they are independent. If the points at \( k = 2, k = 3, \ldots \) are included in addition to the points at \( k = 1 \) in the sum of Eq. 4.8, then these points will not all be independent and the equation no longer holds.

We will now derive the statistical accuracy of the QMC calculation in the case of Markov chain correlations. (Note: the following derivation is the work of the author and, to the best of this author’s knowledge, unique.)

Referring to the derivation of Eq. 4.8 in Appendix J, we see that the assumption of independent samples makes its appearance in Eq. J.3, repeated here:

\[
P_m (m_t) = \int d^N \vec{r} P(\vec{r}_1) P(\vec{r}_2) \ldots P(\vec{r}_N) \delta \left( m_t - \frac{1}{N} \sum_{i}^{N} \frac{\hat{O}_L (\vec{r}_i)}{\langle \Psi_i | \hat{\Psi} \rangle} \right), \quad (7.1)
\]
where $P_m(m_t)$ is the desired probability distribution (spread) of QMC results $m_t$, with $m_t \equiv \frac{1}{N} \sum_{i(\in |\Psi|^2)}^N \hat{O}_L(\overrightarrow{r}_i)$, our estimate of $\langle \hat{O} \rangle$ (see Eq. 4.4).

Let us introduce the notation

$$\langle \hat{O}_x \rangle \equiv \frac{1}{x} \sum_{i(\in |\Psi|^2)}^x \hat{O}_L(\overrightarrow{r}_i)$$ \hspace{1cm} (7.2)

to refer to an estimate of the expectation value of an operator over a finite set of $x$ (possibly correlated) samples.

Also, let us introduce the quantity

$$\langle \hat{O}_j \hat{O}_{j+k} \rangle_N \equiv \frac{1}{N-k} \sum_{i(\in |\Psi|^2)}^{j+N-1-k} \hat{O}_L(\overrightarrow{r}_i) \hat{O}_L(\overrightarrow{r}_{i+k}),$$

a quantity that can be calculated during a QMC run as easily as any other. In the limit that $N \to \infty$ we have

$$\langle \hat{O}_j \hat{O}_{j+k} \rangle \equiv \lim_{N \to \infty} \frac{1}{N-k} \sum_{i(\in |\Psi|^2)}^{j+N-1-k} \hat{O}_L(\overrightarrow{r}_i) \hat{O}_L(\overrightarrow{r}_{i+k}),$$ \hspace{1cm} (7.3)

while the equivalent limit in the case of Eq. 7.2 is given by Eq. 4.5. Eq. 7.3 will be used (Eq. 7.13) to construct the autocorrelation function.

The key distinction between the correlated and the uncorrelated case is that, in Eq. 7.1, if the sample points are correlated, then the various individual probabilities $P$ are not independent. In fact, because the Monte Carlo walk is a Markovian process, each probability depends not only on the current point, but also on the previous point (and only the previous point). The exception is the very first probability $P(\overrightarrow{r}_1) = |\Psi|^2$, which depends only on the first point $\overrightarrow{r}_1$, because $\overrightarrow{r}_1$ is assumed to be selected independently from the distribution $|\Psi|^2$. Therefore, let us introduce the function

$$\tilde{P}(\overrightarrow{r}_j, \overrightarrow{r}_{j-1}) = \text{Probability of moving to } \overrightarrow{r}_j \text{ from } \overrightarrow{r}_{j-1}$$
to account for the correlated nature of the sample points. Because the Markov chain is assumed to be time-independent, this probability is independent of step number $j$.

The function $\tilde{P}$ is non-trivial and highly dependent on both the wave function and the details of the Metropolis-like algorithm used during the run. However, we nonetheless know the result of integrations involving $\tilde{P}$. We will need the following identities, which assume that the wave function $\Psi$ is normalized, as well as time-independent (i.e. $j$-independent) functions $P$ and $\tilde{P}$:

$$
\int d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N P(\mathbf{r}_1) \tilde{P}(\mathbf{r}_2, \mathbf{r}_1) \ldots \tilde{P}(\mathbf{r}_N, \mathbf{r}_{N-1}) = 1 \quad (7.4)
$$

$$
\int d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N P(\mathbf{r}_1) \tilde{P}(\mathbf{r}_2, \mathbf{r}_1) \ldots \tilde{P}(\mathbf{r}_N, \mathbf{r}_{N-1}) \hat{O}_L(\mathbf{r}_j) = \langle \hat{O} \rangle \quad (7.5)
$$

$$
\int d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N P(\mathbf{r}_1) \tilde{P}(\mathbf{r}_2, \mathbf{r}_1) \ldots \tilde{P}(\mathbf{r}_N, \mathbf{r}_{N-1}) \hat{O}_L^2(\mathbf{r}_j) = \langle \hat{O}_j^2 \rangle \quad (7.6)
$$

$$
\int d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N P(\mathbf{r}_1) \tilde{P}(\mathbf{r}_2, \mathbf{r}_1) \ldots \tilde{P}(\mathbf{r}_N, \mathbf{r}_{N-1}) \hat{O}_L(\mathbf{r}_j) \hat{O}_L(\mathbf{r}_{j+k}) = \langle \hat{O}_j \hat{O}_{j+k} \rangle \quad (7.7)
$$

These identities can be proven straightforwardly by recognizing that an integral over all possible sequences of $N$ Markov chain steps of the value of a local operator at a fixed index $j$ (or fixed pair of indices $j$ and $k$), yields a result that is identical to an average over an infinite number of indices (or pair of relative indices) of the local operator in a single Markov chain. Note that $j$ can assume any value in the range $1 \ldots N$ (or $1 \ldots N - k$) in the case of Eq. 7.7. Of course, these identities depend crucially on the time-independent ($j$-independent) nature of the probability distributions.

For the case of Markov chain correlations, then, we have, instead of Eq. 7.1,

$$
\int d^N \mathbf{r} P(\mathbf{r}_1) \tilde{P}(\mathbf{r}_2, \mathbf{r}_1) \ldots \tilde{P}(\mathbf{r}_N, \mathbf{r}_{N-1}) \delta \left( m_t - \frac{1}{N} \sum_{i(\in |\Psi|^2) = 1}^N \hat{O}_L(\mathbf{r}_i) \right).
$$
The derivation proceeds similarly to the case of uncorrelated samples. Eq. J.4 becomes

\[ P_m(m_t) = \int \int d\mathbf{r}_1 P(\mathbf{r}_1) \prod_{j=2}^{N} d\mathbf{r}_j \bar{P}(\mathbf{r}_j, \mathbf{r}_{j-1}) e^{-i\lambda \hat{O}_L(\mathbf{r}_j)} \frac{N}{2\pi} e^{iN\lambda m_t} d\lambda, \]

at which point we move directly to Eq. J.7, which becomes

\[ P_m(m_t) = \frac{N}{2\pi} \int e^{N\{i\lambda m_t + \frac{1}{N} \ln(\int d\mathbf{r}_1 P(\mathbf{r}_1) \prod_{j=2}^{N} d\mathbf{r}_j \bar{P}(\mathbf{r}_j, \mathbf{r}_{j-1}) e^{-i\lambda \hat{O}_L(\mathbf{r}_j)})\}} d\lambda. \]

We now redefine \( g(\lambda) \) from Eq. J.8 as

\[ g(\lambda) = \frac{1}{N} \ln(\int d\mathbf{r}_1 P(\mathbf{r}_1) \prod_{j=2}^{N} d\mathbf{r}_j \bar{P}(\mathbf{r}_j, \mathbf{r}_{j-1}) e^{-i\lambda \hat{O}_L(\mathbf{r}_j)}) \cdot \]

At this point, the derivation proceeds similarly to the case of uncorrelated samples for a few lines (utilizing Eqs. 7.4 and 7.5 along the way). For example, we find that Eq. J.13 becomes

\[ m_t = \frac{\frac{1}{N} \int \hat{O}_L(\mathbf{r}_a) d\mathbf{r}_1 P(\mathbf{r}_1) \prod_{j=2}^{N} d\mathbf{r}_j \bar{P}(\mathbf{r}_j, \mathbf{r}_{j-1}) e^{-i\lambda \hat{O}_L(\mathbf{r}_j)}}{\int d\mathbf{r}_1 P(\mathbf{r}_1) \prod_{j=2}^{N} d\mathbf{r}_j \bar{P}(\mathbf{r}_j, \mathbf{r}_{j-1}) e^{-i\lambda \hat{O}_L(\mathbf{r}_j)}} \quad \text{(7.8)} \]

and the derivation similarly leads to \( \lambda^* = 0 \) so that Eq. 7.8 becomes

\[ m_t = \frac{1}{N} \left( N \left< \hat{O} \right> \right) = \left< \hat{O} \right> \quad \text{(when } m_t = m), \]

so that \( m = \left< \hat{O} \right>, \) even in the case of Markov chain correlations, as expected.

Following the derivation through to Eq. J.17, we see that, again,

\[ \sigma_m^2 = \frac{-g''(\lambda)|_{\lambda=0}}{N}. \]

This time, however, the quantity \( g''(\lambda) \) is more complicated. We find, setting \( \lambda = 0 \)
after performing the double differentation, that

\[
\sigma_m^2 = \frac{1}{N^2} \int \left[ \sum_{a=1}^{N} \hat{O}_L (\mathbf{r}_a) \right]^2 d\mathbf{r}_1 P(\mathbf{r}_1) \prod_{j=2}^{N} d\mathbf{r}_j \tilde{P}(\mathbf{r}_j, \mathbf{r}_{j-1}) \int d\mathbf{r}_1 P(\mathbf{r}_1) \prod_{j=2}^{N} d\mathbf{r}_j \tilde{P}(\mathbf{r}_j, \mathbf{r}_{j-1}) \]

and therefore, again utilizing Eq. 7.4, that

\[
\sigma_m^2 = \frac{1}{N^2} \int \left[ \sum_{a=1}^{N} \hat{O}_L (\mathbf{r}_a) \right]^2 d\mathbf{r}_1 P(\mathbf{r}_1) \prod_{j=2}^{N} d\mathbf{r}_j \tilde{P}(\mathbf{r}_j, \mathbf{r}_{j-1}) \]

Expanding the squared sum in the first term, and utilizing Eq. 7.5 for the second term, yields

\[
\sigma_m^2 = \frac{1}{N^2} \int \left[ \sum_{a=1}^{N} \hat{O}_L (\mathbf{r}_a) \right]^2 d\mathbf{r}_1 P(\mathbf{r}_1) \prod_{j=2}^{N} d\mathbf{r}_j \tilde{P}(\mathbf{r}_j, \mathbf{r}_{j-1}) \]

Using Eqs. 7.6 and 7.7 for the first two terms yields

\[
\sigma_m^2 = \frac{1}{N^2} \left[ N \left\langle \hat{O}^2 \right\rangle \right] + \frac{2}{N^2} \sum_{a=1}^{N-1} (N-a) \left\langle \hat{O}_1 \hat{O}_{1+a} \right\rangle - \frac{1}{N} \left[ N \left\langle \hat{O} \right\rangle \right]^2
\]
At this point we consider the sum that appears in Eq. 7.12. A very useful question is the following: how many total terms of the form \[ D^O \] appear as a result of the complete summation? (For example, \[ 3 \times 2^D^O \] results in 7 terms. Note that \( a \) can vary, because we are merely counting terms to multiply each term by the same constant, regardless of the value of \( a \).) Carefully carrying through the summation, being certain to include the factor \( \frac{2}{N} \), we find that a total of \( N - 1 \) such terms appear. Very conveniently, we therefore find that

\[
\sigma_m^2 = \frac{1}{N} \left\{ \langle \hat{O}^2 \rangle + \frac{2}{N} \sum_{a=1}^{N-1} (N - a) \langle \hat{O}_1 \hat{O}_{1+a} \rangle_N - N \langle \hat{O} \rangle^2 \right\}.
\]  

(7.12)

where the \( \langle \hat{O} \rangle^2 \) terms have been distributed.

The quantity \( \frac{\langle \hat{O}^2 \rangle - \langle \hat{O} \rangle^2}{N} \) is exactly what we would obtain if the samples were uncorrelated. Therefore, the second term within the curly braces is the correction term that represents correlations.

We now make the approximation that the quantity \( \langle \hat{O}_1 \hat{O}_{1+a} \rangle_N \) in the correction term is taken in the limit of an infinite number of samples and we remove the subscript (see Eq. 7.3). Let us now define the function

\[
C(i) \equiv \frac{\langle \hat{O}_j \hat{O}_{j+i} \rangle - \langle \hat{O} \rangle^2}{\langle \hat{O}^2 \rangle - \langle \hat{O} \rangle^2},
\]  

(7.13)

where \( j \) can be any Markov step, because the chain is time-independent. The function
$C(i)$ is the autocorrelation function that represents the correlations in the Markov chain for Markov steps separated by a distance $i$. The function is normalized so that it equals 1 when $i = 0$. Evidently,

$$
\sigma_m^2 = \frac{\langle \dot{O}^2 \rangle - \langle \dot{O} \rangle^2}{N} \left\{ 1 + \frac{2}{N} \sum_{a=1}^{N-1} (N - a) C(a) \right\}.
$$

(7.14)

We now make the further approximation that in the correction term, $N \rightarrow \infty$. This approximation therefore excludes second-order corrections. We have, finally,

$$
\sigma_m^2 = \frac{\langle \dot{O}^2 \rangle - \langle \dot{O} \rangle^2}{N} \left\{ 1 + 2 \sum_{a=1}^{\infty} C(a) \right\}.
$$

(7.15)

Eq. 7.15 is the modified version of Eq. 4.8 in the case of Markov chain correlations. As stated, Eq. 7.15 corresponds to the method shown in Fig. 7-5 in the case that all black points are sampled. The correct value of $\sigma_m^2$ can only be determined with an infinite number of samples; for a finite number of samples, of course, we approximate the expectation values in the standard way.

In fact, the impact of Markov chain correlations can be simplified into a single scaling factor by performing a sum (integration) of the autocorrelation function $C(i)$. Noting that $C(0) = 1$ (the self correlation term), let us define the integrated autocorrelation time $\tau$ as

$$
\tau \equiv 1 + 2 \sum_{i=1}^{\infty} C(i)
$$

where the factor of 2 stems from the double counting that appears in moving from Eq. 7.9 to Eq. 7.10.

We then have a simple form to describe the statistical error, including correlations. We find that

$$
\sigma_m^2 = \frac{\langle \dot{O}^2 \rangle - \langle \dot{O} \rangle^2}{(N/\tau)} = \frac{\sigma_{\text{raw}}^2}{(N/\tau)},
$$

(7.16)

which is the same as in the uncorrelated case (Eq. 4.7), with the exception that the number
of samples is scaled by the factor $\tau$, yielding an effective number of samples $\frac{N}{\tau}$. We have:

$$\frac{N}{\tau} = \text{effective number of samples.}$$

The integrated autocorrelation time $\tau$ is to be distinguished from the decorrelation length $\kappa$, representing the number of Metropolis (or Metropolis-like) steps required for the autocorrelation function to drop below some threshold.

Let us compare the correlated method to the approach in which only the samples at $k = 1$ in Fig. 7-5 are used in the sum of Eq. 4.4. In this case, the number of effective samples is indeed $\frac{N}{\kappa}$ (assuming $N$ is the total number of black points; i.e. the total number of QMC steps, regardless of whether they are sampled). In fact, we therefore must have $\tau < \kappa$.

A direct calculation of the autocorrelation function can be performed utilizing Eq. 7.13. However, a computationally simpler method exists to calculate the integrated autocorrelation time that also reveals the decorrelation length $\kappa$ and may have the capability of shedding light on multiscale electronic behavior.

Flyvbjerg and Petersen [105] were perhaps the first to formally analyze a simpler technique, which we shall introduce shortly, in the context of the QMC community [105]. The method is one of a number of binning approaches that average data in blocks to calculate the correct variance $\sigma_m^2$. The Flyvbjerg method is a renormalization group method in which each data block is itself reblocked. Specifically, every 2 consecutive samples from the previous block are averaged to create 1 sample in the new block. Each block therefore contains exactly half the number of samples as the previous block. The variance of the data in each block is calculated as though the data were completely uncorrelated. Eventually, when the samples become truly uncorrelated, the fixed point is reached and the variances form a plateau. Fig. 7-6 shows an example of such a Flyvbjerg decorrelation plot.

Each point on the horizontal ($x$) axis corresponds to a renormalization stage. The point $x = 0$ corresponds to a set that contains all original sample points ($N$ samples). The point $x = 1$ contains $\frac{N}{2}$ samples, and so on. On the vertical ($y$) axis is plotted a trial determination
Figure 7-6: An example of a Flyvbjerg-style renormalization procedure (one of a variety of “binning” methods) to determine both the decorrelation length $\kappa$ and the integrated autocorrelation time $\tau$. At each renormalization stage (horizontal axis), every consecutive pair of QMC samples from the previous stage is averaged. At each stage, the standard deviation is calculated as though the QMC samples were completely uncorrelated. When the samples have decorrelated, a plateau is reached, corresponding to $\kappa$. The height of the plateau is $\sigma_m$, the true standard deviation of the calculation. It turns out that $\tau$ can be obtained as the ratio of the height of the plateau to the height of the first point. The final points of the plot become scattered because the number of sample points shrinks to 1 at the final renormalization stage, here represented at the 29th renormalization stage by the value $\sigma_t = 0$. The quantity $\sigma_\sigma$ is the “error of the error”, i.e. the standard deviation of the quantity $\sigma_t$. 
of $\sigma_m$, represented as $\sigma_t$, under the assumption that the samples are uncorrelated. Only when the plateau (fixed point) has been obtained does $\sigma_t = \sigma_m$.

The positive slope near the start of the Flyvbjerg plot can be understood from Eq. 4.8. When adjacent samples are averaged, if they are highly correlated they are essentially at the same point in configuration space, the average of each pair of adjacent samples will not vary much from either original value, the total distribution will look the same after the averaging process, but with half the number of sample points, and therefore the raw standard deviation (the top of the fraction in Eq. 4.8) will not change very much. (See the very end of Section 19, and see Eq. 7.17, for the definition of the raw variance). The number of samples $N$ in the bottom of the fraction, on the other hand, will be cut in half. The total value near the beginning of the Flyvbjerg plot therefore has a positive slope. However, when adjacent samples are completely decorrelated, the effect of averaging adjacent samples is to decrease the raw variance of the samples by exactly half, which cancels the change in the bottom half of the fraction. This corresponds to the plateau in the figure.

We see in Fig. 7-6 that a plateau forms at about the value $x = 5$ or $x = 6$. Therefore, because the $x$-axis is a log$_2$ scale, we find that $\kappa \approx 32 - 64$. Also, we find that the height of the plateau ($\sigma_m \approx 0.8$ Ha) is about twice the height of the first point ($\sigma_0 \approx 0.4$ Ha), or $\tau \approx 2$.

If we define the “raw variance” $\sigma_{raw}^2$ (i.e., the variance of the original $N$ samples as though they were uncorrelated) as

$$\sigma_{raw}^2 \equiv \langle \hat{O}^2 \rangle - \langle \hat{O} \rangle^2,$$  \hspace{1cm} (7.17)

we see that Eq. 7.16 becomes

$$\sigma_m^2 = \frac{\sigma_{raw}^2}{(N/\tau)}$$  \hspace{1cm} (7.18)

and that

$$\tau = \left[ \frac{\sigma_m}{(\sigma_{raw}/N)} \right]^2 = \left[ \frac{\sigma_m}{(\sigma_0)} \right]^2.$$  \hspace{1cm} (7.19)

In Fig. 7-6, this corresponds to the (square of the) ratio of the height of the plateau
(\sigma_m) to the height of the first point (\sigma_0).

The Flyvbjerg plots are therefore very useful, not only because we can use them to avoid performing an integral (sum) of the autocorrelation function of Eq. 7.13, but also because they make explicitly clear the distinction between the quantities \( \tau \) and \( \kappa \). The importance of making this distinction is worth a discussion.

### 7.3 Distinction between \( \tau \) and \( \kappa \)

Quantum Monte Carlo is only now making inroads into the study of large clusters, such as \((\text{H}_2\text{O})_{20}\) and \(\text{Li}_{64}\). The hurdles that have limited QMC to very small clusters - both technical and computational - have been discussed in detail in the first chapters of this thesis. However, one hurdle makes its appearance only with the study of large clusters - and it caught this author by surprise. The issue involves the growing divergence between \( \tau \) and \( \kappa \) as the cluster size increases.

Among others, a central issue in the improvement of quantum Monte Carlo methods to handle large clusters is the fact that great attention needs to be paid to minimizing the number of sample points employed in the run. As the example of the equilibration of \(\text{Li}_{64}\) in Fig. 7-2 shows, this molecule demands on the order of 1 s per QMC sample. (Of course this figure is only an order of magnitude measure, as it is highly dependent upon the specific computer architecture, and there are a number of code optimization measures that may not be implemented in any particular QMC program.) The challenge involved in tackling large clusters and the need to minimize samples is one of the motivating forces behind our work in developing the SGA.

Indeed, scaling of the QMC codes to large clusters is a double-edged sword. On the one hand, the time required per sample increases. On the other hand - as this chapter shows - the number of steps required for to decorrelate samples during the data-taking stage also increases.

Although the distinction between the quantities \( \tau \) and \( \kappa \) is mathematically and computationally straightforward, for most cluster sizes that have previously been studied using QMC methods, the values of these two quantities have both been fairly low (for example,
in the case of Li\(_4\) in Fig. 7-6 \(\tau \approx 2\) and \(\kappa \approx 50\). In conjunction with the smaller computational time required per sample, the typical approach has been to simply accumulate a very large number of samples such that \(N \gg \tau\) and \(N \gg \kappa\), not be concerned with the specific values of \(\tau\) and \(\kappa\), and then run a binning method of some sort to obtain the standard deviation after-the-fact.

Before proceeding with the discussion, it is enlightening to provide the context in which the issue revealed itself in the course of our work. The number of samples \(N\) is typically chosen to be much larger than both \(\tau\) and \(\kappa\). Only in the case of very large clusters do either of the conditions \(N < \tau\) or \(N < \kappa\) arise; and here the divergence of \(\kappa\) with respect to \(\tau\) becomes relevant. We find, in the case of Li\(_{64}\), that \(N > \tau\), but that \(N < \kappa\).

Despite the effort to minimize the number of samples in an SGA calculation, at first we assumed that each step of the SGA would be limited at the low end by the need to decorrelate samples. We therefore attempted to utilize the Flyvbjerg methodology of Fig. 7-6 to determine the “natural minimum” \(\kappa\) for an SGA step. We at first imagined that the natural minimum number of samples for a single SGA step would be the number required to observe the appearance of the plateau in a reblocking Flyvbjerg plot. The assumption seemed reasonable for more than one reason: even if \(\kappa\) is not the deciding factor for an SGA step, surely the quantity \(\tau\) limits the number of samples at the low end, and it is impossible to directly obtain the value of \(\tau\) without also obtaining the value of \(\kappa\) (see Fig. 7-6). We did not expect \(\kappa\) to diverge.

However, we now show that the value of \(\kappa\) diverges rapidly with cluster size in comparison with the value of \(\tau\) - so rapidly that it is impossible to obtain \(\kappa\), and in turn it is not possible to directly obtain \(\tau\). Instead, \(\tau\) must be obtained by extrapolating from smaller cluster sizes. The value of \(\tau\) must be extrapolated in order to be confident about the statistical accuracy of the calculation for large cluster sizes, even though it turns out that \(\tau\) is very small even for Li\(_{64}\) (\(\sqrt{\tau} \approx 4\)).

In the remainder of this chapter, we present our results for the scaling of the autocorrelation time in \(\text{H}_2\text{O}\) and Li clusters.
7.4 A study of autocorrelation in Li and H\textsubscript{2}O clusters

We briefly recap the details of the method. For a given many-body wave function $\Psi$, we employ Umrigar’s modified version of discrete Langevin dynamics [106] to generate a sequence of QMC samples. We chose to move all electrons during each QMC step rather than performing single-electron moves; see Appendix G for a detailed discussion of this matter. In all cases, an acceptance ratio of 50% was maintained in the Langevin algorithm; see the same appendix.

Let us use the symbol $h$ to signify the quantity $\langle H(r) \rangle$, the value of the local energy; $h(x) \equiv H \Psi(r)/\Psi(r)$. Estimates of $\langle H \rangle$ are indicated by the symbol $h_t$. The quantities $h_t$ are distributed according to a normal distribution, with variance $\sigma^2_m$ given by $\frac{\sigma_{raw}^2}{(N/r)}$ (Eq. 7.18).

In order to implement the Flyvbjerg binning method (Fig. 7-6), we employed the recently developed Dynamic Distributable Decorrelation Algorithm (DDDA) [107] to block data efficiently. The DDDA performs the blocking with nearly zero overhead both in time and in memory, and for these reasons it is well-suited for our study of the convergence properties of large systems. We do not discuss the DDDA in detail but highly recommend it as the method of choice for performing the binning operation dynamically.

7.4.1 Li clusters

Simulations were carried out on Li clusters with 4, 8, 20, 26 and 64 atoms. The geometry of Li clusters can be found in ref. [72]. For Li64 and Li26, we have extracted the geometry from bulk BCC Li. For our computations in the study of equilibration and autocorrelation, it was not necessary to perform a Jastrow factor optimization or to include electron correlations in the wave function. Instead, we employed Hartree-Fock many-body wave functions. In fact, as mentioned previously, we expect that the HF wave function represents a worst-case scenario for both equilibration and decorrelation, because the variance of the wave function is larger than the improved wave functions that include electron correlations. The single-particle molecular orbitals were constructed with one-particle orbitals obtained with the software Jaguar [92].
Figure 7-7: Normalized trial standard deviation $\sigma_t/\sigma_0$ and its error bar for 4 to 64 atom Li clusters. Samples are decorrelated when $\sigma_t/\sigma_0$ displays a plateau, where the height of the plateau $\sigma_m$ is related from Eq. 7.19 to the square root of the integrated correlation time, i.e. $\sqrt{\tau} = \sigma_m/\sigma_0$. Inset shows the linear scaling of $\sqrt{\tau}$ with the number of electrons $M_{el}$ in the system. Error bars on data points are comparable to dot sizes.
Fig. 7-7 shows the value $\sigma_t/\sigma_0$ plotted as a function of block size for Li clusters varying in size from 4-64 atoms, where $\sigma_t$ indicates an estimate of $\sigma_m$ using sample points which might be correlated. As discussed, the horizontal axis gives the number of adjacent QMC samples (block size) pulled piecewise from the full set of samples and aggregated, creating effective samples which are used in the calculation of $\sigma_t$. Note, in comparison to Fig. 7-6, that the vertical axis has been normalized by $\sigma_0$, the value of the first point of the Flyvbjerg-style plot of Fig 7-6. The appearance of the plateau indicating full decorrelation of samples yields the true value of the normalized standard deviation $\sigma_m/\sigma_0$, which from Eq. 7.19 gives the correct value of the square root of the integrated correlation time, $\sqrt{\tau}$. For example, for the 4 atom cluster with $N_e = 12$ electrons, the $\sigma_t/\sigma_0$ curve (black line) flattens to a value of about 2, which is the value shown for $\sqrt{\tau}$ in the inset. Similarly, the plateau for 20 Li atoms with 60 electrons (deep blue line) appears for $\sigma_t/\sigma_0 = 2.7$.

An increase in the height of the plateau, i.e., in the value of $\sigma_m/\sigma_0$ or equivalently of $\sqrt{\tau}$, with cluster size is evident in Fig. 7-7. More quantitatively, the inset reveals a linear relationship of $\sigma_m/\sigma_0$ with the number of electrons $M$ in the cluster. It thus follows that the autocorrelation time diverges quadratically with system size.

Here we see one of the chief results of this chapter. The value $\kappa$ needed to reach the plateau for a given cluster size - the decorrelation length - diverges in relation to the value of $\tau$, which only increases slowly. This makes performing a calculation of $\kappa$ or $\tau$ practically impossible for large clusters. We spent three months performing the calculation shown in Fig. 7-7, and because this represents a single Markov chain, it cannot be parallelized. Clearly, for realistic research of large clusters, a direct determination of $\kappa$ or $\tau$ is out of the question.

For the 64 atom cluster the plateau appears in Fig. 7-7 at the value 14 or equivalently for $\kappa = 2^{14}$, while $\tau = (4.3)^2 = 18.5$; one sees here the divergence of $\kappa$ with respect to $\tau$. For the SGA, then, it seems clear that the appearance of a plateau is not a reasonable choice to determine the minimum number of samples, and in fact we need to consider the scaling of the autocorrelation time in order to proceed safely with development of the SGA for large clusters.
### 7.4.2 Autocorrelation time and computational efficiency

The total time of a computation can be written as $T = t_s N$, where $t_s$ is the time per step. From Eq. 7.18, we see that in order to maintain a given accuracy $\sigma_m$ for QMC calculations of different clusters, the number of steps $N$ (considered as a function of the number of electrons $M$) must change to balance changes in $\sigma_{\text{raw}}^2$ and $\tau$. For quadratically scaling $\tau$, the number of steps $N$, and therefore the total computation time, will have an additional scaling factor of up to $M^2$ in order to compensate for the scaling of $\tau$ observed in Fig. 7-7. This additional scaling factor for $\tau$ is present whether the quantity being calculated is the energy for the entire system, or the energy per atom. From Fig. 7-7 we obtain the scaling of $\tau$ and find that it is small, in the sense that even calculations of the very large cluster Li$_{64}$ only require 4 times the number of samples as the uncorrelated case. The magnitude and scaling of $\tau$, in fact, is so small in contrast to the scaling of $\kappa$ that we obtain the result that the increase in the number of samples required to maintain a given statistical accuracy is quite mild. This is extremely good news for QMC calculations of large clusters, and our work provides evidence that QMC will continue to be an effective technique even for very large clusters.

Our methodology requires that QMC calculations be performed without the appearance of a decorrelation plateau in the Flyvbjerg plot of Fig. 7-6. As an example of an energy calculation obtained without observing the onset of a decorrelation plateau, we were able to obtain the energy (per atom) for the Li$_{64}$ cluster to within $\sigma_m = 0.1$ eV ($\pm 10\%$) using only $10^5$ QMC steps. Because we are unable to determine the statistical accuracy $\sigma_m$ of this calculation using any direct method (hence the point of this chapter!), we verified our estimate of the accuracy of $\sigma_m$ for this energy calculation by performing 5 independently equilibrated runs and observing the spread of the energy results. Fig. 7-8 shows the Flyvbjerg plot associated with this run. As expected, a decorrelation plateau is not observed. Nonetheless, these data result in a fairly accurate calculation of the energy! This is remarkable, because it indicates that without decorrelating even a single sample point - i.e., the final sample point is in some fashion “near” the initial sample point in configuration space - it is nonetheless possible to perform an accurate QMC calculation. This is a direct result
of the fact that \( \kappa \) diverges with respect to \( \tau \) with cluster size.

This indicates that as the wave function becomes more and more multidimensional (as \( M \) increases), the Quantum Monte Carlo method is able to obtain an accurate analysis of the wave function by “zeroing in” in needle-like fashion to a smaller and smaller region near the “center” of the wave function’s “peak”, and obtaining a dense but highly localized set of sample points there.

### 7.4.3 \( \text{H}_2\text{O} \) clusters

We turn now to consider \( \text{H}_2\text{O} \) clusters, where we have studied clusters of 2, 4, 8, 9, 14 and 20 molecules. For the fixed geometries we used, see ref. [108]. These clusters have similar electron counts to those of the Li clusters discussed above. Fig. 7-9 shows decorrelation plots as a function of block size. All clusters display the onset of the decorrelation plateau. A comparison of the insets in Figs. 7-7 and 7-9 shows that the value of \( \sqrt{\tau} = \sigma_m/\sigma_0 \) varies significantly less rapidly with system size in \( \text{H}_2\text{O} \) clusters. It is striking that all curves in Fig.
7-9 collapse onto an essentially universal curve up to five block transformations. Beyond this block size, however, it appears that other secondary longer-distance correlations play a noticeable role so that the curves begin to rise again and settle into new, weakly size-dependent plateaux. If it were not for this secondary feature, all H$_2$O clusters would achieve their plateaux in the same small number of blocking steps, and the stickiness induced by correlated sampling would not be important. Because of these secondary features, H$_2$O clusters exhibit quadratic scaling of $\tau$ with $M$, but the influence is significantly less severe than for Li. In fact, if $a + bM$ describes a linear fit for the data in the inset for H$_2$O, we see that for the cluster sizes we studied, the constant term in the quadratic expression $\tau = (\sqrt{\tau})^2 = (a + bM)^2$ dominates. This may explain why the phenomenon was not observed in ref. [104]. For Li, the linear term dominates and adds to the scaling of the total computation time for the cluster sizes we studied.
7.5 Flyvbjerg-style plots and multiscale phenomena

These possible secondary longer-distance correlations - represented by the “kink”, or noticeable oscillation of concavity between about 5 and 10 block transformations for water - indicate not only that water exhibits interesting and non-trivial multi-scaled behavior in comparison with Li, but that renormalization blocking methods may be useful in exploring multi-scaled behavior. Differences between the time scales of the core and valence electrons in H$_2$O might account for the behavior [109]; see the end of Appendix G. We have not pursued this research here, but Fig. 7-9 is an exciting indication that the use of Flyvbjerg-style decorrelation plots may provide important insights into the physics of different nanosystems. We believe the interesting structures revealed in the plots of Figs. 7-7 and 7-9 are one of the most exciting results to come out of our work, and we are eager to see the QMC community delve deeper into the use of these seemingly benign renormalization methods as an investigative tool.

In conclusion, we here investigated the scaling of the integrated autocorrelation time $\tau$ in QMC computations of Li and H$_2$O clusters. The quantity $\tau$, which directly yields a measure of sampling correlations in the calculation, is found to diverge quadratically with system size $M$ in both cases, more severely for Li than for H$_2$O, and becomes increasingly difficult to calculate for large clusters. We have shown that brute force decorrelation of samples is simply not feasible for these large clusters. Our study highlights the importance of correlated sampling in QMC computations of large clusters and provides a route for obtaining accurate error estimates by exploiting the scaling properties of $\tau$ with system size, without requiring explicit decorrelation of samples. The present results are directly applicable to the SGA, which operates in the regime of a small number of samples, and the results of this chapter show the necessity of utilizing SGA steps that do not depend on the appearance of a decorrelation plateau.
Chapter 8

The Stochastic Gradient Approximation

In the preceding chapters, we discussed work that involved variational and diffusion QMC calculations. For many of the variational calculations, we deployed the Stochastic Gradient Approximation (SGA), but beyond the background in the introduction, we have not discussed the method in detail. This chapter is devoted to a detailed discussion.

To place the context of the SGA into its Variational Monte Carlo context, we begin by presenting the simple, bare-bones VMC algorithm in the form of a flowchart - see Fig. 8-1.

*Variational Monte Carlo (VMC)*

(I) Choose wave function ansatz $\Psi(\vec{\beta})$ and initial point $\vec{\beta}_0$.

(II) Loop:

(A) Run Metropolis algorithm (brown box). The loop is entered with an initial guess for the variational parameters. The Metropolis algorithm is performed (or a Metropolis-like algorithm such as the Langevin algorithm; see Ch. 4) to obtain a set of $N$ QMC sample points, which are simply $N$ sets of positions for the $M$ electrons in the system, distributed in accordance with $|\Psi|^2$. Running the Metropolis algorithm is the same as moving the walkers.
Figure 8-1: The bare-bones Variational Quantum Monte Carlo (VMC) algorithm. **Brown box:** Sample points are obtained by use of the Metropolis (or related) algorithm. **Orange box:** These points are used to calculate the gradient of the energy (or variance of the local energies). The search direction is the negative of the gradient. **Light blue box:** A line search is performed to obtain the energy (or energy variance) minimum along the search direction. **Dark blue box:** The parameters are set equal to the result of the line search.
(B) Determine a search direction (green box). The sample points from Step (1) are used to calculate the (negative of the) gradient of the energy in order to obtain a search direction in the variational landscape. Note that a Newton’s method, or quasi-Newton’s method approach to obtaining the search direction, both of which involve the Hessian matrix of second derivatives, can also be employed to obtain the search direction.

(C) Obtain a step length (light blue box). A line search must then be performed to determine the step length. It is this stage that performs the actual optimization. To perform the line search, reweighting must be utilized and a number of different points along the search direction must be evaluated according to some line search algorithm.

(D) Move to a new set of variational parameters (dark-blue box). These parameters are the final result of the line search algorithm of Step (3). The algorithm then proceeds with the next iteration of the loop (re-entering the brown box) with this new selection of parameters.

The algorithm is complete when the parameters converge sufficiently between iterations.

Regarding (C), there are many varieties of line searches; see either of the classic texts of ref. [110] or [111]. The issue of a proper line search is a subtle and difficult one - depending on the parameters being optimized, a line search may perform efficiently in one case, but completely fail in another case. A robust VMC code will supply a set of line search options. Line search algorithms lie in two main camps: those that minimize the objective function, and those that locate a root (zero) of the objective function. Within each of these two camps, line search algorithms break into two additional categories: those that employ derivative information (along the search direction), and those that require only function evaluations. For those algorithms that use derivative information, some require the derivative only at the starting point, and some require a calculation of the derivative at every point being evaluated along the search direction.
8.1 The Stochastic Gradient Approximation (SGA)

We introduce the SGA in the context of Fig. 8-1. The SGA is an energy minimization method, as opposed to a variance minimization method. Fig. 8-2 presents a flow-chart of the SGA with the specific implementation details that we find make it the most effective - these will be discussed shortly.

**Stochastic Gradient Approximation (SGA)**

(I) Choose wave function ansatz $\Psi(\beta)$ and initial point $\beta_0$.

(II) Select a reasonable set of boundaries for the variational search.

(III) Determine optimum number of samples $N$ per SGA step by performing a trial run and decreasing the number of samples until the rejection rate during the line search is about 0.1.

(IV) Loop:

(A) Run Umrigar’s modified Langevin algorithm to obtain $N$ samples. (Brown box.)

(B) Accumulate energy results. (Yellow box.)

(C) Accumulate analytical energy gradient data. (Orange box.)

(D) Obtain the search direction by use of quasi-Newton’s method to obtain an approximation of the Hessian. (Green box.)

(E) Obtain the trial point in the variational landscape by performing a line search. Use the line search to find the root of the dot product given in Eq. 8.10. (Light blue box.)

(F) Average all preceding trial parameters to obtain the new parameters. (Dark blue box.)

(III) Calculate final results by averaging energy samples over all locus points of the SGA path.

We have added to the pink box two other substeps that occur simultaneously while running the Metropolis-like algorithm - the accumulation of final results, and the accumulation of search direction information. Because these are clearly distinct computational stages, it is helpful to make the distinction in the flowchart.
Figure 8-2: The SGA algorithm in the form that we have found is simplest and most robust. The figure specializes the flow chart shown in Fig. 10-1 to the specific case of the SGA. Note that the dot product referred to in the light-blue box refers to Eq. 8.10.
Note, from the listing associated with Fig. 8-1, that for standard (deterministic) methods, the new parameters chosen in Step (D) are set exactly equal to the result of the line search in Step (C). The SGA modifies Step (D) by introducing a different method of determining the new trial parameters: it utilizes all previous line search results from Step (C), rather than only the most recent line search result.

Appendix C shows that the difference between the deterministic and the stochastic approach is reflected in the convergence rate criteria for the two methods. In the deterministic case, the convergence rate is given in terms of the preceding step only (Eq. C.1). *Previous steps do not influence the convergence in any way.* In stochastic optimization, however, the convergence is a function of the number of total steps $p$, including all preceding steps (Eq. C.2).

Fundamentally, the reason that all preceding steps are included in the convergence criteria for the SGA is due to the fact that the number of samples per step can be made so small that both the search direction and line search are highly inaccurate. Instead of assuming that previous information is worthless, we utilize the Robbins-Monro theorem (Eq. 8.1) to guarantee convergence as the average over all SGA steps. In contrast, deterministic methods utilize a large number of samples so that the accuracy, per step, is considered so great that the deterministic regime can be assumed for all steps and, as stated, information from the previous steps is considered worthless.

The Robbins-Monro theorem is a rigorous mathematical formulation for the SGA; however, we postpone a presentation of it until Section 8.4. First, we would like to highlight the key details that we have found are required for an effective SGA scheme.

### 8.2 Requirements for effective stochastic optimization

Figs. 8-1 and 8-2 make clear that the SGA shares most of the same options that deterministic algorithms do. Steps (A)-(C), in particular, allow for all of the same options that deterministic methods do. Prior implementations of the SGA [5], [112, 113, 114] have made some poor choices, and in some cases this has caused the method to fail [115, 116]. We discuss these latter cases later.
We provide here a concise list of the requirements and recommendations that we have found result in an effective implementation of the SGA. The first three are requirements for any realistic system of interest; the fourth is likely to be very important, and the fifth has important advantages.

(1) **Adaptive step size (light-blue box).** Previous SGA implementations utilize a poor, trivial choice - a static and unchanging step length, regardless of the variational landscape. Approaches that use the trivial choice do not take advantage of the unique features of QMC that allow the option of utilizing a line search within the stochastic optimization approach. We take full advantage of this possibility within QMC and discuss a good choice for an adaptive step size - a particular line search algorithm - in Section 8.7.1.

(2) **Use of the analytical energy gradient** enhancement, rather than the energy itself, as the objective function - both in the choice of search direction (green box) and in the line search algorithm (light-blue box). Following up on the work of Harju [114], we also observe the remarkable result that by using an analytical energy gradient, we are able to achieve the optimum parameters more quickly than we are able to obtain the energy at that set of parameters. See Fig. 8-6.

(3) **Introduction of a bounded region** for the variational parameters.

(4) **Use of a root-finding line search** (as opposed to a minimization line search). This is distinct from the requirement of an adaptive step size, because different line search algorithms can be employed with an adaptive step size algorithm. We introduce the proper objective function for the optimum root-finding line search - based upon the analytical energy gradient - in Section 8.7.4 (Eq. 8.10).

(5) **Use of a quasi-Newton search direction** (green box), rather than the gradient (steepest-descent) search direction.

We provide a full discussion of each of the five requirements in detail later in this chapter. When these requirements are implemented, we find that the SGA fulfills its potential
of being a robust, massively parallelizable, simple variational Monte Carlo method that is ideally suited for the study of large nanoclusters.

Some recent attempts [115, 116] to utilize the SGA have not been successful because they have not implemented an adaptive step size.

Before proceeding with the formal mathematics of the SGA algorithm, we would like to provide an example of an SGA calculation.

### 8.3 Example SGA computation

Fig. 8-3 presents a typical SGA run. The example here, and the other examples throughout this chapter, involve the cluster Li$_4$. Fig. 8-3 shows an optimization of the opposite-spin Jastrow parameter of Fig. 3-1. The SGA computation in the figure runs here for almost 1,500 iterations, and utilizes 16 samples per iteration, requiring about an hour on a single processor. The true value of the optimum parameter is $\beta = 1.24$.

Fig. 8-4 shows the first 75 iterations of the same SGA run as Fig. 8-3. The first 10 or so iterations oscillate wildly, before beginning to settle down. This indicates excellent convergence for an approximate estimate of the minimum, and it is the direct result of our choice of the analytical energy gradient as the objective function. See Section 8.7.2 for a detailed discussion; in that section, refer to Fig. 8-6 for an explicit demonstration of the rapid convergence. We find that use of the analytical energy gradient (requirement 2) enables the optimization to converge to the minimum more quickly than it can calculate the energy. This has been demonstrated also in Harju [114].

After achieving a rapid convergence in the first 10 or so iterations, during the next 65 or so iterations the parameter oscillates through a range of about $\Delta \beta \approx 0.3$. This reveals that it would be of great use with an SGA optimization to include error bars with the variational computation. In particular, it seems reasonable to suppose that for the SGA run displayed in Fig. 8-3, after about 1,500 iterations we have obtained a statistical accuracy on the order of about $\Delta \beta \approx 0.3$. However, obtaining a statistical accuracy associated with variational parameters is non-standard and is a non-trivial task. We include a discussion of it in Appendix C, and we encourage the reader to study that appendix. We believe the future
of variational Quantum Monte Carlo will involve the incorporation of statistical error bars with the variational parameters to guide computations, and we propose a methodology in the appendix.

8.4 The Robbins-Monro theorem and the SGA

At this point we move on to discuss the mathematical formalism underlying the SGA and stochastic optimization. We present the SGA equation, which is based on the archetypal stochastic optimization formula [3]. We have

$$\bar{\beta}_{p+1} = \bar{\beta}_p - A_p \nabla_{\bar{\beta}_p} \langle H \rangle_p,$$

(8.1)
Figure 8-4: The same SGA run as Fig. 8-3, but displaying 75 iterations.
where the set \( \{ \beta_p \} \) are the locus points defining the SGA path through the variational landscape (see Section 8.5), \( p \) is the iteration count, \( \langle H \rangle_p \) is the calculation of the local energy using only the \( N \) samples obtained at step \( p \), \( \nabla_{\beta_p} \langle H \rangle_p \) is the gradient of this quantity with respect to the variational parameters, and \( A_p \) is a multiplicative factor that depends on \( p \). The Robbins-Monro theorem states that under a set of general conditions, the locus points \( \beta_p \) are guaranteed to converge. We do not go into detail about most of the general conditions, which are typically satisfied by QMC wave functions, but the interested reader can refer to the references that are provided in the next subsection (Section 8.4.1).

However, one of the conditions - that of the choice of \( A_p \) - is critically important for the implementation of the SGA, and corresponds to the essential adaptive step size requirement introduced in Section 8.2.

The necessary conditions on \( A_p \) in Eq. 8.1 are the following.

\[
A_p > 0 \text{ for all } p \tag{8.2}
\]

\[
A_p \to 0 \text{ as } p \to \infty
\]

\[
\sum_{p=0}^{\infty} A_p = \infty
\]

\[
\sum_{p=0}^{\infty} A_p^2 < \infty
\]

We defer a further discussion of the choice of \( A_p \) for Section 8.7.1, in which we discuss the adaptive step size algorithm.

### 8.4.1 History of the Robbins-Monro theorem

To provide a rich and enlightening context for our use of the SGA and the Robbins-Monro theorem, in this subsection we will say a few words about the history of stochastic optimization since the introduction of the Robbins-Monro theorem.

The original Robbins-Monro paper in 1951 [3] was immediately followed by four influential papers that filled in details and expanded the applicability of the theorem. It is insightful to present the papers in chronological order.
1. Robbins and Monro, 1951 [3]. The stochastic approximation is first presented as a root-finding algorithm for a noisy scalar function of a single (scalar) argument. The gradient is not utilized. Note that finding the root (zero) of a 1-dimensional gradient of a function is equivalent to an optimization of the function.

2. Wolfowitz, 1952 [117]. The conditions under which the Robbins-Monro theorem holds are shown to be more general than those presented by Robbins and Monro.

3. Kiefer and Wolfowitz, 1952 [118]. The root-finding Robbins-Monro theorem is placed firmly in the context of optimization (maximization or minimization). The function is still assumed to be a scalar function of a single (scalar) argument. A numerical derivative is employed; no analytical derivative is utilized.

4. Blum, 1954 [119]. The nature of convergence within the so-called domain of attraction (the region in which the algorithm will converge from a given starting point; see references) was proven to be stronger than the previous authors had reported.

5. Blum, 1954 [120]. The author extends both the root-finding algorithm and the optimization algorithm to multiple dimensions (i.e; a vector function of a vector argument), and demonstrates that the same strong convergence criteria apply. This is the form presented in Eq. 8.1, except that in our case we consider a scalar function (the local energy) of the vector quantity \( \bar{\beta} \) (representing the variational parameters).

Since the vector optimization formulas are shown to follow directly from the Robbins and Monro theorem, any form of the Robbins and Monro equation, such as Eq. 8.1, is generally credited to Robbins and Monro.

8.5 Trial points and the SGA path

We now proceed to a conceptually more enlightening framework in which to describe the SGA that highlights the efficiency with which it converges. In the following section, we will prove the equivalence of this framework with the Robbins-Monro theorem of Eq. 8.1.
We begin by referring the reader to Fig. 8-2. As indicated by the figure, a selection of a trial point in the parameter landscape $\overrightarrow{\beta}_{p+1}^{\text{trial}}$ at step $p$ of the variational walk (light-blue box) does not have to imply that $\overrightarrow{\beta}_{p+1}^{\text{trial}} = \overrightarrow{\beta}_{p+1}$.

In the context of QMC, the condition

$$\overrightarrow{\beta}_{p+1} = \overrightarrow{\beta}_{p+1}^{\text{trial}}$$

(8.3)

for every $p$ defines deterministic optimization. This is to be contrasted with Eq. 8.1, which provides the formula for $\overrightarrow{\beta}_{p+1}$ in a stochastic optimization, a formula that takes into consideration that previous steps provide additional information due to the stochastic noise inherent in the estimate $\overrightarrow{\beta}_{p+1}^{\text{trial}}$.

The set of trial points $\left\{ \overrightarrow{\beta}_p^{\text{trial}} \right\}$ obtained in the light-blue box, and the set of points that define the SGA variational path - the points obtained in the dark-blue box of Fig. 8-2 - are non-overlapping. For convenience, let us call the points of the SGA path locus points $\left\{ \overrightarrow{\beta}_p \right\}$. The word locus is not included in the notation.

We here discuss how to obtain the SGA path based on the trial points (red box in Fig. 10-1). The method is simple. The SGA path is obtained by averaging all available trial points. We will prove the equivalence of this method and Eq. 8.1 in the next section.

Arguably the single most important aspect of the distinction between the trial points and the locus points - and the chief reason we are highlighting it in this section - is the fact that the trial points are scattered far and wide throughout the variational landscape even while the locus points of the SGA path converge more and more closely towards the optimum value. This remarkable result has two immediate implications.

(1) The SGA converges quickly to an approximate minimum.

(2) The SGA continues to converge to greater and greater accuracy indefinitely.

Both of these points, especially the second, are in sharp contrast to deterministic methods. Deterministic methods must increase the number of sample points per variational iteration in order to obtain greater accuracy, and a determination of the number of sample
Figure 8-5: A sample of the trial points (green circles) and locus points (blue circles) for an all-electron calculation of Li$_4$ with two variational parameters, the opposite-spin Jastrow parameter and the same-spin Jastrow parameter. The trial points and the locus points form non-overlapping sets. 500 trial points and 500 locus points are shown. The data points are shown as circles so that the region of overlapping points can be observed more clearly, as a smear. Notice that the trial points are widely spread out in comparison with the locus points. The astute reader might also have noticed that the trial points have a tendency to bunch along a line. This tendency is discussed in Section 8.12.
points is a non-trivial task. In the case of the SGA, convergence to greater and greater accuracy is only a function of the number of trial points and therefore of the total computation time - it does not require prior knowledge about the time required or about the number of sample points that will be necessary as the computation proceeds.

The following paragraph summarizes the convergence properties of the SGA.

To run the SGA, don’t think about the goal. Begin a simulation. Watch it converge indefinitely.

This convergence result is guaranteed due to the Robbins-Monro theorem.

The distinction between the trial points and the locus points is also useful in that it helps explain the technical aspects of the SGA algorithm in a concise fashion. Walkers are moved (i.e. the Metropolis-like algorithm is run, and QMC samples are obtained) at the locus points, not the trial points. The trial points are then obtained, filling the variational landscape. As many trial points as possible are obtained.

Before concluding this section, we’d like to note here a distinction between the SGA and the method of Stochastic Reconfiguration (SR) [91], which we employed for an optimization of the RVB parameters discussed in Ch. 6. SR sometimes allows for a somewhat large number of iterations - on the order of \( p = 100 \) [91] - and as a result an average of the variational parameters is sometimes calculated over the final steps of the algorithm. However, this averaging process is imposed after-the-fact, and does not in any way influence the iterations themselves. SR could be enhanced to become a truly stochastic optimization in the formal sense presented in this work. In this case, like the SGA, the selection of each trial point with SR would be directly dependent on the average of all preceding trial points.

8.6 The SGA as an average of trial points

We now show the equivalence of the SGA method as described in Section 8.5, and the SGA method as expressed in Eq. 8.1. Specifically, we show that the average of the set of trial points is equivalent to Eq. 8.1.
Consider the average of the set of trial points \( \{ \overline{\beta}_{\text{trial}} \} \) obtained via the recursive formula

\[
\overline{\beta}_{i+1} = \frac{i \overline{\beta}_i + \overline{\beta}_{i+1}}{i + 1},
\]

where, for general \( i \), \( \overline{\beta}_i \) is the locus point indicating the average of the first \( i \) trial points \( \{ \overline{\beta}_{\text{trial}} \}_i \), where the subscript \( i \) indicates the number of locus points. With \( \overline{\beta}_1 = \overline{\beta}_{1, \text{trial}} \), it is easy to convince yourself that Eq. 8.4 gives the correct average for the set \( \{ \overline{\beta}_{\text{trial}} \} \) as \( i \) is iterated from 1 to \( p - 1 \). If we now make the substitution

\[
A_p \rightarrow \frac{a_p}{p + 1}
\]

in the SGA formula of Eq. 8.1, require that \( \overline{\beta}_{i+1} \) is given by

\[
\overline{\beta}_{i+1} = \overline{\beta}_i - a_i \overline{\beta}_i (H)_i,
\]

and substitute this expression for \( \overline{\beta}_{i+1} \) into Eq. 8.4, straightforward algebra yields the SGA equation (Eq. 8.1), demonstrating the equivalence of the approaches.

This choice of \( A_p \) in Eq. 8.5 is not necessary, however. Any choice that satisfies the conditions in Eq. 8.5 will satisfy the Robbins-Monro theorem.

### 8.7 Details of SGA requirements

Now that we have provided the mathematical formalism underlying the SGA, we are in a position to provide a detailed discussion of the five requirements and recommendations that we introduced in Section 8.2 for a successful SGA optimization. We consider them one at a time.
8.7.1 Adaptive step size

The simplest possible choice for $A_p$ in Eq. 8.1 is

$$A_p = \frac{a}{p},$$

(8.7)

where $a$ is a constant value independent of $p$ which must be carefully determined for each SGA computation. This corresponds to $a_p = a$ in Eq. 8.5.

A major problem with previous implementations of the SGA \([5, 115, 116]\) is that they have employed this simple, static choice for $a_p$. We now discuss the problems associated with a static choice.

With a nearly symmetrical variational landscape, such as that of $H_2$ in Fig. 2-1 or the simple harmonic oscillator utilized by Harju \([112]\), the choice $a_p = a$ works well. However, attempting to utilize this choice with a highly non-symmetric landscape dramatically slows the convergence and makes the SGA impractical. See ref. \([115]\) and \([116]\) for excellent examples of this failure, in which the authors recognized the reason for the failure but did not propose an adaptive step size.

Li clusters - indeed, almost any wave function with a Jastrow factor - provide a good example of a highly non-symmetrical landscape. In the case of the simple Jastrow factor displayed in Fig. 3-1, as $\beta \to 0$, the total energy sharply increases due to the fact that the electrons are forced far apart, even at the cost of a tremendous amount of energy. On the other hand, as $\beta \to \infty$, the increase in energy is very gradual.

The reason for the poor performance of the SGA in this case is simple. Unless the SGA path (the sequence of locus points) has already approached very close to the minimum, even a very small displacement into the region of very steep gradient causes the following trial point to shoot far out of the region of convergence (see Appendix D). In order to prevent this, the constant term $a$ can be chosen to be quite small, to scale down the step length and prevent the trial point from shooting far away. However, on the other side, when the SGA path is in the region of shallow gradient, the small value of $a$ causes the SGA path to crawl painstakingly slowly towards the minimum. In this region, it is preferable for $a$ to be
large, to increase the rate of convergence.

It is impossible for the choice of $a$ to simultaneously satisfy both of these desired criteria. Therefore, the optimum choice of $a$ (about 10 in the case of Li$_4$) is nonetheless associated with a wildly erratic SGA path, competing between the two extremes, and results in an impractically slow convergence. Furthermore, the selection of $a$ is non-trivial and it takes a great deal of experimentation to find an optimum range.

A constant step size is equivalent to the condition of an unchanging value of $a$ and is wrought with these difficulties. An adaptive step size algorithm, on the other hand, allows the value of $a$ to be dynamically determined at each step by the algorithm and avoids the necessity of pre-selecting a constant value for $a$. We discuss the specifics shortly. For now, note that failing to include an adaptive step size algorithm with the Robbins-Monro theorem yields an optimization that requires great care in determining the constant value $a$. Even with the optimum choice of $a$, failing to include an adaptive step size results in a far slower rate of convergence. Both of these drawbacks make the Robbins-Monro theorem impractical in the context of VMC with this trivial choice of step size.

By implementing an adaptive step size, we can simultaneously overcome both problems. First, the dynamic step size can be made small in the region of steep gradient, and large in the region of small gradient, dramatically improving the convergence rate. Second, because the step size is dynamic, it overcomes the fundamental limitation of the necessity of determining an optimum value of $a$.

The adaptive step size algorithm, by its nature, entails a line search to determine the proper step size. In other words, the very concept *step size* implies that a direction has already been chosen (see Fig. 8-2; green box). We have found that a root-finding line search works best. A general line search requirement can therefore be considered equivalent to the adaptive step size requirement; but the *specific* line search that we find works best - the root-finding line search - warrants a separate entry in the list of SGA requirements (item 4), and we defer a discussion of the details of the line search until Section 8.7.4.

As a final note in our discussion of the adaptive step size, the algorithm we employ completely disregards the magnitude of each component of the gradient appearing in Eq.
8.1 - as it must, if it is to overcome the difficulties discussed in this section. It is, nonetheless, simple to demonstrate that the convergence conditions of the Robbins-Monro theorem (Eqs. 8.2) continue to apply. In this context, it is valuable to mention that since the time of the introduction of the Robbins-Monro theorem, the concept of an adaptive step size has been developed in the theory of stochastic optimization (see ref. [6], pp. 95-100), and the optimum adaptive step size has been determined within the small quadratic region surrounding the minimum. Not surprisingly, it turns out to be exactly the Newton step employing the Hessian matrix of second derivatives, just as in the case of the deterministic Newton’s method. Our adaptive step size algorithm has the same purpose as the Newton step - it attempts to land directly at the minimum - but it can be employed even outside the quadratic region. We have observed that it dramatically improves the rate of convergence.

8.7.2 Analytical energy gradient

We now discuss in more detail our use of the analytical energy gradient, both in the determination of the search direction (green box in Fig. 8-2) and in the form of the function \( \vartheta \left( \hat{\beta} \right) \) from Eq. 8.10 which we will discuss shortly as the objective function for use in the root-finding line search.

To begin, let us take this opportunity to highlight the distinction between the analytical gradient, and the numerical gradient, discussed previously in Section 4.8. In this section we discuss the benefits of the analytical gradient. While reading this section, bear in mind that the benefits we describe do not accrue for the numerical gradient. The numerical gradient is subject to the effects of the variance of the local energy, and as we will see in the remainder of this section, the analytical gradient is not subject to these effects. Instead, the analytical gradient is subject to the effects of the variance of the local quantities required by the analytical gradient - which do not include the energy, and which possess a much smaller variance. The fundamental distinction between the analytical gradient and the numerical gradient is precisely the improved variance of the local quantities involved.

The key point, then, behind the choice of the analytical gradient is the fact that due to the reformulation described by Umrigar [47], these fluctuations (i.e. the variance) are
very small and calculations are much more accurate than calculations of the energy itself. Therefore, *we are able to achieve the optimum value quickly* - even before obtaining an accurate calculation of the energy at the optimum point. Fig. 8-6 is an example of the classic graph that demonstrates exactly what is meant by *achieving the optimum value even before obtaining an accurate calculation of the energy*. The phenomenon was first observed explicitly by Harju [114].

The figure shows a plot of the ongoing energy calculation (error bars not shown) as a function of the ongoing SGA variational parameter. The iteration count is not shown, but corresponds to the individual connected line segments shown in the figure.

We see from the figure a very rapid convergence in only a few SGA steps to fairly close to the optimum parameter value - even before the simulation has time to calculate the energy accurately at that point, as evidenced by the fact that the SGA path shoots wildly around in the energy dimension at an approximately fixed value of the variational parameter, before slowing down and beginning a long and arduous crawl which, finally, takes it to an accurate energy calculation.

We have not shown a plot of a direct energy grid for Li$_4$ because it is computationally intensive and burdensome to produce. However, doing so would indicate that a *direct* energy minimization involves relatively large error bars and a correspondingly slow crawl towards the minimum parameter, rather than the rapid convergence exhibited with the analytical energy gradient. See Harju for an excellent example of such a plot in a simpler case where the energy plot is shown, superimposed over a plot similar to the one shown in Fig. 8-6.

In the remainder of this section we present the mathematical form of the analytical energy gradient, followed by the history of the analytical energy gradient within QMC.

**Mathematical form of analytical gradient**

The analytical energy gradient $\vec{\nabla}_{\beta} \langle H \rangle$, can be written strictly in terms of expectation values of the local energy, the wave function, and derivatives of the wave function. The
reformulated version as provided by Umrigar [47] is

\[
\nabla_{\beta} \langle H \rangle = 2 \left\langle \frac{\partial}{\partial \beta} \Psi \left( \hat{H}_L - \langle H \rangle_w \right) \right\rangle_w ,
\]

(8.8)

where \( \hat{H}_L \) is the local energy (the scalar quantity \( \frac{\hat{H}_L}{\Psi} \) discussed in Ch. 4). In this case, in order to gain the benefits of the variance-reduction reformulation of Umrigar, it is critically important that both expectation values in Eq. 8.8 be taken \textit{with respect to the} \( N \) \textit{samples of the given SGA step} (with reweighting, as required for the line search) - and \textit{not} included as the true expectation value. This is indicated by the subscript \( w \).

The necessity of utilizing \( \langle \ldots \rangle_w \), rather than \( \langle \ldots \rangle \), results in the fact that a calculation of the error of the analytical energy gradient is non-trivial. Therefore, error bars are not included with analytical energy gradient plots. In Appendix B, we discuss this issue in detail.

**History of the analytical gradient**

To place the use of the analytical energy gradient in greater context, we review here the history of the analytical energy gradient within QMC.

First, variance minimization with finite differences, in which the search direction is obtained by a \textit{numerical}, rather than analytical, gradient of the local variance, was used almost exclusively in the 12 (or so) year span since it was introduced in 1988 [45] until 2000, at which point new energy minimization techniques were introduced.

To this author’s knowledge, in 1977, Ceperley [121] first wrote down the formulas for the analytical gradients.

In 1990, Schmidt and Moskowitz [122] employed the analytical gradient in some simple QMC calculations (of low-\( Z \) atoms), but did not go into detail.

In 2000, the analytical gradient and the analytical Hessian approaches were first presented by ref. [51] in order to obtain the search direction (green box of Fig. 10-1).

In 2003, Casalegno \textit{et al.} utilized Pulay’s correction [123] to make the variance of the Hellman-Feynman energy finite (see Section 4.12.1). The Hellman-Feynman method is a
Figure 8-6: The figure shows a useful way to observe the rapid convergence of the SGA when the analytical energy gradient is utilized. The horizontal axis is the variational parameter for this Li$_4$ computation (the opposite-spin Jastrow factor). The vertical axis is the energy, as calculated during the run. (Error bars are not shown for the energy.) Because the analytical gradient can be calculated accurately with far fewer sample points, the SGA converges towards the minimum value of the energy well before the actual value of the energy at that point is obtained to the desired accuracy. This can be observed by the fact that the variational parameter remains relatively constant, while the energy slowly drifts towards the exact value. The fact that the energy is initially too low is irrelevant because its statistical error bar is large during the early stage of the computation.
different analytical gradient, but we include it here for completeness.

In 2005, Chiesa, et al. developed the Hellman-Feynman variance-reduction technique further [124]. Since that time it has continued to be utilized (see, for example, ref. [125]).

Also in 2005, Umrigar introduced his significant variance-reduction improvement of the analytical Hessian [47]; the author utilized Newton’s method directly with the improved Hessian to obtain the search direction, and also employed Newton’s method utilizing the analytical Hessian to obtain the trial parameters (light-blue box) without a line search (except for the first few steps which employed steepest descent). We discuss our choice of the quasi-Newton’s method below.

In the same 2005 paper, Umrigar provided an equally valuable reformulation of the analytical gradient that significantly decreases its variance, similar to the variance-reduction of the analytical Hessian. This reformulated form of the analytical gradient, however, is not directly used by the author.

In 2005, the analytical gradient was utilized within the SGA by Harju in a fashion similar to our approach [112].

8.7.3 Parameter boundaries

Another requirement for successful stochastic optimization is not represented by the SGA formula of Eq. 8.1, but has been a critical part of the development of stochastic optimization theory and must be incorporated, as recognized in a QMC context by ref. [116]. Due to the stochastic nature of the path, a noisy step sometimes carries the path outside the domain of attraction (see ref. [6] for a discussion of the domain of attraction). This is such a common occurrence that the stochastic theorems such as Robbins-Monro could not be correct without some method of projecting these faulty points back towards the minimum. See Fig. 2-1 for an example of a wild offshoot in the first few SGA steps - in this case the SGA algorithm recovers, because the variational landscape is smooth for $H_2$, but for more realistic systems with more complicated landscapes, erratic points are less likely to recover.

If a projection method is utilized to project erratic points back towards the minimum,
the modified form of the Robbins-Monro theorem (Eq. 8.1) is

\[
\overline{\beta}_{p+1} = \Xi \left[ \overline{\beta}_p - A_p \overline{\mathbf{V}}_{\overline{\beta}_p} \langle H \rangle_p \right],
\]

(8.9)

where \( \Xi \) is a projection operator which is a user-defined mapping that projects any point not in a previously-defined bounded region to a new point back inside the region.

Convergence to the optimum point has been proven for Eq. 8.9 under a general set of conditions on the projection \( \Xi \), including a projection back onto the closest point inside the domain. The reader is referred to the references ([6], and refs. therein) for details on this work.

As stated, only in the simplest cases does the SGA not require boundaries - the \( H_2 \) example shown in Fig. 2-1 is one such example. Our implementation of the SGA for more complicated systems includes a boundary, as must all realistic SGA implementations.

Note that the SGA method is designed to work well if the boundaries define a region that is much larger than the region near the minimum. This is related to the fact that most of the trial points lie scattered throughout the variational landscape, yet the Robbins-Monro theorem guarantees convergence at the minimum.

It is worth mentioning here than in our implementation of the SGA, we chose to discard out-of-bound points and repeat every SGA step that had a rejected trial point. Stochastic optimization theory [6] discusses a wide set of conditions that satisfy the reflection criteria of \( \Xi \) with boundaries. It is unclear whether our choice of repeating the SGA step until the point lies in-bounds strictly satisfies this criteria. However, if this choice introduces a bias into the calculation, we are unable to discern it, as evidenced by our calculation confirming the correctness of the optimum point obtained with the SGA in the case of Li\(_4\) (Section 14).

Choice of boundaries

Although there is great leeway in the choice of boundaries, in this subsection we discuss technical aspects of the choice of boundaries.
Despite the leeway in the choice of boundaries, it is nonetheless necessary to impose a reasonable set of boundaries. First, consider the case where the boundaries are shrunk tightly around the minimum. In this case, it frequently happens that the line search fails to find a minimum. In this case, the projection function \( \Xi \) will be utilized frequently, the benefits of the adaptive step-size algorithm will not be gained, and the rate of convergence will be drastically slowed. The SGA algorithm \textit{depends} on the fact that the boundaries are spacious to provide breathing room. This corresponds to the fact that the trial points are scattered far and wide throughout the variational landscape, even while the SGA path converges at the minimum, as discussed previously.

In the following subsection we consider the possibility of gaining benefits from shrinking the boundaries - but this represents a theoretical possibility for a future advance with the algorithm. In general the boundaries must not be too small.

On the other hand, the boundaries also must not be too large. We discuss the reasons for this by way of the example of Li clusters that we also discussed in the context of the adaptive step size. In the case of these clusters, problems arise both in the region of very steep gradient as the leading variational parameter \( \beta \rightarrow 0 \), and in the region of very flat gradient as \( \beta \rightarrow \infty \). In the first case, it very occasionally happens that the objective function increases without bound as the line search approaches \( \beta = 0 \) until it overflows (represented by the dreaded \textit{NaN}). In the second case it very occasionally happens that the line search continues all the way out towards infinity. It either finds a minimum very far away, which heavily weights the locus points away from the optimum point, or it never finds a minimum and underflows.

Both of these problems can be easily resolved simply by including a reasonable set of boundaries. The choice of boundaries is unimportant, as long as the boundaries are reasonable. In the case of the Jastrow parameters for Li clusters, we impose boundaries of \( \beta = 0.1 \) to \( \beta = 5.0 \) for both opposite-spin and same-spin electrons.
Shrinking boundaries

It is worth giving a brief discussion about the possibility of shrinking the boundaries as the algorithm proceeds. A shrinking of the boundaries might be undertaken, for example, if we have already performed an optimization and wish to improve upon it. One might suspect that imposing this additional information might help the convergence rate.

If the bounded region is made very small, the primary impact upon the SGA algorithm is that many line searches will fail and the corresponding trial points will be reflected back into the region using the mapping $\Xi$ of Eq. 8.9. This has the effect of dramatically decreasing the rate of convergence. The only way to improve the rejection rate is to increase the number of QMC samples per SGA step. Doing so makes it more likely that the line search will succeed. This point can be understood by noting that an infinite number of QMC samples will always cause the line search to succeed, just so long as the optimum point lies within the bounded region.

In a case with a very small bounded region, then, the bounded region has become a major player in the game - rather than being mostly a spectator. On the other hand, having a very small region is itself equivalent to having obtained convergence. Future work could explore the possibility of providing a small bounded region and perform a detailed study of the relationship between the boundaries, the number of QMC samples per SGA step, the rejection rate, and the convergence rate.

8.7.4 Root-finding line search

The possibility of utilize an adaptive step size is not something that is typically considered in stochastic optimization theory. It is something uniquely made possible within QMC due to the possibility of performing a line search with reweighting, which allows for a much more accurate determination of function differences than function values [1]. In other words, in QMC we are able to take advantage of the correlations between calculations of the objective function using the same set of sample points along the search direction.

For the line search we must determine a good choice for the objective function. We have
chosen to utilize the following scalar objective function for the line search:

\[ \vartheta (\beta) \equiv -\overrightarrow{S} \cdot \nabla_{\beta} \langle H \rangle_w, \]  

(8.10)

where \( \overrightarrow{S} \) is the search direction (normalized to a length of 1) and the quantity \( \nabla_{\beta} \langle H \rangle_w \) with its subscript \( w \), indicates a reweighted calculation of the gradient at points along the direction of the line search. Note that the search direction does not need to be the same as the direction of the gradient (i.e., for a Newton's method approach). Note also that the scalar function \( \vartheta (\beta) \) changes sign as it passes through the smooth reweighted minimum along the search direction. Therefore, we employ a root-finding line search in the light-blue box to locate the zero of \( \vartheta (\beta) \) - rather than performing a minimization. In fact, we experimented around with various objective functions and line search methods and found that the one indicated in Eq. 8.10, in conjunction with a standard root-finding algorithm (see, for example, ref. [111]) works well.

Our choice of \( \vartheta (\beta) \) from Eq. 8.10 allows us to take advantage of the efficiency of the analytical gradient, an issue we discussed in detail in Section 8.7.2.

**Efficiency benefits of SGA computations**

Almost every VMC optimization method that works directly in the variational landscape (see Appendix A for important recent developments in VMC that do not work directly in the variational landscape) performs a line search. In the SGA, we recommend a root-finding line search that employs the function described in Eq. 8.10. However, regardless of the type of line search or the function it employs, all VMC optimization methods that utilize a line search must save the configuration points so that reweighting can be used (Section 4.7.2 discusses this in detail). This fact highlights one of the major benefits of performing calculations using the SGA algorithm, which we discuss here.

As we have emphasized throughout this chapter, stochastic methods do not require a highly accurate calculation of the energy at each variational step. They typically use a small number of sample points at each step. In contrast, standard VMC methods use
an increasingly large number of sample points per step. Generally, the number of sample points becomes so large that it is infeasible to store these sample points in computer memory (RAM). Instead, these sample points must be written to, and read from, the computer’s hard disk in order to perform the optimization. As an example, consider a simulation of a 78-electron system (such as Li$_{26}$) that utilizes 4,000,000 samples. (See ref. [47] for a typical example of a VMC computation that employs this many samples.) If each electron coordinate is stored in 8 bytes of memory, we have, for the necessary memory storage:

\[
\text{Bytes in memory} = 3 \cdot (\# \text{ electrons}) \cdot (\# \text{ samples}) \cdot (\# \text{ bytes per coordinate}) \quad (8.11)
\]

\[
= 3 \cdot (78) \cdot (4,000,000) \cdot (8) = 7,488,000,000 \approx 7.5 \text{ GB}.
\]

Generally, however, Eq. 8.11 is nonetheless an underestimate, because in addition to the electron coordinates, other numerical quantities such as $\ln |\Psi|^2$, the Jastrow factor, etc., are saved for each sample point as well. Therefore, the true amount of memory required is significantly more than indicated by Eq. 8.11. The process of reading from, and writing to the disk slows down the computation, as well as adding an additional layer in the code.

The SGA, on the other hand, requires very few samples per variational step - in our experience, $8 - 256$ samples is sufficient. The amount of required memory is completely negligible, no reading from or writing to the hard disk is required, and very little RAM is used. The SGA is a computer-friendly and server-friendly code which does not require careful memory management.

Similar and related benefits accrue from the SGA when considering parallelization, but in that case regarding the issue of computation time, rather than memory. In Section 8.9 we discuss the computational time required to prepare a standard VMC calculation in order to determine the number of required samples. A careful determination of the number of required samples per variational iteration is essential, and both consumes precious computer resources, and makes the calculation prone to making the wrong choice and thereby running the calculation inefficiently. As we discuss in Section 8.9, the SGA does not require a careful determination of the number of samples and is not subject to either of these disadvantages.
8.7.5 Quasi-Newton’s method search direction

In Section 8.7.2, we discussed Umrigar’s reduced-variance version of the analytical Hessian and analytical gradient. Within a stochastic QMC context, Umrigar’s reformulated version of the analytical gradient can be used with a quasi-Newton approach utilizing previous step information.

We take advantage of this new possibility to utilize the reformulated version of the analytical gradient and develop the SGA utilizing the quasi-Newton method. The reformulated analytical gradient also makes its appearance in the line search in the form of \( \theta \left( \beta \right) \) from Eq. 8.10.

Although we pursue the quasi-Newton method using the analytical gradient in this thesis, it would be worth pursuing the full Newton’s method using the improved analytical Hessian with the SGA to compare the rate of convergence. We suspect, however, that the benefit of building the approximate Hessian over a large number of SGA steps using the quasi-Newton approach will outweigh the benefit of using the improved Hessian at each single SGA step. Perhaps a powerful method would be to average the improved Hessian over multiple SGA steps. We have not pursued it here.

As a final note, we point out that we have made the choice to utilize the quasi-Newton’s method to obtain the search direction, rather than the direction provided by the Robbins-Monro theorem. Technically speaking, there is no proof of convergence in this case. However, it seems unlikely that it will not converge in the quasi-Newton case, which has historically been shown to provide an improvement on the search direction. We assume that the convergence conditions are met even in the quasi-Newton case. Of course, for our single-parameter optimizations the gradient direction will almost always be the same as the quasi-Newton direction.

8.8 Lower bound on the number of samples

As we have discussed, the SGA works in the limit of a small number of samples; however, we have given no discussion of what this limit is.
Use of the adaptive step algorithm provides a natural means to obtain a lower bound on the number of samples.

The lower bound can be obtained by choosing the lowest number of samples that allows the line search to succeed most of the time so that the projection mapping $\Xi$ of Eq. 8.9 is used infrequently. In the case of Li$_4$, for example, a value $N = 8 - 64$ samples is optimum.

Along these lines, it is reasonable to ask whether the choice of the number of samples noticeably impacts the efficiency of the SGA. In our experience, it does not. If we perform an SGA computation with 8 samples, the variational iterations proceed much more rapidly than if we perform the same computation with 64 samples. However, there is also more scatter in the SGA path. We have not noticed a significant influence on the overall efficiency within the range $8 - 64$. However, the optimization noticeably runs less quickly if we use a large number of samples per SGA step, such as 1,024. It is important that the SGA operate in the regime of a small number of samples. Within this regime, however, we have not performed a detailed study of the efficiency of the SGA as a function of the number of samples per SGA step.

### 8.9 Efficiency of the SGA with large clusters

Having laid the groundwork, we can now discuss the benefits of utilizing the SGA in calculations of large clusters, which take a very long time to run (hours, days, or months). In the case of clusters, the time it takes to perform a single calculation of the local energy drastically limits the number of QMC samples that can be evaluated. In such a case, it is essential to avoid overkill.

In general, in order to avoid overkill, it is necessary to introduce a preparation stage in VMC computations, in which the required number of samples per variational iteration is determined. It is, of course, desired to select the smallest number of QMC samples per variational iteration that yields good results. This is a tedious task requiring trial runs during the preparation stage.

As an example of the preparation stage, Umrigar [47] discusses a choice of the number of QMC samples required for a variational calculation. The first 6 iterations utilize 1,000
samples; the following 6 iterations utilize 4,000 samples, and the remaining 11 iterations utilize 4,096,000 samples. The sort of hands-on experimentation to determine the proper number of QMC samples required for different stages of the optimization is thoroughly impractical for cases in which, for example, a single trial run alone requires a week of equilibration time, as we required for Li$_{64}$. These difficulties, which involve a strain on computer resources due to time limitations, are directly related to the strain on computer resources due to memory limitations, discussed in Section 8.7.4.

The SGA solves the problem for the same reason it solves the problem in the case of memory limitations. Namely, the method does not require a careful selection of a large number of samples. It converges with a small number of samples per SGA step, without prior knowledge about either the number of samples or the length of time the simulation must run.

A determination of the proper number of samples $N$ per SGA step is therefore independent of the fact that these are very large clusters - no intensive preparation stage is necessary. It is only necessary to perform trial runs with a small number of samples and a small number of SGA steps.

It is enlightening to discuss the matter of the preparation stage by providing a listing that describes, in practice, the preparation stage required for a successful SGA calculation.
**SGA preparation stage**

(1) Define a reasonable set of boundaries for the variational parameters and select an initial guess.

(2) Perform a very small test run with a small number of sample points on one processor. For example, run 10 steps of the SGA with 64 samples per SGA step.

(3) Observe how many of the trial points remain in-bounds.

(4) If more than 2 or 3 out of 10 trial points go out-of-bounds, increase the number of samples per SGA step and go back to (2).

(5) If none of the trial points go out-of-bounds, decrease the number of sample points, if desired, and go back to (2).

(6) The optimum number $N$ of sample points has now been selected. Perform an SGA calculation.

### 8.10 Parallelization of the SGA

The SGA is nearly ideal for massive parallelization. We discuss this issue in detail in this section, and present our scaling results for the test case of Li$_4$.

Before discussing parallelization further, it’s worth stepping back to reiterate the distinction between QMC and VMC in this regard. Quantum Monte Carlo vanilla calculations are renowned as *embarrassingly parallel* because the processors can accumulate samples independently, without any communication between processors. Only at the very end of the calculation are the accumulated results (yellow box of Fig. 8-2) communicated to the root processor for a single, final calculation of the QMC integral across processors, Eq. 4.4. VMC calculations, on the other hand, are not embarrassingly parallel, because the processors need to communicate before, during, and after the line search (see Fig. 8-1).

There are typically two overall purposes for parallelization.

1. To perform calculations that are otherwise infeasible to perform on a single processor.

   The challenging Li$_{64}$ cluster, discussed in Ch. 7, is a good example. Considering deterministic calculations in this case, inefficiency on a single processor is typically
not exacerbated in proportion to the total number of processors. For example, \( \text{Li}_{64} \) requires about 1 second to perform a single calculation of the wave function \( \Psi \), so that the total computation can take weeks or months on a single processor. In order to perform this calculation using deterministic methods, we take a cue from calculations of smaller clusters to determine the required number of samples, and divide this total number of samples evenly between processors.

2. To increase the accuracy and detail of a calculation that can already be performed on a single processor. The \( \text{Li}_{4} \) cluster is a good example. Considering deterministic calculations in this case, we hope to improve upon the accuracy that can be obtained on a single processor by using the same number of samples for each processor and increasing the number of processors so that the total number of samples increases with respect to a single processor. The wasted time due to inefficiency in this case becomes exacerbated as the number of processors becomes larger and larger, because the wasted time is multiplied by the number of processors.

The excellent efficiency and scalability of the SGA in both cases can be explained in a simple way in terms of the trial points (Section 8.5). The sole purpose of the SGA is to fill the variational landscape with trial points. Each processor can provide a trial point independently, and therefore the variational landscape can be filled in a time that is almost exactly in proportion to the number of processors used for the calculation. No inefficiency is introduced.

In the Motivation section at the beginning of this thesis, we described the ideal balance for parallelization as follows:

The ideal balance for parallel processing is one in which each processor is able to benefit extensively from information available on other processors, and yet one in which this highly beneficial interprocessor communication is limited so that it consumes an optimum fraction of processing time.

The SGA satisfies this criteria because the core building block is the calculation of a trial point. The SGA method essentially scales in direct proportion to the number of
trial points that can be calculated in a given amount of time. This core building block - a calculation of the trial point - is an ideal bite-sized chunk, satisfying the criteria that each processor benefits extensively from information available on the other processors by updating the locus point at every SGA step based on the trial points across processors, and also satisfying the criteria that this communication across processors is limited because the time required to perform a single calculation of a trial point on an individual processor is sufficiently large.

In the remainder of this section we demonstrate the excellent scaling of the SGA with the number of processors by way of an example, the Li$_4$ molecule.

In order to demonstrate the parallelization we perform an optimization of only 1 Jastrow parameter. In general, the landscape for even 2 variational parameters is known to frequently possess multiple local minima of nearly degenerate energy near the global minimum and therefore is not a good test case to compare parallelization runs. See ref. [126], in which such an example has been carefully plotted.

We proceed by demonstrating parallel calculations that optimize the opposite-spin Jastrow factor. Figs. 8-7 and 8-8 compare a parallel calculation with 16 and 1,024 processors, respectively, running for the same number of iterations and plotted with the same scale for the vertical axis so that the smoothness and convergence can be compared. All runs employ 16 Langevin (i.e., Metropolis-like) samples per SGA step and employ the dynamic configuration-space step size algorithm discussed in Appendix G to maintain a Langevin acceptance ratio of 50%. (We discuss the issue of the acceptance rate in Appendix G.) We see that the run with 1,024 processors is much smoother than the run with 16 processors. We also see that the run with 1,024 processors locates the minimum value of 1.24(2) rapidly, in comparison with the run with 16 processors. But even the run with 16 processors, whose initial point is $\beta = 1.0$, moves fairly close to the minimum in just a few steps.

Shown in Fig. 8-9 is the same calculation of 16 processors as Fig. 8-7, but with almost 20,000 iterations shown, rather than 100. We can see that the 16 processor run approaches the optimum value eventually.

Fig. 8-10 is the key figure in the analysis of the scaling properties of the SGA with
Figure 8-7: An example SGA calculation for Li$_4$ with a single variational parameter, the opposite-spin Jastrow factor. This run utilizes 16 processors and 16 samples per processor per iteration. The first 100 iterations are shown.
Figure 8-8: Exactly the same SGA calculation as Fig. 8-7, but utilizing 1,024 processors. The same number of iterations (100) are shown. The scale of the vertical axis is exactly the same, so that the much more rapid convergence of the parameter towards 1.242 is revealed.
Figure 8-9: Exactly the same SGA run as in Fig. 8-7, except that almost 20,000 iterations are shown (requiring about 5 hours), indicating that eventually the 64 processor run arrives at the optimum point with similar accuracy as the much shorter run in Fig. 8-8 with 1,024 processors.
Figure 8-10: Scaling of the inverse of the time required to obtain a fixed accuracy for the variational optimization as a function of the number of processors. Linear scaling is the ideal result. The plot shows data for 16, 64, 256, and 1024 processors. The SGA exhibits outstanding scaling all the way to the limit of 1,024 processors.
respect to the number of processors. The figure shows the inverse of the time required to obtain a fixed accuracy $\sigma_m$ for the determination of the variational parameter. The accuracy was obtained as follows. About 10 runs each with 16, 64, 256, and 1,024 processors were performed. At any given iteration count, these different runs exhibit a scatter of the value of the variational parameter as determined at that iteration; the standard deviation of this scatter can be calculated. An arbitrary desired standard deviation was selected. The iteration count was adjusted for each set of runs until the standard deviation matched the desired standard deviation. Finally, the average amount of wall-clock time required for that number of processors (at that iteration count) was selected for the plot in Fig. 8-10.

A linear plot in Fig. 8-10 would represent ideal scaling. No parallel computation can scale better than a factor of $p$ in comparison to the time taken for a serial run, where $p$ is the number of processors, and the calculation results in an identical statistical accuracy. (The slope is irrelevant and simply represents the inverse of the time required for a single processor for this computation.) We see an excellent linear fit, all the way out to 1,024 processors, indicating that the SGA provides excellent scaling and is an ideal method to use for massively parallel calculations.

We conclude this section with two important technical points. First, there is a difference between a parallel SGA computation and a serial SGA computation, which has the potential to make the scaling of the SGA less than ideal when performing a computation utilizing more processors than we have tested (1,024). In a serial computation, the locus point is updated after every trial point is calculated. However, in a parallel computation, the locus point is updated only after all $R$ processors have calculated a trial point. Therefore, there is a bit of “lag” before the locus point is updated. However, as we demonstrate, this lag was insufficient to interfere with the excellent scaling up to 1,024 processors.

Second, it occasionally happens that a walker “gets cancer” during a QMC calculation; i.e. that due to the statistical fluctuations inherent in many-body wave function calculations, that an overflow occurs, despite all of the variance-reduction, transition function, and other improvements that have been introduced into QMC in order to minimize the risks that lead to this kind of problem. The problem occurs so rarely with modern QMC methods that, in
our experience, it is generally observed in only one out of thousands of walkers in a very long QMC or SGA computation. However, when it does occur in a parallel computation, the cancer can instantly spread to the walkers on every other processor, immediately ruining the entire computation. It is a simple matter, but absolutely necessary, to incorporate a check for overflow (i.e. a check for NaN) before combining the results across processors. If a walker does have cancer, it must be quarantined and permanently removed from the calculation.

8.11 Comparison of the SGA with deterministic methods

Typically, deterministic methods employ overkill at every variational step - i.e. they use more sample points than are necessary to perform the optimization to the same degree of accuracy, and therefore waste time and computational resources. During the line search, if the variational path is far from the minimum, there is no need to perform a calculation with an exceedingly large number of sample points in order to move properly towards the minimum. Only when the path moves close to the desired minimum is it necessary to ramp up the number of samples in order to distinguish nearly degenerate energies in this region.

Fig. 8-11 provides a conceptual picture to help understand overkill\textsuperscript{1}. In early line searches, such as (a) in the figure, rapid progress towards a better position can be made with a small number of samples, because energy differences along the search direction are relatively large. Once a better position has been found, a more detailed line search (b) can be performed by utilizing more samples. Note that (b) lies in a region very close to the minimum, in which energy differences are small.

The fact that the SGA avoids any overkill solves the problem of the need to carefully select the number of samples per variational iteration.

We now provide an example of a deterministic optimization. We employ QMcBeaver [41], a modern, up-to-date VMC code, to perform a deterministic energy-based optimization.\footnote{The example of the Hydrogen molecule energy grid that appears in Fig. 8-11 is adapted from the following talk. D. Nissenbaum, B. Barbiellini, and A Bansil, \textit{Simple geometry optimization with Variational Quantum Monte Carlo method}, American Physical Society, APS March Meeting, March 21-25, 2005, abstract A32.00009.}
Figure 8-11: A graphic with two sample line searches to help understand the inefficiency associated with overkill in a VMC optimization. When the starting point - such as (a) - is far from the minimum, a relatively small number of of samples are necessary to move along the search direction towards the minimum, because energy differences along line (a) are relatively large. In contrast, when the initial point - such as (b) - is close to the minimum, a larger number of samples is required to move a correspondingly shorter distance along the search direction, because energy differences in the region surrounding the minimum are small. The background energy grid is that of H$_2$, with the Jastrow parameter and the nuclear separation as variational parameters.

We perform an optimization that can be compared with the SGA calculation of Li$_4$ shown in Fig. 8-3. The calculation shown in that figure includes about 1,500 iterations, with 16 samples per iteration, for a total of about 24,000 samples. Therefore, we chose to perform our deterministic comparison with 32,768 samples per iteration, which will outperform the SGA computation of Fig. 8-3 if it runs long enough. The calculation in Fig. 8-3 required about an hour. We therefore ran our deterministic comparison on the same machine for the same amount of time as the run shown in Fig. 8-3, for the sake of comparison.

The results are plotted in Fig. 8-12. The blue line shows the characteristic deterministic optimization. The curve is smooth and makes steady progress towards the minimum. However, notice the phenomena regarding overkill that was represented in Fig. 8-11. The initial location of the parameter is far from the minimum and does not benefit from the large number of sample points that were used during the line search at that point. Therefore,
Figure 8-12: A comparison of a deterministic computation and an SGA computation. The SGA computation is the same as that shown in Fig. 8-3. The data is shown plotted against the wallclock time for the calculation. Units of time have been slightly scaled but roughly represent an hour. The total number of samples used during each step of the deterministic computation (32,768) is about 50% greater than the total number of samples used for the complete SGA computation (22,400). The deterministic computation was performed using the state-of-the-art QMcBeaver code. The limiting value of $\beta = 1.24$ has not yet been achieved even by the stochastic optimization; compare to Figs. 8-9 and 8-7, in which it is evident that the stochastic optimization requires 64 processors running for a comparable amount of time to obtain the minimum. The data of this example employs only 1 processor.
the method converges slowly.

An astute reader might have noticed that this is a one-dimensional optimization, and therefore the search direction must pass directly through the minimum, unlike line (a) in Fig. 8-11. However, as Fig. 8-12 shows, even one dimensional deterministic optimizations are not free of the difficulties involving overkill. In this case, the reason is twofold. First, reweighting must be employed during the line search (see Section 4.7.2). The farther the initial point of the line search is from the minimum, the greater the reweighting bias, which causes the line search to land at the wrong point along the search direction.

Second, the line search requires a stopping condition (i.e., a condition that determines when the line search has located a point along the search direction that is satisfactory), an issue we have not discussed in this thesis. Stopping conditions for the line search are non-trivial, and a number of different ones exist, each with advantages and disadvantages [110]. Line searches must strike a balance between accuracy and efficiency. QMcBeaver uses the Wolfe conditions [110] for the line search, which tend to err on the side of efficiency rather than accuracy. A more accurate line search stopping condition would tend towards the minimum more quickly, but it would also cause the line search to run slower, which would be reflected in Fig. 8-12 by fewer iterations during the hour-long run.

8.12 A final example

Now that we have discussed in detail the concepts of the trial points, the SGA path, and the analytical energy gradient, let us present the data from another SGA computation with an eye to highlighting these distinct features. Fig. 8-13 shows an SGA calculation of the identical system as in Fig. 8-5, but with a different random-number seed. Shown in the plot are the first 500 steps. The plot does not, of course, look identical to the one in Fig. 8-5, but similar phenomena can be observed, particularly the fact that the trial points are clustered along the line of the analytic energy gradient near the minimum.

Fig. 8-14 shows steps 22,000 – 23,000 of the same computation, after the simulation has run for about 24 hours. The figure reveals that the analytical energy gradient tends to be very accurate once the SGA path has converged close to a minimum. This figure clearly
Figure 8-13: The first 500 SGA steps in a calculation of the same system as shown in Fig. 8-5, but with a different random number seed. The trial points are shown in green. The locus points are shown in red.
Figure 8-14: The same SGA run as shown in the previous figures, but showing steps 22,000–23,000, after the simulation has run for about a day. The figure clearly demonstrates that the analytical energy gradient is calculated accurately even for a very small number of sample points. The trial points (green dots) each represent a calculation with only 16 samples. The locus points (red dots) all lie at a local minimum. The internal structure of an SGA computation can clearly be observed in this figure.
Figure 8-15: The data corresponding to the final points of Fig. 8-14. The left pane shows the trial points (green) and the locus points at the minimum (red). The right pane zooms in on the locus points.

reveals the internal structure of an SGA computation.

Fig. 8-15 zooms in on the final locus points of Fig. 8-14. Notice the tightness of the scale. This figure clearly shows the accuracy of the analytical gradient. It can be observed that as the SGA run proceeds, the locus points slowly drift in the direction of the gradient attempting to locate the energy minimum. Compare this figure to Fig. 8-6, which demonstrates a rapid convergence toward the \textit{variational} minimum, followed by a slow convergence towards the energy minimum.
Chapter 9

Outlook

This work allowed us to understand and develop concepts involved with detailed, \textit{ab-initio} calculations by working directly in the many-body space that includes all the electrons. The ability to include all or many electrons in a molecule, a computationally very intensive procedure, and yet at the same time study large nanoclusters and more realistic wave functions, is an exciting pursuit that will allow us to understand the physics of nanostructures to a degree not possible previously. In particular, massive parallel computer resources continue to develop and evolve, and making the most efficient use of these resources is no small task.

In this work, we have focused on Li clusters and quantum dots, which are actively being studied today due to their potential in various aspects of photovoltaics, computers, hydrogen storage, and batteries.

We have focused our work on developing efficient Quantum Monte Carlo stochastic methods that allow us to utilize massive servers and study large clusters more easily. However, the work has had its pitfalls. In particular, we had to understand and overcome the nature of the scaling of the autocorrelation time for large clusters (Ch. 7), and various impediments that interfered with the effectiveness of the SGA (Ch. 8). In retrospect it is clear what issues were the most important to fully utilize the SGA; these issues are listed in Section 8.2.

Having developed the method and demonstrated its outstanding scaling abilities, a number of areas are ripe for research that can take advantage of the SGA.
9.1 RVB, JS, and zeta parameters

In particular, we devoted some time to coding the SGA to optimize the zeta parameters, the Slater molecular orbital coefficients (Ch. 3), and the RVB parameters (Ch. 6). However, we did not complete this work. We ran into the following issue: in general, the molecular orbital coefficients and different zeta parameters influence the energy at different scales. Steepest-descent style optimization fails in such cases, whereas the quasi-Newton’s method has been shown to have robust self-correcting properties for poorly scaled parameters (see ref. [110], p. 142).

Unfortunately, during our initial development of the SGA, we did not utilize either the quasi-Newton’s method or the full Newton’s method to obtain the search direction, but instead utilized a steepest-descent search direction. This failure to consider multiply-scaled parameters - our use of steepest descent - during development of the Slater molecular orbital and the RVB optimization may have impeded this development. We are now ready to pursue optimization of a large number of parameters using the SGA with the improvements described in Ch. 8.

9.2 Geometry optimization

Another important endeavor regards geometry optimization. The SGA - as an energy minimization method - could be applied for this purpose. The analytical energy gradient, as discussed in Section 4.13 and as formulated in Eq. 4.29, cannot be used for geometry optimization. However, by using the new Hellman-Feynman variance-reduction methods discussed in Section 8.7.2, we could apply the SGA in this case. Conceivably, the SGA could be used on massively parallel servers to perform detailed, ab-initio calculations of cluster geometries. It was our hope to accomplish some of this work in time to include it in this thesis; we believe this is one of the most promising possibilities for the SGA.
9.3 Natural orbitals

We are excited to pursue work with the natural orbitals that can be obtained with the RVB wave function. As discussed in Section 6.3, only recently have computer hardware and software infrastructures allowed the RVB to be solved using QMC methods. We believe that the possibility of utilizing a basis of natural orbitals (Sections 6.9 and 6.10.3) could provide an important and rich addition to our understanding of the physics of nanomaterials.

By working in this basis of natural orbitals, we could minimize the number of variational parameters in the problem. In this way, we could overcome the challenges of an RVB optimization not by computational horsepower, but - we propose - by utilizing the Hartree-Fock orbitals as the starting guess for the natural orbitals.

9.4 Isolating variational parameters by the inclusion of statistical error bars

During our studies of the RVB wave function, it would have been helpful if there were a statistical accuracy, or error bar, associated with the parameters during the optimization. Despite the presence of the Jastrow factor, the RVB wave function is highly sensitive to changes in some of the parameters, and not very sensitive to changes in others. It is difficult to distinguish between the relevant parameters, and those that are less relevant. Providing statistical error bars would solve this problem. Those parameters with large statistical error bars are not as relevant for the optimization. In Appendix C we discuss a promising method to determine these error bars. We suggest that by solving the Fisher equations (Appendix C) we could obtain, for the first time in QMC, a statistical accuracy associated with the variational parameters.

9.5 Nodal structure effects of VMC optimization

Along these lines, QMC studies rarely report the dependence of the energy on the variational parameters - if they report the optimum variational parameters at all. The SGA has
Figure 9-1: The energy grid shown in this figure is an example of data obtained from a computationally intensive calculation. Such intensive calculations generally cannot be performed within VMC. However, the inclusion of statistical error bars with variational parameters could allow typical SGA calculations to determine relevant regions within the energy landscape. Sample points within these regions along the direction of the energy gradient could be hand-picked for DMC calculations to determine the influence of the variational landscape on the nodal structure of the wave function. This figure provides an imaginary example of this concept by shading in red those regions that might be selected for detailed DMC calculations. The figure shows that we might choose to represent regions with a heavy nodal structure dependence in a darker shade of red. (The energy grid for this plot represents Li clusters and is taken from ref. [126]. It includes a Jastrow parameter along the horizontal axis and a molecular orbital coefficient along the vertical axis.)

allowed us to determine the optimum variational parameters to great accuracy; see Section 8.10. We are now able to determine the energy efficiently in a very tight grid surrounding the minimum point in order to establish the required necessary accuracy for the variational parameter; see Table 14.1. Providing a good sampling of such cases for the QMC community would assist researchers by providing a sense of the energy gains involved and the corresponding required accuracy of the variational parameters. There are currently few such published studies.

Furthermore, by including statistical error bars with variational parameters, it would be possible to develop a detailed nodal structure analysis by intelligently selecting relevant points in the variational landscape, based on the error bars, for DMC computations. This would allow us to determine the influence of the variational wave function on the nodal landscape, as measured by the corresponding energy differences of the DMC calculations.

Fig. 9-1 shows an imaginary example of the simple way that the nodal structure landscape might be represented using this method. The energy grid that forms the background
of the figure is taken from ref. [126]. Such a detailed energy landscape cannot realistically be performed with most VMC calculations. However, the relevant regions of such an energy landscape could be determined in typical SGA calculations by including statistical error bars associated with the variational parameters. These error bars would substitute for the energy landscape by determining relevant ranges of variational parameters surrounding each minimum. A small number of points within each region could be selected for detailed DMC computations to determine the corresponding influence on the nodal structure. Note that the points selected for the DMC computations would be chosen along the direction of the steepest gradient. The figure shows that the results of the DMC calculations could be represented by darker shades of red around those regions with a heavier nodal structure dependence.

In this context, note that changes of variational parameters that lead to significant changes in the variational energy do not necessarily lead to any improvement in the nodal structure or the DMC energy. A good example is provided by the Jastrow parameters. Because the Jastrow factor is positive everywhere, it has no impact whatsoever on the nodal structure, and therefore changes in the Jastrow parameters that lead to a significant improvement in the energy nonetheless leave the DMC energy and the nodal structure unchanged. The Jastrow parameters only indirectly influence the nodal structure and the DMC energy during a variational optimization, by allowing for variational improvement of the other parameters (such as the molecular orbital coefficients). The example of the Jastrow factor demonstrates the importance of understanding the relationship between the variational landscape and the nodal landscape, as suggested by the method we propose in Fig. 9-1.

Such plots of the nodal structure dependence on the energy landscape would be a valuable tool, both for understanding the relevant physics represented by the variational parameters, and to help guide VMC computations to isolate true nodal structure improvements and to understand the corresponding impact on the total DMC energy.
9.6 Comparing variational approaches with a universal measure of efficiency

In Appendix E, we propose a universal measure of efficiency $\alpha$ that would be helpful to compare and contrast the efficiency of different variational methods. Because the last 5–10 years have seen a rapid and confusing increase in new and complicated QMC variational methods, with many overlapping and disparate approaches, we believe that utilizing a universal measure of efficiency to compare any such methods on the same footing would be valuable. This would extend the work of, for example, ref. [127], in which three VMC energy minimization methods are compared.

9.7 Multiscale phenomena and autocorrelation

We are also excited to pursue more detailed studies of the autocorrelation function for different systems, examples of which are shown in Fig. 7-7 and Fig. 7-9. Fig. 7-9, in particular, reveals a fascinating structure that shows promise in understanding and describing multiscale phenomena. Specifically in this case (water), we would like to understand what physics is represented by the oscillation in the concavity of the plot of Fig. 7-9 at different length scales.

9.8 Equilibration studies on massively parallel servers

The cost of equilibration is exacerbated in parallel computations and severely handicaps the feasibility of studying large clusters. A determination of the required equilibration time is non-trivial, as discussed in Section 7.2.1. The equilibration plot of Fig. 7-2 is preliminary. To date, there is no good study of, or repository of, information describing the amount of time required to equilibrate different clusters. Obtaining a variety of detailed plots such as Fig. 7-2 and the corresponding exponential decay plot of Fig. 7-4 would allow researchers to perform QMC calculations of large nanoclusters and be able to carefully determine the necessary equilibration time with confidence.
Figure 9-2: Six different SGA runs are plotted on the same graph. In this case, two variational parameters were optimized - the opposite-spin (horizontal axis) and same-spin (vertical axis) Jastrow factors. The dark blue and green runs correspond to 64 processors running for about an hour. The remaining runs correspond to 1,024 processors running for about 4 minutes. The figure reveals possible multiple, nearly degenerate local minima. This figure should be compared with Fig. 9-1, in which the complexity of the variational landscape even with 2 parameters is revealed with a direct energy grid.

In order to construct the equilibration plot, the computation must be performed in massively parallel mode. This study therefore is a promising use of server technologies such as the ones made available by NERSC.

9.9 Global minimization

The SGA, like other stochastic algorithms, has excellent potential to distinguish the global minimum from among multiple, nearly degenerate local minima. It is known that the variational landscape, even for 2 parameters, tends to have multiple, nearly degenerate local minima. Fig. 9-1 shows an example, taken from ref. [126]. We would like to pursue a detailed analysis of the nature of these local minima, the energy scales involved, and how effectively the SGA can discern these differences.

Fig. 9-2 shows six preliminary parallel SGA calculations that we performed for Li$_4$ with two variational parameters, the opposite-spin and the same-spin Jastrow parameter. The figure reveals that multiple local minima seem to exist in the variational landscape. We would like to construct an energy grid for the variational landscape of Fig. 9-2, similar
to the example energy grid in Fig. 9-1, in order to confirm the existence of multiple local minima, and in order to determine how long it takes the SGA to migrate from one local minimum to the next until it locates the global minimum.

These results could be applied, for example, in geometry optimization, to distinguish ground-state structures between nearly degenerate possibilities. More generally, a deeper understanding of global minimization, utilizing stochastic methods in sample cases, would be of interest across a variety of fields.

9.10 Improved deterministic methods

In Section 8.11, we directly compare deterministic methods and stochastic methods. However, we did not test the deterministic methods in parallel mode, and we did not test the deterministic methods by varying the number of sample points per iteration. Furthermore, we have not yet developed our code to allow for the best possible deterministic calculations. It would be useful both to develop our code along these lines, and to run QMcBeaver or other codes (such as Zori) with more detailed calculations and in parallel mode, to compare and contrast deterministic methods and the SGA.

9.11 Open-source, object-oriented code base and GUI

Finally, over the time involved in this research, the SGA code has been re-written a number of times. In addition, we have utilized two other bodies of object-oriented, C++ QMC code - QMcBeaver [41] and Zori [128]. Both of these have their strengths and weaknesses, as does our code. An attempt to continue the development of truly successful C++ open-source code that might someday become a standard in the field - such as Zori or QMcBeaver - is something we’d like to pursue. In particular, we’d like to introduce a set of objects that exactly reflect the flow chart in Fig. 10-1 of Appendix A.

During the initial course of this work we also developed a useful graphical user interface (GUI) on Windows for VMC code. This GUI has fallen by the wayside, and in the future it would be useful to use open source graphical tools such as OpenGL to develop a user
interface so that QMC calculations will be easily accessible to more researchers.

The most recent QMcBeaver code [41] has begun to implement the Hierarchical Data Format (HDF) [129] for temporary and permanent data storage (i.e., data that is written to and read from the hard disk). The HDF data model is a protocol designed for scientific computations and data exchange. It is somewhat analogous to XML. We believe that the lives of physicists, and the efficiency and value of research, would be improved if physicists adopted a universal method of storing and sharing scientific data. We would like to encourage the use and development of HDF in scientific research.
Chapter 10

Appendix A: Modern VMC methods in context

The past few years have seen a watershed in the development of new VMC methods. The current methods aren’t “what you learn in computational physics 101” any more.

Given the somewhat bewildering state of the field of the new developments in VMC today, this appendix provides an overview of the developments in the context of the flow chart we used in Ch. 8.

We enhance Fig. 8-1 to include two radically new and transformational methods that have been introduced into Variational Monte Carlo in the past few years, one of which (Stochastic Reconfiguration) we used in the optimization of the RVB discussed in Ch. 6.

The new methods fall into one of two general categories, the Effective Fluctuation Potential (EFP) methods and methods involving expansion of the wave function in a Hilbert space of relevant basis functions. Both methods correspond to new developments within the orange, green, and light blue boxes in Fig. 10-1.

Both new methods we now discuss have transformed variational quantum Monte Carlo by operating in the metric of the underlying Hilbert space of the problem, rather than in the configuration space of the electrons. These methods are able to discern the relevant differences between points in the variational landscape as differences in a constructed set of
Figure 10-1: Schematic of modern-day QMC variational algorithms. See text for full details.
basis vectors which capture the relevant effects.

If the basis vectors were known ahead of time, the variational problem would already be solved. Because the vectors are not known ahead of time, the essential problem for these methods is to reconstruct a useful set of basis vectors. The problem is therefore the reverse of a typical quantum mechanical problem. In a typical problem, basis vectors are known ahead of time, and from these basis vectors the coefficients of the desired function are determined. In the present case, instead, it is the function that is known ahead of time, and the relevant basis vectors are determined in the QMC calculation.

The first category of the new energy minimization methods involves a decomposition of the local energy of the wave function into basis functions, rather than the wave function itself. In the second category, the function being decomposed is the wave function itself.

**Effective Fluctuation Potential methods**

Instead of calculating derivative information, Effective Fluctuation Potential (EFP) methods attempt to perform a least-squares-fit (LSF) of the local energy with an effective many-body potential energy function. In order to accomplish this, at each variational step these methods all perform the calculation given by

\[
\langle \Psi \mid \left\{ H - E_0 - \sum_{k=1}^{B} V_k O_k \right\} \mid \Psi \rangle, \quad (A.1)
\]

where \( E_0 \) and \( V_k \) are numerical parameters to be determined at each variational step, \( B \) is the number of variational parameters in the wave function ansatz, and \( O_k \) is some local operator. \( E_0 \) and \( V_k \) are chosen to minimize the integral. Because \( E_0 \) and \( V_k \) are not themselves local quantities, the set \( \{ O_k \} \) need only be calculated once in a QMC calculation during each variational step (orange box), whereupon \( E_0 \) and \( \{ V_k \} \), the trial parameters, are calculated directly in the light-blue box (no search direction required) by solving what turn out (due to the Euler-Lagrange equations) to be an equivalent set of linear equations typified by

\[
\sum_{k=1}^{M} V_k \langle \Delta O_k \Delta O_l \rangle = \langle \Delta E \Delta O_l \rangle, \quad (A.2)
\]
where $\Delta O = O - \langle O \rangle$, $\Delta E = E - \langle E \rangle$, and $\langle \ldots \rangle$ represents a sum over the configuration points of the sample. It is the approximation of the quantities in Eq. A.2 that requires the QMC calculation.

Once $E_0$ and $\{V_k\}$ have been solved, the function $\tilde{V} = \sum_{k=1}^{M} V_k O_k$ acts as an effective potential energy perturbation that is added to the true (original) potential function $V$ for the system. At this point, different methods, depending on the variational parameters involved, are used to recalculate the variational parameters of the wave function utilizing the new effective potential $V + \tilde{V}$. This recalculation corresponds to the light-blue box in Fig. 10-1.

Currently, three types of variational parameters have been developed with the EFP method.

The first are the single-particle molecular orbital coefficients of the Slater determinant. To determine these, standard HF or Local Density Approximation (LDA) calculations are employed, using $V + \tilde{V}$ in place of $V$. (See ref. [130]).

Second are the Jastrow parameters. For these, Prendergast, Bevan and Fahy show how to perform a linear expansion of the Jastrow parameters and obtain an additional set of linear equations, the solution of which provides the new Jastrow parameters (see ref. [131]).

Finally, the parameters of a multideterminant CI-like calculation have also been incorporated into the EFP method. (See ref. [132]).

A key component of all of these methods is the proper selection of the set $\{O_k\}$. Some of the genius of the methods lies in this choice. For the first case, the set $\{O_k\}$ is chosen as an approximate estimate of the local energy function by observing the limiting behavior of this function at points near and far from the nuclei. For the second case, the set $\{O_k\}$ is chosen as the logarithmic derivative of the wave function with respect to the Jastrow parameters (i.e. the derivative of the Jastrow exponent; see Section 3.5). The third case is somewhat complicated and the reader is referred to the reference provided above for details.
Generalized eigenvalue methods

The second of the modern VMC energy minimization methods attempts to recreate a set of generalized many-body basis functions corresponding to a generalized eigenvalue problem associated with the wave function \textit{ansatz}. The basis functions are chosen to be the derivative of the wave function (or its logarithm) with respect to the variational parameters (similar to the second EFP method, above), which is equivalent to linearizing the wave function. The method then performs a QMC calculation of the Hamiltonian, Density, or related matrix elements with respect to these basis functions (\textbf{orange box}).

Once the matrix elements have been calculated, the matrix is diagonalized and, depending on the method, the solutions provide either the search direction in the variational landscape (\textbf{green box}), or both the search direction and trial point (\textbf{green} and \textbf{light blue box}). The latter case is exemplified by the Stochastic Reconfiguration (SR) method (see refs. [133, 134]), which we used in the optimization of the RVB wave function in Ch. 6. The former method is exemplified by very recent work of Umrigar (see ref. [1]). To calculate the trial point, the Umrigar method involves a sophisticated determination of the basis function normalization constants. The SR method is a special case of the choice of normalization constant.

Both the EFP methods and the generalized eigenvalue methods isolate the relevant physical differences between different variational parameters by a selection of basis functions and their coefficients. This allows the configuration points to sample only the relevant regions the most effectively. Fundamentally, the methods work in the Hilbert metric of the system, rather than in the configuration metric. These new energy minimization methods are able to work as efficiently as variance minimization methods, but they are only now starting to be fully developed.
Chapter 11

Appendix B: Statistical accuracy of the analytical gradient

We discuss in this appendix the difficulties involving a determination of the statistical accuracy of the analytical gradient used as the objective function in the SGA (see Section 8.2).

A straightforward (but incorrect) calculation of the statistical error of the analytical gradient might proceed as follows. From Eq. 8.8, defining \( \Psi' \equiv \frac{\tilde{\nabla}\cdot\nabla \Psi}{\Psi} \), we see that the local quantity being averaged in the QMC calculation is

\[
\hat{O}_L = E_L \Psi' - \mathcal{E} \Psi',
\]

where we write \( \mathcal{E} \) in the place of \( \langle H \rangle \). To obtain the statistical accuracy, one calculates the value

\[
\sigma_{\hat{O}_L} = \frac{\sqrt{\langle (\hat{O}_L - \langle \hat{O}_L \rangle)^2 \rangle}}{\sqrt{N}}. \tag{B.1}
\]

However, this quantity assumes that the expectation value is the exact expectation value utilizing an infinite number of sample points. In Umrigar’s reformulated expression of the analytical gradient, Eq. 8.8, as we the subscripts \( w \) indicate, the expectation value must be taken with respect to the finite number of samples \( N \). However, as a result, the law of
large numbers - which is the foundation of formulas for statistical accuracy such as Eq. B.1 - does not hold, and therefore Eq. B.1 does not hold.

However, the entire purpose of the reformulation is to make the quantity much more accurate, and in practice we have found that works extremely well.

The fact that we do not at this time have at our disposal an expression for the statistical accuracy of $\frac{\nabla}{\beta_i} \langle H \rangle$, however, means that we cannot supply or utilize error bars with this quantity. One author [112] performed a direct calculation of $\frac{\nabla}{\beta_i} \langle H \rangle$ in the case of a simple harmonic oscillator (without utilizing Eq. 8.8) and included error bars in a plot of this quantity, demonstrating directly in this case that the statistical accuracy of $\frac{\nabla}{\beta_i} \langle H \rangle$ allows for much more rapid convergence using this quantity, than convergence utilizing $\langle H \rangle$ with its much larger error.
Chapter 12

Appendix C: Statistical error bars for variational parameters

There are no error bars associated with the variational parameter in Fig. 8-3 or Fig. 8-4 (or the other figures that plot the variational parameter/s), and this is typical for plots of variational parameters; see ref. [135] for an example. It is worth noting here that the authors in ref. [135] perform an after-the-fact averaging of variational parameters, which is conceptually similar to the stochastic approach, but not equivalent.

In contrast, the SGA provides the possibility of incorporating statistical error bars for the variational parameters, because stochastic methods fundamentally incorporate the stochastic nature of the optimization. This is an exciting possibility.

Before we proceed with the technical details, it is worth contrasting the stochastic case with the deterministic case. Deterministic methods do not provide a statistical error bar associated with the optimum parameter, because there is no stochasticity involved with these methods. Deterministic methods take advantage of the fact that convergence occurs in a small number of steps (see refs. [136, 47, 1] - all on the order of 10 iterations), with the rate of convergence described by the heavy iterative formula given in Eq. C.1, below. This formula describes convergence only in terms of the preceding step, as befits a deterministic method. It works in the regime of a small number of iterations $p$, and assume that the trial points and the locus points are equivalent. Convergence is represented as a fraction of the
preceeding iteration’s convergence and the large-$p$ regime is never reached.

We now proceed to discuss the mathematical equations that must be solved in order to determine the statistitical error bars in an SGA calculation.

### 12.1 The Fisher information matrix

Stochastic optimization methods fundamentally account for the fact that the final result is associated with a statistical accuracy. However, this has not yet been considered in QMC. The statistical error associated with the variational parameters in a VMC calculation is analogous to the statistical error associated with the energy in a QMC calculation. Deterministic optimization methods do not supply a statistical error, because they fundamentally assume that there is no statistical error associated with the evaluations of the objective function. However, deterministic optimization methods do provide a formal rate of convergence.

We first provide the deterministic rate of convergence. Each point in the path is determined exclusively from the single preceeding point, which is always considered the best current estimate. Therefore, the rate of convergence is given exclusively in terms of the preceeding point and is independent of the number of steps in the variational walk. For deterministic optimization (in the case of the quasi-Newton’s method), we have

$$
\| \beta_{p+1} - \beta_{\text{exact}} \| = c \| \beta_p - \beta_{\text{exact}} \|^2 \quad \text{(deterministic)},
$$

where $p$ is the iteration count, $\beta_{\text{exact}}$ is the value of the parameter at the optimum point in the variational landscape, $\beta_p$ is the estimate of the optimum parameter after iteration $p$, and $c$ is a constant. The equation applies exactly only in the region that the function can be approximated as quadratic, but in practice this region is discovered in only a handful of iterations. Eq. C.1 states that the closeness of any step to the exact value is amplified in quadratic fashion in the next iteration [6].

In the case of stochastic optimization, the matter is very different. In this case, all preceeding steps are employed (or some number of them) to determine the rate of convergence,
and the measure of convergence is not given in the form of Eq. C.1. Instead, due to the stochastic nature of the walk, the only possible way to express convergence information is in the form of a statistical estimate; in particular, we have

\[ \overline{\beta}_p - \overline{\beta}_{\text{exact}} \rightarrow \frac{1}{p^2} \text{Normal} \left( \overline{0}, \overline{F}^{-1} \right) \text{ (stochastic)}, \]  

\[ \text{(C.2)} \]

where \( p \) is the SGA step number, \( \overline{\beta}_{\text{exact}} \) is the value of the parameter at the optimum point in the variational landscape, \( \overline{\beta}_p \) is the estimate of the optimum parameter after iteration \( p \), the arrow indicates that the quantity on the left hand side approaches \textit{in distribution} the quantity on the right hand side as \( p \to \infty \), the right hand side represents a \textit{Gaussian} or normal distribution centered on \( \overline{0} \), \( \overline{F}^{-1} \) is the matrix inverse of the “average” Fisher covariance matrix \( \overline{F} \) (defined momentarily) across all \( p \) SGA steps, and the equation holds only in the case that the step size approaches the optimum selection of step size (provided shortly) in the limit \( p \to \infty \). (See ref. [6], pp. 95-114 and 349-364, and references therein, for a full discussion of the material in this section.) The concept of a \textit{normal distribution} for a \textit{vector} quantity might be less familiar to some readers than the concept of a normal distribution for a \textit{scalar} quantity. In the case of a normally-distributed scalar random variable, the variance of the normal distribution is also described by a scalar quantity. However, in the case of a normally-distributed \textit{vector} random variable, the normal distribution can be described by a \textit{covariance matrix}. This appendix will not provide a review of the statistics involved; see ref. [137] for an introduction, and see ref. [6], p. 358, for more details.

The optimum step “size” required as \( p \to \infty \) in order for Eq. C.2 to hold is given by

\[ A_p = \frac{\left( \frac{\partial^2}{\partial \beta_i \partial \beta_j} \langle H \rangle \right)^{-1}}{p + 1}, \]

\[ \text{(C.3)} \]

where \( \left( \frac{\partial^2}{\partial \beta_i \partial \beta_j} \langle H \rangle \right)^{-1} \) is the matrix inverse of the Hessian matrix of Eq. 4.31 evaluated at the optimum value, \( \overline{\beta}_{\text{exact}} \), which we assume to be well approximated by the average over the \( p \) SGA steps, as recommended in ref. [6]. Note that the optimum step “size” is, in this case, a matrix, rather than a scalar; a matrix is a legitimate object for the quantity.
That appears in Eq. 8.1. With the SGA, we would approximate the Hessian using the quasi-Newton method, or by direct calculation using the approach of Umrigar discussed previously [47].

The Fisher Information matrix $F$ is defined as

$$F \equiv \int \frac{\partial \log \ell}{\partial \beta} \cdot \frac{\partial \log \ell}{\partial \beta^T} \ell d\zeta,$$

where $\beta$ is considered a row vector and $\beta^T$ its transpose in order that the quantity $\frac{\partial \log \ell}{\partial \beta} \cdot \frac{\partial \log \ell}{\partial \beta^T}$ be a matrix, and where the likelihood function $\ell$ is the same as a probability function with the arguments reversed:

$$\ell(\beta | \{\langle H \rangle_N\}_p) \equiv P\left(\{\langle H \rangle_N\}_p | \beta\right).$$

In Eq. C.5, $\{\langle H \rangle_N\}_p$ is a set of $p$ local energy estimates, each performed with $N$ QMC samples (see Eq. 7.2); the function $P$ represents a distribution (histogram) that describes the relative likelihood of obtaining different sets of $p$ estimates of $\langle H \rangle_N$ with $N$ samples per estimate at fixed $\beta$ (conditioned on $\beta$). In other words, $P$ is the relative probability of obtaining a particular set of $p$ results $\{\langle H \rangle_N\}_p$. We have defined $\zeta \equiv \{\langle H \rangle_N\}_p$ - a set of $p$ estimates $\langle H \rangle_N$ at fixed $\beta$ - for convenience. The likelihood function $\ell$ is the same function $P$ with a reversal of conditioning, so that $\ell$ is considered to be the probability distribution for $\beta$, conditioned on $\{\langle H \rangle_N\}_p$. We discuss the interpretation of the integral in Eq. C.4 shortly; we shall see that $F$ is a function of $\beta$ and $p$, which we write as $F_p(\beta)$, with the conditioning on $\{\langle H \rangle_N\}_p$ removed because of the integration, as we shall see. $F$ is also implicitly a function of the number of samples $N$ per estimate within each set of $p$ estimates; the dependence on $N$ is not included in the label. The average $F$ is defined [6] as

$$F \equiv \lim_{p \to \infty} F_p(\beta_{\text{exact}}).$$

For a stochastic optimization, the values $\beta_p$ converge to $\beta_{\text{exact}}$ as $p \to \infty$. According to ref. [6] (p. 356), it is generally safe to calculate $F$ by assuming that all $p$ SGA steps
occur at the optimum value $\beta_{\text{exact}}$. The value of $p$ is therefore set equal to the number of SGA steps.

Given a set of reasonable assumptions that are provided in the reference (see ref. [6], p. 352), it can be shown that the Fisher matrix $F$ is given by

$$F = -\int \frac{\partial^2 \log \ell}{\partial \beta \partial \beta^T} T d\zeta. \quad (C.7)$$

The discussion thus far has provided a review of the necessary technical background of stochastic optimization theory; all of the preceding material can be found in ref. [6]. At this point we switch gears and provide a discussion of the possible application of these ideas in the case of stochastic optimization in a variational Quantum Monte Carlo context. This is preliminary work that has not yet appeared in QMC literature. We have not completed the analysis in this appendix. However, in the remainder of the appendix, we provide a roadmap. If the work can be completed, it will allow a determination of the rate of convergence described by Eq. C.2 in the case of variational QMC, and thus enable us to obtain the statistical accuracy for the variational parameters during an SGA computation.

First, we discuss the integration over $\zeta$ that appears in Eq. C.4 and Eq. C.7. The integration over $\zeta$ removes the conditioning on $\{\langle H \rangle_N \}_p$ by integrating over all possible sets $\{\langle H \rangle_N \}_p$, so that $F$ is a function of $\beta$ and $p$, but no longer conditioned on $\{\langle H \rangle_N \}_p$. Following the examples provided in ref. [6], we analytically construct the function $\ell \left( \beta \mid \{\langle H \rangle_N \}_p \right)$ (given in detail shortly), interpret the integral in either Eq. C.4 or Eq. C.7 as a $p$-dimensional integral over a set of $p$ different values $\langle H \rangle_N$, and assume that this integral can be analytically calculated. The average Fisher information matrix from Eq. C.2 is then computed as discussed above - namely, by setting $p$ equal to the number of SGA steps and assuming that all SGA steps occur at the optimum value $\beta_{\text{exact}}$.

The key to a calculation of the statistical error bars for an SGA computation is therefore a determination of the quantity $\ell$ and the corresponding analytical integral of Eq. C.4 or Eq. C.7 (whichever is more convenient).

To determine $\ell$, we make the assumption that the energy $\langle H \rangle_N$ calculated at a given
value of \( \beta \) for a given number of sample \( N \) is randomly chosen from a Gaussian distribution centered at the unknown value \( E(\beta) \), with a standard deviation \( \sigma_m \) given by Eq. 4.17 - a statement which is exactly correct as the number of samples \( N \) approaches \( \infty \), and which we suggest is approximately correct even for a small number of sample points. Under this assumption, we have, for the distribution \( \tilde{P}_i \) of possible calculated energies \( E_i \equiv \langle H \rangle_N \) that result from the \( i^{th} \) estimate of \( \langle H \rangle_N \) (the “i” is not included in the notation \( \langle H \rangle_N \)) in a set of \( p \) such estimates,

\[
\tilde{P}_i = \frac{1}{\sqrt{2\pi\sigma_m}} e^{-\frac{(E_i - E(\beta))^2}{2\sigma_m^2}},
\]

which takes the form of the standard Gaussian function, where the tilde on \( \tilde{P}_i \) indicates that this distribution represents a single estimate of \( \langle H \rangle_N \). Note that the random variable \( E_i \) is also a function of \( \beta \); however, we choose to describe this random variable by including only a subscript \( i \), with the dependence on \( \beta \) understood. The quantity \( E(\beta) \), on the other hand, is not a random variable.

From the examples given in ref. [6], the probability \( P \) from Eq. C.5 is the product of the quantity \( \tilde{P}_i \) over the \( p \) estimates of \( \langle H \rangle_N \); for the case of our approximation of \( \mathbf{F} \), we take \( p \) to be equal to the number of SGA steps (each with \( N \) samples), with \( i \) ranging from 1 to \( p \). (Note that our proposed function \( \tilde{P}_i \) is based on a similar example from ref. [6], p. 355.) We have

\[
P = \tilde{P}_1 \tilde{P}_2 \ldots \tilde{P}_p. \tag{C.8}
\]

We therefore have

\[
\ell \equiv P = \left( \frac{1}{\sqrt{2\pi\sigma_m}} \right)^p \sum_{i=1}^{p} \frac{e^{-\frac{(E_i - E(\beta))^2}{2\sigma_m^2}}}{\sqrt{2\pi\sigma_m}},
\]

where the identity between \( \ell \) and \( P \) must be understood in terms of the conditioning discussed above regarding Eq. C.5. We have, for \( \log \ell \),

\[
\log \ell = -p \log \left( \sqrt{2\pi\sigma_m} \right) - \frac{1}{\sigma_m} \sum_{i=1}^{p} \left[ E_i - E(\beta) \right]. \tag{C.9}
\]

In order to complete this work and obtain the statistical error bars, we must analytically calculate the integral of Eq. C.4 or C.7 (whichever is more convenient) over \( dE_1 dE_2 \ldots dE_p \).
This integral, once completed, will include factors and terms that are functions of the quantities \(E\), \(\frac{\partial E}{\partial \beta}\), and \(\frac{\partial^2 E}{\partial \beta \partial \beta^T}\). The analytical expression for this integral must then be averaged over all SGA steps to approximate \(\overline{F}\), as discussed above.

An important part of the analysis therefore involves functions of the quantities \(E\), \(\frac{\partial E}{\partial \beta}\), and \(\frac{\partial^2 E}{\partial \beta \partial \beta^T}\). Unfortunately, we do not know these quantities as functions of \(\vec{\beta}\). However, we only need to know \(\overline{F}\), corresponding to the average across all SGA steps. Whether this method will work therefore depends on whether the identity

\[
\overline{f \left( \frac{\partial E}{\partial \beta} \right)} \approx \overline{f \left( \frac{\partial E}{\partial \beta} \right)}
\]  

(C.10)

holds, where \(f\) represents any of the functions that result from the analytical integration of Eq. C.4 or Eq. C.7 (and similarly for functions of the matrix of second derivatives), where the averaging bar that appears over the entire function on the left-hand side and right-hand side of Eq. C.10 represents the average over all SGA steps, and where the averaging bar that appears over \(E\) in \(\frac{\partial E}{\partial \beta}\) in the right-hand side represents the average energy of the system over all SGA steps. Given the assumption that \(\overline{F}\) can be approximated as though all SGA steps are obtained at the optimum value \(\vec{\beta}_{\text{exact}}\), it seems likely that the (approximate) equalities of Eq. C.10 hold; however, we have not completed this analysis.

If the equalities represented by Eq. C.10 do hold, and if the integral of Eq. C.4 or C.7 can be analytically calculated, we then have a powerful tool to provide statistical error bars for the variational parameters in stochastic optimization. We have not yet completed this exciting work.
Chapter 13

Appendix D: Region of convergence and the SGA

The issues raised in the preceding two Appendices can be captured by the concept of a region of convergence, which we have developed during our work with the SGA as a useful, work-a-day way of understanding subtle issues in a simple way. We have not calculated the region of convergence, but employ it for its conceptual appeal. We introduce it in this appendix in the hopes that the concept may prove useful in the long run.

The region of convergence \( r_J \) (or simply \( r_J \), with the dependence on \( \bar{\beta} \) assumed) is a set of points rigorously defined as follows. We assume that we have the exact energy landscape available, as well as all other necessary quantities - i.e., we assume that the energy, the variance of the local energy, and the autocorrelation time \( \tau \) is known to infinite accuracy at every point in the variational landscape. We then choose a number of samples \( J \) and a variational point \( \bar{\beta} \) (typically the optimum point); the region of convergence depends on \( J \) and \( \bar{\beta} \). Using \( J \) and \( \tau \) we employ Eq. 4.17 to determine the statistical accuracy at all points in the variational landscape that results from a calculation with \( J \) samples. The set of points in the landscape whose error bars (centered at the true value of the energy at each point) overlap the true energy at the point \( \bar{\beta} \) form the region of convergence around \( \bar{\beta} \).

Since the region of convergence is a function of some number of samples \( J \), we may now
Figure 13-1: Using the same data as shown in Fig. 8-5, this figure demonstrates the intuitive concept of the region of convergence with an imaginary example (red circle), drawn by “eye”, surrounding most of the locus points. The region of convergence has not actually been determined in this case, and is shown here to demonstrate the concept. In general, calculating the region of convergence is a very computationally intensive task.

define a region of convergence associated with an SGA run as

\[ r_{SGA} \equiv r_K \]  \hspace{1cm} (D.1)

where \( K = \alpha Np \).

and \( \alpha \) is the efficiency parameter defined in Appendix E.

With the region of convergence defined as in Eq. D.1, we can ask rigorously defined questions about the locus points of the SGA path such as, \textit{does any particular locus point lie within the region of convergence} and \textit{what fraction of locus points lie within the region of convergence}. We present the concept of the region of convergence as a useful tool to assist in further developments with the SGA. The concept adheres nicely to intuition as the SGA path converges towards the optimum point, and the locus points shrink into a smaller and smaller region.

Fig. 13-1 shows an imaginary example of a region of convergence using the data shown in Fig. 8-5. In the figure we have drawn a red circle, by “eye”, around our guess of the
region of convergence.

Stochastic optimization can be thought of as a “cat-and-mouse” game, in which the locus points are cornered into the region of convergence, pressing against the edge even while the region of convergence shrinks. Some points spill outside the region of convergence, but others are created on the inside. Our empirical results show that the overall effect is that a sufficient fraction remain inside, and the points outside do not destroy the validity of the energy calculation.

We note here that as the SGA simulation progresses, the region of convergence shrinks, even though almost all trial points lie outside the region of convergence. This fact is a simple and concise way of expressing the remarkable Robbins-Monro result of Eq. 8.1.

In the case of deterministic optimization, we define the region of convergence according to the current step as $r_K$ with $K = N$, ignoring all previous steps. For deterministic optimization, we see that all previous points generally lie outside the region of convergence. This is easily demonstrated by noticing that a large number of sample points are obtained at each iteration, shrinking the error bar with the specific intention of moving to a new location whose energy does not overlap the old point. By definition, this indicates that most or all previous points are located outside the region of convergence. This issue can be viewed from the reverse perspective - by imagining that the deterministic calculation starts within the region of convergence. Inside the region of convergence, deterministic methods must increase the number of sample points in order to shrink the region of convergence [47] until the current point moves outside this radius.

Although a direct calculation of the region of convergence would be computationally intensive, it would be interesting in future work to determine whether the region of convergence provides a simpler, or complementary, way to analyze convergence - in addition to the formal Fisher information matrix methodology discussed in the previous appendix.
Chapter 14

Appendix E: Universal measure of efficiency $\alpha$ in VMC

In this section, we introduce a rough measure of efficiency $\alpha$ and suggest that it could be used as a universal measure to compare different VMC algorithms. We also determine an approximate value of $\alpha$ in the case of the SGA calculations of Li demonstrated in this chapter.

The efficiency parameter we present in this section is limited in applicability to those variational QMC methods whose purpose is to calculate the energy at the optimum point in the variational landscape. Let us call this optimum point $\beta_{\text{opt}}$. In order to define the efficiency parameter, we assume that the maximum possible efficiency (an efficiency $\alpha = 1$) is obtained by way of a QMC computation with $K_{\text{opt}}$ samples with the variational parameter fixed at the value $\beta_{\text{opt}}$. The energy at the optimum will be calculated as $E_{\text{opt}} \pm \sigma_{\text{opt}}$ (with $\sigma_{\text{opt}}$ calculated from Eq. 4.8). There can be no more efficient calculation of the energy with $K_{\text{opt}}$ samples than one that obtains all samples at the optimum point.

In contrast, variational methods that do not obtain all samples at the optimum value $\beta_{\text{opt}}$ must accumulate more samples to obtain the same accuracy $\sigma_{\text{opt}}$. Let us define as $K_{\text{VMC}}$ the total number of required samples for any particular variational calculation in
order to obtain the same accuracy $\sigma_{\text{opt}}$:

$$\sigma_{\text{VMC}} = \sigma_{\text{opt}}.$$ \hspace{1cm} (E.1)

We define the efficiency parameter $\alpha$ as the ratio

$$\alpha = \frac{K_{\text{opt}}}{K_{\text{VMC}}}.$$ \hspace{1cm} (E.2)

If the standard deviation $\sigma_{\text{VMC}}$ of the variational calculation of the energy is arbitrarily selected as the reference value, we have, by definition, the following condition which we shall impose:

Conceptually, the definition in Eq. E.2 for $\alpha$ states that the efficiency is measured by comparing the total number of samples $K_{\text{VMC}}$ that are required by a VMC run to the total number $K_{\text{opt}}$ that would have to be obtained with the parameter fixed at $\beta_{\text{opt}}$ to calculate the energy with the same standard deviation $\sigma_{\text{VMC}} = \sigma_{\text{opt}}$. The optimum efficiency $\alpha = 1$ is only obtained, of course, in the case $K_{\text{VMC}} = K_{\text{opt}}$.

Note that both $\sigma_{\text{VMC}}$ and $\sigma_{\text{opt}}$ are rigorously defined values within a particular method. However, for typical VMC and QMC runs, we generally have available only estimates of $\sigma_{\text{VMC}}$ and $\sigma_{\text{opt}}$; we assume these values provide a good estimate for $\alpha$.

The value $\alpha$ depends on the particular VMC method being used - any modification of the algorithm may alter the value of $\alpha$. In addition, $\alpha$ may be a function of the number of samples.

### 14.1 Deterministic case

The discussion so far has presented only a general definition for the efficiency parameter $\alpha$. We now derive the very simple expression for $\alpha$ in the special case of a deterministic variational optimization with a fixed number of samples $N$ per iteration and $p$ iterations in total. In this case, let us define the statistical accuracy in terms of that obtained in the
variational run. We therefore have

\[ K_{\text{VMC}} = N_p \text{ (simple deterministic case).} \quad (E.3) \]

If, as in the special case under consideration, only the energy from the most recent iteration is used to calculate the final result for the energy, and if furthermore the value of the parameter at this point is taken to be the optimum parameter \( \beta_{\text{opt}} \), we see that we have, for \( K_{\text{opt}} \),

\[ K_{\text{opt}} = N \text{ (simple deterministic case).} \quad (E.4) \]

We then have, straightforwardly,

\[ \alpha = \frac{K_{\text{opt}}}{K_{\text{VMC}}} = \frac{N}{N_p} = \frac{1}{p} \text{ (simple deterministic case),} \quad (E.5) \]

which states that the efficiency for a deterministic optimization under these assumptions is inversely proportional to the number of iterations.

As a hypothetical example, consider a deterministic case in which the variational parameters converge after 15 steps, which is a reasonably small number for a variational optimization (see, for example, ref. [47]). In such a case we find that the efficiency \( \alpha \) is given by \( \alpha = 0.06 \).

However, as we discuss in detail in Section 8.7.2, this model is too simplistic, because deterministic optimization methods rarely utilize the same number of sample points at each iteration. Instead, they begin with a small number and increase the number as the optimization proceeds. Eq. E.5 explains the reason why this is important for the efficiency of deterministic methods. See ref. [47] for a typical example. In this thesis, we do not perform an analysis of the efficiency \( \alpha \) of different variational methods in more realistic cases.
14.2 Stochastic case

The efficiency parameter $\alpha$ is defined in the case of stochastic optimization by considering the set of $p$ iterations that comprise the SGA path and calculating the energy $E_{\text{SGA}}$ as the energy obtained from all SGA iterations as though they all reside at the same point. (We use $E_{\text{SGA}}$ in the place of $E_{\text{VMC}}$ to distinguish the stochastic case from the deterministic case.) For the stochastic case, we define $\tilde{\sigma}_{\text{SGA}}$ similarly to Eq. 4.17 as

$$\tilde{\sigma}_{\text{SGA}} = \frac{\tilde{\sigma}_{\text{SGA-raw}}}{\sqrt{K_{\text{SGA}}}}$$

utilizing all $K_{\text{SGA}}$ samples, where the tildas $\tilde{\sigma}$ and $\tilde{\tau}$ indicate that the quantities are obtained over multiple variational parameters. For the work in this thesis, we assumed that $\tilde{\tau}$ is constant over the variational landscape, $\tilde{\tau} = \tau \approx 4$ (from Fig. 7-7).

We determine the efficiency $\alpha$ in the case of the SGA by extracting the number of samples $K_{\text{opt}}$ from Eq.4.17, and extracting $K_{\text{SGA}}$ from Eq. E.6. We have

$$K_{\text{opt}} = \frac{\tau \sigma_{\text{opt-raw}}^2}{\sigma_{\text{opt}}^2}$$

and

$$K_{\text{SGA}} = \frac{\tau \sigma_{\text{SGA-raw}}^2}{\sigma_{\text{SGA}}^2}.$$ 

If we assume that $\tilde{\sigma}_{\text{SGA}} = \sigma_{\text{SGA}}$ (and therefore that $\tilde{\sigma}_{\text{SGA-raw}} = \sigma_{\text{SGA-raw}}$, from Eq. E.6), and if we apply the condition of Eq. E.1, we find that

$$\alpha_{\text{SGA}} = \frac{K_{\text{opt}}}{K_{\text{SGA}}} = \frac{\sigma_{\text{opt-raw}}^2}{\sigma_{\text{opt}}^2} \frac{\tilde{\sigma}_{\text{SGA}}^2}{\sigma_{\text{SGA-raw}}^2}.$$ 

Applying Eq. E.1, we have

$$\alpha_{\text{SGA}} = \frac{\sigma_{\text{opt-raw}}^2}{\sigma_{\text{SGA-raw}}^2}. \quad (E.7)$$ 

We arrive at the result that the efficiency $\alpha$ of an SGA calculation is determined by the ratio of the raw variance of the local energies at the optimum point and throughout the
SGA run.

Note from Eq. E.6 the very important, but subtle, following point. As in the case of deterministic optimization, we define the value $K_{SGA}$ to correspond to a standard deviation $\sigma_{SGA}$ that matches the standard deviation of the energy calculated from $K_{opt}$ samples at $\bar{\beta}_{opt}$ (see Condition E.1). However, Eq. E.6 does not provide the correct expression for the standard deviation of $K_{SGA}$ samples in an SGA run, due to the fact that the parameters vary during the run. We shall assume that Eq. E.6 is correct, and then perform an empirical analysis to get a sense of the magnitude of this bias. We perform an empirical test of the bias due to the approximation $\tilde{\sigma}_{SGA-raw}^2$ in the next subsection.

### 14.3 Measured value of efficiency for Li$_4$

We shall now give the results of a calculation of the efficiency $\alpha$ for Li$_4$. Tables 14.1 and 14.2 present the data from which we calculate $\alpha$.

First, Table 14.1 shows the results of 3 extensive, full, standard QMC energy calculations (not SGA or VMC calculations) at three different fixed, single Jastrow opposite-spin parameters bracketing the minimum value $\beta = 1.242$ obtained from our SGA calculations of Li$_4$. Each run consisted of 64,000,000 samples at the fixed value of $\beta$. The table reveals that the value $\beta = 1.242$ obtained with the SGA indeed lies at the minimum, confirming the most important fact - namely, that the SGA works. Table 14.1 provides the energy at the minimum value, and the value of $\sigma^2$ for each calculation.

The first row of data in table 14.2 repeats the values from the optimum point, for convenience. The second row provides the results from our SGA runs. In addition to providing the energy and the value $\tilde{\sigma}^2$ for each computation, the table provides the total number of samples $K$ utilized in each case. For all these calculations, we have used the value $\sqrt{r} \approx 2$ from Fig. 7-7. Note that at the optimum point, $\tilde{\sigma}^2 = \sigma^2$ because $\bar{\beta}$ is fixed at the optimum value.

Using Eqs. 4.17 and E.6, and using the value $\tilde{\sigma}_{SGA} = 0.0032$ from Table 14.2, a straightforward calculation shows that
Table 14.1: Detailed QMC calculations performed at fixed variational parameters bracketing the minimum value obtained by the SGA to confirm the correct result. The table shows that the optimum value $\beta = 1.242$ is, indeed, the lowest inergy of the three points. Energies are given in Hartrees.

<table>
<thead>
<tr>
<th>Method</th>
<th>Samples</th>
<th>Energy</th>
<th>$\bar{\sigma}$</th>
<th>Empirical $\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>QMC ($\beta = 1.242$)</td>
<td>$6.4 \cdot 10^7$</td>
<td>$-29.88121$</td>
<td>$\bar{\sigma} = \sigma = 0.00081$</td>
<td>n/a</td>
</tr>
<tr>
<td>SGA (all steps)</td>
<td>$1.4 \cdot 10^7$</td>
<td>$-29.88035$</td>
<td>0.0032</td>
<td>0.0042</td>
</tr>
</tbody>
</table>

Table 14.2: Comparison (in Hartrees) of the exact energy at $\beta = 1.242$ from a direct QMC computation, and the energy obtained from SGA computations. 30 different SGA runs were performed, all reporting approximately the same statistical accuracy of 0.0032. Empirically, the measured spread of results from the SGA runs is 0.0042, indicating that the reported accuracy of the SGA is reliable. The mean SGA energy result corresponds to the exact value, within the reported statistical accuracy.

$$\alpha \approx 0.29,$$  \hspace{1cm} (E.8)

where we describe the result as an approximation for the following reason. The computation of $\alpha$ obtained in Eq. E.8 was obtained utilizing Eq. E.6 to calculate $\bar{\sigma}_{\text{SGA}}$ directly from the raw data. However, as discussed in the previous subsection, we have made the approximation $\bar{\sigma}_{\text{SGA}} \approx \sigma_{\text{SGA}}$. In order to obtain an empirical measure of the true value of validity of $\sigma_{\text{SGA}}$, we ran 30 different identical SGA simulations with different random number seeds, and obtained the mean and empirical standard deviation $\sigma_{\text{SGA}}$, listed in the table as empirical $\sigma$. We find a result

$$\text{Empirical } \sigma_{\text{SGA}} = 0.0042$$

which leads to an efficiency parameter

$$\text{Empirical } \alpha_{\text{SGA}} = 0.16.$$
We find that the empirical result $\alpha = 0.16$ is smaller than the estimated result $\alpha \approx 0.29$ by approximately a factor of 2.

Much more work could be done to study the efficiency parameter $\alpha$ in both the stochastic and the deterministic cases.
Chapter 15

Appendix F: Normalization of the wave function in VMC

Another important issue that must be considered in an implementation of VMC with a Jastrow factor regards the normalization of the wave function. Because it is not discussed in most of the references cited in this work, and because a failure to understand this issue can easily destroy a calculation, we include a discussion of it here.

The normalization constant is unknown when a Jastrow factor is included in the wave function, and it depends on the Jastrow parameters. Because reweighting is utilized during the line search, the reweighting term discussed in Ch. 4 (the ratio of the wave functions at different parameters) therefore includes an additional factor, namely the ratio of normalization constants. Note that the normalization constants do not cancel, as they do for the standard QMC energy integral of Eq. 4.1. Therefore, this ratio of normalization constants introduces a bias into the reweighting. This bias is reflected by the strength of the reweighting factors, and is one reason why the reweighting factors should not deviate strongly from 1, as discussed in Ch. 4. This bias is already known, and VMC has been very successful even in the presence of this bias.

In addition, however, there is a related bias involving the normalization constant when utilizing the analytical gradient. Consider the calculation of the analytical energy gradient $\nabla_{\beta_i} \langle H \rangle$ of Eq. 8.8, which requires the quantity $\nabla_{\beta_i} \frac{\Psi}{\Psi}$, with $\Psi$ assumed to be normalized.
If $\Psi$ is not normalized, we have 
\[
\frac{\nabla^2 \gamma \Psi}{(\gamma \Psi)} = \frac{\nabla^2 \Psi}{\Psi} + \frac{\nabla^2 \gamma}{\gamma},
\]
where $\gamma$ is the unknown normalization constant, which indicates that an additional (unknown) constant term $\frac{\nabla^2 \gamma}{\gamma}$ must be included in the integration to avoid bias. We do not include this term in the formulation of Eq. 8.8. The discussion of Umrigar [47], however, indicates that it is safe to utilize this form due to the variance-reduction reformulation. His results, and our results, show that this additional bias is very small and we have ignored it in this work.

However, a very important note of warning is nonetheless in order. The Jastrow factor as presented in Eq. 3.23, if utilized directly, causes the SGA to fail severely because these biases are not small if the Jastrow is included in exactly that form. From Fig. 3-1, we see that the constant scaling factor $\frac{1}{\sqrt{r}}$ (where the scalar $\beta$ is the leading Jastrow factor that dominates the function for large $r$) yields an asymptote of 1. Therefore, the only deviation of the normalization constant from the Hartree-Fock case, with its known normalization constant of $\frac{1}{(M/2)!}$ (Eq. 3.19), is provided by the relevant region of the decaying Jastrow factor near the origin, which affects only a small fraction of the electrons when carrying out the normalization integral. Without the scaling factor, however, the asymptote of the Jastrow factor increases above 1 and is a function of the leading Jastrow variational parameter $\beta$. This difference in the asymptote at different points in the variational landscape affects not only the small number of electrons which are close together, but also every other electron pair, no matter how far apart they are separated. For $M = 20$, for example, there are 55 opposite-spin pairs. This causes the normalization constant for the two wave functions with different parameters to vary by many orders of magnitude, completely destroying the calculation with reweighting error.

One must include the scaling factor of $\frac{1}{\sqrt{r}}$ in the Jastrow factor, which resets the asymptote to 1 and ensures that only nearby electrons influence the normalization integral.

This discussion also provides a conceptual rationale for the fact that the normalization bias can, in general, be ignored. As stated, the normalization in the Hartree-Fock limit is known. The Jastrow factor has a small (while important) impact on this wave function, so it should come as no surprise that the normalization constant remains roughly constant even with the inclusion of a Jastrow factor, as long as the Jastrow factor includes the proper
scaling factor.
Chapter 16

Appendix G: Single-electron vs. all-electron moves, $\Delta \tau$, and acceptance ratio

In this appendix we revisit the issue of single-electron vs. all-electron moves in the Metropolis-like (in our case, modified Langevin) algorithm - see the brown box in Fig. 8-1, Fig. 8-2, or Fig. 10-1. There is ongoing debate about the use of single-electron vs. all-electron moves. See refs. [106] and [40] for two opposing examples, from the same year, in the case of Umrigar; see ref. [138] for a recent example with all-electron moves; and see also ref. [52] for a discussion. The QMcBeaver code [41] employs all-electron moves while the Casino code [139] employs single-electron moves. The algorithm can fairly easily be changed from one method to the other.

Our work was primarily based on the QMcBeaver code [41], and therefore we utilized all-electron moves. In this appendix we provide a deeper investigation into the issue. We begin with a discussion of the choice of $\Delta \tau$, and proceed with a discussion of single-electron vs. all-electron moves.

We would like the choice of $\Delta \tau$ to optimize the efficiency of the QMC computation. In order to determine the efficiency of the computation as a function of the choice of $\Delta \tau$, we assume that the number of samples $N$ in a given simulation is inversely proportional to the
time step $\Delta \tau$ (Eq. 4.16). This seems like a reasonable assumption because it suggests that the total time (in atomic units) that the electrons diffuse during the simulation, in the sense discussed in Section 4.5.2, must be roughly independent of the step size $\Delta \tau$. The time is therefore independent of the number of electrons.

It is known that decreasing $\Delta \tau$ increases the acceptance ratio $A(\Delta \tau)$ (see Section 4.5.2); we therefore make the further approximation that the number of samples $N$ is also inversely proportional to the acceptance ratio $A$. We also assume that $A(\Delta \tau)$ is exponential so that it can be approximated as $A(\Delta \tau) \approx 1 - a\Delta \tau + O(\Delta \tau^2)$. By minimizing $N$ with respect to $\Delta \tau$, we find

$$A \approx 0.5.$$  \hspace{1cm} (G.1)

This corresponds to the rule of thumb in QMC that the acceptance ratio should be $\frac{1}{2}$ (see ref. [121], p. 3085). The author also gives reasons why somewhat different acceptance ratios might perform better, but does not provide any empirical or analytical justification.

Armed with this guideline for the desired acceptance ratio $\Delta \tau = 0.5$, we implemented in our code the following dynamic $\Delta \tau$ algorithm:

$$\Delta \tau_{\text{new}} = \Delta \tau_{\text{old}} - (0.5 - \frac{N_a}{N_{\text{tot}}})\Delta \tau_{\text{old}},$$  \hspace{1cm} (G.2)

where $N_a$ is the total number of Metropolis (or Metropolis-like) samples that have resulted from accepted steps (see Section 4.5.2), and $N_{\text{tot}}$ is the total number of samples. The modification of $\Delta \tau$ in Eq. G.2 is performed occasionally during the computation; we find (for all-electron moves) that performing the update every 128 or 256 steps works well.

In Fig. 16-1 we demonstrate the dynamic $\Delta \tau$ algorithm in the case of an all-electron calculation of Li$_8$ using the modified Langevin algorithm (discussed in Section 4.5.2). The figure shows the acceptance ratio as it evolves during the simulation. We see from the figure that the algorithm works well in quickly obtaining the desired acceptance ratio of 50%. Fig. 16-2 shows the corresponding evolution of $\Delta \tau$ during the course of the simulation. We see from the figure that a specific value $\Delta \tau \approx 0.3$ is associated with this Li$_8$ calculation and the desired acceptance ratio of 50%. Different cluster sizes have different corresponding values
of $\Delta r$. In Fig. 16-3 we show these values of $\Delta r$ as a function of the inverse of the total number of electrons.

Using Fig. 16-3, we may now return to the issue of single-electron vs. all-electron moves. In order to contrast single-electron moves and all-electron moves, let us consider the total average single-electron distance $r_{tot}$ swept out by all the electrons in the system after all electrons have had a chance to move once. In the case of single-electron moves, this corresponds to $M$ Metropolis (or Metropolis-like) steps for a system of $M$ electrons. In the case of all-electron moves in a system of $M$ electrons, we see that this corresponds to a single Metropolis step. In both cases, we have $r_{tot} = M\overline{r}$ per step, where $\overline{r}$ is the average distance that a single electron moves per step. From the definition of $\Delta r$ in Eq. 4.16, we have $\overline{r} = \frac{1}{2}\Delta r$, where the factor of $\frac{1}{2}$ is the acceptance ratio.

Now let us consider the specific case of Li$_8$ that we have considered here. In Fig. 16-3 we observe approximately a linear relationship. Although a small amount of nonlinearity can be observed, the most important part of the plot is the region approaching the origin, corresponding to a larger electron count; we expect the plot to intersect the origin, and in this region we see a solid linear relationship extending from the origin through the first few points. Therefore, for larger clusters, we evidently have $\Delta r \propto \frac{1}{M}$. Using Eq. 4.16 we then
Figure 16-2: The evolution of $\Delta \tau$ during the same calculation shown in Fig. 16-1.

Figure 16-3: The values of $\Delta \tau$ obtained with the dynamic $\Delta \tau$ algorithm for all-electron calculations of Li clusters using the modified Langevin algorithm, as a function of the inverse of the total number of electrons.
Figure 16-4: The total average distance $r_{\text{tot}}$ swept out by all the electrons in the cluster taken together, per Metropolis (or Metropolis-like) step, as a function of the number of electrons, for the same Li cluster calculations as the ones shown in Fig. 16-3.
have $\Delta r \propto \frac{1}{\sqrt{M}}$; therefore, from the discussion in the preceding paragraph, we find that

$$r_{tot} = M\Delta r \propto \sqrt{M}. \quad (G.3)$$

In Fig. 16-4 we have plotted $r_{tot}$ as a function of $M$. We find that the total distance swept out by the electrons for the larger clusters increases in the case of all-electron moves. We see that it is reasonable to suppose that all-electron moves become an increasingly better choice as the cluster size increases, because the electrons sweep out a larger total distance in configuration space. We have not created a similar plot for the single-electron case, and one might suppose that a similar scaling might be revealed in this case; however, our preliminary calculations employing single-electron moves seemed to run significantly slower for the larger cluster sizes, and as a result we chose all-electron moves.

An additional important consideration is the time required to update the calculation of the Slater determinant of Eq. 3.20 or 3.21 in the two cases. Umrigar [40] has shown that it takes exactly twice as long to perform QMC calculations in the case of single-electron moves than in the case of all-electron moves (note that only 1 calculation is performed per Metropolis step in the case of all-electron moves, whereas in the case of single-electron moves, only 1 row and column needs to be updated for each of the $M$ corresponding Metropolis steps). This factor must be taken into consideration in making a choice between single-electron and all-electron moves.

We would like to acknowledge D. Bressanini and Chip Kent for useful and fascinating discussions regarding the choice between single-electron and all-electron moves. Bressanini [109] has also published interesting related work allowing for differing time scales $\Delta \tau$ for the core and valence electrons. Differences between core and valence electrons might account for the anomalies displayed in Fig. 7-9.
Chapter 17

Appendix H: Alternative constructions of the pair correlation function

It is useful to discuss alternative approaches to constructing the pair correlation function $g_{\sigma\sigma'}(\vec{r})$, because the normalization constant for computer coding applications can take different forms, and it is easy to make mistakes. We must be clear to choose a particular approach when accumulating data for these histograms in a QMC calculation.

To describe one alternative approach, note that since $\langle V \rangle$ is given by Eq. 5.10, we could instead rewrite the definitions in Eq. 5.11, Eq. 5.12, and Eq. 5.13 for $g_{\sigma\sigma'}(\vec{r})$ by defining a new function, $\tilde{g}_{\sigma\sigma'}(\vec{r})$, in terms of $g_{\sigma\sigma'}(\vec{r})$ as

$$\tilde{g}_{\uparrow\uparrow}(\vec{r}) = \frac{1}{(\# \text{ \# pairs})} g_{\uparrow\uparrow}(\vec{r})$$

(H.1)

$$\tilde{g}_{\downarrow\downarrow}(\vec{r}) = \frac{1}{(\# \text{ \downarrow pairs})} g_{\downarrow\downarrow}(\vec{r})$$

(H.2)

and

$$\tilde{g}_{\uparrow\downarrow}(\vec{r}) = \frac{1}{(\# \text{ \uparrow\downarrow pairs})} g_{\uparrow\downarrow}(\vec{r}) ,$$

(H.3)

which has the advantage that when integrated as in Eq. 5.14, we obtain the average value
of \langle V \rangle for a single pair of opposite-spin electrons – the ‘pair interaction energy’ – rather than the total value of \langle V \rangle for the system. The total opposite-spin pair contribution to the potential energy \langle V \rangle, as in Eq. 5.14, instead becomes

$$\int d\mathbf{r}' \frac{M \tilde{g}_{\uparrow \downarrow} (\mathbf{r})}{|\mathbf{r}'|} = \int \frac{|\psi|^2}{r_{\uparrow \downarrow}} d\mathbf{r}'$$

(H.4)

(and similarly for \tilde{g}_{\uparrow \uparrow} (\mathbf{r}) and \tilde{g}_{\downarrow \downarrow} (\mathbf{r})), and hence the total potential energy \langle V \rangle, as in Eq. 5.15, becomes

$$\langle V \rangle = \frac{M (M + 1)}{2} \left\{ \int \frac{M \tilde{g}_{\uparrow \downarrow} (\mathbf{r})}{|\mathbf{r}|} d\mathbf{r} \right\} \ (a)$$

$$+ \frac{M (M + 1)}{2} \left\{ \int \frac{M \tilde{g}_{\downarrow \downarrow} (\mathbf{r})}{|\mathbf{r}|} d\mathbf{r} \right\} \ (b)$$

$$+ M \frac{M + 1}{2} \left\{ \int \frac{M \tilde{g}_{\uparrow \uparrow} (\mathbf{r})}{|\mathbf{r}|} d\mathbf{r} \right\} \ (c).$$

(H.5)

This method of writing the pair correlation function, \tilde{g}_{\sigma \sigma'} (\mathbf{r}) instead of \tilde{g}_{\sigma \sigma} (\mathbf{r}) has the advantage that the same-spin and opposite-spin functions can be compared on the same graph, as they both represent a single pair of electrons.

In this case, instead of Eq. 5.22, Eq. 5.23, and Eq. 5.24, we would have

$$\tilde{g}_{\uparrow \uparrow} (\mathbf{r}) = \frac{1}{\pi n N |\mathbf{r}| \Delta r M_{\uparrow} (M_{\uparrow} - 1)} \text{(total \# \uparrow \uparrow pairs separated by } |\mathbf{r}|)$$

(H.6)

$$\tilde{g}_{\downarrow \downarrow} (\mathbf{r}) = \frac{1}{\pi n N |\mathbf{r}| \Delta r M_{\downarrow} (M_{\downarrow} - 1)} \text{(total \# \downarrow \downarrow pairs separated by } |\mathbf{r}|)$$

(H.7)

and

$$\tilde{g}_{\uparrow \downarrow} (\mathbf{r}) = \frac{1}{2\pi n N |\mathbf{r}| \Delta r M_{\uparrow} M_{\downarrow}} \text{(total \# \uparrow \downarrow pairs separated by } |\mathbf{r}|),$$

(H.8)

and the prefactor has been determined in this case, allowing for direct use in a computer algorithm using this approach.

There is a simpler way to write Eqs. H.6-H.8. When a histogram is composed of all pairs of electrons over all MC points, we have

number of entries from all bins for \uparrow \uparrow = NM_{\uparrow} (M_{\uparrow} - 1) \tag{H.9}

number of entries from all bins for \downarrow \downarrow = NM_{\downarrow} (M_{\downarrow} - 1)

number of entries from all bins for \uparrow \downarrow = NM_{\uparrow} M_{\downarrow}
and hence Eqs. H.6-H.8 become

\[
\tilde{g}_{\uparrow \uparrow}(\vec{r}) = \frac{1}{\pi M |\vec{r}| \Delta r (\# \text{ entries from all } \uparrow \uparrow \text{ bins}) (\text{total } \# \uparrow \uparrow \text{ pairs separated by } |\vec{r}|) \tag{H.10}
\]

\[
\tilde{g}_{\downarrow \downarrow}(\vec{r}) = \frac{1}{\pi M |\vec{r}| \Delta r (\# \text{ entries from all } \downarrow \downarrow \text{ bins}) (\text{total } \# \downarrow \downarrow \text{ pairs separated by } |\vec{r}|) \tag{H.11}
\]

and

\[
\tilde{g}_{\uparrow \downarrow}(\vec{r}) = \frac{1}{2\pi M |\vec{r}| \Delta r (\# \text{ entries from all } \uparrow \downarrow \text{ bins}) (\text{total } \# \uparrow \downarrow \text{ pairs separated by } |\vec{r}|), \tag{H.12}
\]

which is an alternative way to write the prefactor for this approach.

There is a second alternative approach to the construction of \(g_{\sigma\sigma'}(\vec{r})\) that we now provide. Instead of Eq. 5.11, Eq. 5.12, and Eq. 5.13, we introduce the very similar functions

\[
P_{\uparrow \uparrow}(r) = \frac{1}{M} \sum_{i < j} \delta_{\uparrow, \sigma_i} \delta_{\uparrow, \sigma_j} \int \delta (r - r_{ij}) |\Psi|^2 d\vec{r}, \tag{H.13}
\]

\[
P_{\downarrow \downarrow}(r) = \frac{1}{M} \sum_{i < j} \delta_{\downarrow, \sigma_i} \delta_{\downarrow, \sigma_j} \int \delta (r - r_{ij}) |\Psi|^2 d\vec{r}, \tag{H.14}
\]

and

\[
P_{\uparrow \downarrow}(r) = \frac{1}{M} \sum_{i,j} \delta_{\uparrow, \sigma_i} (1 - \delta_{\uparrow, \sigma_j}) \int \delta (r - r_{ij}) |\Psi|^2 d\vec{r}. \tag{H.15}
\]

The functions \(P_{\sigma\sigma'}(r)\) differ from Eqs. 5.11-5.13 only in the definition of the \(\delta\)-function. Instead of the volume integral (5.18), we have a true one-dimensional integral

\[
\int \delta (r - r_{ij}) dr = 1, \tag{H.16}
\]

with

\[
\delta (r - r_{ij}) = \begin{cases} 
\frac{1}{\Delta r} (|\vec{r}| - \frac{\Delta r}{2} < r_{ij} < |\vec{r}| + \frac{\Delta r}{2}) \\
0 \quad \text{(otherwise)}
\end{cases} \tag{H.17}
\]

instead of Eq. 5.17. For proper normalization, notice the difference in the denominator from Eq. 5.17 of the factor \(2\pi |\vec{r}|\). We write \(P_{\sigma\sigma'}(r)\) instead of \(P_{\sigma\sigma'}(\vec{r})\) to emphasize the
one-dimensional nature of the integral with respect to the δ-function, unlike the quantity \( g_{\sigma \sigma'} (\vec{r}) \), as discussed above.

Using this approach, the total opposite-spin pair contribution to the potential energy \( \langle V \rangle \), as in Eq. 5.14, becomes

\[
\begin{align*}
\langle V \rangle &= \int \frac{n P_{\uparrow \downarrow}(r)}{r} \, dr + \int \frac{n P_{\downarrow \uparrow}(r)}{r} \, dr + \int \frac{n P_{\uparrow \uparrow}(r)}{r} \, dr.
\end{align*}
\]  

Analogously to Eqs. 5.22-5.24 and Eqs. H.6-H.8, we have for the computational definition of \( P_{\sigma \sigma'} (\vec{r}) \)

\[
\begin{align*}
P_{\uparrow \downarrow} (r) &= \frac{1}{nN \Delta r} \text{ (total \# \uparrow \downarrow pairs separated by r) (H.20)} \\
P_{\downarrow \uparrow} (r) &= \frac{1}{nN \Delta r} \text{ (total \# \downarrow \uparrow pairs separated by r) (H.21)} \\
P_{\uparrow \uparrow} (r) &= \frac{1}{nN \Delta r} \text{ (total \# \uparrow \uparrow pairs separated by r), (H.22)}
\end{align*}
\]

which can be employed directly in the computer algorithm.

To complete the possibilities for the histogram forms, we have a fourth possibility. Analogously to Eqs. H.1-H.3, we define

\[
\begin{align*}
\tilde{P}_{\uparrow \downarrow} (r) &= \frac{1}{(\# \uparrow \downarrow \text{ pairs})} P_{\uparrow \downarrow} (r) \\
\tilde{P}_{\downarrow \uparrow} (r) &= \frac{1}{(\# \downarrow \uparrow \text{ pairs})} P_{\downarrow \uparrow} (r)
\end{align*}
\]
and
\[
\tilde{P}\downarrow\downarrow (r) = \frac{1}{(#\ \downarrow\downarrow \text{pairs})} P\downarrow\downarrow (r). \quad \text{(H.25)}
\]

The total potential energy \(\langle V\rangle\) becomes
\[
\langle V\rangle = \frac{M_1(M_1-1)}{2} \int \frac{M\tilde{P}\downarrow\downarrow(r)}{r} dr \quad \text{(a)}
\]
\[
+ \frac{M_1(M_1-1)}{2} \int \frac{M\tilde{P}\uparrow\uparrow(r)}{r} dr \quad \text{(b)}
\]
\[
+ M_1M_\downarrow \int \frac{M\tilde{P}\downarrow\uparrow(r)}{r} dr \quad \text{(c)}
\]

and for the histogram definition, we have
\[
\tilde{P}\downarrow\downarrow (r) = \frac{2}{nN\Delta r M_1(M_1-1)} \text{(total # \uparrow\downarrow \text{pairs separated by } r)} \quad \text{(H.27)}
\]
\[
\tilde{P}\downarrow\uparrow (r) = \frac{2}{nN\Delta r M_\downarrow(M_1-1)} \text{(total # \downarrow\uparrow \text{pairs separated by } r)} \quad \text{(H.28)}
\]
\[
\tilde{P}\uparrow\downarrow (r) = \frac{1}{nN\Delta r M_1M_\downarrow} \text{(total # \uparrow\downarrow \text{pairs separated by } r)}. \quad \text{(H.29)}
\]

Also, rewriting the prefactor, similarly to Eqs. H.10-H.12, we have
\[
\tilde{P}\downarrow\downarrow (r) = \frac{2}{M\Delta r \text{ (sum of values from all \uparrow\downarrow \text{bins})}} \text{(total # \uparrow\downarrow \text{pairs separated by } r)} \quad \text{(H.30)}
\]
\[
\tilde{P}\downarrow\uparrow (r) = \frac{2}{M\Delta r \text{ (sum of values from all \downarrow\uparrow \text{bins})}} \text{(total # \downarrow\uparrow \text{pairs separated by } r)} \quad \text{(H.31)}
\]
\[
\tilde{P}\uparrow\downarrow (r) = \frac{1}{M\Delta r \text{ (sum of values from all \uparrow\downarrow \text{bins})}} \text{(total # \uparrow\downarrow \text{pairs separated by } r)}. \quad \text{(H.32)}
\]

Although \(g_{\sigma\sigma'}(\vec{r}), \tilde{g}_{\sigma\sigma'}(\vec{r}), P_{\sigma\sigma'}(r), \text{ and } \tilde{P}_{\sigma\sigma'}(r)\) are satisfactory choices that give the same result, there is a simple conceptual difference between the functions in the families \(g\) and \(P\). From Eqs. 5.22-5.24 (or Eqs. H.6-H.8) and Eqs. H.20-H.22 (or Eqs. H.27-H.29), we see that functions in the \(g\) family have an extra factor of \(2\pi|\vec{r}|\) in the denominator. Conceptually, this means that at any given \(|\vec{r}|\), \(g\) is a density of pairs of electrons \(\vec{r}_i\) and \(\vec{r}_j\).
Figure 17-1: Distinction between $g(\vec{r})$ and $P(r)$ highlighting the fact that $P(r)$ represents electrons separated by the scalar distance $r$, whereas the closely related quantity $g(\vec{r})$ represents electrons separated by the vector displacement $\vec{r}$. The figure makes clear that this is simply the difference between a shell with a radius of $r$, and a point on that shell. Therefore, the difference in normalization is $2\pi r$.

such that $\vec{r}_i - \vec{r}_j = \vec{r}$, whereas functions in the $P$ family give a density of pairs of electrons $\vec{r}_i$ and $\vec{r}_j$ such that $|\vec{r}_i - \vec{r}_j| = r$. Since the problem is symmetric in the polar angle, we find that the $g$ and $P$ functions differ by a simple factor that accounts for integration over the polar angle, $2\pi r$. We have

$$g_{\sigma\sigma'}(\vec{r}) = \frac{P_{\sigma\sigma'}(r)}{2\pi r} \quad \text{(H.33)}$$

and

$$\tilde{g}_{\sigma\sigma'}(\vec{r}) = \frac{\tilde{P}_{\sigma\sigma'}(r)}{2\pi r} \quad \text{(H.34)}$$

with $r = |\vec{r}|$.

The $P$ functions are therefore related to the number of electron pairs whose magnitude of separation is within $\Delta r$ of the value $r$ - in other words, the number of electron pairs whose vector of separation lies in the two-dimensional shell of width $\Delta r$ at radius $r$. In contrast, the $g$ functions are related to the number of electron pairs whose vector separation lies in the element of area of width $\Delta r$ and length $r\,d\theta$ (where $\theta$ is the polar angle). Due
to the symmetry over $\theta$, the $g$ functions need to be multiplied by the entire length of the slice at distance $r$ - namely, $2\pi r$ - and hence we arrive at eqns. (H.33) and (H.34).

Figure 17-1 lays out the scheme and shows the distinction between $g_{\sigma\sigma'}(\vec{r})$ and $P_{\sigma\sigma'}(r)$. In both diagrams, the black arrow represents $\vec{r}_i$. The red arrows correspond to possible choices for $\vec{r}_j$. On the left, any of the red arrows corresponds to a contribution to $P_{\sigma\sigma'}(r)$ at $r$, because the red arrow merely needs to lie anywhere in the shell at radius $r$. On the right, only the red arrow shown corresponds to a contribution to $g_{\sigma\sigma'}(\vec{r})$ at $\vec{r}$, because the red arrow needs to lie in an area element at the position $\vec{r}$. Because of the symmetry in the polar angle, these quantities differ by the quantity $2\pi r$. 
Chapter 18

Appendix I: Derivation of the product of Slater determinants

In this appendix we extend the method discussed in Ch. 3 to provide a full derivation of the standard Hartree-Fock result in the case of the full $M$-body wave function. (Note: the following derivation is the work of the author and, to the best of this author’s knowledge, unique - it includes the spin formulation in a transparent way.) For the $M$-body wave function, it is impractical to start with Eq. 3.1 or Eq. 3.3. However, analogous steps lead to the equivalent of Eq. 3.8 by constructing the many-body time-independent wave function $\Psi_s$ out of different possible spatio-spin tensor combinations $\{\phi\} \otimes \{\xi\}$ as

$$\bar{\Psi}_s = \det \begin{vmatrix} \phi_1 \xi \uparrow & \phi_1 \xi \downarrow & \phi_2 \xi \uparrow & \phi_2 \xi \downarrow & \ldots & \phi_{M/2} \xi \uparrow & \phi_{M/2} \xi \downarrow \\ \phi_1 \xi \uparrow & \phi_1 \xi \downarrow & \phi_2 \xi \uparrow & \phi_2 \xi \downarrow & \ldots & \phi_{M/2} \xi \uparrow & \phi_{M/2} \xi \downarrow \\ \phi_1 \xi \uparrow & \phi_1 \xi \downarrow & \phi_2 \xi \uparrow & \phi_2 \xi \downarrow & \ldots & \phi_{M/2} \xi \uparrow & \phi_{M/2} \xi \downarrow \\ \phi_1 \xi \uparrow & \phi_1 \xi \downarrow & \phi_2 \xi \uparrow & \phi_2 \xi \downarrow & \phi_{M/2} \xi \uparrow & \phi_{M/2} \xi \downarrow \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \phi_1 \xi \uparrow & \phi_1 \xi \downarrow & \phi_2 \xi \uparrow & \phi_2 \xi \downarrow & \ldots & \phi_{M/2} \xi \uparrow & \phi_{M/2} \xi \downarrow \\ \phi_1 \xi \uparrow & \phi_1 \xi \downarrow & \phi_2 \xi \uparrow & \phi_2 \xi \downarrow & \phi_{M/2} \xi \uparrow & \phi_{M/2} \xi \downarrow \end{vmatrix}$$  (I.1)

where each row accepts the spatial and spin coordinates of a single unique electron in the system, and where there are $M$ total functions so that all $M$ electrons are incorporated into
the wave function. This is a simple form of the *Slater determinant* in many-body QMC theory; as stated, we impose the simplification that the number of spin-up and spin-down states is the same (a *closed-shell* description, in the sense that every available single-particle state is fully occupied by a pair of electrons). The spatial functions are also assumed to be orthonormal, so that the spatio-spin functions indeed form an orthonormal set in the space of a single electron. Finally, as stated, we assume that the set of spatial orbitals is the same in the spin-up and the spin-down sets. When all of these conditions hold, we are working within the *restricted, closed-shell* HF formulation. We have not included a normalization factor - this will be considered at the end; we use the symbol $\Psi_s$ to represent the unnormalized wave function.

We now apply a general set of coordinates $\{\vec{r}\}$ and $\{s\}$. We have:

$$
\Psi_s = 
\begin{vmatrix}
\phi_1(\vec{r}_1) \xi_1 (s_1) & \phi_1(\vec{r}_1) \xi_1 (s_1) & \ldots & \phi_{M/2}(\vec{r}_1) \xi_1 (s_1) & \phi_{M/2}(\vec{r}_1) \xi_1 (s_1) \\
\phi_1(\vec{r}_2) \xi_1 (s_2) & \phi_1(\vec{r}_2) \xi_1 (s_2) & \ldots & \phi_{M/2}(\vec{r}_2) \xi_1 (s_2) & \phi_{M/2}(\vec{r}_2) \xi_1 (s_2) \\
\phi_1(\vec{r}_3) \xi_1 (s_3) & \phi_1(\vec{r}_3) \xi_1 (s_3) & \ldots & \phi_{M/2}(\vec{r}_3) \xi_1 (s_3) & \phi_{M/2}(\vec{r}_3) \xi_1 (s_3) \\
\phi_1(\vec{r}_4) \xi_1 (s_4) & \phi_1(\vec{r}_4) \xi_1 (s_4) & \ldots & \phi_{M/2}(\vec{r}_4) \xi_1 (s_4) & \phi_{M/2}(\vec{r}_4) \xi_1 (s_4) \\
\vdots & \vdots & \ldots & \vdots & \vdots \\
\phi_1(\vec{r}_{M-1}) \xi_1 (s_{M-1}) & \phi_1(\vec{r}_{M-1}) \xi_1 (s_{M-1}) & \ldots & \phi_{M/2}(\vec{r}_{M-1}) \xi_1 (s_{M-1}) & \phi_{M/2}(\vec{r}_{M-1}) \xi_1 (s_{M-1}) \\
\phi_1(\vec{r}_M) \xi_1 (s_M) & \phi_1(\vec{r}_M) \xi_1 (s_M) & \ldots & \phi_{M/2}(\vec{r}_M) \xi_1 (s_M) & \phi_{M/2}(\vec{r}_M) \xi_1 (s_M)
\end{vmatrix}
$$

(I.2)

This is the Slater determinant wave function *ansatz*, given the restricted closed-shell HF formulation.

The Pauli exclusion principal demands that if any two electrons have the same position and spin coordinate, or exist in the same single-particle spatial and spin state, the wave function must be identically zero; i.e. this is not a state that can exist in nature. These cases correspond to identical rows, and identical columns, respectively, in the Slater determinant of Eq. I.2 - leading to a value of 0 for the determinant, so that the Slater determinant formulation properly models the Pauli exclusion principle. Also, we immediately see that the proper antisymmetric property of the wave function holds for the exchange of any pair of electrons, because this results in a swapping of two rows of the determinant, which introduces an overall negative sign.
It can be shown that the full $M$-body wave function in Eq. I.2 is an eigenfunction of $S^2 = (S_1 + S_2 + ...S_M)^2$ with eigenvalue 0, in analogy to the case of the hydrogen molecule.

When we write computer code we impose specific spin states $\{s\}$ on the electrons. Suppose, therefore, that we evaluate the wave function in the case that the electrons are ordered in consecutive opposite-spin pairs, so that all odd-indexed particles are spin-up, and all even-indexed particles are spin-down. In this case, we have:

$$\tilde{\Psi}_s^{\uparrow\downarrow} = \begin{vmatrix}
\phi_1 (\vec{r}_1) \xi_1 (s_1^1) & \phi_1 (\vec{r}_1) \xi_1 (s_1^1) & \ldots & \phi_{M/2} (\vec{r}_1) \xi_1 (s_1^1) & \phi_{M/2} (\vec{r}_1) \xi_1 (s_1^1) \\
\phi_1 (\vec{r}_2) \xi_1 (s_2^1) & \phi_1 (\vec{r}_2) \xi_1 (s_2^1) & \ldots & \phi_{M/2} (\vec{r}_2) \xi_1 (s_2^1) & \phi_{M/2} (\vec{r}_2) \xi_1 (s_2^1) \\
\phi_1 (\vec{r}_3) \xi_1 (s_3^1) & \phi_1 (\vec{r}_3) \xi_1 (s_3^1) & \ldots & \phi_{M/2} (\vec{r}_3) \xi_1 (s_3^1) & \phi_{M/2} (\vec{r}_3) \xi_1 (s_3^1) \\
\phi_1 (\vec{r}_4) \xi_1 (s_4^1) & \phi_1 (\vec{r}_4) \xi_1 (s_4^1) & \ldots & \phi_{M/2} (\vec{r}_4) \xi_1 (s_4^1) & \phi_{M/2} (\vec{r}_4) \xi_1 (s_4^1) \\
\ldots & \ldots & \ldots & \ldots & \ldots \\
\phi_1 (\vec{r}_{M-1}) \xi_1 (s_{M-1}^1) & \phi_1 (\vec{r}_{M-1}) \xi_1 (s_{M-1}^1) & \ldots & \phi_{M/2} (\vec{r}_{M-1}) \xi_1 (s_{M-1}^1) & \phi_{M/2} (\vec{r}_{M-1}) \xi_1 (s_{M-1}^1) \\
\phi_1 (\vec{r}_M) \xi_1 (s_M^1) & \phi_1 (\vec{r}_M) \xi_1 (s_M^1) & \ldots & \phi_{M/2} (\vec{r}_M) \xi_1 (s_M^1) & \phi_{M/2} (\vec{r}_M) \xi_1 (s_M^1)
\end{vmatrix},$$

where the superscript on $\tilde{\Psi}_s^{\uparrow\downarrow}$ indicates that we have imposed the spin states of the electrons in this fashion.

Setting appropriate terms to 0, yields

$$\tilde{\Psi}_s^{\uparrow\downarrow} = \begin{vmatrix}
\phi_1 (\vec{r}_1) \xi_1 (s_1^1) & 0 & \ldots & \phi_{M/2} (\vec{r}_1) \xi_1 (s_1^1) & 0 \\
0 & \phi_1 (\vec{r}_2) \xi_1 (s_2^1) & \ldots & 0 & \phi_{M/2} (\vec{r}_2) \xi_1 (s_2^1) \\
0 & \phi_1 (\vec{r}_3) \xi_1 (s_3^1) & \ldots & 0 & \phi_{M/2} (\vec{r}_3) \xi_1 (s_3^1) \\
0 & \phi_1 (\vec{r}_4) \xi_1 (s_4^1) & \ldots & 0 & \phi_{M/2} (\vec{r}_4) \xi_1 (s_4^1) \\
\ldots & \ldots & \ldots & \ldots & \ldots \\
0 & \phi_1 (\vec{r}_{M-1}) \xi_1 (s_{M-1}^1) & \ldots & \phi_{M/2} (\vec{r}_{M-1}) \xi_1 (s_{M-1}^1) & 0 \\
0 & \phi_1 (\vec{r}_M) \xi_1 (s_M^1) & \ldots & 0 & \phi_{M/2} (\vec{r}_M) \xi_1 (s_M^1)
\end{vmatrix},$$
Performing $M/2 - 1$ row permutations leads to

$$
\tilde{\Psi}^\uparrow_s = \pm \det
\begin{pmatrix}
\phi_1 (\vec{r}_1) \xi_1 \left(s^1_1\right) & 0 & \ldots & \phi_{M/2} (\vec{r}_1) \xi_1 \left(s^1_{M-1}\right) & 0 \\
\phi_1 (\vec{r}_3) \xi_1 \left(s^1_2\right) & 0 & \ldots & \phi_{M/2} (\vec{r}_3) \xi_1 \left(s^1_{M-1}\right) & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots \\
0 & \phi_1 (\vec{r}_{M-1}) \xi_1 \left(s^1_{M-1}\right) & \ldots & 0 & \phi_{M/2} (\vec{r}_{M-1}) \xi_1 \left(s^1_{M-1}\right) \\
0 & \phi_1 (\vec{r}_3) \xi_1 \left(s^1_2\right) & \ldots & 0 & \phi_{M/2} (\vec{r}_3) \xi_1 \left(s^1_{M-1}\right) \\
0 & \phi_1 (\vec{r}_4) \xi_1 \left(s^1_3\right) & \ldots & 0 & \phi_{M/2} (\vec{r}_4) \xi_1 \left(s^1_{M-1}\right) \\
\ldots & \ldots & \ldots & \ldots & \ldots \\
0 & \phi_1 (\vec{r}_M) \xi_1 \left(s^1_M\right) & \ldots & 0 & \phi_{M/2} (\vec{r}_M) \xi_1 \left(s^1_M\right)
\end{pmatrix},
$$

with the choice of plus or minus sign depending on whether $M/2$ is even or odd. Finally, performing $M/2 - 1$ column permutations leads to

$$
\tilde{\Psi}^\uparrow_s = \det
\begin{pmatrix}
\phi_1 (\vec{r}_1) \xi_1 \left(s^1_1\right) & \phi_2 (\vec{r}_1) \xi_1 \left(s^1_1\right) & \ldots & 0 & \ldots & 0 \\
\phi_1 (\vec{r}_3) \xi_1 \left(s^1_2\right) & \phi_2 (\vec{r}_3) \xi_1 \left(s^1_2\right) & \ldots & 0 & \ldots & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
0 & 0 & \ldots & \phi_1 (\vec{r}_{M-1}) \xi_1 \left(s^1_{M-1}\right) & \ldots & \phi_{M/2} (\vec{r}_{M-1}) \xi_1 \left(s^1_{M-1}\right) \\
0 & 0 & \ldots & \phi_1 (\vec{r}_3) \xi_1 \left(s^1_3\right) & \ldots & \phi_{M/2} (\vec{r}_3) \xi_1 \left(s^1_3\right) \\
0 & 0 & \ldots & \phi_1 (\vec{r}_4) \xi_1 \left(s^1_4\right) & \ldots & \phi_{M/2} (\vec{r}_4) \xi_1 \left(s^1_4\right) \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
0 & 0 & \ldots & \phi_1 (\vec{r}_M) \xi_1 \left(s^1_M\right) & \ldots & \phi_{M/2} (\vec{r}_M) \xi_1 \left(s^1_M\right)
\end{pmatrix},
$$

where the sign is unchanged from Eq. I.4 because the total number of row and column permutations is $2(M/2 - 1)$, which is even.

Using Eq. I.6, it is simple to show that the only possible choice of spin coordinates for the wave function of Eq. I.2 is one in which half of the electrons have $s = \uparrow$, and half $s = \downarrow$. If this condition is not met, the derivation leading to Eq. I.6 shows that the two sub-matrices of Eq. I.6 are no longer square, resulting in a determinant that is precisely zero. Therefore, any system known to be in the state described by Eq. I.2 has a total component $S_z = 0$ of spin in the $z$-direction; i.e. half the electrons are spin-up and half spin-down. There are no such constraints on which electrons have $s = \uparrow$ and which have $s = \downarrow$, of course, as this would violate indistinguishability of the electrons.

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Our choice here is arbitrary.

Eq. I.6 can be rewritten as

\[
\bar{\Psi}_{s}^{\uparrow \downarrow} = \det \begin{vmatrix}
\phi_{1}(\vec{r}_{1}) \xi_{\uparrow} \left( s_{1}^{\dagger} \right) & \phi_{2}(\vec{r}_{1}) \xi_{\uparrow} \left( s_{1}^{\dagger} \right) & \ldots & \phi_{M/2}(\vec{r}_{1}) \xi_{\uparrow} \left( s_{1}^{\dagger} \right) \\
\phi_{1}(\vec{r}_{3}) \xi_{\uparrow} \left( s_{3}^{\dagger} \right) & \phi_{2}(\vec{r}_{3}) \xi_{\uparrow} \left( s_{3}^{\dagger} \right) & \ldots & \phi_{M/2}(\vec{r}_{3}) \xi_{\uparrow} \left( s_{3}^{\dagger} \right) \\
\ldots & \ldots & \ldots & \ldots \\
\phi_{1}(\vec{r}_{M-1}) \xi_{\uparrow} \left( s_{M-1}^{\dagger} \right) & \phi_{2}(\vec{r}_{M-1}) \xi_{\uparrow} \left( s_{M-1}^{\dagger} \right) & \ldots & \phi_{M/2}(\vec{r}_{M-1}) \xi_{\uparrow} \left( s_{M-1}^{\dagger} \right)
\end{vmatrix}
\]

or

\[
\bar{\Psi}_{s}^{\uparrow \downarrow} = D_{s}^{\uparrow} D_{s}^{\downarrow},
\]

where \( D_{s}^{\uparrow} \) is a spatio-spin Slater determinant composed only of the spin-up electrons and \( D_{s}^{\downarrow} \) is a spatio-spin Slater determinant composed only of the spin-down electrons. The spin component can be factored out, yielding

\[
\bar{\Psi}_{s}^{\uparrow \downarrow} = D^{\uparrow} \left\{ \xi_{\uparrow} \left( s_{1}^{\dagger} \right) \xi_{\uparrow} \left( s_{3}^{\dagger} \right) \ldots \xi_{\uparrow} \left( s_{M-1}^{\dagger} \right) \right\} D^{\downarrow} \left\{ \xi_{\downarrow} \left( s_{2}^{\dagger} \right) \xi_{\downarrow} \left( s_{4}^{\dagger} \right) \ldots \xi_{\downarrow} \left( s_{M}^{\dagger} \right) \right\}.
\]  

The spatial functions \( D^{\uparrow} \) and \( D^{\downarrow} \) are written below.

As Eq. I.4 indicates, Eq. I.9 is the result we obtain by evaluating the wave function with the specific set of spin values \( \{s\} \) such that odd-indexed electrons have \( s = \uparrow \), and even-indexed electrons have \( s = \downarrow \). Making the opposite evaluation, namely that odd-indexed electrons have \( s = \downarrow \) and even-indexed electrons have \( s = \uparrow \), leads to an identical derivation, and the same numerical result for the spatial part of the wave function of Eq. I.9 for any
set of spatial coordinates, but with the spin indices flipped. This yields

\[ \bar{\Psi}_s^{1 \dagger} = D^{\dagger} \left\{ \xi_1 \left( s_1^\uparrow \right) \xi_1 \left( s_3^\uparrow \right) ... \xi_1 \left( s_{M-1}^\uparrow \right) \right\} D^{\dagger} \left\{ \xi_1 \left( s_2^\uparrow \right) \xi_1 \left( s_4^\uparrow \right) ... \xi_1 \left( s_M^\uparrow \right) \right\}. \]

In fact, we find that

\[ D^{\dagger}_{\text{odd}} D^{\dagger}_{\text{even}} = D^{\dagger}_{\text{even}} D^{\dagger}_{\text{odd}}, \tag{I.10} \]

where \textit{even} and \textit{odd} indicate which set of particle indices appear in the determinant. Eq. I.10 holds only in the special case of the restricted closed-shell solution. The derivation proceeds similarly for every choice of even- and odd-indexing. All such choices result in a pair of determinant pairs that satisfy Eq. I.10.

Let us therefore remove the spin-up and spin-down labels from all spin parameters \( s \) in Eq. I.9, and assume that Eq. I.9 is the true many-body wave function for use with spin-free operators, rather than the wave function of Eq. I.2. We may then calculate \( \left\langle \bar{\Psi} \right| \hat{O} \left| \Psi \right\rangle \) for a spin-free operator \( \hat{O} \), as we did for \( H_2 \). We use the symbol \( \bar{\Psi} \) to indicate that this is not the true many-body wave function of Eq. I.2, but instead a wave function with a fixed set of spin states. In the case of Eq. I.9, the spin coordinates straightforwardly integrate out to unity, and we find that

\[ \left\langle \bar{\Psi}_s^{1 \dagger} \right| \hat{O} \left| \bar{\Psi}_s^{1 \dagger} \right\rangle = \int D^{\dagger} D^{\dagger} O \left[ D^{\dagger} D^{\dagger} \right] d\bar{\mathbf{r}} = \int \bar{\Psi}_s^{1 \dagger} O \bar{\Psi}_s^{1 \dagger} d\bar{\mathbf{r}} \tag{I.11} \]

where the subscript \( s \) has been removed from \( \bar{\Psi} \) to indicate that the spin coordinate has been integrated out, and where

\[ \bar{\Psi}_s^{1 \dagger} \equiv D^{\dagger} \]

is a purely spatial wave function - the unnormalized product of up- and down-spin Slater determinants that is the standard form for the Hartree-Fock wave function.

We now proceed to show that, aside from a normalization constant, Eq. I.11 is identical to the correct value \( \left\langle \Psi_s \right| \hat{O} \left| \Psi_s \right\rangle \) (obtained without imposing spin states on the electrons).
We shall therefore prove that
\[ \langle \tilde{\Psi}_s^{\dagger} | \hat{O} | \tilde{\Psi}_s^{\dagger} \rangle \propto \langle \Psi_s | \hat{O} | \Psi_s \rangle. \] (I.13)

Consider the determinant in Eq. I.4. Our choice of spin indices for the spin-up and spin-down electrons was arbitrary; a different choice would result in a similar matrix with 0’s in shifted locations. Let us label the determinant of a matrix of the form in Eq. I.4, with any specific choice of spin-up and spin-down indices, as \( \tilde{\Psi}_s^\lambda \), with a unique value of \( \lambda \) for every possible unique matrix of this form that satisfies the restricted closed-shell Hartree-Fock conditions. (A matrix of this form is unique if the location of the 0’s differs from every other matrix in the set described by \( \lambda \).) The number \( \lambda \) of unique determinants \( \tilde{\Psi}_s^\lambda \) is given by \( \frac{M!}{([M/2]!)^2} \). The proof of Eq. I.13 rests on the following identity:

\[ \tilde{\Psi}_s = \sum_{\lambda=1}^{\frac{M!}{([M/2]!)^2}} (-1)^{r(\lambda)} \tilde{\Psi}_s^\lambda = \sum_{\lambda=1}^{\frac{M!}{([M/2]!)^2}} (-1)^{r(\lambda)} \det \begin{bmatrix} \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \end{bmatrix}^\lambda, \] (I.14)

where in the second line we have written

\[ \tilde{\Psi}_s^\lambda \equiv \det \begin{bmatrix} \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \end{bmatrix}^\lambda \]

so that the nature of the summation is more intuitive.

Eq. I.14 states that an expansion of the full Slater determinant in Eq. I.2 can be decomposed into the sum of sub-Slater determinants of the form of I.4, each with a different combination of zeroed elements corresponding to a different selection of spin-up and spin-down indices \( \lambda \). The sign function \( r(\lambda) \) is defined as 0 if \( \lambda \) corresponds to a choice of indices that requires an odd number of row-shifts from the form shown in Eq. I.4 to obtain 0’s in the correct location for that value of \( \lambda \); and \( r(\lambda) = 1 \) otherwise. (Each row shift swaps the position of two adjacent rows in such a fashion that the location of the 0’s changes.)
Using Eq. I.11, it is straightforward to show that

\[ \langle \tilde{\Psi}_s^\lambda | \hat{O} | \tilde{\Psi}_s^\lambda \rangle = \langle \tilde{\Psi}_s^\nu | \hat{O} | \tilde{\Psi}_s^\nu \rangle \quad \text{for any} \ (\lambda, \nu), \quad (I.15) \]

an identity we need.

Taking the expectation value of the state in Eq. I.14, we have (being somewhat loose
by reverting to ket notation, but a more rigorous proof is straightforward)

\[ \langle \tilde{\Psi}_s | \hat{O} | \tilde{\Psi}_s \rangle = \sum_{\lambda=1}^{\frac{M!}{(M/2)!^2}} (-1)^{r(\lambda)} \sum_{\nu=1}^{\frac{M!}{(M/2)!^2}} (-1)^{r(\nu)} \langle \tilde{\Psi}_s^\lambda | \hat{O} | \tilde{\Psi}_s^\nu \rangle. \quad (I.16) \]

We also need an identity that derives from

\[ \langle \tilde{\Psi}_s^\lambda | \hat{O} | \tilde{\Psi}_s^\nu \rangle = \int \langle \tilde{\Psi}_s^\nu | \tilde{r} s | \hat{O} | \tilde{\Psi}_s^\lambda \rangle d\tilde{r} ds, \]

where \( |\tilde{r} s\rangle \equiv |\tilde{r}_1 s_1 \tilde{r}_2 s_2 ... \tilde{r}_M s_M\). We have

\[ \langle \tilde{\Psi}_s^\lambda | \hat{O} | \tilde{\Psi}_s^\nu \rangle = \int \tilde{\Psi}_s^{\nu*} \hat{O} \tilde{\Psi}_s^\lambda d\tilde{r} ds, \]

where the complex conjugation is included only for consistency with the spin functions
which appear in \( \tilde{\Psi}_s^\nu \) (see Eq. 3.12). Consider now the condition \( \lambda \neq \nu \). All such terms
possess at least one pair \( \xi_1(s_n) \xi_1(s_n) = 0 \) for some \( n \) in the integrand. The product of spin
sums (unaffected by the operator \( \hat{O} \)) in Eq. I.16 therefore vanishes except when \( \lambda = \nu \), and
we find that

\[ \langle \tilde{\Psi}_s | \hat{O} | \tilde{\Psi}_s \rangle = \sum_{\lambda=1}^{\frac{M!}{(M/2)!^2}} (-1)^{r(\lambda)} \langle \tilde{\Psi}_s^\lambda | \hat{O} | \tilde{\Psi}_s^\lambda \rangle = \sum_{\lambda=1}^{\frac{M!}{(M/2)!^2}} \langle \tilde{\Psi}_s^\lambda | \hat{O} | \tilde{\Psi}_s^\lambda \rangle \quad (I.17) \]

We also note that since the functional form of \( \tilde{\Psi}_s^\lambda \) (\( \tilde{\Psi}_s^\lambda \)) is defined similarly as \( \tilde{\Psi}_s^\lambda \)) is
identical for every \( \lambda \), with only the spin indices shifted, that due to the integration in Eq.
I.11, we have

\[ \tilde{\Psi}_s^\lambda \text{ is “equivalent” to } \tilde{\Psi}_s^\nu \text{ for all } \lambda, \nu \quad (I.18) \]
where “equivalent” means, “resulting in an equal value upon taking the inner product of Eq. I.19”. Therefore,

\[ \langle \vec{\Psi}^\dagger_s | \hat{O} | \vec{\Psi}^\dagger_s \rangle = \langle \vec{\Psi}_s^\lambda | \hat{O} | \vec{\Psi}_s^\lambda \rangle, \quad (I.19) \]

for any \( \lambda \).

Using the identity in Eq. I.19, Eq. I.17 becomes

\[ \langle \vec{\Psi}_s | \hat{O} | \vec{\Psi}_s \rangle = \sum_{\lambda=1}^{M!} \langle \vec{\Psi}_s^\dagger | \hat{O} | \vec{\Psi}_s^\dagger \rangle = \frac{M!}{([M/2]!!)^2} \langle \vec{\Psi}_s^\dagger | \hat{O} | \vec{\Psi}_s^\dagger \rangle \]

or that

\[ \langle \Psi_s | \hat{O} | \Psi_s \rangle \propto \frac{M!}{([M/2]!!)^2} \langle \vec{\Psi}_s^\dagger | \hat{O} | \vec{\Psi}_s^\dagger \rangle, \quad (I.20) \]

which is the result we wish to prove.

Eq. I.20 indicates that for the sake of any spin-free observable quantum mechanical property, we may use the wave function defined in Eq. I.12, instead of Eq. I.2.

For the operators considered in this thesis, then, we can consider just the spatial part of \( \Psi_s \), and obtain equivalent results if we use

\[ \vec{\Psi} = D^\dagger D^\dagger, \quad (I.21) \]

where the superscript \( \dagger \dagger \) has been removed from \( \vec{\Psi}_s^\dagger \) due to Eq. I.18, and where

\[
D^\dagger = \det \begin{vmatrix}
\phi_1 (\vec{r}_1) & \phi_2 (\vec{r}_1) & \cdots & \phi_{M/2} (\vec{r}_1) \\
\phi_1 (\vec{r}_3) & \phi_2 (\vec{r}_3) & \cdots & \phi_{M/2} (\vec{r}_3) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_1 (\vec{r}_{M-1}) & \phi_2 (\vec{r}_{M-1}) & \cdots & \phi_{M/2} (\vec{r}_{M-1})
\end{vmatrix}
\]

and

\[
D_\downarrow = \det \begin{vmatrix}
\phi_1 (\vec{r}_2) & \phi_2 (\vec{r}_2) & \cdots & \phi_{M/2} (\vec{r}_2) \\
\phi_1 (\vec{r}_4) & \phi_2 (\vec{r}_4) & \cdots & \phi_{M/2} (\vec{r}_4) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_1 (\vec{r}_M) & \phi_2 (\vec{r}_M) & \cdots & \phi_{M/2} (\vec{r}_M)
\end{vmatrix}
\]
are spin-up and spin down Slater determinants.

The normalization constant can be deduced by counting the number of Hartree-product terms resulting from a full expansion of the spin determinants. For each determinant, the expansion results in a sum of \((M/2)!\) Hartree products. Due to the orthonormality of the spatial functions, we recognize that the square of such a sum of Hartree products, when integrated, is non-zero only in the case when identical Hartree products have been multiplied together, and all such non-zero integrations are straightforwardly equal to 1. This results in a contribution to the squared normalization constant from each determinant equal to the total number of Hartree products in the expansion, \((M/2)!\). Integrations over the two separable determinants are multiplied together, resulting in a squared normalization constant of \([(M/2)!]^2\) for the spatial part of the wave function. The full, normalized wave function then becomes

\[
\Psi = \frac{1}{(M/2)!} D^\dagger D^\dagger. \tag{I.22}
\]
Chapter 19

Appendix J: QMC statistical error

In this appendix, we derive Eq. 4.8, the formula for the statistical error $\sigma_m$ associated with a QMC calculation. Let us define $m$ as the true value of the integral in Eq. 4.1,

$$m \equiv \langle \hat{O} \rangle = \int \Psi \hat{O} \Psi d\mathbf{r} = \int |\Psi|^2 \frac{\hat{O}\Psi}{\Psi} d\mathbf{r} = \int |\Psi|^2 \hat{O}_L d\mathbf{r}, \quad (J.1)$$

and let us define $m_t$ as the QMC approximation of this integral evaluating $N$ samples,

$$m_t = \frac{1}{N} \sum_{i \in |\Psi|^2}^{N} \hat{O}_L (\mathbf{r}_i), \quad (J.2)$$

understanding that the samples are to be drawn randomly from the distribution $P = |\Psi|^2$, as indicated by $i \in |\Psi|^2$ appearing as part of the summation index description.

Each evaluation of $m_t$ will, in general, give a different result, due to the random selection of samples. In order to determine the standard deviation of an infinite set of such results, it suffices to create a function $P_m(m_t)$ that describes the distribution of such results (i.e., a histogram), and then determine the standard deviation of this function. Such a histogram can be constructed by the ingenious use of a Dirac $\delta$-function:

$$P_m(m_t) = \int d^N \mathbf{r} P(\mathbf{r}_1) P(\mathbf{r}_2) \ldots P(\mathbf{r}_N) \delta \left( m_t - \frac{1}{N} \sum_{i \in |\Psi|^2}^{N} \hat{O}_L (\mathbf{r}_i) \right). \quad (J.3)$$
This integral describes a finite set of samples \( N \), and the integration with differential element \( d^N \mathbf{r} \) runs over every coordinate for every such sample. Therefore, for \( 3M \) coordinates and \( N \) samples, this is a \( 3MN \) dimensional integral. The set of \( N \) sets of \( M \) particle coordinates \( \mathbf{r} \) is written \( \{ \mathbf{r} \} \). Using this notation, we could write \( d^N \mathbf{r} = d \{ \mathbf{r} \} \). Note that the term with the sum that appears inside the parentheses in Eq. J.3 is simply equal to \( m_t \), from Eq. J.2. However, embedding the expression in parentheses as the argument to a \( \delta \)-function ensures that the integral will be evaluated as non-zero only when the sum is equal to \( Nm_t \) for any given value of \( m_t \). Recalling that each set of \( N \) random sample points \( \{ \mathbf{r} \} \) used for a calculation of the sum in Eq. J.2 yields possibly a different result \( m_t \), we find that due to the \( \delta \)-function, the integrand provides possibly many non-zero contributions to \( P_m \), each contribution arising from a particular set \( \{ \mathbf{r} \} \) that simply equals \( P(\mathbf{r}_1)P(\mathbf{r}_2)...P(\mathbf{r}_N) \). But in fact, this is just the probability of obtaining the values \( [\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N] \). The integration provides a contribution from all sets \( \{ \mathbf{r} \} \) that yield \( m_t \), so \( P_m \) yields the total probability that \( m_t \) will result from a random selection of samples. It suffices now only to determine the width of the distribution \( P_m \).

To do so, let us employ a useful representation of the Dirac \( \delta \)-function,

\[
\delta (u) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iku} dk.
\]

Substituting \( k \equiv \lambda N \) (assuming \( N \), the number of samples, is fixed for the \( \delta \)-function integration) we have \( \delta (u) = \frac{N}{2\pi} \int_{-\infty}^{\infty} e^{i\lambda Nu} d\lambda \). Inserting into Eq. J.3 yields

\[
P_m (m_t) = \int d\mathbf{r}_j P(\mathbf{r}_j) \int \frac{N}{2\pi} e^{iN\lambda m_t - i\lambda \sum_{a=1}^{N} \hat{O}_a(\mathbf{r}_a)} d\lambda.
\]

Factoring the exponential term yields

\[
P_m (m_t) = \int d\mathbf{r}_j P(\mathbf{r}_j) \int e^{-i\lambda \hat{O}_L(\mathbf{r}_j)} \frac{N}{2\pi} e^{iN\lambda m_t} d\lambda. \tag{J.4}
\]
Rearranging the order of the product and the integrations yields

$$P_m(m_t) = \prod_{j=1}^{N} \int d\mathbf{r}_j P(\mathbf{r}_j)e^{-i\lambda\hat{O}_L(\mathbf{r}_j)} \frac{N}{2\pi} e^{i\lambda m_t} d\lambda$$  \hspace{1cm} (J.5)$$

We see that the $N$ integrations over $\mathbf{r}_j$ are all the same. Therefore, we have

$$P_m(m_t) = \int \left( \int d\mathbf{r} P(\mathbf{r})e^{-i\lambda\hat{O}_L(\mathbf{r})} \right)^N \frac{N}{2\pi} e^{i\lambda m_t} d\lambda,$$  \hspace{1cm} (J.6)$$

or placing everything into the exponent, we find that

$$P_m(m_t) = \frac{N}{2\pi} \int e^{N\{i\lambda m_t + \ln(\int d\mathbf{r} P(\mathbf{r})e^{-i\lambda\hat{O}_L(\mathbf{r})})\}} d\lambda.$$  \hspace{1cm} (J.7)$$

Now, let us define $f(m_t,\lambda)$ and $g(\lambda)$ such that

$$f(m_t,\lambda) \equiv i\lambda m_t + g(\lambda), \text{ with } g(\lambda) \equiv \ln(\int d\mathbf{r} P(\mathbf{r})e^{-i\lambda\hat{O}_L(\mathbf{r})}).$$  \hspace{1cm} (J.8)$$

Therefore, $P_m(m_t)$ can be written simply as

$$P_m(m_t) = \frac{N}{2\pi} \int e^{Nf(m_t,\lambda)} d\lambda.$$  \hspace{1cm} (J.9)$$

We can see that for large $N$, only one value of $\lambda$ dominates the final integral in Eq. J.9. Defining $\lambda \equiv \lambda^*$ at that point, we have $\frac{\partial f}{\partial \lambda}|_{\lambda=\lambda^*} = 0$, and expanding $f$ about that point, keeping only the first non-zero term in $\lambda$, we have $f(m_t,\lambda) \approx f(m_t,\lambda)|_{\lambda=\lambda^*} + \frac{1}{2} \frac{\partial^2 f}{\partial \lambda^2}|_{\lambda=\lambda^*} (\lambda - \lambda^*)^2$. We can perform an asymptotic expansion of the exponential around this point, keeping only this first non-zero term in $\lambda$ as a very good approximation for large $N$. This yields

$$P_m(m_t) \approx \frac{N}{2\pi} e^{Nf(m_t,\lambda)|_{\lambda=\lambda^*}} \int e^{\frac{1}{2} \frac{\partial^2 f}{\partial \lambda^2}|_{\lambda=\lambda^*} (\lambda - \lambda^*)^2} d\lambda.$$  \hspace{1cm} (J.10)$$
In Eq. J.10, the integral is a convenient Gaussian, which can easily be computed, yielding

\[
P_m(m_t) \approx \left(\frac{N}{2\pi} \mathcal{F}(m_t, \lambda)|_{\lambda=\lambda^*}\right)^{\frac{1}{2}} e^{-\frac{N f(m_t, \lambda)|_{\lambda=\lambda^*}}{2}}. \tag{J.11}
\]

Proceeding, we have \(\frac{\partial f}{\partial \lambda} = i m_t + g'(\lambda)\) (where \(g'(\lambda) \equiv \frac{d g}{d \lambda}\)), and setting \(\frac{\partial f}{\partial \lambda} = 0\) at \(\lambda = \lambda^*\) yields

\[
m_t = i g'(\lambda^*). \tag{J.12}
\]

Utilizing Eq. J.8, we have

\[
m_t = \int d\vec{r} P(\vec{r}) \hat{O}_L(\vec{r}) e^{-i \lambda^* \hat{O}_L(\vec{r})} \int d\vec{r} P(\vec{r}) e^{-i \lambda^* \hat{O}_L(\vec{r})} \tag{J.13}
\]

Also, \(\frac{\partial^2 f}{\partial \lambda^2}|_{\lambda=\lambda^*} = g''(\lambda)|_{\lambda=\lambda^*}.\) Hence,

\[
P_m(m_t) \approx \left(\frac{N}{2\pi} g''(\lambda)|_{\lambda=\lambda^*}\right)^{\frac{1}{2}} e^{-\frac{N f(m_t, \lambda)|_{\lambda=\lambda^*}}{2}}. \tag{J.14}
\]

We can now solve for \(\lambda^*\) by noting that, due to Eq. 4.6, \(P_m(m_t)\) has a maximum at \(m\). Since \(\lambda^*\) is a function of \(m_t\) (but not the other way around), we must in this case set the total derivative \(\frac{d P_m}{d m_t}\) equal to zero at \(m_t = m\), rather than the partial derivative, as we did in the case of \(\lambda\). However, Eq. J.14 shows that the maximum of \(P_m\) occurs at the maximum of \(f\), so instead we shall set \(\frac{df}{d m_t}|_{m_t=m} = 0.\) We have \(\frac{df}{d m_t} = \frac{df}{d \lambda^*}|_{\lambda=\lambda^*} \frac{\partial \lambda}{\partial m_t} \frac{\partial \lambda}{\partial m_t}|_{\lambda=\lambda^*} ;\) but \(\frac{df}{d \lambda}|_{\lambda=\lambda^*} = 0\) so \(\frac{df}{d m_t}|_{\lambda=\lambda^*} = i \lambda^*.\) Setting this to 0 yields the result we have been trying to achieve; namely we have found that \(\lambda^* = 0\) when \(m_t = m\), which is clear in retrospect upon inspection (being careful to understand that \(\lambda^* = 0\) only when \(m_t = m\), which, in general, is not the case for finite \(N\)). (Plugging \(\lambda^* = 0\) into Eq. J.13 confirms that \(m = \langle \hat{O}_L \rangle\) from Eq. J.1, as expected.) At this point, note that for large \(N\), the exponential term in Eq. J.14 is dominated by the first non-zero term in the expansion of \(f(m_t, \lambda)|_{\lambda=\lambda^*}\) in terms of \(m_t\) around \(m_t = m\). Performing this expansion, and noting that when \(m_t = m\) it is also true that \(\lambda^* = 0\), we have \(f(m_t, \lambda)|_{\lambda=\lambda^*} \approx f(m_t, \lambda)|_{\lambda=0,m_t=m} + \)

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\[ \frac{1}{2} \frac{\partial^2 f}{\partial m^2} \bigg|_{\lambda=0, m_t=m} (m_t - m)^2, \] or

\[ P_m (m_t) \approx \left( \frac{N}{-2\pi g''(\lambda) \big|_{\lambda=\lambda^*=0}} \right) \frac{1}{2} e^{\frac{N f(m_t, \lambda) \big|_{\lambda=0, m_t=m}}{-2\pi \frac{\partial^2 f}{\partial m^2}} \bigg|_{\lambda=0, m_t=m} (m_t - m)^2. \] (J.15)

From Eq. J.8, \( e^{\frac{N f(m_t, \lambda) \big|_{\lambda=0, m_t=m}}{-2\pi \frac{\partial^2 f}{\partial m^2}} \bigg|_{\lambda=0, m_t=m} = \int d\mathbf{r} P(\mathbf{r}) = 1 \). Calculating \( \frac{\partial^2 f}{\partial m^2} \bigg|_{\lambda=0, m_t=m} \) from Eq. J.8 yields

\[ \frac{\partial^2 f}{\partial m_t^2} \bigg|_{\lambda=0, m_t=m} = (2i \frac{\partial \lambda}{\partial m_t} + (\frac{\partial \lambda}{\partial m_t})^2 \frac{\partial^2 g}{\partial \lambda^2}) \bigg|_{\lambda=0, m_t=m}. \] (J.16)

Taking the partial derivative of Eq. J.12 with respect to \( m_t \) allows us to insert

\[ i \frac{\partial \lambda}{\partial m_t} \bigg|_{\lambda=0, m_t=m} = \frac{1}{g'' \big|_{\lambda=0}} \]

into Eq. J.16, to obtain, finally,

\[ \frac{\partial^2 f}{\partial m_t^2} \bigg|_{\lambda=0, m_t=m} = \frac{1}{g'' \big|_{\lambda=0}}. \]

Hence,

\[ P_m (m_t) \approx \left( \frac{N}{-2\pi g''(\lambda) \big|_{\lambda=0}} \right) \frac{1}{2} e^{\frac{N f(m_t, \lambda) \big|_{\lambda=0, m_t=m}}{-2\pi \frac{\partial^2 f}{\partial m_t^2}} \bigg|_{\lambda=0, m_t=m} (m_t - m)^2. \] (J.17)

Conveniently, Eq. J.17 is exactly the form of a Gaussian function with a mean value \( m \) and variance \( \sigma_m^2 = \frac{-g''(\lambda) \big|_{\lambda=0}}{N} \). A straightforward calculation of \( g''(\lambda) \big|_{\lambda=0} \) from Eq. J.8 yields

\[ \sigma_m^2 = \left\langle \hat{O}_L^2 \right\rangle - \left\langle \hat{O}_L \right\rangle^2 = \frac{\sigma_{\text{raw}}^2}{N}, \] (J.18)

which is identically equal to \( \frac{1}{N} \) times the raw variance of \( \hat{O}_L \). By \textit{raw variance}, we mean the square of the true spread (standard deviation) of the local values \( \hat{O}_L \), independent of the number of sample points \( N \). Evidently, approximations of \( \left\langle \hat{O}_L \right\rangle \) using a finite number \( N \) of sample points chosen randomly from the distribution \( |\Psi|^2 \) have a spread whose variance is given by \( \sigma_m^2 \). Using the usual notation to describe such a statistical spread of results, we
have

\[ \langle \hat{O}_L \rangle \approx m \pm \frac{\sigma_{\text{raw}}}{\sqrt{N}}, \]  

where \( \sigma_{\text{raw}} = \sqrt{\sigma_{\text{raw}}^2} \) is the standard deviation of the values of \( \hat{O}_L \) throughout the space.

The error term \( \sigma_m \) must itself be approximated as the standard deviation of the finite number of samples used during the calculation, and therefore has an associated error; we will not derive it in this thesis (ref. [140] has a detailed derivation), but this “error of the error” was utilized in Ch. 5, in which we described QMC error analysis in greater detail.
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