MONTE CARLO STUDIES IN WEAKLY INTERACTING QUANTUM SYSTEMS

A THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTORATE OF PHILOSOPHY

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Declaration of the Candidate

I certify that except where due acknowledgement has been made, the work is that of the candidate alone. This body of work has not been submitted previously, in whole or in part, to qualify for any other academic award. The content of this thesis is the result of work which has been carried out since the official commencement date of the approved research program. Any editorial work, paid or unpaid, carried out by a third party is acknowledged.

Ryan Springall
December 18, 2008
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To Ajayda and Jude

and in memory of

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Summary

This thesis is composed of two parts. In part one we report results of two quantum Monte Carlo methods - variational Monte Carlo and diffusion Monte Carlo - on the potential energy curve of the helium dimer, the prototypical van der Waals system. In contrast to previous quantum Monte Carlo calculations on this system, we have employed trial wave functions of the Slater-Jastrow form and used the fixed node approximation for the fermion nodal surface. We find both methods to be in excellent agreement with the best theoretical results at short range. In addition, the diffusion Monte Carlo results give very good agreement across the whole potential energy curve, while the Slater-Jastrow wave function fails to bind the dimer at all.

In part two we switch to investigations of many-body systems at finite temperature. We use the path integral representation of statistical mechanics to investigate the symmetry properties of the canonical ensemble partition function and find a representation in terms of irreducible representations of the symmetric group. We use this as a foundation to propose a novel technique for the stochastic sampling of the bosonic partition function for quantum gases. It is shown that in principle we are able to use two operators which enable us to construct a Markov chain through a graph of the irreducible representation of the symmetric group. As an illustration of this method, a test calculation of four particles in a harmonic trap is performed.
Chapter 1

Introduction

1.1 Introduction

There is on occasion in physics a single technological advancement or experimental observation that generates an eruption of theoretical and experimental research, realising the possible resolution of problems that were once in the realm only of academic conjecture. Such was the case with the experimental realisation of Bose-Einstein condensation, which built upon experimental methods in dense quantum liquids such as superfluidity and the advent of laser cooling techniques, achieving a macroscopic occupation of the quantum mechanical ground-state. While the phenomenon of superfluidity had been experimentally confirmed for some time in $^4$He, first observed in 1937 by Pyotr Kapitsa in Moscow and independently by John Allen and Donald Misener at the University of Toronto, the observation of Bose-Einstein condensation in dilute atomic gases was achieved for the first time 70 years after its theoretical prediction in 1925 by Albert Einstein and Satyendra Bose. This curious state of matter, where a quantum phenomenon is illustrated on a macroscopic scale, was first observed in 1995 in atomic vapours containing Rubidium (Anderson et al., 1995), Lithium (Bradley et al., 1995) and Sodium (Davies et al., 1995). Subsequent development of cooling techniques and the construction of novel trapping
potentials has opened new theoretical avenues into the investigation into quantum many-body effects at very low temperatures and represents one of the major emerging areas of physics.

Superfluidity and Bose-Einstein condensation are two examples of macroscopic manifestations of quantum effects which differ substantially from the classical phases of matter; solid, liquid and gas. The primary theoretical attributes that these systems share in common is the absence of chemical bonding between their constituent atoms and the preeminence of spin-statistics. From a reductionist viewpoint they can be qualitatively understood as resulting from long spatial and temporal atomic correlations and occur at temperatures when the thermal de Broglie wavelength becomes comparable to the mean particle separation. However an alternative description of condensation has been offered as being the result of long length permutation cycles as a result of the treatment of particle statistics. That the phenomenon of superfluidity may be linked to Bose-Einstein condensation was first proposed in 1938 by Fritz London (London, 1938a; London, 1938b) who proposed the two fluid model to describe the normal and superfluid components of liquid helium. The superfluid fraction was defined then as the component of the liquid which had condensed to the ground state and made no contribution to the entropy of the liquid. The normal-superfluid transition temperature is traditionally known as the lambda point and is identified as a discontinuity in the specific heat which occurs at 2.17°K at saturated vapour pressure. In contrast to this the critical temperature for Bose-Einstein condensation in alkali gases is in the nK regime with the density of the condensate of the order of $10^{13} - 10^{15}$ atoms.cm$^{-3}$ compared to a typical liquid density of $10^{22}$(Pethick and Smith, 2002).

An alternative theory of superfluidity is obtained by the use of path integrals at finite temperature as a representation of the statistical mechanical partition function. Originally derived as alternative formulation to quantum mechanics, Richard Feynman was able to successfully apply the path integral technique to statistical
mechanics. In the path integral representation, particle statistics is given an elegant intuitive formulation where particles are represented by closed strings whose circumference is proportional to the thermal de Broglie wavelength. The mathematical structure of the partition function for indistinguishable particles is easily recognised and amenable to numerical implementation. As well as providing a powerful alternative route to the dissemination of phenomena, the path integral representation also brings a tantalising connection between quantum theory and statistical mechanics. For many body systems, where a non-perturbative, analytic approach is often not possible and quantum effects cannot be ignored, the Monte Carlo technique can be applied to sample the partition function in the path integral representation in a technique known as path integral Monte Carlo (PIMC) (Ceperley and Kalos, 1979; Ceperley and Pollock, 1986; Ceperley and Pollock, 1989). The PIMC technique stands as one of the most useful non-perturbative methods, and is the only method which incorporates particle indistinguishability at finite temperature, the focus of part two of this work. An excellent text on Bose-Einstein condensation and superfluidity is that of C. J. Pethick and H. Smith, *Bose-Einstein Condensation in Dilute Gases* (Pethick and Smith, 2002).

Helium is a unique element in that it is the only one which exhibits superfluidity, resulting from a large zero point energy and a very weak interatomic interaction. Although in dilute gases the full interatomic potential may be replaced by an effective hard-core interaction, where the coupling constant is proportional to the s-wave scattering length, the accurate description of the He dimer interaction curve has been the focus of theoretical investigations for many reasons and has the most accurately known interatomic potential. Specifically it has been the Helium dimer which has been at the center of intense theoretical investigation to better quantify and understand the nature of the van der Waals force in molecular systems. The Helium dimer is the prototypical van der Waals dimer as it is the smallest system where this is the dominant interaction mechanism. As a result of this weak interaction and
also a large zero-point energy. Helium does not solidify at atmospheric pressures but exists as a liquid down to $T \to 0$. It therefore serves as a convenient benchmark system to test the capability of various approximations in solving the quantum many-body problem, both in condensed matter and electronic structure theory. Electron correlation is seen as being responsible for van der Waals interactions in condensed matter and molecular systems, with the classical result from many-body perturbation theory being the R-6 attraction potential between molecules. However non-perturbative models such as present-day implementations of density functional theory are incapable \textit{a priori} of consistently accounting for van der Waals interactions and other proposed methods such as solutions to the Bethe-Salpeter equation and Green’s functions methods, are restrictive due to their complexity. These interactions are feeble in energy when compared to other bonding types such as covalent and ionic bonding but are known to be the dominant mechanisms in the next size regime which \textit{ab-initio} quantum chemistry will be looked to for application, those of molecular biology and nanotechnology. In these instances we may have aggregates of thousands of interacting electrons, for which it is questionable whether a full many-body wavefunction is a feasible entity. A major approximation in present-day density functional theory is that of the exchange-correlation potential which is usually not transferable between non-similar systems and is not universal. While offering significant increases in computational efficiency this severely restricts its predictive capability. It has been posited that QMC methods are to become an increasingly prominent approach to the many-body bound state problem and offer the promise of a unified approach with the accuracy required to describe van der Waals interactions. This in essence is the central tenet of part one of this investigation.

Are quantum Monte Carlo methods able to give an accurate account of the dominant correlation effects in the prototypical van der Waals bonded system, the He dimer, as well as increase computational efficiency to be applicable to systems containing a larger number of electrons such as other rare gas dimers and more complex
systems? In many ways the phenomenon of van der Waals, or dispersion, interaction epitomises the quantum nature of matter and its theoretical underpinnings. In many other ways it shows how our understanding of interactions on an atomic scale are in instances inadequate. A fundamental understanding of the origin of van der Waals interactions is unattainable without the full machinery of modern theoretical physics.

Van der Waals interactions are ubiquitous in nature, the concept is known to many science students from the earliest of their undergraduate experiences and is used to explain a host of phenomena which cannot be explained within the framework of orbital theory. Van der Waals forces have also been attributed to the adhesive properties of various animals including geckos, spiders and flies (Autumn et al., 2002). There has been much work on understanding and possible technological applications of van der Waals adhesion. Figures 1.1 and 1.2 show electron microscope images of the structure of the feet of the fruit fly (Drosophila Melanogaster) and gecko respectively.

The fruit fly images were obtained by Matthew Taylor and myself on the Phillips XL-30 scanning electron microscope at RMIT University. The gecko images were kindly supplied by Assoc. Prof. Wan Sing of Nanyang Technical University Singapore. The bottom of the foot of the fruit fly is covered with a series of setae, each splayed at its end to form a shovel like profile. The profile is such as to maximise the area of contact of the foot when the fly is on a surface.

The work of Autumn et al (Autumn et al., 2002) was the first to show that gecko adhesion was the result of van der Waals interactions and not capillary forces or pressure differentials. Although gecko feet are highly hydrophobic, strong adhesion was shown on both highly hydrophilic and hydrophobic polarisable surfaces. Therefore surface chemistry is unimportant in adhesion properties which are mainly a function of the geometry of the gecko’s foot. The gecko foot has become a model as a candidate for a universal adhesive which will work well on any surface and in
Table 1.1: Scanning electron microscope images of the foot of Drosophila Melanogaster. Successive magnification of the middle foot are shown in images A, B and C where the profile of the setae are easily recognised. The orientation of image D clearly shows the profile of the foot that allows the fly to become unstuck from the surface it is on. Images C and D are at a magnification of 5212 while images A and B are at magnifications of 81 and 2606 respectively.
Table 1.2: Electron microscope images of the branching structure of the base of the gecko foot. This allows adhesion to both smooth and undulating surfaces as the contact area is maximised. Coupled with its self cleaning properties, the gecko foot has become the basis of the fabrication of gecko tape. (Reproduced with permission of Tanu Suryadi Kustandi, Institute of Materials Research and Engineering, Singapore)
1.2 Overview of Thesis

This thesis is devoted to the theoretical understanding of weakly interacting atomic systems using both zero and finite temperature quantum Monte Carlo methods. This thesis is then naturally divided into two parts. In part one we look at electron correlation in the Helium dimer, the prototypical van der Waals bonded atomic system, by calculating its potential energy curve using the variational and diffusion Monte Carlo methods. In Part Two we shall use path integral techniques to look at the behaviour of many-body bosonic systems at finite temperature, which manifest at low temperatures in the observation of superfluidity and Bose-Einstein condensation.

It is hoped at the conclusion of this thesis that we will have presented a clear view of not only quantum Monte Carlo methods, but also the difficulties that will need to be overcome in order to that it may continue to be a benchmark computational procedure.

Part One - Zero Temperature Quantum Monte Carlo Methods and the Helium Dimer

- **Chapter Two**: We review the theoretical basis of two quantum Monte Carlo methods, variational Monte Carlo (VMC) and fixed node-diffusion Monte Carlo (FN-DMC). We describe the Metropolis sampling scheme, present a general trial wave function of the Slater-Jastrow form and outline the two most important limitations of the diffusion Monte Carlo method, the fermion sign problem and finite time-step errors.

- **Chapter Three**: We report results from VMC and DMC calculations on the potential energy curve of the helium dimer with interatomic separations in the range \( r \in [0.9, 7.4] \) a.u.. We find both methods to be in excellent agreement
with the best theoretical results at short range. In addition, the diffusion Monte Carlo results give very good agreement across the whole potential energy curve, while the Slater-Jastrow wave function fails to bind the dimer at all.

Part Two - Path Integral Statistical Mechanics

• **Chapter Four:** We give a brief overview of theoretical and experimental investigations into Bose-Einstein Condensation and superfluidity.

• **Chapter Five:** Since being formally presented in 1939 by Richard Feynman, the path integral representation of quantum mechanics has provided an alternate and in some instances the only description of the behaviour of Nature. The path integral representation naturally lends itself to an intuitive understanding of particle dynamics and is the foundation of the diagrammatical approach to the many-body problem. In this chapter we review the foundations of the path integral in quantum and statistical mechanics and give some consequences resulting from this approach.

• **Chapter Six:** The structure of the partition function under the action of the permutation group reveals a deeper mathematical structure where correlation lengths may be related to permutation cycle lengths. In this chapter we give a description of the bosonic partition function in terms of the conjugacy classes of the symmetric group. We connect the partition for bosons and fermions to the symmetric polynomials and show how they relate to each other.

• **Chapter Seven:** The principal ideas behind the path integral Monte Carlo method are presented such as the primitive action and the sampling of the density matrix. We present a novel permutation space sampling algorithm which maps between conjugacy classes of the symmetric group and apply it to the well characterised problem of bosons confined to a one dimensional harmonic trap.
Part One
Chapter 2

Quantum Monte Carlo Methods

2.1 Introduction

The main concern of current theoretical and computational investigations of electronic structure in atomic and condensed matter physics is an increasingly accurate account of correlation effects of interacting quantum particles. Of particular interest is the accurate account of dispersion interactions in systems where physical bonds are the predominant interaction mechanism, such as noble gas dimers and layered solids such as graphite and micas. The main characteristic of such systems is a distinct absence of electron-dense regions along the bond vector, and large non-local contributions to the correlation energy.

Quantum Monte Carlo (QMC) methods are an alternative to traditional approaches to the quantum many-body problem, variational Monte Carlo (VMC) via the use of explicitly correlated, variational wave-functions and diffusion Monte Carlo (DMC) via numerically projecting out the exact ground-state wave-function.

In this chapter a theoretical outline of two quantum Monte Carlo techniques, VMC and DMC, shall be presented. They are presented as per application to the evaluation of expectation values in the quantum mechanical many body problem, in particular solving the many-body Schrödinger equation at zero temperature. The
interested reader is referred to (Foulkes et al., 2001; Needs et al., 2005) and references therein for a more in-depth discussion on the QMC method and the CASINO QMC code which is used in the calculations presented in Chapter 3. In part two of this thesis we will look at the path integral Monte Carlo method, a technique for investigating quantum systems at finite temperature.

2.2 The Monte Carlo Method

The term Monte Carlo as applied to numerical calculations pertains to the use of stochastic methods in order to numerically solve various mathematical problems. On the most fundamental level one can consider two realms of application of the Monte Carlo method. For problems which are explicitly probabilistic in nature, the Monte Carlo method may be applied directly to obtain quantitative information regarding the outcome of a large number of independent measurements. Systems of this type include for example the scattering of an electron beam through the collimator of a linear accelerator, nuclear decay pathways or option prices in the stock market. The second type is one in which although the problem is not explicitly probabilistic, stochastic methods may be used to deduce results.

An example of the latter case is the calculation of the constant π. Consider a 2-dimensional random vector \( \{(x, y) \mid x, y \in (-r, r)\} \) and the geometric arrangement of a circle of radius \( r \) fitted to the inside of a square such that their perimeters are coincident. Denote the area inside the circle as \( A \) and the area outside the circle, but inside the square as \( B \). The probability that a random vector will lie in each of these areas is proportional to the ratio of their areas and is given by

\[
Pr(B) = 1 - \frac{\pi}{4} \\
Pr(A) = \frac{\pi}{4}
\] (2.1)
For a set of $N$ random vectors, denote as $n$ the number of vectors that lie inside the circle. The number $n$ will then be representative of $Pr(A)$, which substituting into equation 2.1 gives an expectation value of $\pi$

$$\langle \pi \rangle = \frac{4n}{N}.$$ 

The results of this algorithm are shown in figure 2.2.

In the problems we are to pursue in the ensuing chapters, our primary task is calculating integrals of the form

$$I = \frac{\int dX \hat{h}(X) P(X)}{\int dX P(X)} \quad (2.2)$$

That is, we need to calculate the expectation value of an observable represented by the operator $\hat{h}(X)$ associated with the distribution $P(X)$. To do this requires a more sophisticated approach than the example given above for the calculation of $\pi$, which the Metropolis algorithm is the basis of.
Figure 2.2: Estimation of $\pi$ via stochastic sampling as a function of samples. The rate of convergence is also plotted which is proportional to $1/\sqrt{N}$

### 2.2.1 The Metropolis Monte Carlo Method

The power of the Metropolis scheme (Metropolis et al., 1953) is the ability to calculate expectation values of distributions without the explicit requirement of normalisation, which is implicitly fulfilled by the algorithm.

Given an arbitrary distribution, the Metropolis algorithm allows us to construct a Markov chain through configuration space, which will return a sequence of values indicative of this distribution. Consider a $3N$ dimensional vector $\mathbf{R} = \{r_1, r_2, ..., r_N\}$, where $r_i$ labels the position of an artificial particle known as a walker, and the associated scalar density $\pi(\mathbf{R})$. If the field is positive definite over its entire domain, that is $\pi(\mathbf{R}) \geq 0 \ \forall \ \mathbf{r} \in \mathbb{R}$, then it may be interpreted as a probability distribution and expectation values of quantities associated with this field given as

$$
\langle f \rangle = \frac{\int_a^b d\mathbf{R} f(\mathbf{R}) \pi(\mathbf{R})}{\int_a^b d\mathbf{R} \pi(\mathbf{R})}
$$

(2.3)

Given a set of walkers $\mathbf{R} = \{\mathbf{R}_1, ..., \mathbf{R}_M\}$ distributed as $\pi(\mathbf{R})$, then the mean value of an estimator of $f$ which is a function of $\mathbf{R}$ on the field $\pi(\mathbf{R})$ may be computed
as

$$\langle f \rangle = \frac{1}{M} \sum_{i=1}^{M} f(R_i). \quad (2.4)$$

Equation 2.4 is exact in the limit $M \to \infty$. The associated statistical error may be estimated by the standard deviation

$$\sigma_{\langle f \rangle} = \sqrt{\frac{1}{N(N-1)} \sum_{i=1}^{N} [f(R_i) - \langle f \rangle]^2} \quad (2.5)$$

The error associated with estimators is theoretically independent of the dimensionality of the problem. A walker is stochastically guided through the configuration space of $\pi(R)$ by the specification of new configurations via the transition probability $P(R \to R')$, the probability that a walker moves from $R$ to $R'$. This transition probability is composed of two components, $T(R \to R')$ the probability that a move is proposed and $A(R \to R')$ the probability that the move is accepted.

$$P(R \to R') = T(R \to R') A(R \to R'). \quad (2.6)$$

Once the new configuration is chosen it is accepted with the probability

$$A(R \to R') = \min \left( 1, \frac{\pi(R') T(R' \to R)}{\pi(R) T(R \to R')} \right) \quad (2.7)$$

If accepted, the configuration is updated to the new configuration and if rejected, the old configuration maintained. In this way rejected as well as accepted configurations are used for the evaluation of averages. A proof of the convergence of the
procedure can be found in (Narayan and Young, 2001). There is no restriction on the form of $T(R \rightarrow R')$, other than that required to satisfy the ergodicity condition known as detailed balance. This ensures that the flow of walkers into a region is the same as the flow out of the region and hence equilibrium is reached. If the move $R \rightarrow R'$ has a finite probability of being proposed, then so should $R' \rightarrow R$, although it is not necessary that this should be with the same probability. Common forms of $T(R \rightarrow R')$ are to set it equal to a constant within some range $\tau$ and zero elsewhere or a Gaussian with variance $\tau$. The quantity $\tau$ is a user defined parameter which is usually adjusted such that approximately half of all moves are accepted. There is no explicit reason for this to be so, however it can be argued that an acceptance ratio of 50% is the optimal value for minimising serial correlation biases.

At the beginning of the algorithm, particle positions are allocated randomly and then equilibrated. Once equilibrated they are then used to sample $\pi(R)$, returning a set of vectors $\{R_1, R_2, ..., R_N\}$ representing this distribution, which in turn are used to evaluate $\langle f \rangle$.

## 2.3 The Many-Body Schrödinger Equation and the Variational Theorem

The modern basis for the computation of the electronic structure of atoms, molecules and solids is the many-body Schrödinger equation in the Born-Oppenheimer approximation, whereby the relaxation of electrons to their equilibrium configuration occurs instantaneously compared to the time scale of nuclear motions

$$\hat{H}\Psi(X) = E\Psi(X). \quad (2.8)$$

Here $\Psi(X)$ is the many-body wave-function, $X = \{x_i\} = \{r_i, \sigma_i\}$ the n-particle
space-spin degrees of freedom and \( E \) the energy. In first quantised form the Hamiltonian operator \( \hat{H} \), is

\[
\hat{H} = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \sum_{i} \sum_{A} \frac{Z_{A}}{|R_{A} - r_{i}|} \\
+ \frac{1}{2} \sum_{i} \sum_{j \neq i} \frac{1}{|r_{i} - r_{j}|} + \frac{1}{2} \sum_{A} \sum_{B \neq A} \frac{Z_{A}Z_{B}}{|R_{A} - R_{B}|}
\]  

(2.9)

where \( Z_{A} \) denotes the atomic number of the \( A^{th} \) nucleus and \( R_{A} \) its position.

In the Born-Oppenheimer approximation, the nucleus-nucleus interaction potential is independent of the electron configuration, being constant within the specified geometry. Throughout this work we shall use this Hamiltonian operator as the basis for approaches to the quantum many-body problem.

The foundation for many attempts at approximate solutions to the Schrödinger equation is the variational principle. Consider some hermitian operator and corresponding eigenvalue equation

\[
A|e_{i}\rangle = \lambda_{i}|e_{i}\rangle.
\]  

(2.10)

The set of eigenvectors \( \{|e_{i}\}\) define a complete basis for the inner product Hilbert space \( \mathcal{H} \). Since the basis vectors span \( \mathcal{H} \) we may express an arbitrary vector \( |f\rangle \in \mathcal{H} \) as a linear combination of the basis vectors as \( |f\rangle = \sum_{i=1} c_{i}|e_{i}\rangle \). The normalisation requires that \( \sum_{i} |c_{i}|^{2} = 1 \) and we may now calculate the expectation value of \( A \) along \( |f\rangle \) as
\[ \langle f | \hat{A} | f \rangle = \sum_{m} \sum_{n} c_{n}^{*} c_{m} \langle e_{n} | A | e_{m} \rangle \]
\[ = \sum_{m} \sum_{n} c_{n}^{*} c_{m} \lambda_{m} \langle e_{n} | e_{m} \rangle \]
\[ = \sum_{m} \sum_{n} c_{n}^{*} c_{m} \lambda_{m} \delta_{mn} \]
\[ \lambda_{f} = \sum_{m} |c_{m}|^{2} \lambda_{m} \]

(2.11)

If the eigenvalue spectrum is bounded from below then it is not difficult to see that for any function \( |f \rangle \in \mathcal{H} \), \( \lambda_{f} \geq \lambda_{0} \), \( \lambda_{0} \) being to the lowest eigenvalue. For the case of the Schrödinger equation, this implies that expectation values of the Hamiltonian operator with respect to a trial wave-function \( |\Psi_{T} \rangle \) will give an energy that is always greater than or equal to the true ground-state energy, as long as it satisfies the requirements of single valuedness and square integrability,

\[ E_{T} = \langle \Psi_{T} | \hat{H} | \Psi_{T} \rangle \]
\[ \geq E_{0} \]

(2.12)

This is the basis for the variational approach to the many-body Schrödinger equation and methods such as the Hartree-Fock method, density functional theory and other variational methods. One of the powers of the variational approach is that we now have a criterion for wave-function construction and optimisation for many-body systems which is independent of empirical observation. By this it is meant that to ascertain the ability of different forms of trial wave-function to incorporate the appropriate fermion physics, we are required only to compare their respective energies. For the case of practical DFT, where approximations are introduced by the
use of a non-exact exchange correlation functional, this universal validity is no longer applicable as variational solutions for the many-body wave-function give a lower bound with respect to the particular form of the implemented exchange-correlation functional (Dreizler and Gross, 1990) which can be lower than the true ground-state energy. Further it is not guaranteed that the correct physics is incorporated into this functional.

2.4 The Variational Monte Carlo Method

The Variational Monte Carlo (VMC) method is the more straightforward of the Monte Carlo techniques used for quantum many-body calculations. Its successful implementation requires two basic ingredients, the Metropolis algorithm to sample the distribution $|\Psi_T|^2$ and the variational theorem. The primary quantity which controls the overall accuracy of a VMC calculation is a judicious choice of trial wave-function, that which is able to encapsulate the major physics which is manifest in many body correlation effects, as well as being compact in form to allow rapid evaluation. Although more sophisticated QMC methods may obtain more accurate estimators for observables, they can be all broadly cast as projector techniques in that they project out exact ground state properties, however giving less information regarding the physical nature of many-body correlations. VMC on the other hand is systematically improvable by building in more complicated correlation effects into the trial wave-function. A specific case in point is the work of Drake et al. (Drake et al., 2002) in the use of Hyleraas-Jastrow type trial wave-function for He, H$^-$ and Ps$^-$ (positronium) with the explicit inclusion of dipole-dipole terms.

Given a trial wave-function $\Psi^\alpha$ containing a set of free parameters $\{\alpha\}$, the expectation value of the Hamiltonian operator $\hat{H}$, denoted $E_T$, will be a strict upper bound to the true ground-state energy as given by the variational principle. The expression for the expectation value of the energy given in Equation 2.12 is not
appropriate for evaluation via the Metropolis Monte Carlo method, which must be recast into a form similar to Equation 2.3. Such an expression is

$$E_T = \frac{\int dR |\Psi(\mathbf{R})|^2 E_L(\mathbf{R})}{\int dR |\Psi(\mathbf{R})|^2}, \quad (2.13)$$

where the quantity $E_L = \Psi^{-1}_\alpha \hat{H} \Psi_\alpha$ is the known as the local energy. The complete set of electrons is represented by a $3N$ dimensional walker with the coordinate set $\mathbf{R} = \{r_1, ..., r_n\}$ representing electron positions. Using the Metropolis algorithm, a set of configurations $\{\mathbf{R}\} = \{\mathbf{R}_1, ..., \mathbf{R}_M\}$ is obtained which are distributed as $|\Psi(\mathbf{R})|^2$. To sample the many-body trial wave-function we construct a Markov chain in configuration space by considering the Metropolis acceptance probability $A(\mathbf{R} \rightarrow \mathbf{R}') = \min(1, q)$, where $q = |\Psi(\mathbf{R}')/\Psi(\mathbf{R})|^2$. For an electron-by-electron sampling algorithm, a single electron move is proposed from an existing position as

$$r_i' = r_i + A(\tilde{\varepsilon} - 0.5). \quad (2.14)$$

Here $A$ is the step size and $\tilde{\varepsilon}$ is a 3-dimensional vector of uniformly distributed random numbers in the interval $[0, 1]$. Once the new walker configuration is posited, the move is accepted or rejected by calculating the Metropolis acceptance probability and if accepted the walker position updated. Each point in configuration space has a corresponding value of the local energy, and the total energy of the system with respect to the trial wave-function may be computed as the statistical average of each point in the sampled configuration space, i.e.

\footnote{From here we shall drop the $T$ subscript indicating the use of the trial wave-function unless clarification is required}
\[ E_T = \frac{1}{M} \sum_{i=1}^{M} E_L(R_i). \quad (2.15) \]

In practice the local energy is not evaluated after each Metropolis move as successive electron configurations are highly correlated and the error can be underestimated if this expression is used. In practice we reduce errors arising from serial correlation by calculating the local energy at every \( n^{th} \) step, \( n \) being defined by the user, or employing post calculation methods such as data reblocking (Needs et al., 2005). The value of the correlation period will depend on the system investigated and for the calculations in the following chapter a value of between 2 and 10 is used.

### 2.4.1 Variance minimisation

Given that we may obtain an estimate for the expectation value of the local energy for a fully interacting quantum system, we can use the variational theorem to obtain better approximations to the wave-function of the system and hence a better description of electron correlation. The basis of the variance minimisation technique was the proposal of Umrigar et al. (Umrigar et al., 1988) that instead of energy minimisation as the criteria for optimisation of trial wave-functions, one should instead look at the variance in the local-energy, arguing that for a good quality trial wave-function the variance of the local-energy will approach zero. In practice the merit of variance minimisation over minimisation of the local-energy is that variance minimisation algorithms are numerically more stable (Needs et al., 2005). Recently Toulouse and Umrigar (Toulouse and Umrigar, 2007) have proposed a generalised wave-function optimisation algorithm for trial wave-functions of the Slater-Jastrow type and applied it to the \( \text{C}_2 \) molecule. Unlike energy minimisation where the ground-state energy differs between different systems, the zero variance principle also offers a universal measure of wave-function accuracy and gives a lower bound
to optimise wave-function parameters. The variance in the energy will then be a function of the parameter set \( \{ \alpha \} \) and can be calculated as

\[
\sigma^2_{\{ \alpha \}} = \frac{\int |\Psi^{\{ \alpha \}}(\mathbf{R})|^2 [E^\alpha_L - E^\alpha] d\mathbf{R}}{\int |\Psi^{\{ \alpha \}}(\mathbf{R})|^2 d\mathbf{R}},
\]

where \( E_L \) is the energy of one configuration and \( E \) is the mean energy of all configurations. To calculate the variance as given Equation 2.16 then requires that we have the additional condition that \( \int \Psi^* T \hat{H}^2 \Psi_T < \infty \) (Foulkes et al., 2001). For a set of walker configurations, the variance in the energy is computed as

\[
\sigma^2 = \frac{1}{N-1} \sum_i \left( E^\alpha_L (\mathbf{R}_i) - E^\alpha_L \right)^2
\]

We shall discuss the specific form of the implemented wave-function in this and other works on the noble gas atoms presently.

### 2.5 The Fixed Node Diffusion Monte Carlo Method

Diffusion Monte Carlo is one of a class of projector techniques whereby a set of walkers is evolved in imaginary time from some initial starting approximation of the ground-state wave-function, to a statistical distribution that is proportional to the true ground-state one. Like the path integral Monte Carlo method, which shall be discussed in part two of this thesis, it utilises the connection between quantum mechanics and statistical mechanics through the analytic continuation of time to the imaginary axis of the many-body Green’s function. Like VMC, DMC uses a set of random walkers to sample the configuration space associated with the ground state probability distribution. However unlike VMC where the probability distribution is given as an approximated form of the many-body wave-function, in principle DMC
solves the Schrödinger equation for a given Hamiltonian \textit{exactly}. In practice there are two major approximations required for the successful implementation of DMC, the fixed node approximation to deal with the antisymmetry of fermionic wave-functions and the finite time-step value for the many-body Green’s function. DMC has had great success in predicting many properties for a large range of systems including periodic solids and small van der Waals and hydrogen bonded molecules (Maezono et al., 2007; Benedek et al., 2006; Acioli, 1996), giving the correct quantitative behaviour of the van der Waals binding energy curve. However whether DMC will be sufficiently efficient and accurate enough for larger systems or van der Waals solids such as graphitic carbon, has yet to be decided.

2.5.1 Theoretical Basis

Diffusion Monte Carlo lends its name from the form of the Schrödinger equation in imaginary time, which is equivalent to the inhomogeneous diffusion equation

\[- \partial_\tau \Psi (\mathbf{R}, \tau) = \left( \hat{H} - E_T \right) \Psi (\mathbf{R}, \tau).\]  (2.18)

Here $E_T$ is an energy offset term whose purpose will become clear momentarily and $\tau$ is the imaginary-time variable. As usual, the many-body Hamiltonian $\hat{H}$ is composed of two parts, a kinetic term and potential term. In the absence of potential energy terms, Equation 2.18 describes the free diffusion of a set of walkers in $3N$-dimensional configuration space from some initial configuration. The inclusion of potential terms act to guide walkers into or away from regions in configuration space. For atomic systems, the initial configuration of a set of walkers is derived from a density given by some previously optimised trial wave-function, which in our circumstance will be of the Slater-Jastrow form from an earlier VMC calculation. Given the initial walker distribution $\{ \mathbf{R} \}$ at time $t$, the time evolution of the system
can be cast into integral form by making use of the Green’s function, which for all intents and purposes here may simply be defined as the inverse of the Hamiltonian, i.e.

\[ \hat{H}G(R, \tau; R', \tau') = \delta (R' - R) \delta (\tau' - \tau), \] (2.19)

for which the imaginary-time Schrödinger equation is cast in integral form as

\[ \Psi (R', \tau) = \int dR G(R, R'; \tau) \Psi (R). \] (2.20)

Here \( G(R, R'; \tau) \) is the Green’s function, or the propagator. Equation 2.20 is simply a re-expression of Equation 2.18 and contains no new information on particle time evolution, however there are advantages in representing it in this form. Firstly in the position representation we may express the Green’s function as a c-number function and are no longer required to use a unitary time evolution operator to describe the temporal evolution of the system. Secondly the integral formulation is ideal for implementation of the Monte Carlo integration method. The implementation of the DMC technique rests on the properties of the long time limit of Equation 2.20. Consider the formal definition of the Green’s function in the position representation (cf. the definition of the thermal density matrix in part 2),

\[ G(R, R'; \tau) = \langle R | e^{-\tau(\hat{H} - E_T)} | R' \rangle. \] (2.21)

If we denote \( \{|\phi_i\rangle\} \) as the complete basis of the Hilbert space corresponding to the full many-body Hamiltonian and the initial state of the system as \( \Psi_T \), we can use the spectral expansion of the Green’s function to prove that in the limit that
$\tau \to \infty$, the system will evolve to the exact ground-state of the Hamiltonian. Using the identity $\sum |\phi_i\rangle \langle \phi_i| = 1$ Equation 2.21 can be written

$$
G(R, R', \tau) = \sum_i \langle R | \exp \left[ -\tau \left( \hat{H} - E_T \right) \right] | \phi_i \rangle \langle \phi_i | R' \rangle
$$

$$
= \sum_i \phi_i^*(R') \phi_i(R) e^{-\tau(E_i - E_T)},
$$

where $E_i$ is the corresponding eigenvalue of the eigenfunction $\phi_i$. Substituting this representation of the Green’s function into Equation 2.20 gives

$$
\Psi (R', t + \tau) = \int dR \sum_i \phi_i^*(R') \phi_i(R) e^{-\tau(E_i - E_T)} \Psi_T (R, t)
$$

$$
= \sum_i \phi_i (R') e^{-\tau(E_i - E_T)} \langle \phi_i | \Psi_T \rangle,
$$

which in the $\tau \to \infty$ limit gives

$$
\lim_{\tau \to \infty} \Psi (R, t + \tau) = C \phi_0 (R).
$$

Here $C$ is a normalisation constant. By choosing the trial energy $E_T$ to be the exact ground-state energy, the weight of all states except the ground-state in the spectral expansion of the Green’s function will be exponentially damped and hence tend to 0 in the $\tau \to \infty$ limit. In this way the ground-state is projected out, the only proviso being that the initial state and the true ground state are not orthogonal. This is the theoretical foundation for the DMC technique.
2.5.2 The Green’s function

The purpose of doing DMC calculations is to find numerical solutions to the Schrödinger equation which is too difficult to be solved analytically. This means we are required to approximate the form of the Green’s function consequently introducing errors into any calculation performed. Consider the free, single particle Hamiltonian operator $\hat{H} = -\frac{1}{2} \nabla^2$ and corresponding Green’s function

$$\langle \mathbf{r} | e^{-\tau \hat{T}} | \mathbf{r}' \rangle = (2\pi\tau)^{-\frac{3}{2}} \exp \left[ -\frac{(\mathbf{r}' - \mathbf{r})^2}{2\tau} \right].$$  \hspace{1cm} (2.24)

When substituted into the time evolution equation 2.20, Equation 2.24 describes the time-dependent density of particles diffusing in space. For a system of $n$ free discrete walkers, the Green’s function will be simply the product of product of single particle Green function of the form of equation 2.24. Using the diffusion analogy, Equation 2.24 can then be considered as prescribing the transition probability for a walker to complete the move $\mathbf{r} \rightarrow \mathbf{r}'$, which can be successively applied in the construction of a Markov chain describing diffusing Brownian particles.

The inclusion of particle interaction terms means that we can no longer decompose the n-particle Green’s functions into single particle components. To proceed we separate the Hamiltonian into kinetic and potential components and use the Baker-Campbell-Hausdorff formula for operator exponential expansions,

$$e^{\tau (\hat{T} + \hat{V})} = e^{\tau \hat{T}} e^{\tau \hat{V}} e^{\tau^2 \hat{C}}.$$  \hspace{1cm} (2.25)

One can obtain this expression via a Taylor series expansion about $\tau = 0$ and grouping appropriate terms. Doing so $\hat{C}$ evaluates to

---

Note: The result $\hat{C}$ is derived in part 2 of this thesis.

---
\[ \hat{C} = \frac{\tau^2}{2} [\hat{T}, \hat{V}] + \frac{\tau^3}{12} [\hat{T}, [\hat{T}, \hat{V}]] - \frac{\tau^3}{12} [\hat{V}, [\hat{T}, \hat{V}]] + \ldots \] (2.26)

For small values of \( \tau \), an approximation to the Green’s function is obtained by disregarding all the terms contained in \( \hat{C} \), which in the literature is sometimes referred to as the primitive approximation. Using this we may derive an explicit form of the Green’s function,

\[
\langle R'| e^{-\tau(\hat{T}+\hat{V})} | R \rangle \approx \langle R'| e^{-\tau\hat{T}} e^{-\tau\hat{V}} | R \rangle = \int dR'' \langle R'| e^{-\tau\hat{T}} | R'' \rangle \langle R''| e^{-\tau\hat{V}} | R \rangle = (2\pi t)^{-\frac{3N}{2}} \int dR'' \exp \left( -\frac{(R'' - R')^2}{2\tau} \right) e^{-\tau V(R)} \delta(R - R'')
\]

(2.27)

In the final line we have replaced the energy offset term as defined in equation 2.18. The added potential term describes a decay-growth process such as population growth or nuclear decay. In the case of DMC it is used to determine walker creation or annihilation such that the population is a statistical representation of the ground-state density \( |\Psi_0|^2 \). It acts to increase walker numbers in areas of high density and decrease the population in places with low probability. Using a finite value for the time-step in the Green’s function introduces errors into the calculated averages, referred to as time-step errors. In practice one is required to perform calculations over a range of time-step values and extrapolate these values to zero. We will look at the effects of this in the next chapter especially since in the energy regime with which we are working they become more pronounced.

Representing the wave-function as a summation over a set of walkers \( \Psi(R) = \)
\[ \sum_j \delta(r - r_j) \] and substituting into Equation 2.23 gives the walker evolution equation for a single time-step to be

\[ \phi(r, \tau) = \sum_j G(r_j(t) - r; \tau) \]  \hspace{1cm} (2.28)

Initially the walkers will be statistically distributed as the trial wave-function, successive applications evolving the system to the ground-state.

### 2.5.3 Wave-function Nodes and the Fixed Node Approximation

The appeal of the diffusion Monte Carlo method as an exact numerical method for the many-body problem is offset by the sign problem in fermionic systems. The origin of this problem is the interpretation of the wave-function as a probability density in the imaginary time Schrödinger equation. The necessary anti-symmetry
of the many-body fermion wave-functions gives regions having positive and negative values. When constructing fermionic wave-functions, trial functions need to satisfy the exchange anti-symmetry condition condition for same spin fermions

$$\Psi(..., r_i, ..., r_j, ...) = -\Psi(..., r_j, ..., r_i, ...).$$  \hspace{1cm} (2.29)

As such the fermion ground-state wave-function is not positive definite and therefore cannot be strictly considered as constituting a probability measure over its entire domain. This is the so called 'fermion sign problem' and is one of the major barriers to obtaining exact solutions to the fermion many-body problem for systems containing more than a few particles (Ceperley, 1991). There have been several proposals for methods to overcome this problem, for example the released node method (Ceperley and Alder, 1980), being based on the theorem that the fermion nodal surface is variational and thus optimisable. For systems containing few particles this is indeed achievable, however the method quickly becomes inhibited by exponential computational scaling with the systems degrees of freedom. The initial solution to the fermion nodal problem and the most commonly implemented is the fixed node approximation (Anderson, 1976). The orthogonality of Hilbert space vectors, $$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$ has the implication that wave-functions have regions where they are equal to zero. The zeroes of the many-body wave-function are called nodes and the fixed node approximation circumvents the fermion sign problem by fixing the nodal surface of the wave-function to be that of the trial wave-function throughout the calculation. The use of variational trial wave-function renders a variational nodal surface and thus energies obtained in DMC calculations will be an upper bound to the true ground-state energy. It is found to be surprisingly accurate, in most cases yielding energies far more precise than traditional variational calculations. Some graphical examples of wave-function densities and nodal structures for two-particle systems in
Table 2.1: Wave-functions of one-dimensional two fermion systems, red representing positive regions and blue negative. a. Ground state wave-function for two particles in a unit length box. b. The first excited state and c. the eighth excited state. d. shows the radial component of two noninteracting fermions in the 1s and 2s states of a coulombic field respectively. Figure a. is the ground-state wave-function which has a single node defined by the curve $x_1 = x_2$, which manifests itself as fermion repulsion, the wave-function approaching zero as $|x_1 - x_2| \to 0$.

The fixed node approximation is implemented by restricting the region in which walkers may propagate. When a walker move is proposed $\mathbf{R} \to \mathbf{R'}$, a comparison of the sign of the trial wave-function is made. If $\Psi(\mathbf{R'})/\Psi(\mathbf{R}) < 0$, then the move is rejected and the walker position maintained. The lower value of the wave-function near nodes is such that the walker will drift away from the nodes into higher density regions. This ensures that the anti-symmetry of the wave-function is maintained and that the correct physics is present in the final distribution.
2.5.4 Importance Sampled DMC

Using equation 2.27 as the guiding condition for the movement of walkers turn out in practice to be very inefficient. The branching rate which controls walker population diverges as two particles interacting via the Coulomb potential approach each other. This originates from the branching rate being proportional to the interaction term and results in large fluctuations in the population of diffusing walkers and consequently a large variance in the energy estimator. To overcome this problem we move to importance sampled DMC, where the probability distribution is multiplied by a trial or guiding wave-function (Kalos et al., 1974; Ceperley and Kalos, 1979).

Substituting the wave-function \( f(\mathbf{R}, \tau) = \Psi_T(\mathbf{R}) \phi(\mathbf{R}, \tau) \) into the imaginary-time Schrödinger equation and reorganising terms gives

\[
- \partial_\tau f(\mathbf{R}, \tau) = -\frac{1}{2} \nabla^2 f(\mathbf{R}, \tau) + \nabla \cdot \left[ \mathbf{v}_D f(\mathbf{R}, \tau) \right] + \left[ E_L - E_T \right] f(\mathbf{R}, \tau), \tag{2.30}
\]

Here \( E_L \) is the local energy similarly used in VMC

\[
E_L(\mathbf{R}) = \frac{\hat{H}\Psi_T(\mathbf{R})}{\Psi(\mathbf{R})}, \tag{2.31}
\]

where \( \nabla \) is the 3N-dimensional gradient operator. The \( \mathbf{v}_D \) term is known as the drift velocity in 3N-dimensional configuration space and is given by

\[
\mathbf{v}_D = \nabla \ln |\Psi_T(\mathbf{R})| = \frac{\nabla \Psi_T}{\Psi_T}, \tag{2.32}
\]

which can be interpreted as a quantum ‘force’. The inclusion of the drift velocity term serves to enhance walker population in regions where the trial wave-function \( \Psi_T \) is large as the walker current is proportional to the gradient of \( \Psi_T \). An advantage
of importance sampled DMC is the modified form of the imaginary-time Green’s function which is no longer a function of $\hat{V}(r)$ energy but the local energy. For good quality trial wave-functions the local energy is roughly constant and wild fluctuations in walker population are reduced. Conversely this places a greater importance on the accuracy of the trial wave-function for accurate DMC calculations. However this condition is somewhat negated by the fixed node approximation as in general one would use the same trial wave-function for the fermion nodal surface and importance sampled DMC. As we shall see for the case of the Helium dimer in the next chapter, importance sampled DMC can still suffer from catastrophic population explosions and divergences.

2.6 The Trial Wave-function

High quality trial wave-functions are important in all QMC calculations. As with any variational method, accurate wave-functions mean lower energies. For VMC, the accuracy of the calculation is directly determined by the trial wave-function and the ability to recover a large percentage of electron correlation. In DMC, which is theoretically independent of the initial wave-function, good quality trial wave-functions can reduce statistical errors and time-step biases and general instability problems. DMC is dependent on an accurate description of the electron nodal surface, which should be adequately approximated by the trial wave-function. Further the trial wave-function should be compact and easy to evaluate, as one of the most computationally expensive operations is the continual evaluation of the wave-function and its derivatives. Of specific interest in this thesis is the ability of the proposed trial wave-function to incorporate van der Waals interactions within VMC.

The simplest wave-function obeying antisymmetry under fermion exchange is the Slater determinant of single particle orbitals.
\[
\Psi (\mathbf{R}) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(\mathbf{r}_1, \sigma_1) & \cdots & \psi_N(\mathbf{r}_1, \sigma_N) \\
\vdots & \ddots & \vdots \\
\psi_1(\mathbf{r}_N, \sigma_N) & \cdots & \psi_N(\mathbf{r}_N, \sigma_N)
\end{vmatrix}.
\] (2.33)

Variational calculations with this wave-function and the Hamiltonian operator given in equation 2.9 are known as Hartree-Fock (HF) calculations and represent the first attempts at constructing fermionic bound state wave-functions. HF contains no correlation effects by definition, and the correlation energy is indeed defined as the difference between the HF energy and the exact non-relativistic energy. Although in many instances variational energies obtained are 99% of the experimental value, it is the remaining energy that largely responsible for bonding which is unaccounted for in HF theory. For spin-independent Hamiltonians, the single Slater determinant may be decomposed into the product of spin up and spin down components, reducing the task of evaluating a determinant of \( n \) rows,

\[
D(\mathbf{X}) = D_\uparrow(\mathbf{r}_1, \ldots, \mathbf{r}_k) D_\downarrow(\mathbf{r}_{k+1}, \ldots, \mathbf{r}_N)
\] (2.34)

The single electron orbitals in the Slater determinant are commonly constructed from atomic centered Gaussian basis functions, implemented in many commercially and freely available atomic and solid-state \textit{ab initio} simulation packages such as Gaussian (Frisch et al., 2004), Crystal (Dovesi et al., 2006) and a proliferation of others.

To move beyond the HF approximation we can consider implementing the constraints on the wave-function which are known exactly. The wave-function cusp conditions are such constraints. When two charged particles come into contact the potential energy diverges which in the instance of an exact eigenfunction, is can-
Figure 2.4: The local energy of the hydrogen atom where the wave-function is given by three different functions. The blue and black lines show the local energy as a function of distance for an STO-nG basis (Frisch et al., 2004). The green line shows the value of the local energy for the exact ground state wave-function.

...celled by a corresponding divergence in the kinetic energy (cf. Figure 2.4). Boundary conditions of the many-body Schrödinger equation require wave-function ‘cusps’ at the electron-electron and electron-nucleus coalescence points (Foulkes et al., 2001; Kato, 1957). Orbitals constructed from gaussian basis functions do not satisfy the electron-nuclear cusp conditions. However methods which employ larger bases, such as the configuration interaction method which uses linear combinations of Slater determinants, overcome this problem and obtain a better profile of wave-function cusps. The tradeoff is that slow convergence and the use of extensive computational resources limits the size of the systems that may be modeled using these methods.

To improve upon the Slater determinant wave-function we have used a wave-function of the Slater-Jastrow type

\[ \Psi (X) = \exp \left[ J (X) \right] D (X). \]
Here $D(X)$ is a Slater determinant of single electron orbitals as given in equation 2.33 and $J(X)$ is the Jastrow correlation factor (Jastrow, 1955). The Slater-Jastrow wave-function has the advantage of being relatively compact with fermionic antisymmetry satisfied by the Slater determinant. The Jastrow term is a purely real, symmetric and hence nodeless function of inter-electron and electron-nuclear separation and allows the inclusion of wave-function cusp constraints and correlation effects more compactly than those based on a linear combinations of determinants. In this work we have used a Jastrow factor composed of one, two and three body terms

$$J(X) = \sum_{i \neq j}^{N} u(r_{ij}) + \sum_{I=1}^{N_{\text{ions}}} \sum_{i=1}^{N} \chi_{I}(r_{iI}) + \sum_{I=1}^{N_{\text{ions}}} \sum_{i \neq j}^{N} f_{I}(r_{iI}, r_{jI}, r_{ij}).$$ (2.36)

The $u$ term is a function of relative electron positions, $|r_{i} - r_{j}|$, the $\chi$ term electron-nuclear positions $|R_{I} - r_{j}|$ and the $f$ term electron-electron-nuclear positions. In this work, each of the terms is a polynomial with coefficients optimised to minimise the variance of the local energy (see equations 2.16 and 2.17). (Needs et al., 2005; Drummond et al., 2004).

To date there has been no VMC study showing that a trial wave-function of the Slater-Jastrow type will give the correct binding energy curve for van der Waals bonded systems. It has been argued that a wave-function of Slater-Jastrow form equation 2.36 will be unable to account for bonding of the van der Waals type due to the incorrect long range correlations of the Jastrow function (Dobson et al., 2001). It is expected that to properly account for van der Waals bonding, the wave-function is required to explicitly contain multi-pole coupling terms which from perturbation theory are seen to be responsible for van der Waals interactions.
2.7 Summary

In this chapter we have introduced two quantum Monte Carlo techniques as per application to the many-body bound state problem. We have presented a wavefunction of the Slater-Jastrow type which in the next chapter will be used to investigate electron correlation effects for He$_2$, the prototypical van der Waals bonded molecule.
Chapter 3

Quantum Monte Carlo

Investigation of He Dimer


3.1 Van der Waals and the rare gas dimers

The prototypical systems whereby van der Waals interactions become manifest are the rare gas dimers. The inert gases are theoretically characterised by closed outer shells, hence their reluctance to interact chemically and their relatively late experimental detection\(^1\). The simplest of these and arguably the most interesting is helium, which exhibits a range of idiosyncratic behaviour like superfluidity, originating from a large zero point energy.

For the accurate description of amalgamations of helium atoms into condensed phases, the accurate description of dimer and in some instances trimer effects are essential, which are best parameterised by the potential energy surface.

The theoretical study of the helium dimer has a long history with increasingly ac-

\(^1\)The first experimental confirmation of helium was in 1868 by Pierre Janssen. Its existence was posited for the completion of the periodic table and confirmed by spectroscopic analysis of sunlight. Thus the origin of the name helium, in reverence to Helios the Sun God.
<table>
<thead>
<tr>
<th>Method</th>
<th>Binding Energy (K)</th>
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<td>Greens Function QMC (1993) (Anderson et al., 1993)</td>
<td>-11.01 ± 0.10</td>
</tr>
<tr>
<td>Explicitly correlated CC (Klopper and Noga, 1995)</td>
<td>-11.00</td>
</tr>
<tr>
<td>SAPT (Korona et al., 1997)</td>
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<tr>
<td>MR-CI (van de Bovenkamp and van Duijneveldt, 1999)</td>
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<tr>
<td>Fixed node HF-DMC (Springall et al., 2008)</td>
<td>-10.89 ± 0.17</td>
</tr>
</tbody>
</table>

[1] This work

Table 3.1: Summary of calculations of the He-He potential well depth at 5.6 a.u.

Accurate descriptions of the binding energy curve largely correlated to the growth in computer power. The first direct calculation of the helium dimer potential energy was by Slater (Slater, 1928) who used the repulsive interaction as derived by Heitler and London and combined it with an attractive component obtained from a long-range calculation of Wang (Wang, 1927) on the interaction of two hydrogen atoms. Compared to modern theoretical estimates for the well-depth and position this result is remarkably accurate, with a well depth of 8.9K at 5.6 a.u. compared with the current accepted values of around 11.0K also at 5.6 a.u. As more sophisticated approaches were developed in order to treat the quantum many-body problem, it became apparent that the description of the type of electron correlation responsible for interactions of the vdW type was not consistently described. A summary of results using a variety of theoretical techniques to calculate the potential well depth of the helium dimer at an atomic separation of 5.6 a.u. is presented in Table 3.1.

The introduction of density functional theory (DFT) revolutionised the theoretical approach to the quantum many-body problem and has since become the computational paradigm for quantum chemists and solid state physicists. DFT is the primary theory which uses the mean field approach, in which many-body interactions are replaced by single particle equations, with each particle moving in an effective external potential. However in recent years the approximations which in the past have seen DFT applied successfully to many systems have been shown to be fundamentally inadequate. The failure of DFT to
give the correct binding energy curve for van der Waal’s systems which is even qualitatively correct has been well documented (Andersson et al., 1996; Kamiya et al., 2002). The use of the modern hybrid functionals further exacerbates the problem, with the recent proposal of a so-called X3LYP functional (extended hybrid functional combined with Lee-Yang-Parr correlation functional), parametrised to give the properties of hydrogen bonded and van der Waals complexes (Xu and III, 2004). One may construct an exchange-correlation functional which will give the correct well depth and equilibrium separation for the noble gas dimers with relative ease, much as one may approximate the volume of a cow to be that of an ellipsoid. Indeed we looked at approaching this problem in this manner and were able to construct a hybrid functional for the helium dimer. However, although the correct interaction energy and position at equilibrium was optimised, there are spurious long range fluctuations which are not physical and it is unlikely to result in a universally applicable functional. As much as many people would care for cows to be ellipsoids, particularly in aid of transportation and butchering, only to be disappointed to find variations upon the regular four legged variety, hybrid functionals are no more than an exercise in parameter fitting and lack a sound physical basis, giving little or no insight into the underlying nature of the physics. There has been progress in constructing functionals with the correct physical basis (Dobson and Wang, 1998; Rydberg et al., 2003), however these functionals are only appropriate for specific cases. The situation for solid state systems is different, where the local density approximation (LDA) can in many cases be seen as a logical approximation. Still this approximation to the exchange correlation functional, along with its other incarnations, fails for inhomogeneous systems like graphite and the micas. Alternative approaches to the many-body problem are found in computationally more expensive approaches such as configuration interaction, the coupled cluster method and many-body perturbation theory. However as the complexity of the systems investigated increases, these methods become untenable, scaling as $N^{7-8}$, and the use of more subtle approaches is required. The density functional approach to the quantum many problem has been the usual recourse to unfavourable computational scaling, however as yet no-one has been able to devise a universal scheme to account for the electron correlation responsible for van der Waals interaction.
I do no wish here to go into the theoretical foundations of DFT, as this will greatly add to the length of this thesis for the sake of a minor critique. Suffice it for me to say that although in principle there seems no insurmountable difficulties in constructing exact exchange-correlation functionals for any particular system one would care to investigate via the adiabatic connection formula (Parr and Yang, 1989), the case for a universally valid functional would seem to be very weak, simply due the lack of system which is prototypical across all energy regimes. The inability of current functionals to consistently predict geometric as well as electronic properties should not act as further incentive to clarify the theory, but warn us of the limitations of theories involving convoluted approximations.

Another issue concerning the theoretical description of vdW interactions is the absence of one theoretical method which is applicable to the desired accuracy across all length scales. The situation can be best represented by the current form of the helium dimer potential as given in (Hurly and Moldover, 2000). In this paper the authors use eleven theoretical methods across multiple ranges to determine the 12 parameters used in the potential.

It has been posited that QMC methods are to become an increasingly prominent approach to the many-body bound state problem and offer the promise of a unified approach with the accuracy required to describe van der Waals interactions. In contrast to other methods of comparable accuracy which scale as $N^{7-8}$, quantum Monte Carlo methods typically scale as the cube of the number of electrons. However there are still some doubts with regards to a ubiquitous method to account universally for van der Waals interactions within QMC. Previous QMC calculations on the helium dimer have been performed, most notably that of Anderson et al. (Anderson et al., 1993) using exact QMC and helium dimer calculations at 5.6 a.u. of Mella and Anderson (Mella and Anderson, 2003). The VMC and FN-DMC calculations of Mella and Anderson employ very accurate trial wave-functions of the Hylleraas-type multiplied by a Jastrow function term which explicitly contains dipole-dipole terms. The accuracy of the trial wave-function is reflected in the FN-DMC result where there is relatively little dependence on the time-step used and an a very accurate VMC energy. This in itself is no problem and the results achieved are indeed remarkably accurate. However for QMC to become a universal calculation procedure, it must contain
generalisable wave-functions which scale at least as favourably with system size as convention quantum chemical methods. QMC will always be a more involved procedure due to its innate complexity and the need for a rigorous error analysis, but one would like as many transferable attributes as possible. A particular type of wave-function which may be of universal form is of the Slater-Jastrow type (see equations 2.35-2.36). However the inclusion of a Jastrow factor to account for non-local correlations has been questioned, with no investigation yet to provide a conclusive argument otherwise (Dobson et al., 2001). The work of Anderson et al. employed the Green’s function Monte Carlo method and although exact, again becomes prohibitively expensive as the number of degrees of freedom is increased. Further as the separation was reduced beyond 5.6 Bohr, the calculated binding energies were accompanied by large statistical errors.

In this chapter we present the results of variational Monte Carlo (VMC) and fixed-node diffusion Monte Carlo (FN-DMC) calculations for the helium dimer with atomic separations in the range $r \in [0.9, 7.4]$ a.u.. All of our QMC calculations have been performed with the CASINO code (Needs et al., 2005).

### 3.2 The Trial Wave-function and Method

The determinant component of the trial wave-function for the helium atom and the dimer was constructed from a Gaussian basis containing 17-s, 4-p and 3-d type functions, optimised to be within $4 \times 10^{-8}$ Hartree of the He atom Hartree-Fock limit. The Slater determinants were constructed using Hartree-Fock (HF) orbitals generated using Gaussian03 (Frisch et al., 2004) which were cusp-corrected using the scheme of Ma et al. (Ma, Towler, Drummond and Needs, 2005). For the atom a Jastrow function containing a total of 135 optimisable parameters including cutoffs, optimised using 100,000 electron configurations. For the dimer the Jastrow function term contained 173 optimisable parameters. Each of the $u-$ and $\chi-$terms contain 28 parameters, 14 for each spin correlation ($\uparrow\uparrow=\downarrow\downarrow\neq\uparrow\downarrow$ for the $u$-term), along with optimisable cutoffs, and the $f$-term contains a total of 114 parameters plus optimisable cutoff, with dependence of the coefficients the same as the $u$-term. These coefficients were variance optimised using a total of 1 million configurations.
Table 3.2: Energy as a function of time-step value for the Helium atom

<table>
<thead>
<tr>
<th>time-step</th>
<th>Energy (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-2.903 724 48(65)</td>
</tr>
<tr>
<td>0.0025</td>
<td>-2.903 724 63(17)</td>
</tr>
<tr>
<td>0.005</td>
<td>-2.903 724 30(16)</td>
</tr>
<tr>
<td>0.01</td>
<td>-2.903 724 52(16)</td>
</tr>
<tr>
<td>0.02</td>
<td>-2.903 724 43(17)</td>
</tr>
</tbody>
</table>

Table 3.3: Total energy of the helium atom for various calculation methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-2.861 679 63</td>
</tr>
<tr>
<td>HF limit(^1)</td>
<td>-2.861 667 999</td>
</tr>
<tr>
<td>VMC(^4)</td>
<td>-2.903 724 30(26)</td>
</tr>
<tr>
<td>DMC(^4)</td>
<td>-2.903 724 48(17)</td>
</tr>
<tr>
<td>DMC(^2)</td>
<td>-2.903 732(5)</td>
</tr>
<tr>
<td>Exact(^3)</td>
<td>-2.903 724 377 034</td>
</tr>
</tbody>
</table>

For the DMC calculations, the VMC optimised wave-functions were used and calculations performed over a range of time-step values to check the dependence of the energy on the time-step. As the ground state wave-function of helium is nodeless, the DMC result is essentially exact and does not suffer from errors resulting from the fixed-node approximation. Actual errors do arise however via the use of the discrete time Green function and statistical errors associated with Monte Carlo procedure. As can be seen from Table 3.2, the DMC energy for the atom is relatively independent of the time-step value used. As such the final result for the atom DMC energy was taken as the average of four the values shown. For the case of the dimer we used an error weighted quadratic fit to extrapolate to the $\tau = 0$ limit. All calculations were performed with a target population of 4000 walkers. These were spread across 16 processors and all calculations contained a minimum of $3 \times 10^6$ Monte Carlo samples, with extra calculations being performed until the desired error was obtained.
3.3 Results

The results of calculations for the helium atom are shown in Table 3.3 with comparisons to modern values. As mentioned in the previous chapter, the accuracy of the VMC method is wholly dependent on the quality of the trial wave-function used. The VMC result for the atom is extremely good, being an order of magnitude more accurate than the DMC calculation of Ma et al (Ma, Drummond, Towler and Needs, 2005), where they employed trial wave-functions also of the Slater-Jastrow type using both a Gaussian and numerical basis for the Slater component. This suggests that the form of the Jastrow function used is suitable for the description of correlation effects in such systems. In the work of Ma et al. where QMC calculations were performed for the noble gas atoms up to xenon, it was found that the percentage of the correlation energy recovered via the use of a Slater-Jastrow trial wave-function decreases with increasing atomic number. This may be expected as even though non-additive correlations are implicitly accounted for with a Jastrow function containing only two-electron correlation terms, the explicit inclusion of higher order terms may be required to recover the remaining correlation energy.

To calculate the binding energy for the dimer we use the supermolecular approach, where the interaction energy is calculated as the energy difference between the molecular system and each of its constituents. This method amounts to taking the difference in energy between two large numbers to obtain a small residual binding energy and care must be taken to ensure that all residual effects are accounted for, the classic case in basis-set dependent theories being basis-set superposition error. Table 3.4 shows the VMC and FN-DMC binding energy values for the dimer over all separations investigated. A full table of results of these calculations is given in Appendix A. For comparison we include the binding energy values of the Hurly-Mehl potential (Hurly and Mehl, 2007).

Although agreeing well with the potential of Hurly and Mehl in the $r \to 0$ limit, our results clearly show that VMC fails to give any binding. To investigate the reason for this, in Fig.3.1 we have plotted the percentage of the FN-DMC correlation energy retrieved by VMC using the Slater-Jastrow trial wave function. The FN-DMC energy is the lowest energy consistent with the given nodal surface, and so is the same result one would obtain
Table 3.4: Binding energy values of the helium dimer at different values of inter-atom separation. The binding energies are given in Kelvin.

<table>
<thead>
<tr>
<th>Separation (a.u.)</th>
<th>VMC</th>
<th>DMC</th>
<th>Hurly and Mehl, 2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>315889.69 ± 72.63</td>
<td>314409.15 ± 3.79</td>
<td>319211.08</td>
</tr>
<tr>
<td>1.9</td>
<td>46759.27 ± 47.37</td>
<td>45959.52 ± 4.11</td>
<td>45840.26</td>
</tr>
<tr>
<td>2.3</td>
<td>20781.23 ± 26.84</td>
<td>20159.33 ± 0.64</td>
<td>20108.76</td>
</tr>
<tr>
<td>2.8</td>
<td>5931.68 ± 29.05</td>
<td>5575.28 ± 5.37</td>
<td>5549.73</td>
</tr>
<tr>
<td>3.2</td>
<td>2460.70 ± 21.79</td>
<td>2271.94 ± 1.45</td>
<td>2259.18</td>
</tr>
<tr>
<td>3.8</td>
<td>639.31 ± 10.42</td>
<td>537.78 ± 1.77</td>
<td>535.64</td>
</tr>
<tr>
<td>4.3</td>
<td>162.50 ± 11.68</td>
<td>102.24 ± 0.32</td>
<td>100.67</td>
</tr>
<tr>
<td>4.5</td>
<td>102.18 ± 11.05</td>
<td>49.76 ± 0.29</td>
<td>50.538</td>
</tr>
<tr>
<td>4.7</td>
<td>62.27 ± 3.03</td>
<td>19.49 ± 0.27</td>
<td>21.020</td>
</tr>
<tr>
<td>5.6</td>
<td>2.91 ± 1.52</td>
<td>-10.89 ± 0.17</td>
<td>-11.05</td>
</tr>
<tr>
<td>5.9</td>
<td>0.22 ± 1.39</td>
<td>-10.31 ± 0.15</td>
<td>-10.40</td>
</tr>
<tr>
<td>7.4</td>
<td>0.82 ± 0.92</td>
<td>-2.57 ± 0.18</td>
<td>-3.412</td>
</tr>
</tbody>
</table>

Figure 3.1: Percentage of the FN-DMC correlation energy of the helium dimer retrieved by VMC, as a function of separation. The inset shows a closeup of the main figure around the region of the potential well minimum.
Table 3.5: DMC binding energy at 5.6 a.u. as a function of the time-step $\tau$. Statistical uncertainty in the last figures are quoted in parentheses.

<table>
<thead>
<tr>
<th>$\tau$ (a.u.)</th>
<th>Binding Energy (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-10.89(17)</td>
</tr>
<tr>
<td>0.001</td>
<td>-10.55(16)</td>
</tr>
<tr>
<td>0.0025</td>
<td>-10.12(18)</td>
</tr>
<tr>
<td>0.005</td>
<td>-10.09(17)</td>
</tr>
<tr>
<td>0.01</td>
<td>-9.158(16)</td>
</tr>
</tbody>
</table>

in VMC with a ‘perfect’ Jastrow function. Because of this, a comparison of the VMC correlation energy with the FN-DMC correlation energy is a direct measure of the quality of the Jastrow function. It shows a monotonic decrease in the quality of the wave function as the separation between the atoms decreases. The loss in quality is slow at first, but becomes more rapid below 3.2 a.u., with a linear drop-off in correlation energy. The reason for the lack of any binding seems to be simply that the intra-atomic correlation effects are described more accurately than the inter-atomic effects. The improved agreement for VMC at short range occurs because the correlation energy becomes a small fraction of the potential energy in this region. The incorrect description of the interaction curve can therefore be reasonably be attributed to the inability of the implemented form of the Slater-Jastrow wave-function to include interaction effects of the van der Waals type.

Our FN-DMC results are mostly within 1% of the Hurly-Mehl curve, and we obtain a binding energy of $-10.89 \pm 0.17$K at a separation of 5.6 a.u., which is in agreement with the previous results presented in Table 3.1. The binding energy of the dimer at 5.6 a.u. as a function of time-step value $\tau$ is shown in Table 3.5. This can be compared with Table I of the previous FN-DMC study of the He dimer at 5.6 a.u. by Mella and Anderson (Mella and Anderson, 2003), which reports the same quantities using a very accurate trial wave function. Our use of the less accurate but more generalisable Slater-Jastrow wave function results in a slower convergence to the $\tau = 0$ limit.

We would also like to mention one further point. To calculate the dimer binding energy, Mella and Anderson (Mella and Anderson, 2003) have used the exact atomic energy value of $-2.903\,724\,377\,034$ a.u. If we use this value to calculate the dimer binding energy rather than our atomic DMC energy, we obtain a binding of $-10.96 \pm 0.15$K which is in even
better agreement with the values calculated by other methods presented in Table 3.1.

3.4 Conclusion

In summary, we have used two quantum Monte Carlo methods, VMC and FN-DMC, to investigate the binding energy curve of the helium dimer. For the variational Monte Carlo method where we have employed trial wavefunctions of Slater-Jastrow form, we have found that the method is unable to account for the many-body correlations responsible for van der Waals bonding. This suggests that one would be required to include higher order correlation terms explicitly, as has been done in (Mella and Anderson, 2003). A problem with this however is the increased time required for the optimisation of coefficients resulting from larger wave-function and generalisation to many-electron systems.

Using FN-DMC and the VMC optimised trial wavefunctions, we have performed calculations for each separation at several time-steps and used an error weighted quadratic fit to extrapolate to the $\tau = 0$ limit. The results show that FN-DMC recovers the electron-correlation leading to van der Waals bonding. The two inherent errors associated with FN-DMC are the fixed node approximation for the treatment of fermions and the finite time-step value. From the atomic calculations, the calculated energy is independent of the time-step value used as a result of the use of a very accurate trial wave-function. The time-step error in the dimer calculations is found to be quadratic using a trial wave-function of the same form and the extrapolated results are in very good agreement with previously published results.
Part Two
Chapter 4

Many-body interacting systems at finite temperature

4.1 Introduction

Irrespective of their experimental realisation, the theoretical existence of condensed phases of noninteracting media is indeed remarkable and the mathematical structures with which they are imbued can lead to a variety of interesting observations. It is not difficult to show that a system of noninteracting indistinguishable particles with bosonic symmetry will undergo a second order phase transition if the spatial dimension is greater than two (Pethick and Smith, 2002) (Hohenberg, 1967). While for \( d \leq 2 \) it has been rigorously been shown by Hohenberg that a bosonic system will not undergo phase transition for \( T > 0 \) if there is translational invariance, it is not the general case. Bagnato and Kleppner (Bagnato and Kleppner, 1991) have shown that the presence of a localised confinement potential allowed the existence of a condensate in one and two dimensions, which was experimentally confirmed in 2001 by a group at MIT who observed condensation in quasi-2-D traps (Görlitz...
Since the observation of Bose-Einstein condensation (BEC) in atomic vapours in 1995 there has been an explosion in experimental and theoretical research in low temperature physics. Experimentalists have constructed BEC’s in systems with both positive and negative s-wave scattering lengths(Anderson et al., 1995; Bradley et al., 1995; Davies et al., 1995)\(^2\), constructed novel trapping potentials, for example periodic and random optical and magnetic lattices (Greiner, Mandel, Esslinger, Hänsch and Bloch, 2002; Greiner, Mandel, Hänsch and Bloch, 2002; Günther et al., 2005) as well as quasi-one and two dimensional harmonic traps (White et al., 2006; Burger et al., 1999; Görlitz et al., 2001). This has been complimented on the theoretical side by a renewed impetus to the theoretical description of low temperature atomic gases.

Bose-Einstein condensation and superfluidity have been identified as potential mechanisms for the properties of many physical systems. In the astrophysics community it is widely accepted that neutron superfluidity plays a major role in the aberration of pulsar periodicity(Pizzochero et al., 1997; Link and Riper, 1992), in solid-state physics exciton condensation in semiconductor systems has been studied both theoretically and experimentally (Eisenstein and Macdonald, 2004) and a theoretical understanding of the vacuum state in nuclear physics has led to the theoretical postulation of superconducting quark-antiquark condensates(Pethick and Smith, 2002). Modern experimental methods have made it possible to compare idealised theoretical models to quantitative experimental results in systems which were never thought to be realiseable in the laboratory. Ultracold atomic and molecular gases in optical lattices are almost perfect realisations of lattice models like the Hubbard model(M. Lewenstein and Sen, 2007) and density profiles obtained for condensate in quasi-one dimensional cigar traps can be compared to theoretical results

\(^1\)This was the same group which first observed Bose-Einstein condensation in atomic vapours of \(^{22}\)Na.
of one dimensional hard-sphere systems (Hofferberth et al., 2007).

4.2 The Critical Temperature and the Condensate Fraction

Just as electronic structure theory is built on fermionic antisymmetry, the fundamental mechanism for the formation of a condensate of bosons is symmetric indistinguishability. Bose-Einstein condensation occurs as the mean nearest neighbour distance becomes comparable to the thermal de Broglie wavelength $\lambda_T$,

$$\lambda_T = \left[ \frac{2\pi \hbar^2}{mk_B T} \right]^{1/2} = L. \quad (4.1)$$

Here $m$ is the mass, $T$ the temperature and $k_B$ Boltzmann’s constant. At this temperature, particles are sufficiently delocalised to be indistinguishable from neighbouring particles, with the mathematical result that the probability of occurrence of long length permutation cycles become more than negligible. By approximating the mean inter-particle separation as the inverse cube root of the number density we can estimate the critical temperature, which after substitution and rearrangement of equation 4.1, which gives

$$T_c \sim \frac{2\pi \hbar^2}{mk_B \rho^{2/3}}. \quad (4.2)$$

2 The condensation in these three systems differ in one important respect. The atomic interaction in the $^{23}$Na and $^{87}$Rb have a positive scattering length while the scattering length in $^7$Li is negative. This implies for the latter an attractive interaction (Ueda and Huang, 1999; K. M. O’ Hara and Thomas, 2000; Bradley et al., 1995), which was previously thought to be unstable as the gas would condense to the liquid phase prior to the formation of a bose-einstein condensate.
By substituting in the properties for liquid helium we obtain a lambda transition temperature of $T_c = 5.39\, K$, a good estimate when compared to the experimental value of $2.17\, K$ (Pethick and Smith, 2002). Equation 4.2 defines an important length scale in condensation and can be used to identify the demarcation between classical and quantum behaviour.

London first proposed that the process responsible for fluid-superfluid transition in $^4$He is the same as that for the condensation of a non-interacting Bose-Einstein gas, albeit masked by molecular interactions and its manifestation as a liquid and not a gas (London, 1938b). The present day identification of the theoretical existence of the BEC is particles occupying the zeroth fourier mode, the order parameter given by the long-range off-diagonal correlation first introduced by Penrose and Onsager (Penrose and Onsager, 1956). Although this is still an important theoretical approach, in recent times there has been a shift in emphasis from the identification of condensation with long-range spatial correlation functions to the enumeration of long permutation cycles (Ueltschi, 2006; Mullin, 2000). In particular is has been postulated that there is a relationship between the derivative of the probability distribution with respect to the permutation cycle length of permutation cycles and the condensate probabilities (Chevallier and Krauth, 2007).

As is the case with electronic structure, the equations that govern Bose-Einstein condensation are explicitly simple in form. For the general case of D-spatial dimensions, noninteracting harmonically trapped Bose gases are defined by the single particle Hamiltonian

$$H = \sum_{n=1}^{\infty} \left( \frac{p_n^2}{2m} + \frac{1}{2} m \omega_n^2 x_n^2 \right)$$

We approximate the inter-particle separation as the cube root of the inverse of the number density, that is $L = \rho^{-1/3}$. The density of liquid helium at boiling point at atmospheric pressure is $125\, kg/m^3$, giving a number density of $\rho = 1.88 \times 10^{28}\, atoms/m^3$. Data taken from http://www-safety.deas.harvard.edu/services/helium.html.
\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \frac{m}{2} \sum_{i}^{D} \omega_i^2 x_i^2 \]  

(4.3)

where \( \omega_i \) are the trapping frequencies in the \( x_i \) direction. The many-body eigenvalues of this Hamiltonian is the sum of the occupation numbers of each state, that is

\[ \epsilon_{n_1...n_D} = \sum_{i=1}^{D} \left( \frac{2n_i + 1}{2} \right) \hbar \omega_i, \]  

(4.4)

the numbers \( n_i \) being nonnegative integers. The ground-state wave-function for a \( N \)-body system is obtained by putting all the particles in the lowest eigenstate, that is \( \phi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \prod_{j=1}^{N} \phi_0(\mathbf{r}_i) \), giving the density distribution \( n(\mathbf{r}) = N|\phi(\mathbf{r})|^2 \). The size of the condensate then is independent of the number of particles in the system. In real systems, the size of the particle cloud will be larger due to thermal excitation of particles to higher eigenstates\(^5\). However for a system with a large condensate fraction, ballistic expansion will give a density profile containing a spike at its center representing the condensed particles. We have calculated non-normalised density profiles for noninteracting particles in a two dimensional hard-walled trap, using a path integral Monte Carlo code, as shown in figure 4.1.

### 4.3 Path Integral Monte Carlo

The path integral Monte Carlo technique is broad numerical approach to the low temperature behaviour of both continuous and discrete systems. As the name suggests, the path integral Monte Carlo technique has a foundational basis in Feynman’s sum over histories approach to quantum dynamics.

\(^5\)For example the number of particles in a condensate is relatively small, on the order of \( 10^7 \).
Table 4.1: Unnormalised density profiles obtained from path integral Monte Carlo calculations for noninteracting particles in a 2-dimensional box. The image on the left is of particles treated with Boltzmann statistics and the image on the right with boson statistics.

The first work to exploit the path integral representation of the partition function for the numerical evaluation of properties of quantum-statistical ensembles was that of Fosdick and Jordan, implementing the Monte Carlo method to evaluate the diagonal component of the two particle thermal density matrix for He\textsuperscript{4} (Fosdick and Jordan, 1965). The identification of the classical polymer isomorphism by Chandler and Wolynes (Chandler and Wolynes, 1981) and the seminal work of Ceperley and Pollock (Ceperley and Pollock, 1986) in the study of the superfluid transition of bulk He\textsuperscript{4} at saturated vapor pressure gave validity to the PIMC method and realised the possibility of its application to previously unresolved theoretical questions in statistical mechanics in the quantum regime. Subsequent to the pioneering work of Ceperley and Pollock for the evaluation of the low temperature properties of liquid $^4$He (Ceperley and Pollock, 1986; Ceperley and Pollock, 1989) the PIMC technique has grown to become an important tool in the investigation of many-body quantum phenomena at finite temperature. It has been successfully applied to spatially confined Helium and finite clusters and droplets in the superfluid regime (Draeger and Ceperley, 2003; Sindzingre and Klein, 1989), including studies of vortices in He droplets (Sola et al., 2007). The experimental verification of Bose-Einstein condensation has also seen the PIMC technique applied to weakly interacting cold atomic...
gases, two examples of which can be found in (Pilati et al., 2006; Nho and Landau, 2004).

Significant progress has been made for identifying the superfluid and BEC phases of particles with periodic boundary conditions which has been extended to very large system sizes. Holzmann and Krauth (Holzmann and Krauth, 1999) have performed calculations for 20000 weakly interacting particles, calculating the shift in the critical temperature for small values of the coupling constant. Although successful, this method relies on the identification of the critical temperature of a non-interacting counterpart for which the permutation structure of the partition function is decomposable.

In PIMC calculations for interacting bosons, there are two distributions that require sampling, the configuration space of particle trajectories and the permutation space of particle exchange cycles. The construction of Markov chains in configuration space is accomplished via the identification of the density matrix as probability density. The transition probability in the Metropolis rejection algorithm is then a function of the change in the Euclidean action accompanying the change in configuration from $R$ to $R'$ in a manner similar to the DMC method discussed Part 1 of this thesis. In contrast to the continuous integration measure over configuration space, the probability measure associated with the probability density in permutation space is over the conjugacy classes of the symmetric group which is inherently discrete.

The symmetric group is central in the study of the physics of systems of indistinguishable particles, giving a mathematical framework for studying the permutational symmetry of the many-particle Hamiltonian. It is also central to the study of finite groups by virtue of Cayley’s theorem, implying that every finite group $G$ is isomorphic to a subgroup of the permutation group on $G$, $S_{|G|}$. The representation theory of the symmetric group has a very deep and well understood structure and incorporates many areas of mathematics. The theory of symmetric
functions is intricately tied to the representation theory of the symmetric group and therefore it is not a surprise that they should occur in different contexts within physics. Symmetric polynomials occur for instance in relation to the eigenvalues of the Calogero-Sutherland model and the Boson-Fermion correspondence of importance to integrable systems. In the context of finite temperature mechanics, the occurrence of the symmetric polynomials in the partition function has been noted on several occasions (Balantekin, 2001; Schmidt and Schnack, 2002), however they rarely go to dissemination of phenomenology and are most often appreciated on a purely theoretical basis. The work of Balantekin is especially interesting and to the knowledge of the author, goes the furthest to put symmetric polynomials in the context of statistical mechanics (Balantekin, 1992).

The literature on the representation theory of finite fields is vast and it is almost impossible to give a complete account of its application to physics in general. One would like to point to a review article on the subject, however one does not exist. A simple application of the symmetric polynomials as occurring in the partition function is presented in (Schmidt and Schnack, 2002).

Of the theoretical approaches to the finite temperature quantum many-body problem, path integral Monte Carlo (PIMC) techniques stand as one of the most useful non-perturbative methods, and is the only method able to give quantitative insights into quantum many-body systems at finite temperature (Boninsegni, 2005). One of the ubiquitous problems in all approaches to evaluating the partition function for bosonic systems is a transparent way of sampling the permutation space inherent in all problems involving indistinguishable particles. Previous approaches such as those in (Ceperley, 1995; Boninsegni, 2005; Holzmann and Krauth, 1999) advocate either the sampling of some cyclic subset of $S_n$, the symmetric group of order $n!$, typically up to $C_4$ or $C_5$, or approximate the interacting partition function structure to that of a noninteracting system, which is only strictly valid for systems which are weakly coupled. Further, identifying the critical temperature of a bosonic system
by considering correlation length requires the evaluation of off-diagonal elements of the density matrix, which in PIMC can be very inefficient and ambiguous.

In Part 2 of this thesis we look at the path integral representation of statistical mechanics and aspects of its implementation within the Monte Carlo method. Specifically this investigation will look at the theory underpinning macroscopic manifestations of indistinguishability effects in confined geometries and the establishment of a novel sampling routine which gives accurate predictions of the correct permutation structure. As part of this investigation we will be temporarily led to theory involving symmetric polynomials and elements of group representation theory, the work of which is currently ongoing and hopefully published in the near future. Excellent references for a general introduction to the path-integral representation of statistical mechanics are (Feynman, 1972; Reif, 1965; Kleinert, 2004).
“At the arithmetic level this connection comes merely from the fact that the central objects in quantum physics $e^{-i\hat{H}t}$ and in thermal physics $e^{-\beta\hat{H}}$ are formally related by analytic continuation. Some physicists, myself included, feel that there may be something profound here that we have not quite understood.”

A. Zee, Quantum Field Theory in a Nutshell

“But except in rather simple cases there is practically no evidence that results obtained after a Wick rotation have anything to do with reality....One feature of it however, is that it maps the equation for quantum mechanical time evolution into the equation for probabilities in statistical mechanics, imaginary time corresponding to inverse temperature. And while it is conceivable that this mapping may have deep significance, none has so far been identified.“

Stephen Wolfram, A New Kind of Science
5.1 Introduction

It is quite a remarkable coincidence and an epiphanic moment when one realises its significance, that the subjects of statistical and quantum mechanics are formally related via the consideration of time as having an imaginary projection. The analytic continuation of time to the imaginary axis was first considered by Gian-Carlo Wick in determining boundary conditions for the Bethe-Salpeter equation (Wick, 1954). In this paper he states that ‘While the concept of an imaginary time variable does not help physical intuition, it has mathematically several advantages’. Quantum field theorists have been using the analytic continuation of time to the imaginary axis ever since and while it seemingly keeps a lot of things mathematically well behaved, no physical interpretation has ever been attributed to this connection between quantum and statistical mechanics, as has been noted by several authors [See quotations on the previous page]. In the case of the path integral formulation of statistical mechanics, we are offered not only an alternative mathematical description of systems at finite temperature and thus another path to dissemination of phenomena, but also a conceptual tool in qualitatively understanding of particle behaviour at finite temperatures. We will come to see that this is especially true of the temperature dependence of particle non-locality and the treatment of particle indistinguishability.

A further consideration of the relevance of the path-integral is its aesthetic value. In Thomas Kuhn’s work on the nature of scientific discovery and progress (Kuhn, 1962), his main thesis is that of a paradigm by which scientists will work with. It is not until a crisis in the current paradigm which is unable to resolve some issue regarding obvious discrepancies between theory and empirical sources that a new paradigm is put forward, with the two methods necessarily being mutually exclusive. Work in understanding the foundations of new theory describing natural (rational) phenomena, in particular quantum versus classical mechanics, can reveal a link between the new and the old paradigm with the old theory being a limiting case.
of a more general theory. As opposed to the canonical formulation of quantum mechanics and its extension to quantum field theory in terms of operator algebra, the path integral formulation gives a greater impetus to the 'rationality' of quantum mechanics in that its connection to classical mechanics is manifest in the action principle. The operator correspondence principle, the replacement of commutators with Poisson brackets, although achieving the desired connection between classical and quantum dynamics, is not transparent in that one does not clearly see how this connection arises from more than an empirical basis. The path-integral on the other hand makes this connection clear as the limit $\hbar \to 0$ or more accurately $\text{mass}/\hbar \to \infty$ and one is easily able to identify the domain in which classical dynamics is a valid approximation to full quantum behaviour. The advantage of this is that the theory becomes more transparent and in turn extendible. However, we do not here wish to divert into a sometimes nubilous discussion on the philosophical foundations of quantum theory and the interested reader is directed to the following articles(Kuhn, 1962; Popper, 1959; Bell, 2004). Although canonical quantisation of field theories is generally successful, it has several drawbacks, most notably extremely involved derivations involving operators and its difficulty when dealing with non-perturbative phenomena. However much can be said on the elegance of operator algebras and the like and integrable models. The path-integral has several of its own drawbacks, the major concern being the lack of rigorous mathematical definition of exactly what a path integral over a field signifies. Also significantly in the case of discrete lattice systems, a large emerging area (of the past 20 years) of mathematical physics, the path integral is not well defined.

In this chapter we shall derive both the path integral formulation of quantum mechanics and statistical mechanics in the canonical ensemble, much of which can be found in the texts on path integrals including those of Kleinert and Feynman and Hibbs (Kleinert, 2004; Feynman, 1972). For the path-integral representation of quantum mechanics we will start from Huygen’s principle of the time-evolution of
a distribution and the properties of the time-evolution operator. For the statistical mechanical path integral, we will begin with the operator representation of the thermal density matrix and arrive at an expression for the partition function where the dynamical quantity of interest, the Euclidean action, is now rendered a $c$-number quantity. There is another route to the path integral representation of the partition function based upon the Wick rotation of time onto the imaginary axis (Wick, 1954). Path integrals make the connection between quantum and statistical mechanics, or quantum field theory and statistical field theory clearly evident and is a rich area of research in both mathematics and theoretical physics. This connection will become manifest with specific examples of the harmonic oscillator and free particle propagator. However the main aim of this chapter is to lay down the theoretical framework for a numerical approach to the evaluation of the partition function within the path integral Monte Carlo method and for analysis of the mathematical properties of ensembles of bosonic particles in terms of irreducible representations of the symmetric group.

### 5.2 Path Integral Quantum Mechanics

In quantum mechanics, the wave-function of a particle at $x_f$ at time $t_f$, given its wave-function at $x_i$ at time $t_i$ can be represented by

$$\Psi (x_f, t_f) = \int K (x_f, t_f; x_i, t_i) \Psi (x_i, t_i) dx_i, \quad (5.1)$$

that is Huygens’s principle. Here $|K (x', t'; x, t)|$ is proportional to the propagation amplitude and equation 5.1 is an integral form of the usual Schrödinger equation. Abstractly, $K (x', t'; x, t)$ can be written as a generalised inner product between the space-time vectors $\langle x', t'| x, t \rangle$, from which we can utilise the unitary time evolution operator to connect these two states $\langle x'| U(t', t)|x \rangle$. The time evolution operator is
constructed in such a way so as to have the following properties;

1. Composition Law

\[ U(t_c, t_a) = U(t_c, t_b)U(t_b, t_a) \]

2. Unitarity

Since we have

\[ U(t, t) = U(t, t')U(t', t) = 1 \]

we get

\[ U(t', t) = U^{-1}(t, t') \]

\[ U(t', t) \] is an anti-causal or advanced evolution operator

therefore

\[ U(t', t) = \exp^{-\frac{i}{\hbar}(t' - t)H} = U^{-1}(t, t') = U^\dagger(t, t') \]

3. \( U(t_b, t_a) \) Obeys the Schrödinger equation

\[ i\hbar \partial_t U(t_b, t_a) = \hat{H}U(t_b, t_a) \]

\[ i\hbar \partial_t U^{-1}(t_b, t_a) = -U^{-1}(t_b, t_a)\hat{H} \]

This property will play a central part in the connection of quantum and statistical mechanics through an isomorphism of this equation and the Bloch equation for density matrices.

Also we have the relationship between eigenstates of the system as different times

\[ \langle x_b t_b | x_a t_a \rangle = \langle x | \hat{U}(t_b, t_a) | x_a \rangle. \]

In non-relativistic theory we consider only the retarded time evolution amplitude

\[ \langle x_b t_b | x_a t_a \rangle^R \equiv \langle x_b | \hat{U}^R(t_b, t_a) | x_a \rangle \Theta(t_b - t_a) \langle x_b t_b | x_a t_a \rangle. \]

The derivation of the propagator in the path integral formalism follows mostly from the composition law (1). In developing the path integral representation for
propagation amplitudes, Feynman realised that due to the composition law of the canonical evolution operator, one may break this up into a product of evolution operators acting over shorter duration

\[ \hat{U}(t_b, t_a) = \hat{U}(t_b, t_n)\hat{U}(t_n, t_{n-1})\hat{U}(t_{n-1}, t_{n-2})...\hat{U}(t_1, t_a). \] (5.2)

7.3

Inserting the complete set of eigenstates between each of the \( U(t, t') \) with the identity \( \int dx_n |x_n\rangle\langle x_n| \) gives

\[
\langle x_b t_b | x_a t_a \rangle = \int dx_n dx_{n-1}...dx_1 \langle x_b | \hat{U}(t_b, t_n) | x_n \rangle \langle x_n | \hat{U}(t_n, t_{n-1}) | x_{n-1} \rangle ... \langle x_1 | \hat{U}(t_1, t_a) | x_a \rangle
\]

\[
= (\prod_n \int dx_n) \prod_n \langle x_n | \hat{U}(t_n, t_{n-1}) | x_{n-1} \rangle; \quad (5.3)
\]

where \( x_b = x_{N+1} \) and \( x_a = x_0 \). We have broken up the full propagator in the time-interval \( t_i \rightarrow t_f \) into a product of infinitesimal propagators, each of which defines a time-slice of constant duration \( \epsilon \). Considering one of the time-slices and the operator definition of the time-evolution operator, we can rewrite the evolution operator as

\[
\hat{U}(t_n, t_{n-1}) = \exp \left[ -\frac{i}{\hbar} \int_{t_{n-1}}^{t_n} \hat{H}(t)dt \right].
\]

By setting \( t_{n-1} = t_n - \epsilon \), we can then make the approximation that the Hamiltonian is time-independent over this period and write (cf. figure5.1)
\[
\int_{t_{n-\epsilon}}^{t_n} \dot{H}(t) \approx \epsilon \dot{H}(t_n).
\] (5.4)

Thus the integral for one time-slice becomes

\[
\langle x_n | x_{n-1} \rangle = \langle x_n | \exp \left( -\frac{i}{\hbar} \epsilon \dot{H}(t_n) \right) | x_{n-1} \rangle.
\]

In the absence of a vector potential, the Hamiltonian operator is composed of kinetic and potential components, i.e. \( \dot{H}(x, p, t) = \dot{T}(p, t) + \dot{V}(x, t) \) and we may write

\[
\exp \left( -\frac{i}{\hbar} \epsilon \left( \dot{T} + \dot{V} \right) \right) = \exp \left( -\frac{i}{\hbar} \epsilon \dot{T} \right) \exp \left( -\frac{i}{\hbar} \epsilon \dot{V} \right) \exp \left( -\frac{i}{\hbar} \epsilon^2 \dot{X} \right)
\] (5.5)

where \( \dot{X} = \frac{i}{\hbar} \left[ \dot{V}, \dot{T} \right] - \frac{\epsilon}{\hbar} \left( \frac{1}{6} \left[ \dot{V}, \left[ \dot{V}, \dot{T} \right] - \frac{1}{3}\left[ \dot{V}, \dot{T} \right] \right] \right) + \ldots \) via the Campbell-Baker-Haussdorf formula (Kleinert, 2004). For the limit that the number of time-slices approaches infinity we may use the Trotter formula to obtain an exact result.
for the path-integral, i.e.

\[
\exp \left[ -i \frac{\epsilon}{\hbar} (T + V) \right] = \lim_{N \to \infty} \left[ \exp \left( -\tau T \right) \exp \left( -\tau V \right) \right]^N
\]

(5.6)

where \( \tau = \frac{\epsilon}{\beta N} \). We are justified therefore in ignoring terms of order \( \epsilon^2 \) and higher and are now in a position to rewrite the infinitesimal propagator as

\[
\langle x_n|x_{n-1} \rangle = \int dx \langle x_n \mid \exp \left( -\frac{i \epsilon}{\hbar} \hat{V} \right) \mid x \rangle \langle x \mid \exp \left( -\frac{i \epsilon {p_n^2}}{2m} \right) \mid x_n \rangle
\]

The propagator is now the product of two terms, one of the kinetic energy and the other of the potential energy. Let us first evaluate the kinetic energy term.

\[
\langle x \mid \exp \left( -\frac{i \epsilon}{\hbar} \frac{p_n^2}{2m} \right) \mid x_{n-1} \rangle = \int \frac{dp_n}{2\pi\hbar} \langle x \mid \exp \left( -\frac{i \epsilon}{\hbar} \frac{p_n^2}{2m} \right) \mid p_n \rangle \langle p_n \mid x_{n-1} \rangle
\]

\[
= \int \frac{dp_n}{2\pi\hbar} \exp \left( -\frac{i \epsilon}{\hbar} \frac{p_n^2}{2m} \right) \langle x \mid p_n \rangle \langle p_n \mid x_{n-1} \rangle
\]

\[
= \int \frac{dp_n}{2\pi\hbar} \exp \left( -\frac{i \epsilon}{\hbar} \frac{p_n^2}{2m} \right) \exp \left( \frac{i}{\hbar} p_n(x - x_{n-1}) \right)
\]

Here we have used the relationship \( \langle x \mid p \rangle = A \exp(ipx/\hbar) \), momentarily dropping the normalisation term\(^1\). To evaluate the potential term we make use of the fact that the basis vectors \( \mid x_n \rangle \) are eigenstates of the potential operator \( V(x_n) \) and \( \langle x_n \mid x \rangle = \delta(x - x_n) \) giving

\[
\int dx \langle x_n \mid \exp \left( -\frac{i \epsilon}{\hbar} \hat{V}(x_n, t_n) \right) \mid x \rangle = \int dx \delta(x_n - x) \exp \left( -\frac{i}{\hbar} V(x_n, t_n) \right)
\]

\[
= \exp \left( -\frac{i}{\hbar} \epsilon V(x_n, t_n) \right)
\]
Combining each of the results for the kinetic and potential integrals gives us an expression for a single time-slice of the propagator containing no operators but instead c-number quantities. Substituting this expression for each time-slice into the full propagator, equation 5.2, gives

$$\langle x_b t_b | x_a t_a \rangle = \int \mathcal{D}x \mathcal{D}p \exp \left[ \frac{i}{\hbar} \epsilon \sum_{n=1}^{N+1} \left( \frac{p_n (x_n - x_{n-1})}{\epsilon} - \frac{p_n^2}{2m} - V(x_n, t_n) \right) \right]$$

$$= \int \mathcal{D}x \mathcal{D}p \exp \left[ \frac{i}{\hbar} \int_{t_1}^{t_f} dt \left( p \dot{x} - H(x, p, t) \right) \right]$$

(5.7)

where in the final line we have taken the limit $\epsilon \to 0$, defined the classical Hamiltonian and have defined the functional integration measures as

$$\int \mathcal{D}x = \prod_{n=1}^{N} \left[ \int dx_n \right]$$

$$\int \mathcal{D}p = \prod_{n=1}^{N+1} \left[ \int \frac{dp_n}{2\pi\hbar} \right].$$

A simplification of expression 5.7 can be found if $H(p, q)$ is quadratic in $p$. In the absence of external magnetic fields for which we have derived the path-integral, the

---

1The proof of this identity is fairly straight forward. Firstly we use the following two relationships

$$\hat{p} |p\rangle = p |p\rangle \quad \text{and} \quad \langle x|\hat{p} = -i\hbar \partial_x \langle x|$$

taking the inner product with the momentum space eigenvector gives

$$\langle x|\hat{p}|p\rangle = -i\hbar \partial_x \langle x|p\rangle = p \langle x|p\rangle$$

The right hand side defines a differential equation, the solution of which gives our desired identity.
Hamiltonian will take the form $H(p, q) \to \frac{p^2}{2m} + V(x)$ (In the presence of an external magnetic field, momentum couples to the vector potential $\mathbf{A}$ via the replacement $\vec{p} \to \vec{\pi} = (\vec{p} - \frac{e}{c} \vec{A})$). Equation 5.7 becomes an $N + 1$ dimensional gaussian integral in $p$, which we are able to evaluate.

$$K(x_f, t_f; x_0, t_0) = \int \mathcal{D}x \mathcal{D}p \exp \left[ \frac{i}{\hbar} \int \mathcal{D}t \left( p \dot{x} - \frac{p^2}{2m} - V(x) \right) \right]$$

$$\simeq \int \mathcal{D}x \left[ \prod_{n=1}^{N+1} \int \frac{dp_n}{2\pi \hbar} \right] \exp \left[ \frac{i}{\hbar} \sum_{n=1}^{N+1} \epsilon \left( p_n \delta x - \frac{p_n^2}{2m} - V(x) \right) \right]$$

where we have fully discretised momentum space, and semi discretised coordinate space via $\dot{x} \to \frac{\delta x}{\epsilon}$, with $\epsilon$ being the infinitesimal time-step. The potential term $V(x)$ here is independent of $p$, and therefore may be taken outside the $p$ integral and the $p_n$ integrals performed.

$$K \simeq \int \mathcal{D}x \exp \left[ -\frac{i}{\hbar} \int_{t_i}^{t_f} dt V(x) \right] \left[ \prod_{n=1}^{N+1} \int \frac{dp_n}{2\pi \hbar} \exp \left[ -\left( \frac{i\epsilon}{2m\hbar} p_n^2 - i\delta x p_n \right) \right] \right]$$

$$\simeq \int \mathcal{D}x \exp \left[ -\frac{i}{\hbar} \int_{t_i}^{t_f} dt V(x) \right] \int \frac{dp_1}{2\pi \hbar} \exp \left[ -\frac{i}{\hbar} \left( \frac{\epsilon}{2m} p_1^2 - \delta x p_1 \right) \right] \times \ldots$$

$$\times \int \frac{dp_i}{2\pi \hbar} \exp \left[ -\frac{i}{\hbar} \left( \frac{\epsilon}{2m} p_i^2 - \delta x p_i \right) \right] \times \ldots \int \frac{dp_{N+1}}{2\pi \hbar} \exp \left[ -\frac{i}{\hbar} \left( \frac{\epsilon}{2m} p_{N+1}^2 - \delta x p_{N+1} \right) \right]$$

From this last line we see that the functional integral is a product of gaussian integrals, with gaussian integrals having the property that the product of any number of gaussian's is again a gaussian\(^2\). Integrating out the momentum, our path-integral becomes

\(^2\)The integral of two gaussians with the same coefficient is

$$\int dx_n e^{-a(x_n-x_{n-1})^2} e^{-a(x_{n+1}-x_n)^2} = \sqrt{\frac{\pi}{2a}} \exp \left[ -\frac{1}{2} a(x_{n-1} - x_{n+1})^2 \right]$$
\[
K \simeq \int \mathcal{D}x \exp \left[ -\frac{i}{\hbar} \int_{t_i}^{t_f} dt V(x) \right] \left[ \frac{m}{2\pi \hbar \epsilon} \right]^{\frac{N+1}{2}} \exp \left[ \frac{i}{\hbar} \sum \epsilon \frac{m}{2} \dot{x}^2 \right]
\]

\[
\simeq \left[ \frac{m}{2\pi \hbar \epsilon} \right]^{\frac{N+1}{2}} \int \mathcal{D}x \exp \left[ \frac{i}{\hbar} \sum \epsilon \left( \frac{m}{2} \dot{x}^2 - V(x) \right) \right]
\]

which in the limit \( N \to \infty \) gives us,

\[
K (x_f, t_f; x_0, t_0) = N \int \mathcal{D}x \exp \left[ \frac{i}{\hbar} S [x, \dot{x}] \right] \quad (5.9)
\]

where \( \lambda = \lim_{N \to \infty} \left[ \frac{m}{2\pi \hbar \epsilon} \right]^{\frac{N+1}{2}}. \) The central quantity in the definition of the path-integral is the classical action, which is written as the time integral of the Lagrangian \( S [x, \dot{x}] = \int dt L(x, \dot{x}) \) and takes the place of the Hamiltonian operator in the canonical formalism.

So we have arrived at a formulation of quantum mechanics where the entity defining the dynamics is the classical Lagrangian. This is an attractive feature of the path integral treatment, as the Lagrangian always offers us easy access to the classical limit via the principle of least action and the stationary phase approximation. In principle, the method used to define the path integral method from the canonical formalism of quantum mechanics is reversible, and as such we can a priori claim equation 5.9 as defining the quantum mechanics.

In general when doing calculations in the path integral formalism, we break up phase space into discrete portions, and at the conclusion of the derivation, take the limit that the volume of these discrete units go to zero. One of the most impressive things about the path integral representation is that the Lagrangian (and correspondingly the Hamiltonian) contains only c-number quantities. This means all quantities in the exponent commute, and the action of any path can be evaluated via classical means. On the downside, there are infinitely many paths to integrate.
over, even classically forbidden ones!

5.2.1 Free Particle Propagation

As a first example of a calculation with the path integral method, let us look at the motion of a particle in free space. The Lagrangian for free particle motion is

\[ L(x, \dot{x}) = \frac{1}{2} m \dot{x}^2 \]  

(5.10)

For which our path integral (equation 5.9) is

\[ K(x_f, t_f; x_0, t_0) \simeq \left[ N \prod_{i=1}^{n} \int dx_i \right] \exp \left[ \frac{i \epsilon}{\hbar} \sum_{i=1}^{n} \left( \frac{x_{i+1} - x_i}{\epsilon} \right)^2 \right] \]  

(5.11)

To evaluate this integral, we proceed in a manner similar to that when we performed the p integration in the previous section, that is slice up the functional integral into a product of discrete blocks.

\[ K \simeq N \int dx_1 \exp \left[ -a(x_1 - x_0^2) \right] \int dx_2 \exp \left[ -a(x_2 - x_1^2) \right] \times \]  

\[ ... \int dx_n \exp \left[ -a(x_n - x_{n-1}^2) \right] \exp \left[ -a(x_{n+1} - x_n^2) \right], \]  

(5.12)

where we have made the temporary substitution \( a \rightarrow \frac{im}{2\hbar\epsilon} \). Also note that here \( x_{n+1} = x_f \) and \( x_0 = x_i \) are not integrated over. To evaluate this integral we begin by evaluating the integral over \( x_n \) and integrate subsequent terms down to \( x_1 \). Performing the integrations over \( x_i |i \in [1, N] \), the free particle propagator is
\[ K_{\text{free}} \approx N \left( \prod_{n=1}^{N} \left[ \pi \frac{1}{a(1 + \frac{1}{n})} \right]^{\frac{1}{2}} \right) \exp \left[ -\frac{a}{n+1} (x_f - x_i)^2 \right] \]

\[ \approx \left[ \frac{m}{2\pi\hbar\epsilon} \right]^{\frac{N+1}{2}} \left[ \frac{\pi^N}{N+1} \left( \frac{-2\hbar\epsilon}{im} \right)^N \right]^{\frac{1}{2}} \exp \left[ \frac{im}{2\hbar\epsilon(N+1)} (x_f - x_0)^2 \right] \]

\[ \approx \left[ -\frac{im}{2\pi\hbar\epsilon(N+1)} \right]^{\frac{1}{2}} \exp \left[ \frac{im}{2\hbar\epsilon} (x_f - x_i)^2 \right] \]  \quad (5.13)

In the limit \( n \to \infty, \epsilon \to 0 \). We are free to set the initial time which we choose to be \( t_i = 0 \) such that \( \epsilon(N+1) = \Delta t = t_f - t_i = t \). With this, the free particle propagator is

\[ K(x_f, x_i; t) = \left[ \frac{m}{2\pi\hbar\epsilon} \right]^{\frac{1}{2}} \exp \left[ \frac{im}{2\hbar\epsilon} (x_f - x_i)^2 \right] \]  \quad (5.14)

This is the one dimensional, non-relativistic free particle propagator.

### 5.2.2 The Classical Limit

Using the result for the free particle propagator from the previous section, we will give two examples of extracting the classical dynamics from the path-integral. The first is by calculating the expectation value of the action giving the classical equations of motion of a point particle and the second is for a particle described by a box-car distribution as an example of a hard-sphere particle.

Firstly let’s calculate the expectation value of the action for a free particle by making the following ansatz

\[ \langle S \rangle = \frac{1}{K} \int DxS \exp \left( \frac{i}{\hbar} S \right) \]  \quad (5.15)
temporarily setting $-\alpha = \frac{i}{\hbar}$ (and stepping aside from the issue of constant nature of $i$ and $\hbar$), we are able to arrive at the expression

$$\langle S \rangle = -\frac{1}{K} \int Dx \frac{\partial}{\partial \alpha} e^{-\alpha s[x]}$$

$$= -\frac{1}{K} \frac{\partial}{\partial \alpha} K[\alpha]$$

$$= -\frac{\partial}{\partial \alpha} \ln K[\alpha]$$  \hspace{1cm} (5.16)

in a manner similar that one is able to calculate ensemble averages for the energy is statistical mechanics. Using the result for the free particle propagator (equation 5.14) and substituting it into the above expression gives

$$\langle S \rangle = -\frac{\partial}{\partial \alpha} \ln \left( \frac{\alpha m}{2\pi t} \right)^{\frac{1}{2}} \exp \left[ -\frac{\alpha m}{2t} (x_f - x_i)^2 \right]$$

$$= -\frac{1}{2} \frac{\partial}{\partial \alpha} \ln \left( \frac{\alpha m}{2\pi t} \right) + \frac{\partial}{\partial \alpha} \left[ -\frac{\alpha m}{2t} (x_f - x_i)^2 \right]$$

$$= -\frac{i}{2} + \frac{m}{2t} (x_f - x_i)^2.$$  \hspace{1cm} (5.17)

For free particle propagation where the Lagrangian is simply $L = \frac{1}{2}m\dot{x}^2$, we may evaluate the classical equations of motion via the Euler-Lagrange equations

$$\frac{\partial}{\partial t} \frac{\partial L}{\partial \dot{x}} = m\ddot{x} \rightarrow \ddot{x} = 0$$  \hspace{1cm} (5.18)

The solution of which is simply

$$\dot{x} = \dot{x}_0 = \frac{(x_f - x_i)}{t}.$$
Thus the classical action is

\[
S[x] = \int_0^t dt \frac{1}{2} m x_0^2 \\
= \frac{1}{2} m x_0^2 t \\
= \frac{1}{2} m (x_f - x_i)^2 \\
\]

(5.19)

We thus have a closed form expression for the expectation value of the action for a particle which propagates in a manner described via path integral. Apart from the complex constant, this is the same as the expectation value of the action evaluated through the path integral method. At the field level this is also present, albeit in infinite form.

### 5.2.3 Time-evolution of a particle distribution

It is a natural question to ask under what conditions do quantum and classical theory coincide? A qualitative argument for the cross-over point from quantum mechanical to classical behaviour was put forward by Neils Bohr, who posited that when the parameters describing quantum dynamics become large, the equations of motion will revert to the classical form. An analysis of the time behaviour of wave-packet spreading for a free particle shows that the corresponding parameter is the particle mass, which in the limit \( m \to \infty \) gives the classical equations of motion.

By definition, in the limit that \( \Delta t \to 0 \), the propagator reduces to the Dirac delta function, that is

\[
\lim_{t \to 0} K(x_f, x_i; t) = \delta(x_f - x_i). 
\]

(5.20)

This is simply a mathematical statement of the obvious, that if a particle is
prepared in some initial state and no time has elapsed, the particle remains in that state. For the free particle we can see this explicitly (cf. Equation 5.14), this limit is a formal definition of the delta-function (Hussani, 1999)

$$\lim_{\hbar \to 0} \left[ \frac{a}{2\pi} \right]^{1/2} \exp \left[ -a(x - x')^2 \right] = \delta(x - x')$$ (5.21)

We will now show how this directly affects particle dynamics by utilising equation 5.1. We start with a free particle which initially has a boxcar wave-function in one dimension, namely

$$\psi(x_i, t_i) = \frac{1}{\sqrt{2a}} (\Theta(x + a) - \Theta(x - a))$$ (5.22)

for which we wish to evaluate the behaviour of the particle at future times, with the initial condition being that \langle p \rangle = 0. In the propagator formalism, the time evolution is given by

$$\psi(x', t') = \left[ \frac{\alpha m}{2t\pi} \right]^{1/2} \frac{1}{\sqrt{2a}} \int_{-\infty}^{\infty} [\Theta(x + a) - \Theta(x - a)] \exp \left[ -\frac{\alpha m}{2t}(x' - x)^2 \right] dx$$

$$= \left[ \frac{\alpha m}{4at\pi} \right]^{1/2} \int_{-a}^{a} \exp \left[ -\frac{\alpha m}{2t}(x' - x)^2 \right] dx$$ (5.23)

which integrates to give

$$\psi(x', t) = \frac{1}{2\sqrt{2a}} \left( Erf \left[ \sqrt{\frac{\alpha m}{2t}}(x' + a) \right] - Erf \left[ \sqrt{\frac{\alpha m}{2t}}(x' - a) \right] \right)$$ (5.24)
We may formally define the Heaviside step function as the following limit (Arfken and Weber, 2000)

\[ \Theta(x) = \frac{1}{2} \lim_{\epsilon \to 0} \text{Erfc}\left(\frac{x}{\epsilon}\right) \] (5.25)

where \( \text{Erfc}(x) = 1 - \text{Erf}(x) \) is the complimentary error function. Using this expression for the Heaviside step function it is trivial to show that our original boxcar wave-function is reproduced in the limit as \( m \to \infty \) And hence, given the wave-function of a particle \( \Psi(x_1, t_1) \) at some time, the particle remains localised for all future times. No uncertainty relations, no imaginary time diffusion. When mapping statistical mechanics in the density matrix formulation to the path integral method we shall see that a particle, or rather the partition function, is represented by a closed loop. As the temperature is decreased, the mean radius of this loop increases so that in the zero temperature limit it becomes infinitely delocalised. This should be seen as an expression of the third law of thermodynamics and thus has deep consequences for the laws of quantum mechanics.

5.3 Statistical Mechanics and the Thermal Density Matrix

Consider a system of quantum particles in thermal equilibrium whose dynamics are governed by the time-independent operator equation

\[ \int_{-a}^{a} \exp \left[ -b(x' - x)^2 \right] dx = \frac{1}{2} \sqrt{\frac{\pi}{b}} \left[ \text{Erf} \left( \sqrt{b}(x' + a) \right) - \text{Erf} \left( \sqrt{b}(x' - a) \right) \right] \]

\(^3\)

Although we will be dealing with non-relativistic particles, this is equally applicable to relativistic and spin dependent systems.
The state of an ensemble of particles is statistically determined by the state functions $|\psi_n\rangle$ which characterise microstates of the system. From the state functions one may determine the macroscopic or bulk properties of many-particle systems by assigning a temperature dependent statistical weight to each microstate. The operator which gives a statistical weight to each eigenstate, relating to each a probability amplitude for occurrence, is the density matrix. For the Hilbert space $\mathcal{H}$, the most general density matrix is of the form

$$\rho = \sum_n w_n |\psi_n\rangle\langle \psi_n|,$$  \hspace{1cm} (5.27)

where $w_n > 0$ and $\sum_n w_n = 1$. Equation 5.27 gives a statistical representation of the state of the system, where the coefficients $w_n$ relate to the proportion of the ensemble for distinguishable particles in the $n^{th}$ state. In the canonical ensemble, specified by the fixed quantities of particle number($N$), volume($V$) and temperature($T$), the probability of a measurement on the ensemble giving the $n^{th}$ eigenstate is governed by the Boltzmann factor $\exp (-\beta E_n)$, where $\beta = 1/k_B T$ is the Boltzmann weight. Substituting $w_n = \exp (-\beta E_n)$ into equation 5.27, gives the thermal density matrix in the canonical ensemble. Going one step further, we can give an expression which is independent of representation for any basis $\{\psi_n\} \in \mathcal{H}$, whereby the exterior product of basis functions is equal to unity, i.e. $\sum_n |\psi_n\rangle\langle \psi_n| = \hat{I}$.
\[ \rho = \sum_n e^{-\beta E_n} |\psi_n\rangle \langle \psi_n| \]
\[ = e^{-\beta \hat{H}} \sum_n |\psi_n\rangle \langle \psi_n| \]
\[ = e^{-\beta \hat{H}}. \quad (5.28) \]

The operator \( e^{-\beta \hat{H}} \) is defined by the series

\[ e^{-\beta \hat{H}} = \sum_l \frac{(-\beta)^l}{l!} \hat{H}^l, \quad (5.29) \]

from which all proofs follow. Formally one may then write the partition function \( Z = Z(T, V, N) \) as the trace of the density matrix as

\[ Z = \sum_n e^{-\beta E_n} = \text{Tr} \left( e^{-\beta \hat{H}} \right). \quad (5.30) \]

Although the density matrix does not contain any new physical information on the properties of the ensemble not already present in the partition function, it establishes a notation which is explicitly independent of representation (Huang, 1987). The trace of an operator in one representation is equivalent to the trace in any representation via a unitary transformation and the property of the trace operation \( \text{Tr} (AB) = \text{Tr} (BA) \). As the partition function contains all extensive information of the statistical ensemble, knowledge of the properties of the density matrix is equivalent to a complete characterisation of the system and therefore is the central quantity in the evaluation of macroscopic quantities.

The expectation value of an ensemble measured observable associated with the
operator $O$ can then be calculated as

$$\langle O \rangle = \frac{\sum_n \langle \psi_n | \hat{O} | \psi_n \rangle e^{-\beta E_n}}{Z} = \frac{\text{Tr} (\hat{O} \rho)}{\text{Tr} (\rho)} \quad (5.31)$$

An ensemble measured observable should be taken to mean that we take a randomly selected microstate of the system and measure the observable $O$. Repeating this, the linear average of the set $O = \{O_i\}$ gives us the expectation value of $\hat{O}$ (Long et al., 2006).

For infinite dimensional Hilbert spaces with which we will be primarily concerned, it is often convenient to work in the position representation

$$\rho (R', R; \beta) = \langle R' | e^{-\beta \hat{H}} | R \rangle \quad (5.32)$$

where $|R\rangle = |r_1, r_2, ..., r_N\rangle$ denotes the coordinate representation of the full $N$ particle Hilbert space. We can easily show that this expression is equivalent to equation 5.30 if we recognise the continuum version of the Trace operation as requiring that $R' = R$ and integrating over $R$

$$Z = \text{Tr} (\rho) = \int dR \langle R | e^{-\beta \hat{H}} | R \rangle = \int dR \sum_n \langle R | e^{-\beta \hat{H}} | \phi_n \rangle \langle \phi_n | R \rangle = \sum_n e^{-\beta E_n} \int dR \phi_n^* (R) \phi_i (R) = \sum_n e^{-\beta E_n} \quad (5.33)$$
The Hamiltonian operator $\hat{H}$ in general contains q-number quantities representing particle kinetic and potential terms and equation 5.30 represents that of an interacting many body quantum problem for distinguishable (Boltzmannian) particles.

5.3.1 The Harmonic oscillator

As a model system we shall be using the quantum harmonic oscillator as its thermal properties can be derived analytically. For a system of non-interacting distinguishable particles, all properties are contained in the single particle density matrix, the eigenvalues and eigenfunctions of the Hamiltonian operator:

$$\hat{H}\psi_i = \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} \omega^2 x^2 \right) \psi_i$$

$$= E_i \psi_i$$  \hspace{1cm} (5.34)

for which $E_i = (n + \frac{1}{2}) \hbar \omega$. If we substitute the eigenvalues and eigenfunctions into Eq.5.30 we are able to evaluate the canonical partition function:

$$Tr(\rho) = \sum_i \exp \left[ -\beta \left( n + \frac{1}{2} \right) \hbar \omega \right]$$

$$= \exp \left[ -\frac{\beta \hbar \omega}{2} \right] \left[ 1 + \exp \left[ -\beta \hbar \omega \right] + \exp \left[ -2\beta \hbar \omega \right] + \ldots \right]$$

$$= \frac{\exp \left[ -\frac{\beta \hbar \omega}{2} \right]}{1 - \exp \left[ -\beta \hbar \omega \right]}$$

$$= \frac{1}{2} \text{Csch} \left[ \frac{1}{2} \beta \hbar \omega \right]$$  \hspace{1cm} (5.35)

We can evaluate the expectation value of the energy by employing the thermodynamic relationship of the energy as the derivative of the partition function with respect to inverse temperature giving (Huang, 1987)
\[ \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z \]
\[ = \frac{1}{2} \hbar \omega \coth \langle \frac{1}{2} \beta \hbar \omega \rangle. \quad (5.36) \]

We shall compare this result with a numerical calculation in PIMC in later chapters of this thesis.

### 5.3.2 Derivation of the Path Integral Representation of the Partition Function

The basis of the path integral formulation of statistical mechanics is the convolution property of the many body density matrix in the position representation \( \rho (R, R'; \beta) \) and the resulting classical configuration integral for calculating the properties of quantum systems (Feynman, 1972; Ceperley, 1995). Consider the Trotter product formula for self-adjoint operators

\[ e^{- (\hat{A} + \hat{B})} = \lim_{M \to \infty} \left( e^{- \hat{A}/M} e^{- \hat{B}/M} \right)^M. \quad (5.37) \]

Henceforth \( M \) shall be referred to as the Trotter number. A trivial consequence of equation 5.37 is that when \( \hat{A} = \hat{B} \), this identity becomes exact for finite \( M \) as every operator is self commutative. In our case we wish to apply this to the density matrix and we can use the Trotter formula to express the partition function as a product of \( M \) density matrices. Let us apply this to the thermal density matrix for the case of \( M = 2 \)
\begin{align}
\langle R | e^{-\beta \hat{H}} | R' \rangle &= \langle R | e^{-\beta \hat{H}/2} e^{-\beta \hat{H}/2} | R' \rangle \\
&= \int dR_1 \langle R \left| e^{-\beta \hat{H}/2} | R_1 \right\rangle \langle R_1 | e^{-\beta \hat{H}/2} | R' \rangle \\
&= \int dR_1 \rho(R, R_1; \beta/2) \rho(R_1, R'; \beta/2)
\end{align}

(5.38)

where we have inserted the identity \( \int dR_1 |R_1\rangle \langle R_1| = 1 \). The convolution property of the density matrix is exact and gives a representation of the ensemble at inverse temperature \( \beta \) as the convolution of two density matrices, each at the higher temperature \( \beta/2 \). A generalised expression for the density matrix for the case of arbitrary Trotter number is

\begin{align}
\rho(R, R'; \beta) &= \int dR_1 \ldots dR_M \rho(R, R_1; \beta/M) \rho(R_1, R_2; \beta/M) \ldots \rho(R_M, R'; \beta/M) \\
&= \prod_{i=1}^{M} \left[ \int dR_i \right] \prod_{i=0}^{M} \langle R_{i+1} | e^{-\tau \hat{H}} | R_i \rangle,
\end{align}

(5.39)

where we have set \( R_{M+1} = R' \), \( R_0 = R \) and \( \tau = \beta/M \). This re-expression of the thermal density matrix in itself serves no useful purpose as we still have the problem of evaluating many-body operator equations of the form \( \langle R_{i+1} | e^{-\tau \hat{R}} | R_i \rangle \), albeit at a higher temperature. To proceed, let us consider the thermal density matrix for a non-interacting system in the limit \( \tau \to 0 \). For a typical matrix element from equation 5.39, we can use the Baker-Campbell-Hausdorff formula for the operator exponential expansion to independently evaluate the noncommutative kinetic and potential terms in the Hamiltonian, i.e.

\begin{align}
\langle R_{i+1} | e^{-\tau \hat{H}} | R_i \rangle &= \langle R_{i+1} | e^{-\tau \hat{T}} e^{-\tau \hat{V}} e^{-\hat{O}(\tau^2)} | R_i \rangle
\end{align}

(5.40)
For small $\tau$, the operator expansion will be dominated by the terms linear in $\tau$ and we can approximate the density matrix as a product of kinetic and potential terms, ignoring higher order terms. The final expression we will obtain here will be in the $\tau \to 0$ limit, for which this decomposition exact. However in practical implementations of path integral statistical mechanics for which we will use a finite value of $\tau$, we should be mindful that this introduces errors in any calculations performed. Proceeding with the evaluation of the matrix element in 5.40, we can now evaluate each of the kinetic and potential terms independently by again utilising the identity operator $\int dR |R\rangle \langle R| = \hat{I}$

\[
\langle R_{i+1}|e^{-\tau\hat{H}}|R_i\rangle = \int dR \langle R_{i+1}|e^{-\tau\hat{T}}|R\rangle \langle R|e^{-\tau\hat{V}}|R_i\rangle. \tag{5.41}
\]

In the position basis, the potential energy operator is usually diagonal such that we may write

\[
\langle R|e^{-\tau\hat{V}(R_i)}|R_i\rangle = e^{-\tau V(R_i)} \delta (R - R_i). \tag{5.42}
\]

To evaluate the kinetic term, we insert the momentum space identity $\int dP|P\rangle \langle P| = \hat{I}$, where $|P\rangle = |p_1,...,p_N\rangle$ is the momentum space representation of the $N$-particle Hilbert space.

\[
\langle R_{i+1}|e^{-\tau\hat{T}}|R\rangle = \int dP \langle R_{i+1}|e^{-\tau\hat{T}}|P\rangle \langle P|r \rangle \\
= \int dP e^{-\tau\lambda p^2} \langle R_{i+1}|P\rangle \langle P|R \rangle \\
= \int dP \exp \left(-\tau\lambda p^2 - iP \cdot (R_{i+1} - R)\right), \tag{5.43}
\]
where we have used the identity $\langle P|R \rangle = e^{iP.R}$ and set $\lambda = \frac{k^2}{2m}$. The resulting integral is a standard $ND$-dimensional gaussian integral, an explicit evaluation of which is given in appendix E. The kinetic integral then evaluates to

$$
\langle R_{i+1}|e^{-\tau H}|R_i \rangle \approx \left[ \frac{\pi}{\lambda \tau} \right]^{\frac{ND}{2}} \int dR \exp \left[ -\frac{(R_{i+1} - R_{i})^2}{4\lambda \tau} \right] \quad (5.44)
$$

Recombining the results for the kinetic and potential terms, the small $\tau$ approximation for the matrix element in equation 5.40 becomes

$$
\langle R_{i+1}|e^{-\tau H}|R_i \rangle \approx \left[ \frac{\pi}{\lambda \tau} \right]^{\frac{ND}{2}} \prod_{i=1}^{M} \int dR_i \exp \left[ -\frac{(R_{i+1} - R_{i})^2}{4\lambda \tau} \right] \quad (5.45)
$$

Substituting 5.45 into 5.39 gives us an expression for the thermal density matrix for Trotter number $M$, i.e.

$$
\rho (R_0, R_{M+1}; \beta) \approx \left[ \frac{\pi}{\lambda \tau} \right]^{\frac{MN}{2}} \prod_{i=1}^{M} \int dR_i \exp \left[ -\frac{(R_{i+1} - R_{i})^2}{4\lambda \tau} - \tau V (R_i) \right] \quad (5.46)
$$

To calculate the partition function, the trace condition requires that $R_{M+1} = R_0$ and we integrate over $R_0$. In the limit that $M$ tends to infinity, the summation in the exponential becomes an integral evaluating to the classical Euclidean action
\[ S[R] = \int_{0}^{\beta} d\tau \left( \frac{1}{4\lambda} \left( \frac{\partial R}{\partial \tau} \right)^2 + V(R) \right) \]  

(5.47)

and one may formally write the partition function as,

\[ Z[\beta] = \int dR \langle R | e^{-\beta H} | R \rangle = \Lambda \oint_{R(0)}^{R(\beta)=R(0)} DR e^{-S[R]} . \]  

(5.48)

Here we have set \( \Lambda = \lim_{M \to \infty} \left[ \frac{\pi}{\lambda \tau} \right]^{M N D} \) and

\[ \oint DR = \lim_{M \to \infty} \prod_{i=0}^{M} \int dR_i \]

is the functional integration measure. Equation 5.48 establishes the path integral representation of the partition function in the canonical ensemble. The major benefit of this formulation is the removal of operator dependence of the partition function and replacement by the classical action. However there is a price we must pay, this being that the integration measure is now over an infinite dimensional functional space.

The formal evaluation of Eq. 5.48 for noninteracting particles in arbitrary potential gives the partition function to be the product of the single particle partition function, i.e.

\[ Z_N[\beta] = Z_1[\beta]^N \]  

(5.49)
5.3.3 The free particle density matrix

Now that we have the path integral representation of the density matrix, we may ask what we may calculate with it. In the previous section of this chapter we calculated the propagator for a free non-relativistic particle using path integrals, the most trivial example of an analytically solvable Hamiltonian. So we shall follow this example and calculate the thermal density matrix for the free particle or more accurately, an infinite non-interacting gas. However instead of proceeding to perform a calculation of the convolution of an infinite number of Gaussian integrals, we shall exploit the relationship between quantum mechanics and statistical mechanics via the Wick rotation. Recall the properties of the quantum mechanical propagator the previous section, in particular that it is a solution of the Schrödinger equation. For the free particle this is

\[ i\hbar \frac{\partial}{\partial t} K(x, x'; t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} K(x, x'; t). \] (5.50)

Similarly observe for the exponential operator representation of the thermal density matrix the relationship

\[ \frac{\partial}{\partial \beta} e^{-\beta \hat{H}} = -\hat{H} e^{-\beta \hat{H}} \]

which for the free particle Hamiltonian gives

\[ \frac{\partial}{\partial \beta} \rho(R, R'; \beta) = \frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} \rho(R, R'; \beta) \] (5.51)

This equation is the continuous form of the Bloch equation, first introduced in (Bloch, 1932)(Kirkwood, 1933) as an attempt at a quantum equivalent of the
Gibbs phase space integral for the calculation of classical thermodynamic quantities.

To make the simplest connection between Eqs. 5.50-5.51, equivalence between the propagator and the thermal density matrix can be found by setting \( t = -i \hbar \beta \) and \( x = R \)

\[
\rho (R, R'; \beta) = K (R, R', -i \hbar \beta). \quad (5.52)
\]

Using this relationship we obtain the free \( N \)-particle density matrix

\[
\rho (R, R'; \beta) = \left[ \frac{m}{2\pi \hbar \beta} \right]^{Np} \exp \left( -\frac{m}{2\hbar^2 \beta} (R' - R)^2 \right). \quad (5.53)
\]

where \( D \) is the spatial dimension. The partition function is calculated by setting \( R' = R \) and integrating over \( R \), giving the familiar result for the non-interacting Boltzmann gas

\[
Z_N [\beta] = \left[ \frac{m}{2\pi \hbar \beta} \right]^{Np} \frac{1}{V} \int_0^L dR
\]

\[
\langle E \rangle = \frac{D}{2} Nk_B T \quad (5.55)
\]

where we have included the volume normalisation term \( 1/V \).

This is the basis of the path-integral formulation of statistical mechanics, equation 5.48 the starting point of the PIMC method for distinguishable particles. One important aspect of quantum theory however has yet to be considered and that is the case of particle indistinguishability. In the next chapter we will see how incorporating particle statistics in the density matrix leads to some very fascinating physical
and mathematical structures.
Chapter 6

The partition function for
indistinguishable particles

6.1 Particle Statistics

The formalism presented in the previous chapter is the high temperature limit of a more fundamental theory and does not take into account the full symmetry of the Hamiltonian. The Hamiltonian as parametrised by the position labels $R = \{r_1, r_2, \ldots, r_n\}$ is invariant under permutation of particle labels with the familiar consequence of Bose-Einstein and Fermi-Dirac statistics, resulting in new phenomenology as the temperature of the ensemble is reduced. The effects of particle indistinguishability can qualitatively be said to become manifest when the thermal wavelength $\lambda_T = \left[\frac{2\pi \hbar^2}{mk_B T}\right]^{1/2}$ becomes comparable to the mean interparticle separation. Essentially it is a quantum measurement problem in that we are no longer justified in labeling particle trajectories with known starting and finishing points. The characterisation of symmetries necessarily involves elements of group theory and a study of invariance under the group action. Mathematically, permutational symmetry is best described in terms of representation theory of the symmetric group, knowledge of which has a large area of importance including the theory of
symmetric functions and many fundamental questions in quantum theory. In this thesis we shall be concerned solely with representations of the symmetric group as it applies to the theory of bosons and the many-body thermal density matrix. This will form a basis for the development of a novel stochastic sampling algorithm for sampling particle exchange cycles in confined geometries.

### 6.1.1 The Partition Function for Bosons

For the well-ordered set of particle position labels \( \{R\} = \{r_1, r_2, ..., r_N\} \), denote as \( S_N \) the symmetric group of order \(|S_N| = N!\), the group of all permutations of \( N \) symbols. If we denote as \( \{\phi\} \in S_N \) the corresponding set of operators which exchange particle labels, then the \( N \)-particle bosonic density matrix can be written as a sum over all such operators

\[
\rho_B (R, R'; \beta) = \frac{1}{N!} \sum_{\phi \in S_N} \rho (R, \phi R'; \beta).
\] (6.1)

For noninteracting systems of identical particles, the convolution property of the density matrix leads to a decomposition and the partition function becomes the product of density matrices at various temperatures. This property of the density matrix can be utilised to find an expression for the boson partition function which is enumerated in terms of the length of cyclic exchanges in the symmetric group. Consider a system of two non-interacting particles in an arbitrary external potential with the Hamiltonian operator

\[
\hat{H} = \hat{H}_1 + \hat{H}_2,
\] (6.2)

such that \([\hat{H}_1, \hat{H}_2] = 0\). The density matrix for this system will be the sum of
two components, one relating to the identity element of $S_2$ and other the transposition of $\{1, 2\}$. The identity element of the density matrix will be the same as the non-interacting Boltzmann case for which we have $\rho(r_1r_2, r'_1r'_2; \beta) = \rho(r_1, r'_1; \beta)\rho(r_2, r'_2; \beta)$. Permuting particle labels for the second element gives the partition function

$$Z_0[\beta] = \frac{1}{2} \int dr_1 dr_2 \rho(r_1, r_1; \beta)\rho(r_2, r_2; \beta) + \frac{1}{2} \int dr_1 dr_2 \rho(r_1, r_2; \beta)\rho(r_2, r_1; \beta)$$

(6.3)

Using Equation 5.39 for the second integral in Equation 6.3 the partition function can be written exactly as (cf. Figure 6.1)

$$Z_0[\beta] = \frac{1}{2} \left[Z_1[\beta]^2 + Z_1[2\beta]\right],$$

(6.4)

$Z_1$ denoting the single particle partition function. As is frequently noted, the partition function of statistical mechanics is related to the propagator of quantum theory via rotation of time to the imaginary axis (Kleinert, 2004), and so the effect of permuting particle labels in the two particle case is to wind the trajectory twice around imaginary time.

A general expression can be obtained for the $N$-body *interacting* partition function, involving the irreducible representations of the symmetric group (Springall et al., 2007). The representation theory of groups is usually concerned with the representation of a group $G$ as a set of invertible matrices, that is $\rho : g \rightarrow GL(n, F)$ where $g \in G$ (James and Liebeck, 1993) and all proofs regarding the relationship between group elements can be constructed in this framework. An important property of group elements is that of conjugacy. For $x, y \in G$, we say that $x$ and $y$ are conjugate elements if $x = g y g^{-1}, \forall g \in G$. The set of all conjugate elements of
Figure 6.1: Graphical representation of the trace operation on the density matrix for indistinguishable particles

\[ G \] are called a conjugacy class with the number of conjugacy classes of \( S_N \) given by the number-theoretic partition function \( P(N) \), the number of ways the number \( N \) may be written as the sum of positive integers (James and Liebeck, 1993; Macdonald, 1999; Goldschmidt, 1993). Each element of the group will belong to only one conjugacy class and therefore the conjugacy operation partitions the group into nonintersecting sets. Denoting the set of conjugacy classes of \( G \) as \( \phi_i \) we then have

\[
\bigcup_{i=1}^{P(N)} \phi^i = S_N
\]

\[
\bigcap_{i=1}^{P(N)} \phi^i = \emptyset
\]

(6.5)

where \( \phi^i \) denotes the \( i^{th} \) conjugacy class. Each permutation is composed of a number of disjoint cycles with the sum of cycle lengths equal to \( N \). It is then not difficult to show that elements of the same conjugacy class have the same cycle structure using the matrix representation of \( S_N \) which consist of the permutation matrices.
Figure 6.2: Graphical representation of the conjugacy classes of $S_4$ (Springall et al., 2007)

### 6.1.2 Graphical Representation of Conjugacy Classes

Each conjugacy class can be graphically represented via the standard Young Tableaux, with an equivalence relation between conjugacy classes and partitions of $N$ corresponding to a summation based on exchange cycle lengths (Fulton, 1997). However for application to the thermal density matrix in the path integral representation it is instructive to consider diagrams of the form shown in Fig. 6.2 showing the conjugacy classes of $S_4$ which has 5 conjugacy classes and 24 elements.

An explanation is in order as to the origin of these diagrams. In the path integral representation of the density matrix each particle is represented as a string whose length is proportional to the thermal de Broglie wavelength. The act of taking the trace of the density matrix for distinguishable particles is to connect the start of the string ($\tau = 0$) to its corresponding end ($\tau = \beta$) and integrate. For the indistinguishable case, the action of elements of $S_N$ on the density matrix is to exhaust all possibilities in connecting particle start and finish positions to form closed loops, the identity element corresponding to the case of Boltzmann statistics. From the
diagrams in Figure 6.2 it can be seen that elements of a particular conjugacy class are topologically equivalent which specify an irreducible representation of the group.

In order to enumerate all conjugacy classes of \( S_N \), one is required to find all distinct cycle structures which as mentioned is equivalent to the number of ways one may partition \( N \) into a summation of positive integers. We can index partitions of \( N \) with the weakly decreasing sequence

\[
\bar{\phi}_i = \{ \bar{\lambda}_1^i, \bar{\lambda}_2^i, ..., \bar{\lambda}_\rho^i \},
\]

(6.6)

each element having the property that \( \bar{\lambda}_1^i \geq \bar{\lambda}_2^i \geq ... \geq \bar{\lambda}_\rho^i \), or as the strongly decreasing sequence

\[
\phi_i = \{ (\lambda_1^i)^{k_{i,1}} , (\lambda_2^i)^{k_{i,2}} , ..., (\lambda_\gamma^i)^{k_{i,\gamma}} \},
\]

(6.7)

where \( \lambda_1^i > \lambda_2^i > ... > \lambda_\gamma^i \). Here \( k_{i,j} \) will be denoted as the multiplicity of a particular loop size. The dimension of each conjugacy class is equal to the number of Young tableaux with shape \( \phi_i \), that is the number of equivalent diagrams, which is given by

\[
\dim (\phi_i) = \frac{n!}{\prod_{j=1}^{\gamma} ((\lambda_j^i)^{k_{i,j}} k_{i,j}!)} = d_i,
\]

(6.8)

where each partition satisfies
For the purpose of this work we need to identify two numbers \(|\bar{\phi}^i| = \rho\), the number of elements in a partition, which is equal to the number of rows on the equivalent Young tableaux and \(|\hat{\phi}^i| = \gamma\), the number of distinct elements. For example if we denote \(\Phi\) as the set of all Young tableaux with \(N\) boxes, for the case of \(S_4\) we have the conjugacy classes labeled by the partitions

\[
\Phi = \{\{1, 1, 1, 1\}, \{2, 1, 1\}, \{2, 2\}, \{3, 1\}, \{4\}\}
\]

\[
= \{\{1^4\}, \{2, 1^{2}\}, \{2^2\}, \{3, 1\}, \{4\}\}
\]

\[
= \{\phi^1, \phi^2, \phi^3, \phi^4, \phi^5\},
\]

with the dimension of each conjugacy class given as (cf. Figure 6.2)

\[
\dim (\Phi) = \{\frac{24}{1^4 \cdot 4!}, \frac{24}{2 \cdot 1^2 \cdot 2!}, \frac{24}{2^2 \cdot 2 \cdot 3!}, \frac{24}{3 \cdot 1}, \frac{24}{4}\}
\]

\[
= \{1, 6, 3, 8, 6\} = \{d_1, d_2, d_3, d_4, d_5\}.
\]

With this notation, we are able to write down a general expression for the partition function of a noninteracting bosonic system of \(N\) particles. Since for each element of a conjugacy class the contribution to Equation 6.1 will be equivalent, the number of equivalent elements is equal to the dimension of the conjugacy class and we may write the partition function as

\[
Z_b[\beta] = \frac{1}{N!} \sum_{i=1}^{P(n)} \left( d_i \prod_{j=1}^{\frac{|\hat{\phi}^i|}{\rho}} Z_1[\lambda^i_j \beta]^{k_{i,j}} \right),
\]
where the superscript \( k_{i,j} \) denotes raising the power of the partition function to the multiplicity of this particular loop with cycle size \( \lambda_j \). We see that to each partition is associated exactly one function and therefore they define class functions of the symmetric group via the mapping

\[
Z : g \rightarrow \prod_{j=1}^{|\phi|} Z_1 \left[ \lambda_j \beta \right]^{k_{i,j}}.
\] (6.13)

To obtain an understanding of Equation 6.12, let us again consider the example of \( S_4 \) for which \( P(4) = 5 \). Written out fully, the partition function takes the form (cf. Figure 6.2)

\[
24 \times Z_b = \prod_{j=1}^{\phi_1} Z_1 \left[ \lambda_j \beta \right]^{k_{1,j}} + 6 \prod_{j=1}^{\phi_2} Z_1 \left[ \lambda_j \beta \right]^{k_{2,j}} + 3 \prod_{j=1}^{\phi_3} Z_1 \left[ \lambda_j \beta \right]^{k_{3,j}} + 8 \prod_{j=1}^{\phi_4} Z_1 \left[ \lambda_j \beta \right]^{k_{4,j}} + 6 \prod_{j=1}^{\phi_5} Z_1 \left[ \lambda_j \beta \right]^{k_{5,j}}
\]

\[
= Z_1[\beta]^4 + 6Z_1[2\beta]Z_1[\beta]^2 + 3Z_1[2\beta]^2 + 8Z_1[3\beta]Z_1[\beta] + 6Z_1[4\beta]
\] (6.14)

This is the exact form of the bosonic partition function for 4 noninteracting particles in d-dimensions in an arbitrary external potential. Each conjugacy class will have a temperature dependent contribution to the partition function which defines a natural probability measure on the set of partitions.
6.1.3 The Symmetric Polynomials

It has been noted on several occasions that the partition function for both bosons, fermions and para-statistical systems related to the symmetric polynomials (Balantekin, 2001; Schmidt and Schnack, 2002; Chaturvedi, 1996) and also occur in relation to the eigenfunctions of the Celogero-Sutherland model (Hallnäs, 2007). This is not surprising as the symmetric polynomials are important in the representation of the symmetric group (Macdonald, 1999). The analysis in these papers however is restricted primarily to the occupation number representation in systems containing only a finite number of eigenstates. The theory of symmetric polynomials and their connection to representation theory is expansive and mostly formal and as such we present here only a small component which is of relevance and comprehensible to the author. A symmetric function is one which remains unchanged under the permutation of particle labels, that is

\[ f(x_1, x_2, ..., x_N) = f(x_{P_1}, x_{P_2}, ..., x_{P_N}) \] (6.15)

There are two bases that satisfy the algebra for symmetric functions. Given the set of monomials \( \mathbf{x} = \{x_1, x_2, ..., x_N\} \), the complete symmetric homogeneous polynomials are functions which are invariant under label permutation and can be obtained by the generating function

\[ \prod_{i=1}^{N} (1 - x_i)^{-1} = \sum_m h_m(\mathbf{x}). \] (6.16)

Here are the first few complete homogenous symmetric functions:
\[
\begin{align*}
h_1(x) &= \sum_{i=1}^{N} x_i \\
h_2(x) &= \sum_{j \leq i} \sum_{i=1}^{N} x_i x_j \\
h_3(x) &= \sum_{k \leq j \leq i} \sum_{i=1}^{N} x_i x_j x_k \\
\end{align*}
\] (6.17)

The complete symmetric homogeneous polynomials may also be represented another way. Given a matrix \( \hat{A} \) for which the monomials \( x \) are the eigenvalues, then the complete symmetric polynomials obey trace relationships. The first three are

\[
\begin{align*}
h_1(x) &= \text{Tr}[\hat{A}] \\
h_2(x) &= \frac{1}{2} \left( \text{Tr}[\hat{A}^2] + \text{Tr}[\hat{A}]^2 \right) \\
h_3(x) &= \frac{1}{6} \left( \text{Tr}[\hat{A}]^3 + 3 \text{Tr}[\hat{A}] \text{Tr}[\hat{A}^2] + 2 \text{Tr}[\hat{A}^3] \right). \\
\end{align*}
\] (6.18)

That is, they satisfy Equation 6.12, connecting the partition function for \( N \) bosons with the symmetric polynomials;

\[
\begin{align*}
h_N(x) &= \frac{1}{N!} \sum_{i=1}^{P(n)} d_i \prod_{j=1}^{[\delta_i]} \text{Tr}[\hat{A}^\lambda]^{k_{i,j}}. \\
\end{align*}
\] (6.19)

To understand the context of the appearance of the monomials \( \{x\} \) it will be useful to examine the occupation number representation of the partition function. In the occupation number representation for a system containing \( N \) particles with \( m \) energy levels, we may write the canonical ensemble partition function as
\[ Z_B[\beta] = \sum_{n_1} \sum_{n_2} \cdots \left[ \prod_{i} x_i^{n_i} \right] \delta(N - \sum_j n_i) \]  

(6.20)

where \( x_i = \exp(-\beta \epsilon_i) \). Here the delta function is a particle number constraint, with \( n_i = Z^* \) for bosons and \( n_i \in [0, 1] \) for fermions. Expanding Equation 6.20 gives for the bosonic case

\[
Z^b_N = \sum_{n_1} \sum_{n_2} \cdots [x_1^{n_1} x_2^{n_2}] \delta(N - \sum_i n_i) \\
= (x_1^0 + x_1^1 + x_1^2 + x_1^3 \cdots) (x_2^0 + x_2^1 + x_2^2 \cdots) \cdots \delta(N - \sum_j n_i) \\
= \frac{\delta(N - \sum_i n_i)}{\prod_i (1 - x_i)} = h_m(x),
\]

(6.21)

Note that if the number of energy levels is the same as the number of particles, we may replace \( m \) in the above equation with \( N \) and the partition function becomes that given in Equation 6.19. We can do a similar analysis for fermions which gives

\[
Z^f_N = (x_0^0 + x_1^1) (x_1^0 + x_1^1) (x_2^0 + x_2^1) \cdots \\
= \prod_i (1 + x_i) \delta(N - \sum_i n_i)
\]

(6.22)

So the natural question to ask at this point is, “does the fermionic partition function correspond to the symmetric polynomials?” This leads us to the elementary symmetric polynomials which are
\[ a_1(x) = \sum_{i=1}^{N} x_i \]
\[ a_2(x) = \sum_{j<i}^{N} \sum_{i=1}^{N} x_i x_j \]
\[ a_3(x) = \sum_{k<j}^{N} \sum_{j<i}^{N} \sum_{i=1}^{N} x_i x_j x_k \]
\[ \prod_{i=1}^{N} (1 + x_i) = \sum_{m} a_m(x), \quad (6.23) \]

the final line giving the generating function. By enforcing the particle number constraint we get

\[ Z_N^f = a_m(x) \quad (6.24) \]

If the set of monomials \( x = \{x_1, \ldots, x_n\} \) are the eigenvalues of some matrix \( \hat{A} \) then the elementary symmetric polynomials satisfy the trace relationship

\[ a_1(x) = \text{Tr}[\hat{A}] \]
\[ a_2(x) = \frac{1}{2} \left( \text{Tr}[\hat{A}] - \text{Tr}[\hat{A}^2] \right) \]
\[ a_3(x) = \frac{1}{6} \left( \text{Tr}[\hat{A}]^3 - 3 \text{Tr}[\hat{A}] \text{Tr}[\hat{A}^2] + 2 \text{Tr}[\hat{A}^3] \right). \quad (6.25) \]

The negative sign arises in the path integral representation of the fermionic partition function when a permutation is even which is a result of fermion wave-function antisymmetry. Thus we may write
\[ a_N = \frac{1}{N!} \sum_{i=1}^{P(n)} \left( \text{sgn}(\phi_i) d_i \prod_{j=1}^{\lvert \phi_i \rvert} Z_1 \lambda_j \beta^{k_{i,j}} \right), \quad (6.26) \]

where \( \text{sgn}(\phi) \) is +1 for an even permutation and −1 for an odd one. For the case of fermions it is worth mentioning one point. A problem in all Monte Carlo calculations, where a positive definite probability is required, is the fermion sign problem. For the case of PIMC the fermion sign problem manifests itself in the negative sign associated with the density matrix of odd permutations. However as represented by the elementary symmetric polynomials, the fermionic density matrix suffers no such problem if the monomials are positive definite. In the case of the occupation number representation over a finite number of energy levels it is clear what the monomials are, namely the exponents of the energy levels. However what these monomials do not correspond to are the occupation numbers in the path integral form of the partition function that we derived in equation 6.12. Equation 6.12 is written as a sum over the conjugacy classes of the symmetric group and is independent of the number of levels in the system. The matrix operator \( \hat{A} \) in this instance is the density matrix \( \exp \left( -\beta \hat{A} \right) \) which obeys

\[ \exp(-\beta \hat{H})^k = \exp(-k\beta \hat{H}) \quad (6.27) \]

The trace operation represents the group character in the permutation cycle representation over an arbitrary number of energy levels, whereas the monomials give the group characters in the occupation number representation over only a finite number of energy levels. Balantekin presented the result \( Z_N = h_N(x) \) in (Balantekin, 2001) connecting the partition function to the complete homogeneous symmetric functions in the occupation number representation. However the connec-
tion to the permutation cycle representation as in equation 6.19 was not made. A search of the literature has failed to turn up any previous mention of this connection explicitly. This has important consequences for the construction of estimators of the condensate fraction defined by loop cycle probabilities in PIMC, and the specification of transition probabilities for the construction of Markov chains in permutation space.

6.2 Calculating Permutation Cycle Probabilities

There is an interesting question that arises when one studies the partition function for indistinguishable particles in terms of representation theory of the symmetric group. Is there a relationship between long permutation cycles and the condensate fraction? That particle statistics are connected to the representation theory of the symmetric group is well known. What is less well understood is the connection between different representations of particle-statistics and how they relate to each other. Of particular interest is the connection of loop cycle probabilities in quantum gases to the condensate fraction, a fundamental quantity in the determination of the properties of BECs. Whereas the occurrence of BEC has traditionally been identified with long spatial correlations in the many-body density matrix, recently there has been a shift in emphasis to the evaluation of long permutation cycles and their connection to the condensate fraction (Ueltschi, 2006; Mullin, 2000; Chevallier and Krauth, 2007). This is the so-called loop gas approach.

Given Equation 6.12, the probability of randomly choosing a particular partition $\phi^i \in \Phi$, as a function of temperature is given by

$$
\pi (\phi_i \in \Phi) = \frac{d_i}{Z_b} \prod_{j=1}^{\phi_i} Z_1 |\lambda_j^i|^2 \beta^{k_{i,j}}. \tag{6.28}
$$

We have plotted these the conjugacy class probabilities in Figure 6.3 for $S_4$ where
the probabilities are those in Equation 6.14.

In this figure, the contributions from various elements of the permutation group are clearly evident, showing that at high temperatures the identity dominates, leading to the usual classical statistics (Feynman, 1972; Ceperley, 1995). Also in the $T \to 0$ limit, the partition function reduces to

$$Z_b[\beta \to \infty] = \frac{1}{N!} \sum_{i=1}^{P(n)} d_i$$  \hspace{1cm} (6.29)

which is exact for all noninteracting bosonic systems. For systems in which the particles interact, the evaluation of partition function elements will generally not be decomposable as a product of single particle functions (Holzmann and Krauth, 1999), but the loop structure based upon the conjugacy classes of $S_N$ will still be present.

The question is, does the loop structure directly relate to the condensate fraction in atomic gases, defined as the probability of $N_0/N$ particles occupying the ground-state? Or to be more precise, is $\langle l \rangle \sim \langle N_0 \rangle$ where $\langle l \rangle$ is the expectation value of the
longest permutation cycle? If so, then knowing the expectation value of the loop size then becomes crucial to the evaluation of the condensate fraction and other superfluid and BEC properties.

So we ask then, what is the probability of occurrence of individual cycles of length $l$? In (Chevallier and Krauth, 2007), the authors propose the following definition of cycle probabilities of length $l$

$$\pi_l = \frac{1}{Z^b} \sum_{\{\phi|l \in \phi\}} Z[\phi; \beta]$$

(6.30)

Where the sum is over all conjugacy classes containing a cycle of length $l$. In general a cycle of length $l$ will be associated with more than one partition and so the sum is over all partitions containing loops of length $l$. However this is the incorrect probability measure to use over cycle lengths as is does not take into account that the probability of a particle being in a cycle of length $l$ in a particular partition is also dependent on the other cycles in the partition. In this instance, the probability measure fails to be unitary and is therefore inappropriate. An example of this is shown in Figure 6.4, where we have plotted the probability of each loop length for 4 particles in a one-dimensional harmonic trap (cf Figure 6.3).

In short, the reason for this is simple. The given probability measure is the probability that a conjugacy class will contain a cycle of length $l$, not the probability that a particle will be in a cycle of length $l$. The measure is not unitary as partitions are double counted if they contain cycles of more than one type. To correct this we must take into account that the probability of a particle being in a cycle of length $l$ is a function of the length of the cycle. Consider for a moment equation 6.12 but with temperature dependence removed, that is
Figure 6.4: Cycle probabilities for 4 particles in a one-dimensional harmonic trap as given by Equation 6.30. The solid red line gives the sum over the probabilities which is not unitary.

$$Z^b = \frac{1}{N!} \sum_{i=1}^{P(N)} d_i$$ \hspace{1cm} (6.31)

If we denote the set of all conjugacy classes which contain a cycle of length \( l \) as \( \{ i | l \in \phi_i \} \) then for each cycle length in \( S_N \) the following relationship holds

$$\sum_{\{ \phi | l \in \phi_i \}} d_i l k_{i,l} = N!$$ \hspace{1cm} (6.32)

The summation is over all partitions containing cycles of the same length. Table 6.1 gives the corresponding formulas for \( S_5 \) which contains 7 conjugacy classes.

Since for each cycle length equation 6.32 gives the same value, then
Table 6.1: The conjugacy classes of $S_5$ and loop cycle weights as calculated from Equation 6.32. In the case each loop weight evaluates to 120, which is given in the final row on the righthand side.

<table>
<thead>
<tr>
<th>Conjugacy Class</th>
<th>Partition</th>
<th>$d_i$</th>
<th>Cycle length(l)</th>
<th>$\Pi_l = \sum_{i(l \in \phi_i)} d_i l_k_{i,l}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_1$</td>
<td>${1^5}$</td>
<td>1</td>
<td>1</td>
<td>$5d_1 + 3d_2 + d_3 + 2d_4 + d_6$</td>
</tr>
<tr>
<td>$\phi_2$</td>
<td>${2, 1^3}$</td>
<td>10</td>
<td>2</td>
<td>$2 (d_2 + 2d_3 + d_5)$</td>
</tr>
<tr>
<td>$\phi_3$</td>
<td>${2^2, 1}$</td>
<td>15</td>
<td>3</td>
<td>$3 (d_4 + d_5)$</td>
</tr>
<tr>
<td>$\phi_4$</td>
<td>${3, 1^2}$</td>
<td>20</td>
<td>4</td>
<td>$4d_6$</td>
</tr>
<tr>
<td>$\phi_5$</td>
<td>${3, 2}$</td>
<td>20</td>
<td>5</td>
<td>$5d_7$</td>
</tr>
<tr>
<td>$\phi_6$</td>
<td>${4, 1}$</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\phi_7$</td>
<td>${5}$</td>
<td>24</td>
<td></td>
<td>120</td>
</tr>
</tbody>
</table>

$$ \sum_{l=1}^{N} \left[ \sum_{\{\phi | l \in \phi_i\}} d_i l_k_{i,l} \right] = N \times N! $$

$$ = \sum_{l=1}^{N} \Pi_l, \quad (6.33) $$

where we have denoted the inner summation on the left hand side of the above equation as $\Pi_l$ in the final line. The natural conclusion is that using this, the probability of a particle belonging to a cycle of length $l$ is $1/N$, that is

$$ \pi_l = \frac{\Pi_l}{\sum_{k=1}^{N} \Pi_k} = \frac{1}{N} \quad (6.34) $$

Reinserting the temperature dependence in Equation 6.33, we then give the loop probability as a function of temperature as

$$ \pi_l = \frac{1}{\bar{Z}^b} \sum_{\{\phi | l \in \phi_i\}} d_i l_k_{i,l} Z[\phi_i; \beta] $$

$$ \bar{Z}^b = \frac{1}{N(N!)} \sum_{l=1}^{N} \Pi_l \quad (6.35) $$
Figure 6.5: The probabilities of cycle lengths as a function of temperature for 4 bosons in a one-dimensional harmonic trap. The red line gives the sum over cycle length probabilities, which is unitary at all temperatures. The correct result of equal probability in the $T \to 0$ is clearly evident.

where the $\bar{Z}^b$ indicates a summation over loops and $Z[\phi_i; \beta]$ the class function associated with conjugacy class $\phi_i$. Employing this equation, we will look at the example of 4-particles in a one-dimensional harmonic trap. The loop cycle probabilities are

$$
\pi_1 = \frac{1}{4} (4Z_1[\beta]^4 + 6.2Z_1[2\beta]Z_1[\beta]^2 + 8Z_1[3\beta]Z_1[\beta]) \\
= Z_1[\beta]^4 + 3Z_1[2\beta]Z_1[\beta]^2 + 2Z_1[3\beta]Z_1[\beta] \\
\pi_2 = \frac{1}{4} (6.2Z_1[2\beta]Z_1[\beta]^2) \\
= 3Z_1[2\beta]Z_1[\beta]^2 + 3Z_1[2\beta]^2 \\
\pi_3 = \frac{1}{4} (8.3Z_1[3\beta]Z_1[\beta]) = 6Z_1[3\beta]Z_1[\beta] \\
\pi_4 = \frac{1}{4} (6.4Z_1[4\beta]) = 6Z_1[4\beta].
$$

The results of which are plotted in Figure 6.5. Equation 6.35 is the correct expression for calculating cycle probabilities.
Now to the question we originally asked. Do loop cycle probabilities correspond to the ground state probabilities? It is not difficult in this case to calculate the expectation value of 4 particles in the ground state. Since the ground-state eigenvalue is \( \exp \left( -\frac{1}{2}\hbar \omega \beta \right) \), the expectation value that 4-particles will occupy the ground-state as a function of temperature is given by

\[
\langle n_0(4) \rangle = \frac{e^{-2\hbar \omega \beta}}{Z_b}
\]

(6.37)

Comparing this to Equation 6.36 we clearly see that this is not equal to the 4 loop probability which is given by

\[
\langle l = 4 \rangle = \frac{1}{Z_b} 6 \times \frac{1}{2} \text{Csch}[2\hbar \omega \beta]
\]

\[
= \frac{3}{Z_b} \text{Csch}[2\hbar \omega \beta].
\]

(6.38)

It is clear then that the probability of having \( n \) particles in the ground state is not equivalent to the probability of a particle being in a permutation cycle of length \( n \).

We have one further identity to prove. Since the value of the partition function is independent of whether we sum over loops or over partitions, then it follows that \( \bar{Z}^b = Z^b \). For non-interacting systems we may then write

\[
\frac{1}{N(N!)} \sum_{l=1}^{N} \left( \sum_{\phi | l \in \phi_i} d_l k_{i,l} \prod_{j=1}^{\phi^i} Z_1 [\lambda^i_j \beta]^{k_{i,j}} \right) = \frac{1}{N!} \sum_{i=1}^{P(n)} \left( d_i \prod_{j=1}^{\phi^i} Z_1 [\lambda^i_j \beta]^{k_{i,j}} \right)
\]

(6.39)
This equivalence is not difficult to prove. In the summation on the left hand side we take all elements which have as a common factor the conjugacy class dimension \( d_m \) which we suppose is equal to the corresponding term for the \( m^{th} \) conjugacy class on the right hand side, that is

\[
\frac{1}{N} \sum_{j=1}^{\vert \phi_m \vert} \lambda_{m,j} k_{m,j} \prod_{j=1}^{\vert \phi_m \vert} Z_1 [\lambda_j^m \beta]^{k_{m,j}} = \prod_{j=1}^{\vert \phi_m \vert} Z_1 [\lambda_j^m \beta]^{k_{m,j}}
\]

The product term containing the single particle functions is common to both sides, leaving

\[
1 = \frac{1}{N} \sum_{j=M}^{\vert \phi_j \vert} \lambda_{m,j} k_{m,j}
\]

\[
N = \sum_{j=1}^{\vert \phi_M \vert} \lambda_{m,j} k_{m,j}.
\]

This relationship is that given in equation 6.9 and therefore the equivalence in equation 6.39 proven.

### 6.3 Summary

In this chapter we have derived a form of the partition function for bosonic systems in the canonical ensemble based upon the irreducible representations of the symmetric group of \( n \) objects. It was shown that the partition function can be decomposed into a sum over the conjugacy classes of \( S_n \) which defines a probability measure over Young tableaux which is a function of temperature. Further we have related the partition function for bosonic and fermionic systems to the symmetric polynomials and identified monomials which correspond to the eigenvalues of the single particle density matrix for non-interacting systems. However we have left unresolved what
the monomials \{x_1, x_2, ..., x_N\} represent in terms of the fermionic and bosonic density matrices, which makes no explicit reference to the eigenvalue spectrum of the Hamiltonian.

Although research into the appearance of symmetric polynomials in statistical mechanics is relatively recent, their mathematical origin is in Newton’s attempts at finding polynomial roots in the seventeenth century. The subsequent development of group theory and the role the symmetric polynomials play in understanding the symmetric group has resulted in a large amount of literature expounding their properties. There are many occasions where the generating function of the symmetric functions has appeared in connection with particle statistics, for example equation 8.62 of Huang, 1987, however without reference to the symmetric polynomials themselves.

Their connection to group representation theory should see application to problems in statistical mechanics progress rapidly, as representation theory of the symmetric group is a widely studied area of mathematical physics. Work is likely to continue in this area and a wider knowledge of symmetric polynomials by physicists sought, which will enable an alternative and mathematically rigorous approach to particle statistics.
Chapter 7

Computational Implementation of
Path Integral Monte Carlo

7.1 Introduction

In chapter six we have seen how we may use the convolution property of the many-body density matrix to re-express the partition function as a functional integral in configuration space, the dynamical quantity now being the classical action of particle trajectories and not the sum over Hilbert space basis vectors. Like any interacting many-body problem however, the range of problems for which analytic solutions exists is limited and one must look to methods for obtaining approximate numerical solutions.

The path integral Monte Carlo (PIMC) method is a computational technique which allows the accurate numerical description of quantum many-body systems at finite temperature. Recoverable information from PIMC calculations include the energy, radial distribution function and density profile, the pressure, specific heat and where bosonic symmetries are included, the superfluid density. A central quantitative measure of the state of the system is the energy. There are several different ways that one may obtain the energy in PIMC. A thermodynamic estimator
is obtained by the relationship between the energy and the derivative of the partition function. Another estimator is based on the virial theorem and typically yields lower variances than the thermodynamic estimator. In any case, any evaluation of the energy from a calculation will be dependent upon the action implemented and if the functional form of the action is changed, say from the primitive action to the harmonic action, then the expression of the energy within the code must be altered accordingly. However the evaluation of the energy is not the only end to a PIMC calculation and there are emerging techniques for analysis of condensation behaviour.

At the commencement of the coding of a PIMC code, the aim was to develop a method to treat Helium in the superfluid phase to complement the zero-temperature quantum Monte Carlo investigations in part one of the thesis. As is often with proposed research, the problems that would be encountered were not foreseen and subsequently the work on this very interesting area of physics was not engaged. There is a plethora of results of PIMC studies of Helium, as highlighted in chapter four, and it would have proved difficult to complete a novel calculation that would have added to this body of research. Instead there came to our attention a fundamental discrepancy in the rigor with which one tackles treating particle statistics within a computer code. Whereas for continuous probability measures methods have been developed which give significant improvements on a purely random sampling approach, none had been developed for discrete measures, as is encountered when Bose-Einstein statistics is to be strictly enforced. The bosonic configuration space has an inherent $N!$ scaling owing to the size of the permutation group of $N$ particle labels and although ingenious methods, along with their explanations, have been put forward, to us none of these seemed entirely satisfactory. This should be seen as the impetus of the work contained in the previous chapter which included elements of representation theory and this chapter with regard to a sampling technique for the Bosonic partition function which maps between conjugacy classes of the symmetric
group.

In this chapter we shall use the formalism presented in chapters five and six to outline the three main components of a working PIMC code, the action, sampling and the evaluation of properties. Of specific concern is the contrasting nature of sampling configuration space and permutation space. With regard to the latter, we will address the issue of appropriate integration measures over permutation space and outline a novel sampling method based upon a probability measure on the space of Young Tableaux as indexed by partitions\(^1\). As for choosing an appropriate action, we include only a synopsis of the primitive action, the simplest approximation for a discretised action. This has been implemented in the Fortran 90 code EPICURUS.

### 7.2 The Path Integral Monte Carlo Method

#### 7.2.1 Configuration space sampling

Recall from the previous chapter the exact representation of the partition function as a product of density matrices,

\[
Z[\beta] = \int dR_0...dR_M \\
\rho(R_0, R_1; \beta/M) \rho(R_1, R_2; \beta/M) ... \times \rho(R_{M-1}, R_M; \beta/M) \rho(R_M, R_0; \beta/M).
\]

For sufficiently high temperatures, approximations to the density matrix are known which renders equation 7.1 a classical multi-dimensional integral. For dilute systems where n-body interactions are dominated by pairwise contributions, an appropriate approximation to the density matrix is that of the pair-product form\(^1\).

\(^1\)This work specifically was published by the author in reference (Springall et al., 2007)
\[ \rho(R, R'; \tau) = \left[ \prod_{i=1}^{N} \rho_1(r_i, r'_i; \tau) \right] \left[ \prod_{i<j} \tilde{\rho}(r_{ij}, r'_{ij}; \tau) \right]. \quad (7.2) \]

Here \( \rho_1 \) is the single particle density matrix for an ideal gas at temperature \( \tau = \beta/M \) and \( \tilde{\rho}_2 \) is the two body density matrix divided by the ideal gas terms. The ideal gas term, derived and given in equation 5.53 is

\[ \rho_1(R, R'; \tau) = \left( \frac{m^2}{2 \pi \tau} \right)^{\frac{N}{2}} \exp \left[ -\frac{m}{2 \tau} \sum_{i=1}^{N} (r_i - r'_i)^2 \right]. \quad (7.3) \]

For a scalar potential field, the potential energy operator will be diagonalisable in the position representation and the two-body density matrix will simply be the exponent of the potential at a point in configuration space. However one should be aware of an approximation introduced using this method. For real systems, the potential energy of a particle will vary along its trajectory which is quantitatively reflected in a continuous line integral along that trajectory. The use of a finite number of time-slices has the result that we average out spatial variations in the potential energy, which becomes a spatial average of the full interaction curve (cf. figure 7.1). This places a length scale on the spatial variation of the potential as a function of Trotter number (and hence temperature), and the validity of equation 7.2 as an approximation to the true density matrix. In practice a better approximation to the potential term is (Feynman, 1972),

\[ \tilde{\rho}_2(r, r'; \tau) = \exp \left[ -\frac{\tau}{2} (V(r) + V(r')) \right]. \quad (7.4) \]

This representation of the many-body density matrix is exact only in the limit that \( \tau \to 0 \), as the decomposition of the operator exponential contains commutator
terms of higher order in $\tau$ which decay faster than the linear terms as $\tau \to 0$. In this case we are forced to use a finite value of the Trotter number $M$ in the formula $\exp(-\beta \mathcal{H}) = \exp(-\tau \mathcal{H})^M$ while integrating out any q-number dependence in the density matrix. The form of the density matrix we have presented here is of the simplest kind and is known as the primitive approximation and has a variance proportional to $(\beta/M)(\text{Raedt and Raedt, 1983})$. Higher order corrections based on the evaluation of commutator terms are available for most propagator QMC methods (Li and Broughton, 1987; Cuervo et al., 2005; Acioli, 1996) however in this work we will use solely the primitive approximation.

We are able to use equation 7.2 as the basis of a sampling approach based in the Metropolis algrithm. Let $s$ represent the state of the system as labeled by the bead and particle configuration $\{s^N_M\}$ and $\pi(s)$ the corresponding probability distribution given by the thermal density matrix of Equation 7.2.

$$P_{s \to s'} = \min \left[ 1, \frac{\pi(s')}{\pi(s)} \right]$$

(7.5)

For a bead-by-bead sampling algorithm where one Metropolis move is made by displacing a single bead of a “polymer”, the transition probably will be the function of the change in action for a single bead that is
\[
\frac{\pi(s')}{\pi(s)} = e^{-\Delta S(r_i^\mu, s_i^\mu)}
\] (7.6)

where \(r_i^\mu\) denotes the position of the \(i^{th}\) bead of the \(\mu^{th}\) particle and the full expression for the change in the action is

\[
\Delta S (r_i^\mu, r_i'^\mu) = (r_{i+1} - r_i')^2 + (r_i' - r_{i-1})^2 + V(r_i') + \sum_{\nu \neq \mu} v (r_i^\mu, r_i'^\nu) \\
-(r_{i+1} - r_i)^2 - (r_i - r_{i-1})^2 - V(r_i) - \sum_{\nu \neq \mu} v (r_i^\mu, r_i'^\nu)
\] (7.7)

The bead-by-bead algorithm satisfies all the criterion for Metropolis sampling set out in chapter two, such as detailed balance for ergodicity and is therefore guaranteed to converge. For the calculations in this thesis we have used as an \textit{a priori} move probability \(T (s \rightarrow s') = c\) where \(c\) is a step-size set to give an acceptance probability of 0.5. The value of \(c\) is optimised through the equilibration period before being set constant for accumulation of statistics.

### 7.2.2 The Polymer Isomorphism

The trace condition on the density matrix for the evaluation of the partition function requires that the particle trajectories form closed paths. For the discretised case, the \(N\)-particle partition function can be viewed as classically interacting ring polymers, each polymer described by a ring containing \(M\) nodes interacting harmonically with coupling constant \(k = mM/h^2\beta\) (Chandler and Wolynes, 1981). As the spring constant increases with increasing temperature, the mean particle radius of curvature decreases and the particle becomes more localised. In the classical limit the particles behave as classical point like structure.
Figure 7.2: In PIMC, particles are represented by a set of beads with nearest neighbour harmonic interactions. The circumference of each particle loop is proportional to the thermal de Broglie wavelength.

Figure 7.3: Particle radial distributions as a function of temperature for free, non-interacting particles composed of ten beads in one dimension calculated using PIMC. On the outer graph, the y-axis is the relative probability of the mean particle radius as calculated in center of mass coordinates. The inner graph shows the peak value of the radius as a function of temperature which obeys a $1/r$ relationship.
7.2.3 The inter-particle potential

We mention two types of interparticle potential which were implemented in the course of this thesis. For dilute systems we introduce a contact interaction as found in the Gross-Piteavskii equation, which has its origins in $\phi^4$ theories and may be given as (Dalfovo et al., 1999)

\[ V(\mathbf{r} - \mathbf{r}') = g\delta(\mathbf{r} - \mathbf{r}') \]  

(7.8)

where the coupling constant is related to the s-wave scattering length $a$ by

\[ g = \frac{4\pi \hbar^2 a}{m}. \]  

(7.9)

This potential however is impractical for systems with a dimension greater than one. A more practical effective potential is the hard-sphere system

\[ V(\mathbf{r} - \mathbf{r}') = \begin{cases} 0, & |r > a| \\ \infty, & |r < a| \end{cases} \]  

(7.10)

The hard-sphere interaction is a valid approximation only when the s-wave scattering length is much smaller than the mean inter-particle separation and the condensate fraction is a significant proportion of the total number of particles in the system. For the case of superfluid Helium these condition are not valid and thus we are required to use an accurate inter-particle potential. We have used the Hurly and Moldover (Hurly and Moldover, 2000) 12-parameter potential.
\[ \phi_{\text{rep}} (r) = A \exp \left( a_1 r + a_2 r^2 + a_{-1} r^{-1} + a_{-2} r^{-2} \right) \]

\[ \phi_{\text{att}} (r) = -\sum_{n=3}^{8} \frac{f_{2n}(r) C_{2n}}{r^{2n}} \left[ 1 - \left( \sum_{k=0}^{2n} \frac{(\delta r)^k}{k!} \right) \exp (-\delta r) \right] \quad (7.11) \]

John Hurly of the National Institute of Standards and Technology has been kind enough to offer his fortran code of this potential, which for a set of discrete separations lists the relevant value of the potential. This potential is also very close to the QMC potential energy curve calculated in chapter three (see table 3.4 in this work and (Springall et al., 2008)).

7.2.4 Calculating the Energy

Although in the subsequent work we have not used classical properties, one of the thermodynamic estimators we do use is the energy. The thermodynamic estimator for the energy is obtained from the density matrix via the thermodynamic relationship

\[ \langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \]

\[ = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \quad (7.12) \]

We may then easily calculate the expectation value of the energy in PIMC in a way analogous and almost identical to that of DMC. Applying equation 7.12 to equation 5.46 gives the thermodynamic estimator for a configuration of any dimensionality;
\[
\langle E_s \rangle = \frac{N M k_B T}{2} \left[ D - m k_B T \sum_{i=1}^{M} \sum_{\mu=1}^{N} (x_{i+1}^{\mu} - x_i^{\mu})^2 \right] \\
+ \frac{1}{M} \sum_{\mu=1}^{N} V(x_i^{\mu}) + \frac{1}{2M} \sum_{\mu=1}^{N} \sum_{\nu \neq \mu}^{n} v(x_i^{\mu}, x_i^{\nu}),
\]

(7.13)

where \( D \) is the spatial dimension. The expression in the brackets on the right hand side gives the correction to the classical kinetic energy expression for \( M \) beads. To calculate the mean energy we sum over configurations for \( p \)-statistics accumulation steps to obtain the PIMC estimated energy

\[
\langle E \rangle = \sum_{s}^{p} \langle E_s \rangle.
\]

(7.14)

Alternative estimators for the energy have been derived, primarily in response to the large intrinsic variance in the thermodynamic estimator and higher order corrections to the primitive action. The virial estimator was proposed in Hermal et al., 1982 and is an energy estimator which is dependent only on the potential energy and its derivatives. For the purpose of this work, we will only implement the thermodynamic estimator. We have therefore outlined the basic components of a working PIMC code for distinguishable particles. We now move onto the problem of incorporating particle statistics.

### 7.3 Permutational sampling. A new approach for treating Bosons

One of the ubiquitous problems in all approaches to evaluating the partition function for bosonic systems within PIMC is a transparent way of sampling the permutation space arising from the exchange symmetry of the Hamiltonian. Permutation space
is an inherently discrete space with a conventionally ill defined metric, lacking the concept of local neighborhoods and a distance between elements in contrast to continuous probability distributions. This makes it difficult to propose an accurate method which will provide a good approximation to the true loop configuration probabilities. Previous approaches such as those in Ceperley, 1995; Ceperley and Pollock, 1989; Boninsegni, 2005 and Holzmann and Krauth, 1999, advocate either the sampling of some cyclic subset of $S_n$, the symmetric group of order $N!$, typically up to $C_4$ or $C_5$, or approximate the interacting partition function structure to that of a noninteracting system, only strictly valid for systems which are weakly coupled and unable to give an account of the ultra-low temperature properties nor properties where interactions are strong. The strong interaction regime is important especially for the case of repulsive interactions. It is specifically the strongly interacting regime where the PIMC method is an important theoretical method as perturbation theory becomes divergent. The cyclic subset method, henceforward referred to as the Ceperley method, is equivalent to the treatment of parastatistics (Green, 1953; Polychronakos, 1996) and has been successfully applied to the calculation of properties of Helium in the superfluid phase. To be precise Ceperley was able to calculate the specific heat of an infinite Helium system and identify the signature lambda curve. As the results relied on thermodynamic energy estimators, the variance in the specific heat results was subsequently large. These methods are unable however to give an accurate representation of the permutational structure of bosonic systems. As has been alluded to by Krauth, specific information regarding the condensate is contained in the permutational structure itself (Chevallier and Krauth, 2007; Holzmann and Krauth, 1999). Although the intrinsic $N!$ scaling involved in the sampling of permutation space has largely been overcome, this has been replaced with algorithms which scale exponentially, still problematic for large $N$. A recent proposal for a size independent algorithm has been reported by Boninsegni et. al. in (Boninsegni et al., 2006a) which also looks promising for investigations into large systems and
calculating off-diagonal elements of the density matrix. In this work however we will not be concerned with treating large systems \( (N > \mathcal{O}(1000)) \) and confine ourselves to small, finite systems.

In recent years mathematical methods have been developed regarding the random growth of partitions of the symmetric group, the probability measure known as the Plancherel measure and random matrices (Borodin et al., 2000; Polychronakos, 1996; Okounkov, 2000). Although up to the present time the investigation of these structures have been of abstract mathematical interest only, one would like to ascertain if these methods could help in the very physical application of predicting the permutational structure of BEC’s and superfluid’s at arbitrary temperatures.

In this section we present an algorithm which allows us to construct a Markov chain through permutation space for an explicit probability measure which maps between conjugacy classes of the symmetric group. It is partially inspired by the recent work regarding Markov processes on Young tableaux (Borodin et al., 2000; Borodin and Olshanski, 2004a; Borodin and Olshanski, 2004b; Okounkov, 2000), the connection between irreducible representations of the symmetric group and the analytic form of the bosonic partition function for noninteracting systems which was derived in the previous chapter. Unlike a previous method (Holzmann and Krauth, 1999), which is restricted to weakly interacting systems, we propose that this method samples the ring configuration structure at any temperature without any \( a \ priori \) knowledge of the noninteracting counterpart. This enables us to quantify ring configuration probabilities over a larger temperature scale and evaluate the relative importance of certain structures to the partition function. In practice this amounts to the construction of a graph of partitions giving rise to a concept of neighbouring points and a way to sample permutation space, giving a realistic distribution of loop structures at equilibrium.
7.3.1 Permutation Sampling

Recall the expression for the partition function for a system of noninteracting bosonic particles written as a sum over the conjugacy classes of the symmetric group

\[ Z[\beta] = \frac{1}{N!} \sum_{i=1}^{P(n)} \left( d_i \prod_{j=1}^{\phi^i} Z_1[\lambda_j^i \beta]^{k_i,j} \right), \tag{7.15} \]

where \( d_i \) is the dimension of the conjugacy class (the number of equivalent diagrams), \( \phi^i \) the number of cyclic sub-classes of the \( i^{th} \) conjugacy class, \( \lambda_j^i \) the permutation cycle length and \( k_{i,j} \) the multiplicity of a particular cyclic permutational structure in the conjugacy class (cf. Figure 6.2). Each partition of \( S_N \) will have a contribution to the canonical partition function and can be seen to define a temperature dependent probability measure on the set of partitions \( \Phi \). In the simplest implementation of a stochastic sampling method, one would randomly select a partition with a Metropolis acceptance probability given by

\[ Pr(\phi^i \rightarrow \phi^j) = \frac{d_j \prod_{m=1}^{\phi^j} Z_1[\lambda_m^j \beta]^{k_j,m}}{d_i \prod_{n=1}^{\phi^i} Z_1[\lambda_n^i \beta]^{k_i,n}}, \tag{7.16} \]

with \( d_i = \text{dim}(\phi^i) \) given by

\[ \text{dim}(\phi^i) = \frac{N!}{\prod_{j=1}^{\gamma} (\lambda_j^i)^{k_j^i} k_j^i !}. \tag{7.17} \]

However, as derived by Ramanujan and Hardy, for large \( n \) the number of partitions is given by (Hardy and Ramanujan, 1918)

\[ P(n) \simeq \frac{1}{4\sqrt{3n}} e^{\pi \sqrt{\frac{2n}{3}}}. \tag{7.18} \]
which becomes prohibitively inefficient for large $n$, as the rejection rate for transitions between uncorrelated partitions would be large. The overhead required for the construction of probability measures as given above is minimal, with only knowledge of the current permutational structure and the proposed structure required and thus memory requirements kept to a minimum. What would seem to be the most troublesome to implement is the ratio of conjugacy class dimensions as given in equation 7.16. This is presumably the probability used in Holzmann and Krauth, 1999 to construct partitions, which was then applied to the case of a weakly interacting Bose gas. However in this work there is no mention of including conjugacy class dimension in the calculation of transition probabilities. What we would like is a binary operation from which we are able to move between the conjugacy classes of $S_N$ which is more efficient than unguided sampling.

### 7.3.2 A new permutation space sampling algorithm

We propose a set of operators which enable us to construct a Markov chain through the conjugacy classes of $S_N$. A similar formalism can be found in Borodin and Olshanski (Borodin and Olshanski, 2004a; Borodin and Olshanski, 2004b) in constructing partitions, identifying an operation which maps between partitions. Again consider a partition as the weakly decreasing sequence

$$\bar{\phi}^i = \{\lambda^i_1, \lambda^i_2, \ldots, \lambda^i_j, \ldots, \lambda^i_{\rho-1}, \lambda^i_{\rho}\} \quad (7.19)$$

but with the restriction that at least one element, namely $\lambda^i_{\rho}$, has the value of 1. Consider two operators $a_j$ and $\bar{a}_j$ which act on a partition by either combining two loops together, one of which is a single particle loop, or separating a loop into two components with one a single particle loop, that is

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such that

$$\begin{align*}
|a_j\bar{\phi}_i| &= |\bar{\phi}_i| - 1 \\
|\bar{a}_j\bar{\phi}_i| &= |\bar{\phi}_i| + 1.
\end{align*}$$ (7.21)

These operators create and destroy $C_1$ subgroups of the conjugacy classes, in the process creating a new partition which is also a conjugacy class of the relevant permutation group. The action of these operators is to effectively move up and down a graph with $P(n)$ vertices of the partitions of $S_N$, leaving the sum of the elements of partitions invariant (cf. Figure 7.4).

If we denote partitions which are related via a single application of $a_j$ or $\bar{a}_j$ as
neighbouring partitions, we can construct a probability measure over neighbouring partitions to give a formula for the transition probability under \( a_j \) and \( \bar{a}_j \) as

\[
\begin{align*}
\rho^\downarrow (\phi_i; a_j \phi_i) &= \frac{\dim(a_j \phi_i)}{\sum_j \dim(a_j \phi_i)} \\
\rho^\uparrow (\phi_i; \bar{a}_j \phi_i) &= \frac{\dim(\bar{a}_j \phi_i)}{\sum_j \dim(\bar{a}_j \phi_i)}
\end{align*}
\tag{7.22}
\]

One can easily see that these transition probabilities satisfy the criterion that the sum of probabilities over neighbours is equal to one. In the construction of a Markov chain through permutation space, one could suppose that these are the correct transition probabilities to be used. Ergodicity, in the sense that the correct weight of each partition will be reproduced, is not assured via these relations. It is not however difficult to prove that all partitions are accessible under this scheme. If we consider the partition denoting the identity of \( S_N \) as \( \{1\}_N \), then we may construct any other partition using a repeated application of \( a_j \), that is

\[
\{\lambda_1, \lambda_2, ..., \lambda_\rho\} = \prod_{i=1}^\rho a_i^{\lambda_i} \{1\}_N.
\tag{7.23}
\]

Since we are able to perform the reverse of this operation, that is reach the identity from any partition, via the use of \( \bar{a}_j \), all partitions are connected. Once a partition is chosen then it can be accepted or rejected via the Metropolis scheme. One hinderance to the successful application of these transition probabilities is that there does not exist any formula for the sum over neighbours which would be relatively easy to implement on a computer within a Monte Carlo code, especially for systems containing a large number of particles.

An alternative option which is relatively easy to implement would be to give all neighbours the same weight. Then one may choose a particular element of a
partition to act upon with the probabilities

\[
p^\uparrow (\phi_i; a_j \phi_i) = \frac{k_j}{|\phi_i| - 1} \quad p^\downarrow (\phi_i; a_j \phi_i) = \frac{k_j}{|\phi_i| - k_{i,\gamma}}.
\]

(7.24)

The action of \(\bar{a}_j\) on a partition element is to give \(\bar{a}(\lambda) \rightarrow (\lambda - 1, 1)\) and so the normalisation is the number of elements in a partition which are not equal to one. The action of \(a_j\) on a partition element is to give \(a(\lambda, 1) \rightarrow (\lambda + 1)\) such that at least one element must have value one, giving a normalisation factor of the number of elements in a partition less one. Metropolis sampling is not involved at this point, the use \(a\) and \(\bar{a}\) being a prescription that a permutation move be proposed. Boninsegni used the \(a_j\) operator to construct permutation cycles for the superfluid phase of \(^4\text{He}\), containing 64 atoms. However in this work permutation cycles were constructed at each sampling move from the identity. Again, from equation 7.23 we can see that each permutation cycle will be accessible via this scheme, however it is not guaranteed that the correct weights will be reproduced.

### 7.3.3 Calculating Conjugacy Class Dimensions

To calculate the Metropolis acceptance probability, we are required to calculate the ratio of the dimensions of each conjugacy class which in general will be the ratio of factorial functions(cf. equation 7.16). For conjugacy classes which are related by a single application of \(a\) or \(\bar{a}\), the ratio of their dimension is considerably simplified. For these derivations we alter our notation of partitions to the following. For an \(N\) particle system a partition is labeled by

\[
\phi = \{n^{k_n}, (n - 1)^{k_{n-1}}, ..., 2^{k_2}, 1^{k_1}\}
\]

(7.25)
that is, different partitions are distinguished only by a difference in the multiplicity of any of the elements of the partition. For example consider $n = 10$ and the partition $(3^2, 2^2, 1)$ which in the above notation is labeled as

$$
\phi = \{10^0, 9^0, 8^0, 7^0, 6^0, 5^0, 4^0, 3^2, 2^2, 1^1\}.
$$

Consider two conjugacy classes related via $\phi = a_j \phi'$ labeled by the partitions,

$$
\phi' = \{n^k, \ldots, (n-j)^{k_{n-j}}, (n-j-1)^{k_{n-j-1}}, \ldots, 1^{k_1}\}
$$

$$
\phi = \{n^k, \ldots, (n-j)^{k_{(n-j)-1}}, (n-j-1)^{k_{(n-j)-1}+1}, \ldots, 1^{k_1+1}\}.
$$

There are two cases that need to be considered separately, one where a cycle of length 2 is operated on and all others. Firstly consider the case of $l \neq 2$. Applying the formula for conjugacy class dimension gives

$$
\frac{\text{dim}(\phi')}{\text{dim}(\phi)} = \frac{n^k \ldots (n-j)^{k_{(n-j)-1}} (n-j-1)^{k_{(n-j)-1}+1} \ldots k_n! (k_{(n-j)})! \ldots (k_1 + 1)!}{n^k \ldots (n-j)^{k_{(n-j)}} (n-j-1)^{k_{(n-j)-1}} \ldots k_n! (k_{(n-j)} - 1)! (k_{(n-j)-1} + 1)! \ldots (k_1)!}
$$

$$
= \frac{(n-j)^{k_{(n-j)-1}} (n-j-1)^{k_{(n-j)-1}+1}}{(n-j)^{k_{(n-j)}} (n-j-1)^{k_{(n-j)-1}}} \frac{k_{(n-j)}! k_1!}{k_{(n-j)}! (k_{(n-j)} - 1)! (k_1 + 1)!}
$$

$$
= \frac{(n-j) k_{n-j-1} k_1}{(n-j-1) k_{n-j}}.
$$

The case for $l = 2$ is subtly different as separating into two components gives two single loops and one may work through the algebra to get

$$
\frac{\text{dim}(\phi')}{\text{dim}(\phi)} = \frac{2^{k_2-1} k_1+2 (k_2 - 1)! (k_1 + 2)!}{2^{k_2} k_1 (k_2! k_1!)}
$$

$$
= \frac{k_1 + 2}{2^{k_2}}.
$$
There are further instances of simplifications, for example when acting on loop sizes whose lengths are greater than half the number of particles in the system where multiplicities cannot be greater than one, however they offer little in the way of computational advantage. One also has the feeling that this relationship could prove beneficial to working out a recursion relations for conjugacy class dimensions. These relationships coupled with the conjugacy class transition rules enable us to calculate the Metropolis acceptance probability and construct a Markov chain through permutation space based upon the decomposition of the partition function into a sum over conjugacy classes of the symmetric group which is easily implemented on a computer.

7.3.4 Calculating Cycle Probabilities

An important quantity associated with low temperature atomic systems is the fraction of particles in the lowest eigenstate, i.e. the condensate fraction. The classical understanding of the superfluid or lambda transition in liquid helium is a divergence in the specific heat \(C_v\) (Feynman, 1972; Ceperley and Pollock, 1989) at constant volume. However as was noted earlier, energy estimators tend to have large variances and as \(C_v\) is the derivative of the energy this transition can be difficult to identify unless one knows where to look. There are however other indicators of the occurrence of a phase transition, such as an abrupt change in the superfluid density or the condensation fraction, which are direct signatures of the transition. Another indicator of a phase transition is the presence of stable long permutation cycles, which are linked to many-body correlations. As the correlation length of a condensate approaches infinity, this requires that we must calculate off-diagonal elements of the density matrix. In PIMC this can be very inefficient, however methods have been devised to investigate such behaviour in large systems, notable the worm algorithm of lattice QFT calculations (Boninsegni et al., 2006b).

Our strategy for calculating permutation cycle length probabilities is to count
Figure 7.5: Loop probabilities for 64 hard-sphere particles in a isotropic 3-dimensional harmonic trap as calculated by equation 7.30. The data set contains 12,800,000 samples taken with 10 moves between samples.

permutation cycle lengths at each iteration in the statistics accumulation phase, then calculate the probabilities as

$$ \pi_k = \frac{n_k}{\sum \lambda n_{\lambda \lambda}} $$  \hspace{1cm} (7.30)

where $n_k$ is the total number of loops of size $k$. This result should coincide with the result given in equation 6.35, which is displayed in figure 7.30.

7.3.5 Non-interacting Bosons in a one dimensional harmonic trap

As a simple test of the proposed scheme with the analytic results given in Figure 6.3, we performed a path integral Monte Carlo calculation on 4 bosons in a one
dimensional harmonic trap. We essentially use the method outlined in (Ceperley, 1995) and (Springall et al., 2008). The Trotter number was chosen such that the single particle energy was comparable to the analytic expression $\langle E \rangle = \frac{1}{2} \coth \left( \frac{1}{2} \beta \right)$, however small enough that chosen permutations were accepted with a reasonable probability.

We implemented two schemes for permutation sampling. In the first, the results of which are summarised in figure 7.6, particle labels were randomly shuffled at each move and were accepted or rejected according to the Metropolis scheme. This was used primarily as a test for the validation of the code. In the second scheme we constructed a random walk through permutation space based upon the transition probabilities given in Equations. 7.22 between partitions. At each move a partition list is created and an up or down move ($a_j$ or $\bar{a}_j$) proposed with equal probability. In the case that a partition is at the end of a path (cf. Figure 7.4), then the algorithm forces a move to the next connected vertex. In the case of $a_j$, once a partition element is chosen, then the nearest single loop structure is found such that the acceptance probability in the following Metropolis sampling move is maximised. The results of this method are shown in Figure 7.7

As can be seen, randomly shuffling particle labels reproduces the analytic decomposition of the partition function very well. We would however expect this method to become diminishingly inefficient as the particle number increased, and as the confining potential becomes significantly weaker, where the thermal wavelength of the particles will no longer be comparable to the mean particle separation, and thus would not be a viable option for a general PIMC code. Further the results of our method show that even though every partition is accessible via this algorithm, this does not guarantee that the method will reproduce the analytical result of Equation. 6.14.

An interesting feature of the results of the two methods of permutational sampling investigated is that, while they did not coincide with regard to the predicted
Figure 7.6: Partition structure of four bosons in a 1-d harmonic trap from PIMC calculations, with partitions created via a random shuffling of particle labels. The solid line is the exact answer as given by Equation. 6.14

Figure 7.7: Partition structure of four bosons in a 1-d harmonic trap with partitions created the new method. The solid line is the exact answer as given by Equation. 6.14
permutation cycle structure, the resultant energy of the two methods was nearly identical (cf. Figure 7.8). Although the new method proposed was unable to reproduce the exact analytic form of Equation 6.14 for this basic model, we would expect that as the number of particles is increased that this would become more accurate. As the number of paths between vertices of the partition graph is increased, a walk on this graph will not be required to pass through a disproportionate number of low weight vertices. Our results show that the weight of the larger cycle lengths is underestimated, which is reflected by the fact that they lie on the end points of the graph of $S_4$. The larger cycle lengths contribute to quantities such as the superfluid fraction which is proportional to the mean squared winding number (Ceperley and Pollock, 1989). This method does have the advantage over other methods in that the only approximation is the form of the transition probabilities. After a period of equilibration, where the cycle structure is constructed from the identity, we will be able to sample the local permutational structure by using $a_j$ and $\bar{a}_j$ without any a priori knowledge of cyclic structure of the partition function.

Figure 7.8: Energy as a function of temperature for 4-particles bosonic particles using two different methods for sampling permutation space. The statistical errors in these calculations are beyond the resolution of this graph.
7.4 Summary

In this chapter we have given an account of the theory for a practical implementation of the path integral Monte Carlo method, with an emphasis on application to the evaluation of equilibrium properties of bosons in the canonical ensemble. We have proposed a novel algorithm for the construction of a Markov chain through permutation space, suggesting the use of one loop operators which define a stochastic walk through the graph of partitions and given a proof of ergodicity.

An interesting mathematical question also arises which we have not explicitly addressed here, but may be a useful connection between the theory of indistinguishable many-body systems and a large body of work in probability theory and the random growth of Young tableaux. Is one able to construct a Markov chain via the use of $a_j$ and $\bar{a}_j$ in the canonical ensemble that in the infinite time limit will give probabilities distributed according to equation 6.28? Further, what is the limit shape of Young tableaux in the $N \to \infty$ limit as a function of temperature (Borodin et al., 2000; Okounkov, 2000)? As $T \to \infty$ we expect this to be $x\theta \left( x + \frac{1}{2} \right)$, where $\theta$ is the Heaviside step function, as the identity will become dominant in this limit. In the $T \to 0$ limit, where the partition function reduces to equation 6.29, the limit shape in the grand canonical ensemble has been established and so one would expect a continuous transformation between these limit shapes, the mapping being a function of temperature. This will be related to finding eigenvalues of random matrices as a function of temperature.
References


Appendices
Appendix A

QMC Figures and Tables
Table A.1: Summary of all calculations

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Table A.2: The results of the varmin runs

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[1] All parameters in the Jastrow factor were set to zero then optimised, except cutoffs, which were given a finite value between 3 and 4 Bohr’s. [2] Parameters in the Jastrow-factor were initially given finite values, which were those of the optimised 2.96 Å Jastrow factor values. This was due to convergence problems i.e. energy blowups and very large errors if the parameters were initially set to zero then optimisation performed.
Figure A.1: Graphical representation of the energy as a function of time-step for the DMC calculations of the helium atom. Shown in red are the individual time-step results, in blue the calculated VMC energy and in black the extrapolated DMC value.
Appendix B

Invariances on Complex Inner Product Spaces and the Wick rotation

Derived here is the analytical form of the Wick rotation of a Lagrangian which contains second order time derivatives. We will see that under this rotation the action does not remain invariant, however its modulus does. This is a consequence of measurement, that it is $|K(x', t' : x, t)|^2$ which is proportional to the measured probability amplitude, not $K(x', t' : x, t)$.

In complex space the invariant infinitesimal line element is given by:

$$ds^2 = du^2 + dv^2$$

$$= (du + idv) \ast (du + idv), \quad \text{(B.1)}$$

such that the length of a curve is given by

$$s = \int (du + idv)^\ast (du + idv). \quad \text{(B.2)}$$
We can parametrise a curve as a function of a single variable, i.e.

\[ u = u(t) \quad \text{and} \quad v = v(t), \]  

(B.3)
such that the line integral becomes

\[ s = \int_{t'}^{t''} \left( \frac{\partial u}{\partial t} + i \frac{\partial u}{\partial v} \right)^* \left( \frac{\partial u}{\partial t} + i \frac{\partial u}{\partial v} \right) dt. \]  

(B.4)

Now consider the particular case where \( u(t) = t, v(t) = 0 \), that is time is purely a real number. For this curve, the length almost trivially evaluates to

\[ s = \int_{0}^{t'} dt = t' \]  

(B.5)

We can easily show that the length of a curve in complex space is invariant under the unitary rotation \( z' = e^{i\theta} z \)

\[
\begin{align*}
s &= \int (\partial_t u + i\partial_t v)^* (\partial_t u + i\partial_t v) \\
 &= \int (\partial_t u + i\partial_t v)^* e^{-i\theta} e^{i\theta} (\partial_t u + i\partial_t v).
\end{align*}
\]  

(B.6)

This is clearly true. What we desire is a complex representation of time such that we are able to perform a rotation of time into the complex plane.

\[
\int dt f (u(t) + iv(t)) = \int du f(u) \quad \text{for} \quad v(t) = 0
\]  

(B.7)

In the usual formulation of equations involving time and its derivatives, time is purely real number, i.e. \( u(t) = t, v(t) = 0 \). A generalisation of this so complex time will give integrals (in that we shall be considering the action, which is the time
integral of the Lagrangian) of the form

\[ \int' \int'' f(z)dz = \int' \int'' (\partial_t u + i\partial_t v)^* f(u(t) + iv(t)) dt \]

\[ = \int' \int'' (\partial_t u + i\partial_t v)^* e^{-i\theta} f' (e^{i\theta} (u(t) + iv(t))) dt \]

where in the last line we have performed a unitary rotation. If we let \( \theta = \frac{\pi}{2}, u(t) = t \) and \( v(t) = 0 \). This defines how the integration measure is transformed.

\[ \int' \int'' e^{-i\frac{\pi}{2}} (\partial_t u) f' (e^{i\frac{\pi}{2}} u(t)) dt = i \int' \int'' (it) dt. \]

The factor of \( i \) is simply a statement that now the action has an amplitude in the complex direction as opposed to real. That is compare with the directional derivative. In most instances we deal with integrals of kinetic energy and so we wish to find how functions of the second derivative transform, i.e. \( f' = \frac{\partial x(t)}{\partial t} \). Consider the Laplacian in complex space

\[ \nabla^2 = \frac{\partial^2}{\partial u^2} + \frac{\partial^2}{\partial v^2} = (\partial_u + i\partial_v)^* (\partial_u + i\partial_v). \]

If we use the usual the general parametrisation given in equation B.3, the Laplacian becomes

\[ (\partial_t^2 + \partial_v^2) \partial_t f(z(t)) + ((\partial_u t)^2 + (\partial_v t)^2) \partial_t^2 f(z(t)) \quad (B.8) \]

setting \( u = t \) and \( v = 0 \) this becomes \( \partial_t^2 f \). If we perform a rotaion by \( \frac{\pi}{2} \) we get \( \partial_t^2 f(it) = -\partial_t^2 f(t) \)

The Wick rotation cannot be viewed as a rotation on a complex vector space that has a conventional norm and a metric induced by the definition of an inner
product as in this space the rotation would have no effect, and therefore performing
the rotation would have no mathematical advantage. The Wick rotation is a specific
case of a Mobius transformation, and for these transformations we can draw a Rie-
mann surface to see the effect of the transformation on the structure of the complex
plane. The time derivative of the wavefunction, when time is considered complex,
is a projection operator which projects out only real component. It is possibly the
investigation of this structure which is required as we wish to see how line integrals
transform under these transformations.