Path Integral Method for Calculating Work Statistics in Quantum Thermodynamics

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ABSTRACT

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The definition of work, one of the cornerstones of classical thermodynamics, must be reformulated in quantum thermodynamics because of the inherent uncertainty in position and energy in microscopic systems. To account for this uncertainty, I calculate and use the propagator from quantum mechanics, which gives the probability amplitude that a particle will move from a initial position to a final position. I discuss the notion of work in microscopic systems, as well as the two-point method, the most current method for calculating work. I then present an alternative method to calculate work, which utilizes the path integral formulation of quantum mechanics to find the work. I consider two applications, a free particle interacting with a rigid wall moving at constant velocity, and a free particle inside an infinite square well where one wall is moving at constant velocity. In both cases, I calculate the propagator using a semiclassical approximation to the path integral for both systems, and calculate the work for the infinite square well system. The path integral result is compared to the result from the two-point method, and shown to be an equivalent, but more powerful method.

Keywords: quantum thermodynamics, work statistics, path integral, van Vleck, work probability distributions

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Chapter 1

Introduction

Quantum thermodynamics is a branch of physics that has been recently developed (Griffiths 2005). In this chapter, I give a brief overview of quantum thermodynamics and related fields of physics. The tension between quantum thermodynamics and these related fields of physics leads to the need for a new definition of the fundamental concept of work and new methods to evaluate it. This research problem is illustrated by an evaluation in two specific examples.

1.1 Classical Thermodynamics

Thermodynamics is the theory of macroscopic quantities, like heat, work, and temperature of a system and how these quantities relate to energy and entropy. It is a theory that describes the average behavior for every physical system. In that sense, thermodynamics is the most general theory in physics (Kreuzer & Tamblyn 2010).

Thermodynamics was mainly developed in the 19th century in order to better understand complex, macroscopic systems like steam engines. These systems were too complicated to analyze each component individually, and, as a result, thermodynamics was developed to give an overall understanding of these systems (Deffner & Campbell 2019). In what follows I give a brief introduction of

the most important concepts in thermodynamics in my work.

1.1.1 Work in Classical Thermodynamics

The fundamental idea behind thermodynamics is that systems transform from one equilibrium state to another equilibrium state. These states are described using state equations, which describe how the thermodynamic quantities are related.

Work W is one of the most important quantities in thermodynamics because work is one of the primary ways through which a state can be transformed. This transformation is described by the first law of thermodynamics (Kreuzer & Tamblyn 2010)

$$dE = đW + đQ, \tag{1.1}$$

where E is the internal energy, W is the work, and Q is the heat. The symbol $đ$ is used to denote that the differential quantity is not exact. In other words, the first law of thermodynamics states that the change in energy for a system is dependent on the change in work and heat of a system. From this thermodynamic perspective, work can be thought of as the energy transferred to or from a particle via the force applied on the particle.

The exact mathematical definition of work done on a particle is

$$W = \int_C \vec{F} \cdot d\vec{s}, \tag{1.2}$$

where C is the trajectory a particle follows, $\vec{F}$ is the force applied to the particle, in is in the direction of $d\vec{s}$, which is a infinitesimal displacement. The work is the sum total of the force infinitesimally parallel to the displacement applied to the particle.

One of the most important theorems in classical mechanics is the work-energy theorem, which states that the change in kinetic energy of a system corresponds to the amount of work done on the system. This can be expressed as

$$W = \Delta T, \tag{1.3}$$

where T is the kinetic energy (this is only true if $Q = 0$, which means no heat is transferred into or out of the system).

1.2 Quantum Mechanics

Quantum mechanics is the second branch of physics that is relevant in quantum thermodynamics. Quantum mechanics was developed to better explain microscopic systems, and has also been proven to be accurate and useful. In this section, I will discuss the main properties of quantum mechanics that are needed to understand the results in this thesis.

1.2.1 Probability Distributions

One of the most common problems in classical mechanics is to calculate the positions of a particle as a function of time based on the forces the particle feels. Using Newton's second law and the initial conditions of the particle, we can determine the position of the particle at any time. In quantum mechanics, we are not interested in finding the position of a particle (because finding the exact position of a particle is impossible! See Section 1.2.2), we are instead interested in determining the wavefunction, $\psi(x,t)$, of a particle, where x indicates position and t is time. The wavefunction of a particle is a statistical quantity that gives the probability amplitude of finding the particle at a specific position and time and is typically found by solving the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \hat{H}\,\psi(x,t), \tag{1.4}$$

where $\hbar$ is the reduced Planck's constant, i is the imaginary unit, and $\hat{H}$ is the Hamiltonian operator (which gives the total energy of the system).

In microscopic systems, we can only determine where the particle is likely to be. The norm square of the wavefunction gives the probability distribution for the position of the particle. In

mathematical terms,

$$\int_a^b |\psi(x,t)|^2 \, dx. \tag{1.5}$$

This integral shows the probability that the particle can be found between positions $x = a$ and $x = b$ at time t (Griffiths 2005). In order to conserve probability, all wavefunctions must be normalized, which means the particle must be found somewhere in space. This can be expressed as

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx = 1. \tag{1.6}$$

1.2.2 Uncertainty Principle

The uncertainty principle in quantum mechanics gives a lower limit to the joint uncertainty uncertainty in position and momentum simultaneously. It is related to the statistical interpretation introduced in section 1.2.1, and is the reason why we can't know the exact position of a particle. The uncertainty principle is expressed mathematically as

$$\Delta x \Delta p \geq \frac{\hbar}{2}. \tag{1.7}$$

where p is the momentum.

There is also an uncertainty principle that gives a lower limit to how well we can know the energy of the system. This energy uncertainty principle is defined as

$$\Delta E \Delta t \geq \frac{\hbar}{2}. \tag{1.8}$$

In quantum mechanics, we can't know the exact position and momentum, or energy and total time span of a particle (we can know the momentum and energy of particle simultaneously, however). Specifically, a particle in a microscopic system does not follow a well-defined trajectory, and the particle does not have a definitive energy (Griffiths 2005). The inherent uncertainty and statistical interpretation in quantum systems is arguably the main difference between quantum and classical systems.

1.2.3 Propagators

Propagators in quantum mechanics are functions that give the probability amplitude that a particle will go from some start point x_a to an end point x_b in a given time interval, t_a to t_b. The propagator is either denoted as $K(x_a,t_a;x_b,t_b)$ (Feynman & Hibbs 2010), or as a transition amplitude using the Dirac notation, $\langle x_b|\hat{U}|x_a\rangle$, where $\hat{U}$ is the evolution operator. From this point on, I will use the Dirac transition amplitude definition to express the propagator.

The propagator can be found from the wavefunction of the particle. Once you find the wavefunction, you can calculate the propagator by using (da Luz & Cheng 1992)

$$\langle x_b|\hat{U}|x_a\rangle = \int_0^\infty \psi^*(x_a,t_a)\psi(x_b,t_b)dk, \tag{1.9}$$

where $k = 2\pi/\lambda$, and is the wavenumber of the wavefunction. The wavenumber is related to the wavelegth, and hence the momentum of the particle by the de Broglie relation, which is

$$p = h/\lambda = \hbar k. \tag{1.10}$$

1.2.4 Density Matrices

The density matrix is a generalization of mass density to quantum systems. The density matrix describes the state of some system. Density matrices can be thought of as more general versions of wavefunctions. Wavefunctions can only describe pure states, while density matrices can also represent mixed states (which occur when the exact state is unknown or when two states are entangled).

The density matrix can be calculated from the wavefunction and the initial state of the system. The mathematical definition of the density matrix is

$$\rho(x) = \sum_n \frac{\exp(-\beta E_n))}{Z_0} |\psi_n(x)\rangle \langle\psi_n(x)|. \tag{1.11}$$

where β is the inverse temperature ($\beta = 1/k_B T$, where k_B is the Boltzman constant and T is the temperature), Z_0 is the initial partition function, E_n is the energy of the n^{th} level, and $|\psi_n\rangle\langle\psi_n|$ is the outer product of the initial wavefunction (Deffner & Campbell 2019). For systems with real wavefunctions, the outer product turns into standard multiplication.

1.3 Quantum Thermodynamics

Quantum Thermodynamics combines elements of quantum mechanics and classical thermodynamics and studies how the laws of thermodynamics can be applied to microscopic systems. Classical thermodynamics has been proven to be accurate in the classical limit, but has three major shortcomings: (i) it does not contain any information about microscopic systems; (ii) thermodynamics cannot describe non-equilibrium states as it is an equilibrium theory; and (iii) the mathematical framework is classical in nature (Deffner & Campbell 2019). Due to these shortcomings, we need to develop a quantum version of thermodynamics to help us fully describe microscopic systems.

1.3.1 Motivation for the Development of Quantum Thermodynamics

One of the main motivations for quantum thermodynamics is to help us better understand quantum machines, like quantum computers. Quantum computers have the potential to immensely improve our computational abilities and increase the accuracy of computational models. It is crucial to have an understanding of quantum thermodynamics to further develop quantum computers. Other machines, like quantum heat engines, have the potential to be even more efficient than classical heat engines (Preskill 2012). Quantum thermodynamics will help to maximize the efficiency and output of these quantum machines, and has the potential to lead to an improvement in quantum technologies, just like classical thermodynamics helped to improve the efficiency of steam engines in the 18th century.

One of the main differences between classical thermodynamics and quantum thermodynamics is the presence of fluctuations. Because quantum systems are microscopic, they are susceptible to sudden changes in thermodynamic quantities, which lead to fluctuations in these quantities. In order to deal with fluctuations, a branch of thermodynamics was developed called Stochastic Thermodynamics. Stochastic thermodynamics is a branch of thermodynamics is centered around analyzing small systems that are far from thermodynamic equilibrium. Recent developments in stochastic thermodynamics include the Jarzynski Equality (Jarzynski 1997) and Crook's fluctuation theorem (Crooks 1999). The fundamental idea behind stochastic thermodynamics is that thermodynamics can be generalized to single particle dynamics (Sekimoto 1998). Single particle dynamics is the focus of my work, and has lots of applications to other quantum systems. The development of stochasic thermodynamics was crucial to the development of quantum thermodynamics (Deffner & Campbell 2019).

1.3.2 Calculating Work Statistics

The classical definition of work Eq.(1.2), does not apply to microscopic systems because particles do not follow a single trajectory (from Section (1.2.2). We need to develop another understanding for quantum work, one that is more closely related to the work-energy theorem classical mechanics or the first law of thermodynamics.

The typical method for calculating work in quantum systems is by using the two point measurement (Deffner & Campbell 2019). The two point measurement is done by initializing a system and measuring the instantaneous energy E_n^0 at time $t = 0$, moving the system forward in time using a force protocol, and measuring the instantaneous energy E_l^τ at some time $t = \tau$. The quantum fluctuating work is then the difference in energies

$$W_{l,n} = E_l^\tau - E_n^0, \tag{1.12}$$

where n and l are arbitrary states. This is very similar to the work-energy theorem in classical,

Eq. (1.3). However, there is some uncertainty that the system is actually in the state E_n^0 at time $t = 0$ because of the time and energy uncertainty principle. Because of that, we need to define the probability of finding the system at the n^{th} energy level at $t = 0$. This is defined as p_n, and can be calculated using

$$p_n = \langle E_n^0 | \hat{\rho}(0) | E_n^0 \rangle \,, \tag{1.13}$$

where $\hat{\rho}(0)$ is the initial density matrix. The initial system is set up in some ensemble with partition function Z_0 and energy level E_n. In order to extract work out of the system, we use a time-dependent potential that is controlled by an external parameter, which is called the work parameter, λ_t. At $t = 0$, the work parameter is at its initial value, λ_0, so we can write the energy at $t = 0$ as the Hamiltonian as a function of λ_0.

The probability of observing the work $W_{l,n}$ is then going to be the probability p_n of the system being in E_n at $t = 0$ multiplied by the probability of the system going from E_n to E_l. The probability of observing the work can be expressed as

$$p(n,l) = p_n | \langle E_l^\tau | \hat{U} | E_n^0 \rangle |^2, \tag{1.14}$$

where $\hat{U}$ is the evolution operator

$$\hat{U} = \hat{T} exp\left(-\frac{i}{\hbar} \int_0^\tau dt \hat{H}(\lambda_t) \right),$$

and $\hat{H}$ is the Hamiltonian operator and$\hat{T}$ is the time ordering operator, which is needed because $H(\lambda_0)$ and $H(\lambda_\tau$ do not commute. Because of the uncertainty in energy and position , the amount of work W is also uncertain, and we need to represent the work done as a probability distribution , $P(W)$. This distribution can be expressed as

$$P(W) = \sum_{l,n} \delta(W - W_{l,n}) p(l,n). \tag{1.15}$$

where $W_{l,n}$ is the work associated with going from an arbitrary state l to another arbitrary state n. This distribution can be difficult to find. An easier quantity to calculate is the characteristic function

of work, which is the Fourier Transform of the work distribution. After taking the Fourier transform, we get that the characteristic function of work can be defined as

$$\chi_W(\nu) = \int dW P(W) exp(i\nu W), \tag{1.16}$$

where ν is the Fourier transform conjugate variable of work W. The characteristic function of work is the quantity I will be calculating using a path integral approach. Using Eq. (1.15) we can rewrite the characteristic function of work as

$$\chi_W(\nu) = \int dW \sum_{l,n} \delta(W - W_{l,n}) p(n,l) exp(i\nu W).$$

Using now use the definition for $p(n,l)$, from Eq. (1.14), we get

$$\chi_S(\nu) = \int dW \sum_{l,n} \delta(W - W_{l,n}) p_n |\langle E_l^\tau | \hat{U} | E_n^0 \rangle|^2 exp(i\nu W)$$

We can now use the definition of p_n, from Eq. (1.13), to get

$$\chi_w(\nu) = \int dW \sum_{l,n} \delta(W - W_{l,n}) \langle E_n^0 | \rho(0) | E_n^0 \rangle \langle E_l^\tau | \hat{U} | E_n^0 \rangle \langle E_n^0 | \hat{U}^\dagger | E_l^\tau \rangle exp(i\nu W).$$

We can simplify this by replacing the W in the exponent with $E_l^\tau - E_n^0$, as well as evaluating the integral to get

$$\chi_w(\nu) = \sum_{l,n} \langle E_l^\tau | \hat{U} | E_n^0 \rangle \langle E_n^0 | \hat{\rho}(0) | E_n^0 \rangle \langle E_n^0 | \hat{U}^\dagger | E_l^\tau \rangle exp(i\nu E_l^\tau - i\nu E_n^0).$$

Further simplification leads to

$$\chi_w(\nu) = \sum_{l,n} \langle E_l^\tau | \hat{U} exp(-i\nu E_n^0) | E_n^0 \rangle \langle E_n^0 | \hat{\rho}(0) | E_n^0 \rangle \langle E_n^0 | \hat{U}^\dagger exp(i\nu E_l^\tau) | E_l^\tau \rangle .$$

At this point, we can replace the energy at each time with the equivalent Hamiltonian since it is acting on the energy eigenstates. This gives that at $t = 0$, E_n^0 is equivalent to $H(\lambda_0)$ and the energy at $t = \tau$, E_l^τ is equivalent to $H(\lambda_\tau)$. Substituting these results gives

$$\chi_w(\nu) = \sum_{l} \langle E_l^\tau | \hat{U} \exp(-i\nu H(\lambda_0)) \hat{\rho}(0) \hat{U}^\dagger \exp(i\nu H(\lambda_\tau) | E_l^\tau \rangle .$$

At this point, there is only one summation left, which means this equation is equivalent to taking the trace. This gives the final equation for the characteristic function of work

$$\chi_w(\nu) = Tr\left[\hat{U}\exp(-i\nu\hat{H}(\lambda_0))\hat{\rho}(0)\hat{U}^{\dagger}\exp(i\nu\hat{H}(\lambda_\tau)\right] \tag{1.17}$$

(Funo & Quan 2018). This is the standard definition for the characteristic function of work. It involves the evolution operator and the adjoint of the evolution operator, the initial density matrix, and the energy at the initial and and final time. By calculating the characteristic function of work, we can easily find the work probability distribution by taking the inverse Fourier transform of the characteristic function of work.

1.4 Research Question

My research was focused on calculating the work distribution for two different quantum configurations, using an alternative method to the two-point measurement, which will be described in Chapter 2. These configurations are

1. A free particle of mass m starting at x_a and t_a, initially moving with velocity v, and ending at x_b at t_b interacting with one rigid wall moving at a constant velocity u.
2. A free particle of mass m starting at x_a and t_a, initially moving with velocity v, and ending at x_b at t_b inside an infinite square well with one wall moving at a constant velocity u.

In Chapter 2, the path integral method for calculating the work distribution will be introduced, and Chapter 3 will focus on calculating the work distribution for the specific configurations above.

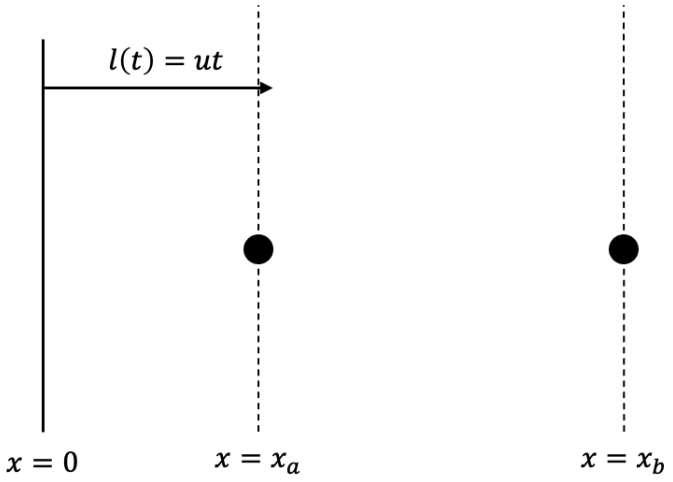

Figure 1.1 . The wall's equation of motion is $l(t) = ut$, where u is the velocity of the wall. The particle starts at $x = x_a$ and ends at $x = x_b$.

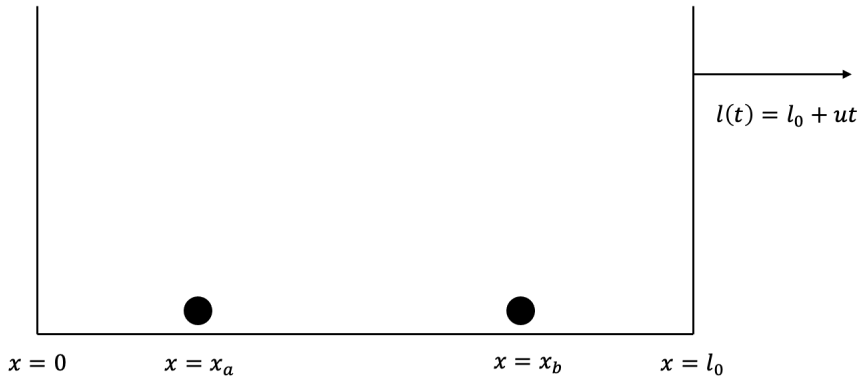

Figure 1.2 A quantum infinite square well is shown with one wall moving at a constant velocity u, and the equation of motion is $l(t) = l_0 + ut$, where l_0 is the initial position of the wall. The particle starts at $x = x_a$ and ends at $x = x_b$.

Chapter 2

Methods

Traditionally, there are two formulations of quantum mechanics, the operator formulation and the path integral formulation. For my project, I was specifically interested in using the path integral formulation to calculate work statistics in quantum thermodynamics. This chapter gives a basic introduction to path integrals and how to use path integrals to calculate work distributions.

2.1 Lagrange's Equations

The path integral formulation of quantum mechanics is rooted in the Lagrangian formulation of classical mechanics, which is an alternative method to Newton's Laws for calculating the equations of motion for a system using Lagrange's equations.

The Lagrangian $\mathscr{L}$ is defined as the difference between the kinetic and potential energy,

$$\mathscr{L} = T - V, \tag{2.1}$$

where T is the kinetic energy and V is the potential energy. The kinetic energy of a particle with mass m is given by

$$T = \frac{1}{2}m\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right) = \frac{1}{2}m\,\vec{\dot{r}}^{\,2} \tag{2.2}$$

where x, y, z are the cartesian components of position ($\vec{r}$ is the overall position vector) and $\dot{x}$, $\dot{y}$, $\dot{z}$ are the cartesian components of velocity ($\vec{\dot{r}}$). The potential energy has the form

$$V = V(x,y,z) = V(\vec{r}\,). \tag{2.3}$$

Based on these definitions of the energies, it is clear that the Lagrangian is a function of both position and velocity. The first step when finding the equations of motions using the Lagrange's equations is to identify the potential energy and the kinetic energy (which involves finding the velocity) and use them to express the Lagrangian.

In order to find the equations of motion using the Lagrangian, we define a functional, called the action S, as

$$S = \int_{t1}^{t2} \mathscr{L}(r,\dot{r})\,dt. \tag{2.4}$$

Using the calculus of variations, it can be shown that

$$\frac{\partial \mathscr{L}}{\partial x} = \frac{d}{dt}\frac{\partial \mathscr{L}}{\partial \dot{x}} \tag{2.5}$$

is the equation of motion for the particle in the x-component, with similar equations for the y and z directions.

This result says that the actual trajectory a particle follows in a given time interval is such that the action is stationary (Taylor 2003). This idea was crucial for the development of path integrals, as well as for approximate methods that can be used to solve the path integrals.

2.2 Path Integrals

Paul Dirac was interested in using the Lagrangian in quantum mechanics as an alternative to the canonical quantization procedure, which starts from the Hamiltonian version of classical mechan-

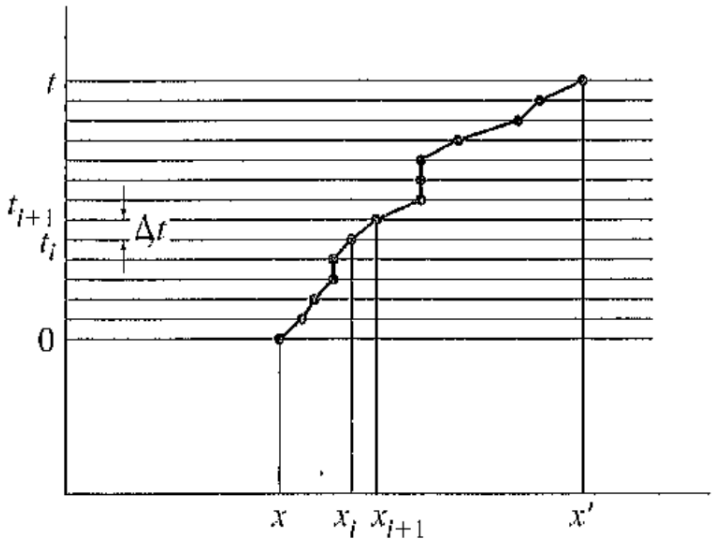

Figure 2.1 The overall time interval is divided up into N pieces of length Δt. We need to consider the propagation through each time interval (Tannor 2007).

ics. Richard Feynman then used this result to develop the path integral formulation of quantum mechanics, which gives an alternative method to finding the propagator in quantum mechanics. As discussed in Section1.2.3, the propagator is typically defined by using the wavefunction $\psi(x,t)$ as

$$\langle x_b|\hat{U}|x_a\rangle = \int_0^\infty \psi(x_a,t_a)\psi^*(x_b,t_b)dk, \tag{2.6}$$

where x_a is the initial position of the particle, x_b is the final position of the particle, and $\hat{U}$ is the evolution operator. Instead of using this definition of the propagator, Richard Feynman found another way using the Lagrangian and Action to calculate the propagator in a quantum system.

In quantum systems, each possible path between positions x_a and x_b in a time interval $t_b - t_a$ contributes to the total probability amplitude of going from x_a to x_b. Each path contributes an equal magnitude, but the phase from each path varies with the phase factor, $\exp(iS/\hbar)$ where S is the action from Section 2.1 (Feynman & Hibbs 2010).

To calculate Feynman's path integral definition of a propagator, we first divide the time interval into N pieces of size $\Delta t = (t_b - t_a)/N$, as is shown in Figure 1. The propagator is then the

accumulation of infinitesimal propagation through each of these pieces

$$\langle x_b|\exp\left(-iHt/\hbar\right)|x_a\rangle = \int dx_1 dx_2 ... dx_N \langle x_b|\exp\left(-i\hat{H}\Delta t/\hbar\right)|x_N\rangle \langle x_N|\exp\left(-i\hat{H}\Delta t/\hbar\right)|x_{N-1}\rangle$$
$$... \langle x_2|\exp\left(-i\hat{H}\Delta t/\hbar\right)|x_1\rangle \langle x_1|\exp\left(-i\hat{H}\Delta t/\hbar\right)|x_a\rangle \tag{2.7}$$

where $\hat{H}$ is the Hamiltonian operator. The Hamiltonian is the operator representing the total energy the particle, which we can define as

$$\hat{H} = \hat{T} + \hat{V},$$

where $\hat{T}$ and $\hat{V}$ are the kinetic and potential energy operators.

As the time interval goes to zero, the number of intervals will go to infinity, which means we can ignore the non-commutative nature of the $\hat{p}$ and $\hat{V}$ operators and write the evolution operator as

$$\exp\left(-i\hat{H}t/\hbar\right) \approx \exp\left(-i\hat{T}t/\hbar\right)\exp\left(-i\hat{V}t/\hbar\right). \tag{2.8}$$

Using the form for $\hat{T}$ and $\hat{V}$ in Section 1.1, we get the evolution between between two points in the interval, x_1 and x_2, to be

$$\langle x_2|\exp\left(-iH\Delta t/\hbar\right)|x_1\rangle = \langle x_2|\exp\left(-i\hat{p}^2\Delta t/2m\hbar\right)\exp\left(-iV\Delta t/\hbar\right)|x_1\rangle. \tag{2.9}$$

We can use the definition of the inner product, and the completeness relation for the position and momentum operator to write this as

$$\int\int\int \langle x_2|p\rangle \langle p|\exp\left(-i\hat{p}^2\Delta t/2m\hbar\right)|p'\rangle \langle p'|x\rangle \langle x|\exp\left(-iV\Delta t/\hbar\right)|x_1\rangle \, dp\, dp'\, dx. \tag{2.10}$$

We then use the definitions of the inner product of the position and momentum operator, evaluate

the integral, and simplify to get

$$\begin{aligned}
&\langle x_2|\exp(-iH\Delta t/\hbar)|x_1\rangle \\
&\qquad = \int \frac{1}{\sqrt{2\pi\hbar}}\exp(ipx_b/\hbar)\exp\left(-ip^2\Delta t/2m\hbar\right)\frac{1}{\sqrt{2\pi\hbar}}\exp(ipx_a/\hbar)\exp(-iV\Delta t/\hbar)\,dp \\
&\qquad = \frac{1}{2\pi\hbar}\exp(-iV\Delta t/\hbar)\int_{-\infty}^{\infty}\exp\left(-ip^2\Delta t/2m\hbar\right)\exp(ip(x_b-x_a)/\hbar)\,dp \\
&\qquad = \sqrt{\frac{m}{2\pi i\hbar\Delta t}}\exp(-iV\Delta t/\hbar)\exp\left(im(x_b-x_a)^2/2\Delta t^2\right).
\end{aligned} \tag{2.11}$$

Since $(x_b - x_a)/\Delta t$ corresponds to the average velocity during the time interval, we can replace it with $\dot{x}$ which gives us

$$\langle x_b|\exp(-iH\Delta t/\hbar)|x_a\rangle = \sqrt{\frac{m}{2\pi i\hbar\Delta t}}\exp\left(i\left(\frac{m\dot{x}^2}{2}-V\right)\right)\Delta t/\hbar. \tag{2.12}$$

We see that the Lagrangian $\mathscr{L} = m\dot{x}^2/2 - V$ is in the exponent, so we can rewrite this in terms of the Lagrangian to get

$$\langle x_b|\exp(-iH\Delta t/\hbar)|x_a\rangle = \sqrt{\frac{m}{2\pi i\hbar\Delta t}}\exp(i\mathscr{L}\Delta t/\hbar). \tag{2.13}$$

This is the contribution to the probability amplitude from one spatial point in the interval to the next. We need to connect the N intermediate points together over the time t, which we do by multiplying the amplitudes of each intermediate point. Since there are no operators here (all of the expressions are classical), this corresponds to a sum in the exponent. This gives

$$\langle x_b|\exp(-iHt/\hbar)|x_a\rangle_{path} = \sqrt{\frac{m}{2\pi i\hbar\Delta t}}\exp\left(i\sum_n \mathscr{L}_n\Delta t/\hbar\right), \tag{2.14}$$

where the path refers to a single path between points x_a and x_b. As we take the time interval goes to zero, the discrete sum over n can be replaced by an integral. The exponent now has the form of the action , $S = \int \mathscr{L}\,dt$, so we can write the contribution to the trajectory for one path as

$$\langle x_b|\exp(-iHt/\hbar)|x_a\rangle_{path} = \sqrt{\frac{m}{2\pi i\hbar\Delta t}}\exp(iS/\hbar). \tag{2.15}$$

This propagator is only the contribution from one path. We need to consider the contribution of each path, since each possible path contributes to the total probability amplitude. The complete expression for the propagator is then

$$\begin{aligned}\langle x_b|\exp\left(-i\hat{H}t/\hbar\right)|x_a\rangle &= \sqrt{\frac{m}{2i\pi\hbar t}}\sum_{all\ paths} e^{iS/\hbar} \\ &= \sqrt{\frac{m}{2i\pi\hbar t}}\int \mathscr{D}[x]e^{iS/\hbar},\end{aligned} \tag{2.16}$$

where $\mathscr{D}[x]$ represents the integral over all paths between x_a and x_b. In other words, this propagator requires us to consider every single path between the end points, of which there can be infinitely many (Tannor 2007). The term in front of the integral is a normalization constant for a single particle, so it is necessary to determine the normalization constant for other systems.

In the classical limit , where the action is much bigger than $\hbar$, a small change in the actual trajectory results in large changes in the phase. This leads to high oscillations from positive to negative values. These oscillations will add to zero, which means the total contribution to the trajectory from paths close to the trajectory is zero. In summary, except for regions where the action is stationary, $\delta S/\delta x = 0$, the phases from nearby paths cancel out, and only one path is physically possible. This path becomes the trajectory the particle will follow, and explains why a single trajectory emerges from all possible quantum trajectories in the classical limit (Feynman & Hibbs 2010).

The fact that the classical trajectory comes out of a quantum expression suggests that nature is inherently quantum, and that classical laws arise out of quantum laws in the classical limit.

2.2.1 Path Integrals for Successive Events

It is important for this project to find the propagator for two successive events. For two events that happen successively, there is a different action for each event and therefore a different formula for the path integral propagator . If we take an intermediate step between x_a and x_b, called x_{int}, we can

write the action as

$$S[x_b, x_a] = S[x_b, x_{int}] + S[x_{int}, x_a]. \tag{2.17}$$

The propagator from x_a to x_b through x_{int} is then defined as

$$\langle x_b | \exp\left(-i\hat{H}t/\hbar\right) | x_a \rangle = \int \mathscr{D}[x] e^{(i/\hbar)S[x_b, x_{int}] + (i/\hbar)S[x_{int}, x_a]}. \tag{2.18}$$

We are integrating over all paths from x_a to x_{int}, and then integrating over all paths from x_{int} to x_b. We then integrate over all possible values of x_{int} to get

$$\langle x_b | \exp\left(-iHt/\hbar\right) | x_a \rangle = \int_{-\infty}^{\infty} dx_{int} \int_{x_a}^{x_{int}} \mathscr{D}[x] \exp\left(iS[x_{int}, x_a]/\hbar\right) \int_{x_{int}}^{x_b} \mathscr{D}[x] \exp\left(iS[x_b, x_{int}]/\hbar\right). \tag{2.19}$$

This is equivalent to

$$\langle x_b | \exp\left(-iHt/\hbar\right) | x_a \rangle = \int_{-\infty}^{\infty} \langle x_b | \exp\left(-iHt/\hbar\right) | x_{int} \rangle \langle x_{int} | \exp\left(-iHt/\hbar\right) | x_a \rangle \, dx_{int}. \tag{2.20}$$

In other words, the probability amplitude to go from x_a to x_b through an intermediate point x_{int} is the probability amplitude to go from x_a to x_{int} multiplied by the probability amplitude to go from x_{int} to x_b (this is just like multiplying probabilities in statistics), and then integrating over all possible x_{int}. The general rule is that probability amplitudes for events occurring in succession in time multiply (Feynman & Hibbs 2010).

2.2.2 Van Vleck Propagator

In practice, these path integrals are difficult to evaluate, and approximations are often used. One of the most important approximations is called the van Vleck propagator. The van Vleck propagator is a semiclassical approximation, which means the only paths that contribute to the van Vleck propagator are paths possible in classical mechanics. The full derivation of the van Vleck propagator is given in (Tannor 2007). The van Vleck propagator has the form

$$\langle x_b | \exp\left(-i\hat{H}t/\hbar\right) | x_a \rangle = \sum_{all\ classical\ paths} \left(-\frac{1}{2\pi i\hbar} \frac{\partial^2 S}{\partial x_b \partial x_a} \right)^{1/2} \exp\left(iS/\hbar\right), \tag{2.21}$$

where S is the action , and the summation is only over classical paths. There are several possible problems where counting only the classical paths leads to the full quantum propagator, and these problems in this thesis are two of them.

2.3 Path Integral Approach to Calculating Work Statistics

From Chapter 1, we have that the characteristic function of work can be written as

$$\chi_W(\nu) = Tr\left[\hat{U}\exp\left(-i\nu\hat{H}(\lambda_0)\right)\rho\hat{(}0)\hat{U}^\dagger\exp\left(i\nu\hat{H}(\lambda_\tau)\right)\right]. \tag{2.22}$$

We rewrite this using the defintion $\hat{U} = \exp(-i\hat{H}t/\hbar)$ and simplify to get

$$\begin{aligned}\chi_W(\nu) &= \langle x_b|\hat{U}\exp\left(-i\nu\hat{H}\right)|x_a\rangle\langle x_a|\hat{\rho}(0)|x_a\rangle\langle x_a|\hat{U}^\dagger\exp\left(i\nu\hat{H}\right)|x_b\rangle \\ &= \langle x_b|\hat{U}|x_a\rangle\exp\left(-i\nu\hat{H}\right)\langle x_a|\hat{\rho}(0)|x_a\rangle\langle x_a|\hat{U}^\dagger|x_b\rangle\exp\left(i\nu\hat{H}\right).\end{aligned} \tag{2.23}$$

Using the (unnormalized) path integral definition of the propagator, we can rewrite this as

$$\chi_W(\nu) = \int D[x]\exp\left(iS/\hbar\right)\exp\left(-i\nu\hat{H}\right)\langle x_a|\rho(0)|x_a\rangle\int D[x]\exp\left(-iS/\hbar\right)\exp\left(i\nu\hat{H}\right). \tag{2.24}$$

This is equation for the characteristic function of work which we will use (Funo & Quan 2018).

2.4 Potential as a Work Parameter

In order to extract work out of a system, we will use a time-dependent potential with a time-dependent parameter λ_t called the work parameter. Work is done on the system when the work parameter is changed by an external agent. In both of the configurations in this thesis, the work parameter is the position of the moving wall. Another examples of the work parameter is a changing angular frequency in the quantum harmonic oscillator.

It is standard to have two propagations involving the work parameter [5]. The first propagation is when the work parameter is held at a constant value, λ_0 from $t = 0$ to $t = \hbar\nu$, where ν is the Fourier conjugate variable of work, from Chapter 1. After the initial propagation, the work parameter is changed from λ_0 to λ_τ over the time period $t = \hbar\nu$ to $t = \tau + \hbar\nu$. In order to account for the changing work parameter, we insert an intermediate position x_{int} at t_{int}, and at this point, the work parameter begins to change. Using the results from the Section on successive events, the propagator would be

$$\langle x_b|\hat{U}|x_a\rangle = \int_{-\infty}^{\infty} dx_{int} \int_{x_a}^{x_{int}} \mathscr{D}[x] \exp\left(-iS_1[x]/\hbar\right) \int_{x_{int}}^{x_b} \mathscr{D}[x] \exp\left(-iS_2[x]/\hbar\right), \tag{2.25}$$

where $S_1[x]$ and $S_2[x]$ are defined as

$$S_1[x] = \int_0^{\hbar\nu} dt\, \mathscr{L}\left(\lambda_0, x\right), \qquad S_2[x] = \int_{\hbar\nu}^{\tau+\hbar\nu} dt\, \mathscr{L}\left(\lambda_t, x\right). \tag{2.26}$$

The characteristic function of work involves the adjoint of the propagator, which is called the "backwards" propagator. In order to avoid confusion, the backward propagator is characterized by the action $S[y]$, and the time variable s. During this propagation, the work parameter is changed from λ_0 at $s = 0$ to the final value λ_τ at $s = \tau$. It is then held at λ_τ from time $s = \tau$ to $s = \tau + \hbar\nu$. This means the propagator for the backwards propagation is

$$\langle x_a|\hat{U}^\dagger|x_b\rangle = \int_{-\infty}^{\infty} dy_{int} \int_{x_b}^{x_{int}} \mathscr{D}[y] \exp\left(iS_1[y]/\hbar\right) \int_{x_{int}}^{x_a} \mathscr{D}[y] \exp\left(iS_2[y]/\hbar\right), \tag{2.27}$$

and the actions are defined as

$$S_1[y] = \int_0^{\tau} ds\, \mathscr{L}\left(\lambda_s, y\right), \qquad S_2[y] = \int_{\tau}^{\tau+\hbar\nu} ds\, \mathscr{L}\left(\lambda_\tau, y\right). \tag{2.28}$$

We will use these definitions to calculate a propagator for the forward and backward progressions, which will then be used to calculate the characteristic function of work (Qiu et al. 2020).

Chapter 3

Results

In order to calculate the characteristic function of work , from which we can find the work probability distribution, we need to calculate the action . To calculate the action, we need to find the kinetic energy and potential energy to include in the Lagrangian. In order to calculate the kinetic energy, we need to find the velocity. This process was done to calculate the work distribution for the problems introduced in Chapter 1. For both of these problems, we only consider classical paths so we can use the van Vleck propagator.

3.1 Classical Action Results

3.1.1 Calculating Action for Problem 1

For the first problem, there are two classical paths that the particle could follow to go from $x_a(t_a)$ to $x_b(t_b)$; A direct path where the wall isn't involved, and an indirect path where the particle hits off the wall. The wall moves at a constant velocity u, and the position is given by $L(t) = ut$. Figure 1 shows the physical set up for the indirect path.

We assume that $x_a > L_a$ (x_a and L_a are the position of the particle and the wall, respectively, at

time t_a), and $x_b > L_b$.

Direct Path

For the direct path, the average velocity is

$$v = \frac{x_b - x_a}{t_b - t_a}. \tag{3.1}$$

We put this in the Lagrangian to get

$$\mathscr{L} = \frac{1}{2}mv^2 = \frac{1}{2}m\frac{(x_b - x_a)^2}{(t_b - t_a)^2}. \tag{3.2}$$

Using this to calculate the action for the direct path, S_D, we get

$$S_D = \int_{t_a}^{t_b} dt \frac{m(x_b - x_a)^2}{2(t_b - t_a)^2} = \frac{m(x_b - x_a)^2}{2(t_b - t_a)^2}(t_b - t_a).$$

This is the first of two actions we need to calculate for the first problem.

Indirect Path

The indirect path involves a collision with the moving wall, which is moving at velocity u. By conservation of momentum, when the particle collides with the wall, it will gain velocity $2u$.

We divide the interval $t_b - t_a$ into two times, t' and t''. t' is the time from t_a until the particle hits the wall at a time we call t_{int}. t'' is the time from when the particle hits the wall at t_{int} until t_b. Using these definitions, we can write the equations of motion for the wall and particle. Starting with the first time segment, t' we have for the wall

$$L_{int} - L_a = ut' \tag{3.3}$$

and for the particle

$$L_{int} - x_a = -vt' \tag{3.4}$$

We have two equations and two unknowns. Solving this system of equations with substitution gives

$$t' = \frac{x_a - L_a}{(v+u)}. \tag{3.5}$$

Using this definition for t', we can solve for L_{int}, which gives

$$L_{int} = \frac{ux_a + vL_a}{u+v}. \tag{3.6}$$

We now use these definitions to solve for t''. The distance the particle travels after the collision is $x_b - L_{int}$, and the velocity of the particle is $v+2u$. This means we can express t'' as

$$t'' = \frac{x_b - L_{int}}{v+2u}.$$

We use the expression for L_{int} to get

$$t'' = \frac{u(x_b - x_a) + v(x_b - L_a)}{(v+2u)(v+u} . \tag{3.7}$$

We know that adding t' and t'' gives the total time interval, $t' + t'' = t_b - t_a$. This gives us

$$t' + t'' = \frac{-2L_a + x_a + x_b}{2u+v}. \tag{3.8}$$

We can use the definition of constant velocity to write the velocity of the wall as $u = (L_b - L_a)/(t_b - t_a)$. Plugging this into our equation for total time we get

$$t_b - t_a = \frac{-2L_a + x_b + x_a}{2\frac{L_b - L_a}{t_b - t_a} + v}.$$

Solving this equation for v we get our initial velocity in terms of know quantities,

$$v = \frac{x_b + x_a - 2L_a}{t_b - t_a}. \tag{3.9}$$

Now that we have the velocity, we can write the action for the indirect path as

$$S_I = \int_0^{t'} \frac{1}{2} m v^2 dt + \int_{t'} t'' \frac{1}{2} m (v+2u)^2 dt.$$

Using the equations for v, t', and t'' derived above, we can evalute this integral to get

$$S_I = \frac{m}{2}(v^2 t' + (v+2u)^2(t''-t')).$$

This simplifies to

$$S_I = \frac{m}{2(t_b - t_a)}\left[(x_a + x_b)^2 - 4u(x_a t_b + x_b t_a - u t_a t_b)\right]. \tag{3.10}$$

We now have the classical action for both of the classical paths possible for Problem 1.

3.1.2 Calculating Action for Problem 2

In this problem, we consider an infinite square well with one wall moving constant in time, such that it follows $L(t) = L_0 + ut$, where L_0 is the position of the wall at $t = 0$.

This problem is uniquely challenging because there are an infinite number of number classical paths between x_a and x_b because of the possible reflections between the particle and the wals.

In order to deal with the infinite number of classical paths, we classify the paths into 4 classes based on which wall the particle collides with first and last (da Luz & Cheng 1992). These classes are

(1) The first collision with the moving wall and the last collision with the fixed wall or no collision at all

(2) Both the first and the last collisions with the fixed wall

(3) The first collision with fixed wall and last collision with the moving wall

(4) Both the first and last collisions with the moving wall

We define three variables to help find the initial velocity: L_j (with $j \geq 1$) is the position of the moving wall when the particle hits it for the jth time. t'_j is the time the particle spends traveling from $x = 0$ to arrive at $x = L_j$ before the the jth collision with the moving wall. t''_j is the time the particle spends traveling from $x = L_j$ to arrive at $x = 0$ after the jth collision with the moving wall.

Example Calculation for the Simplest Case

As an example, we will calculate the initial velocity and the action for the case when $x_a = x_b = 0$, and use the results to find a general expression for each of the classes. For this case, all paths will belong to class 1 because the first collision must happen with the moving wall.

By conservation of momentum, the particle will lose velocity $2u$ after each collision with the moving wall, but will keep the same velocity magnitude but change direction with a collision with the stationary wall. The equation of motion for the particle before the first collision (traveling from $x = 0$ to L_1 is

$$L_1 - 0 = vt_1'.$$

After the particle collides with the moving wall, the particle will switch direction and travel to the stationary wall. This trajectory can be described as

$$0 - L_1 = -(v - 2u)t_1''.$$

The particle will collide with the stationary wall at $x = 0$ and travel to the wall which will be at $x = L_2$. This gives us

$$L_2 - 0 = (v - 2u)t_2'.$$

This pattern continues, and after the next collision with the moving wall we have

$$0 - L_2 = (v - 2u - 2u)t_2'',$$

which is followed by

$$L_3 - 0 = (v - 2u - 2u)t_3'.$$

This gives us the position of the wall at the jth collision, which is

$$L_j = (v - 2ju)t_j''. \tag{3.11}$$

Additionally, if we consider the equations of motion for the wall, we have that

$$L_1 - L_0 = ut_1$$

for the time period when the particle moves from it's starting position to the first collision. For the next period, when the particle travels from the first collision with the moving wall to the second collision with the moving wall, we get

$$L_2 - L_1 = u(t_1'' + t_2').$$

It follows that, in general, we can say

$$L_{j+1} - L_j = u(t_j'' + t_{j+1}1). \tag{3.12}$$

Finally, we need to find the initial equation of motion for the wall using t_a. At t_a, the wall will be at $L(t_a) = L_0 + ut_a = L_a$. This implies that

$$ut_1' = L_1 - L_0 - ut_a = L_1 - L_a. \tag{3.13}$$

We will now solve for L_j in terms of known variables.

We introduce another variable n which signifies the total number of collisions with the moving wall. For $n = 1$, we can set up a system of equations to find L_1.

$$L_1 = vt_1', \qquad L_1 - L_a = ut_1'.$$

Solving this for L_1 we get

$$\implies L_1 = \frac{vL_a}{v-u}. \tag{3.14}$$

For two collisions, we have (including the result from above

$$L_1 = \frac{vL_a}{v-u}, \qquad L_1 = (v-2u)t_1'', \quad , \quad L_2 = (v-2u)t_2', \qquad L_2 - L_1 = u(t_2' + t_1'').$$

Solving these we have

$$\implies L_2 = \frac{vL_a}{v-3u}. \tag{3.15}$$

For three collisions we have (including the results from above) we get

$$L_2 = \frac{vL_a}{v-3u}, \qquad L_2 = (v-4u)t_2'', \qquad L_3 = (v-4u)t_3', \qquad L_3 - L_2 = u(t_3' + t_2'')$$

Solving these for L_3 we have

$$\implies L_3 = \frac{vL_a}{v-5u}. \tag{3.16}$$

By comparing these equations, we can see the pattern, which gives us

$$L_n = \frac{vL_a}{v-u(2n-1)}. \tag{3.17}$$

We can now find t_j' and t_j'' in terms of known variables. Setting Eq. (3.12) and Eq. (3.17) equal to each other we get

$$\frac{vL_a}{v-u(2j-1)} = [v-u(2j-2)]t_j'$$

which implies

$$t_j' = \frac{vL_a}{(v-u(2j-1))(v-u(2j-2))}. \tag{3.18}$$

Similarly y, we can use set Eq. (3.12) and Eq. (3.17) equal and solve for t_j''. This gives us

$$t_j'' = \frac{vL_a}{(v-2ju)(v-u(2j-1))}. \tag{3.19}$$

If we add these two times, we get the total time it takes the particle to go from $x = 0$, collide with the moving wall for the jth time, and return to $x = 0$. We call this time t_j, which is given by

$$t_j = t_j' + t_j'' = \frac{2L_a v}{(2u(j-1)-v)(2ju-v)}. \tag{3.20}$$

The total time elapsed between x_a and x_b is the sum of all the t_j, which can be represented as

$$t_b - t_a = \sum_{j=1}^{n} t_j. \tag{3.21}$$

Evaluating this sum we get that the total time elapsed between x_a and x_b must be

$$t_b - t_a = \frac{2nL_a}{v-2nu}. \tag{3.22}$$

Solving this equation for the initial velocity v we get

$$v = \frac{2nL_b}{t_b - t_a}. \tag{3.23}$$

Now that we have the initial velocity, we can calculate the classical action,

$$S = \int \frac{1}{2} m v^2 dt$$

Just like in Problem 1, we split the action into time periods of constant velocity. This gives

$$S(0,t_b;0,t_a) = \frac{m}{2}\left(\int_0^{t_1'} v^2 dt + \sum_{j=2}^{n}\int_{t_{j-1}'}^{t_j'} (v-2ju)^2 dt + \int_{t_n'}^{t_b} (v-2nu)^2 dt\right), \tag{3.24}$$

which yields

$$S = \frac{2mn^2 L_a L_b}{t_b - t_a}. \tag{3.25}$$

Calculation for General Case

To generalize this result to each of the four cases, we need to add the extra distance the particle will travel if it starts at an arbitrary position x_a and ends at x_b. In general, we can write the initial equation of motion as

$$vt_1' = L_1 + d_1,$$

where d_1 is determined by the specific case. t_1' is now the time it takes the particle to go from $x = x_a$ to $x = L_1$.

The final trajectory the particle takes (when $j = n$) can be described as

$$(v - 2nu)t_n'' = L_n + d_2,$$

where d_2 is the distance traveled by the particle after the last collision with the moving wall, and is determined by the specific case. t_n'' is the time the particle takes to go from L_n to the ending point x_b.

We can determine what d_1 and d_2 will be based on each specific case. For Case 1, the particle collides with the moving wall first and the fixed wall last, or has no collision with the moving wall. In order for this to happen, we need $d_1 = -x_a$, which leads to the initial condition

$$L_1 - x_a = vt_1'.$$

We must have $d_2 = x_b$ since the particle goes from $x = L_n$ to $x = 0$, reflects off the stationary wall, than travels to $x = x_b$. This leads to the final condition

$$L_n + x_b = (v - 2nu)t_n''.$$

Case 2 is when the particle collides with the fixed wall for both it's first and last collision. For this case, d_1 must be $d_1 = x_a$, since the total distance the particle travels to hit the moving wall is $L_1 + x_a$. The initial condition is

$$L_1 + x_a = vt_1'.$$

Since both Case 1 and Case 2 have a fixed wall collision as the last collision, $d_2 = x_b$ for both of them. The particle follows

$$L_n + x_b = (v - 2nu)t_n''.$$

Case 3 is when the first collision of the particle is with the fixed wall and the last collision is with the moving wall. Just as in Case 2, $d_1 = x_a$, and the initial condition is

$$L_1 + x_a = vt_1'.$$

The total distance traveled after the last collision in Case 3 is $L_n - x_b$, which means $d_2 = -x_b$, and the particle follows

$$L_n - x_b = (v - 2nu)t_n''.$$

Case 4 is when both the first and last collision of the particle is with the moving wall. As in Case 1, $d_1 = -x_a$, and the particle has the initial condition

$$L_1 - x_a = vt_1'.$$

As in Case 3, $d_2 = -x_b$, because the kinematic equation for the particle after L_n and until x_b is

$$L_n - x_b = (v - 2nu)t_n''.$$

Using these results, we can derive a formula for the initial velocity for the general case. The initial velocity in terms of known quantities becomes

$$v = \frac{2nL_b + d_1 + d_2}{t_b - t_a}. \tag{3.26}$$

The Action in the general case becomes

$$S = \int_{t_a}^{t_1'} v^2 dt + \sum_{j=2}^{n-1} \int_{t_{j-1}''}^{t_j''} (v - 2ju)^2 dt + \int_{t_n'}^{t_b} (v - 2nu)^2 dt.$$

This evaluates to our final action on Problem 2

$$S_n^{(j)}(x_b, t_b; x_a, t_a) = \frac{m}{2T}\left((2nL_0 + d_1 + d_2)^2 + 4nu[(d_1 t_b + d_2 t_a) + nL_0(t_a + t_b)] + 4n^2u^2 t_a t_b\right), \tag{3.27}$$

where j refers to the case number ($j = 1, 2, 3, 4$) and n refers to the number of collisions with the moving wall.

3.2 Propagator Results

Now that we have calculated the action for both problems, we can use the path integral formulation to calculate the propagators . Since we only considered classical paths in calculating the action, we will use the van Vleck formula to calculate the propagator found in (Tannor 2007).

3.2.1 Calculaing the Propagator for Problem 1

The van Vleck propagator is defined as

$$\langle x_b | \exp\left(-i\hat{H}t/\hbar\right) | x_a \rangle = \sum_{all\ classical\ paths} \left(-\frac{1}{2\pi i\hbar}\frac{\partial^2 S}{\partial x_b \partial x_a}\right)^{1/2} \exp\left(iS/\hbar\right).$$

There are only two classical paths, so the van Vleck propagator will have two terms, one corresponding to the direct path and the other term corresponding to the indirect path.

Evaluating the partial derivatives we get

$$\frac{\partial^2 S_D}{\partial x_b \partial x_a} = \frac{-m}{t_b - t_a}$$

and

$$\frac{\partial^2 S_I}{\partial x_b \partial x_a} = \frac{m}{t_b - t_a}.$$

We use these expressions to get

$$\langle x_b | \exp\left(-i\hat{H}t/\hbar\right) | x_a \rangle = \left(\frac{1}{2\pi i\hbar} \cdot \frac{m}{T}\right)^{1/2} exp\left(\frac{im(x_b - x_a)^2}{2T\hbar}\right) + \left(\frac{1}{2\pi i\hbar} \cdot \frac{-m}{T}\right)^{1/2} exp\left(\frac{im}{2T\hbar}\left[(x_b + x_a)^2 - 4u\left(x_a t_b + x_b t_a - u t_a t_b\right)\right]\right).$$

This simplifies to

$$\langle x_b | \exp\left(-i\hat{H}(\lambda_t)t/\hbar\right) | x_a \rangle = \left(\frac{m}{2\pi i\hbar T}\right)^{1/2} \left(exp\left(\frac{im}{2\hbar T}(x_b - x_a)^2\right) - exp\left(\frac{im}{2\hbar T}\left[(x_a + x_b)^2 - 4u\left(x_a t_b + x_b t_a - u t_a t_b\right)\right]\right)\right). \tag{3.28}$$

This propagator can be shown to be equal to the propagator found when solving Schrödinger's equation and using the spectral definition of the propagator.

In order to extract work out of the system, we have the wall stationary for the first part of the forward propagation, as discussed in Chapter 2 . The propagator for this period of time is found by substituting $u = 0$ into the propagator above. This gives

$$\langle x_b | \exp\left(-i\hat{H}(\lambda_0)t/\hbar\right) | x_a \rangle = \left(\frac{m}{2\pi i\hbar T}\right)^{1/2} \left(exp\left(\frac{im}{2\hbar T}(x_b - x_a)^2\right) - exp\left(\frac{im}{2\hbar T}(x_a + x_b)^2\right)\right). \tag{3.29}$$

This expression matches the expression found in (da Luz & Cheng 1992).

We can find the entire propagator for the entire forward propagation with the propagators for each section. We do this by following the method in Chapter 2 in successive events. We introduce an intermediate point x_{int}, multiply the two propagators together, and integrate over the intermediate point. By introducing the intermediate point, the starting position for the stationary wall propagation is x_a and the ending point is x_{int}. Similarly, for the moving wall propagation, the starting point will be x_{int} and the ending point will be x_b. We can write this as

$$\int_{-\infty}^{\infty} \langle x_{int}| \exp\left(-i\hat{H}(\lambda_0)t/\hbar\right) |x_a\rangle \langle x_b| \exp\left(-i\hat{H}t/\hbar\right) |x_{int}\rangle \, dx_{int}.$$

The Hamiltonian in the evolution operator is shown as a function of the work parameter λ, where λ_0 represents the work parameter holding at it's original position, which is when the wall is not moving, while λ_t represents when the work parameter is changing, which is when the wall is moving. We can evaluate this integral to get the propagator for the entire forward propagation. This propagator was not found by me, and could be a starting point for someone elses research .

3.2.2 Calculating the Propagator for Problem 2

Using the action derived for our second problem, we can evaluate the partial derivatives necessary for the van Vleck Propagator. For Case 1, we have

$$\frac{\partial^2 S_n^{(1)}}{\partial x_a \partial x_b} = -\frac{m}{T}.$$

For Case 2, we have

$$\frac{\partial^2 S_n^{(2)}}{\partial x_a \partial x_b} = \frac{m}{T}.$$

For Case 3, we have

$$\frac{\partial^2 S_n^{(3)}}{\partial x_a \partial x_b} = -\frac{m}{T}.$$

and for Case 4, we have

$$\frac{\partial^2 S_n^{(3)}}{\partial x_a \partial x_b} = \frac{m}{T}$$

It is of interest to see that in both physical scenarios, the derivative of the action for different paths only varies by an overall sign. The physical reason behind it could be attributed to the phase change associated with the number of collisions.

Now that we have the partial derivatives, we can find the van Vleck propagator by summing over all possible paths. As stated before, there are an infinite number of classical paths between the starting and ending positions, so our sums in the propagator will be infinite, but the starting index for the summation is different for the different Cases. Based on the definitions for Case 1 and Case 2, it is possible for the particle to complete a trajectory between the starting and ending positions without a collision with the moving wall, which means we can say that $n = 0$ is a possible classical path. For the path to be considered Case 3 or 4, the particle must collide with the moving wall at least once, so $n = 1$ is the shortest classical path.

The propagator will be

$$\begin{aligned}\langle x_b|\exp\left(-i\hat{H}t/\hbar\right)|x_a\rangle = &\sum_{n=0}^{\infty}\left(\frac{1}{2\pi i\hbar}\cdot\frac{m}{T}\right)^{1/2}\exp\left(\frac{i}{\hbar}S_n^{(1)}\right)\\ &+\sum_{n=0}^{\infty}\left(\frac{1}{2\pi i\hbar}\cdot\frac{-m}{T}\right)^{1/2}\exp\left(\frac{i}{\hbar}S_n^{(2)}\right)\\ &+\sum_{n=1}^{\infty}\left(\frac{1}{2\pi i\hbar}\cdot\frac{m}{T}\right)^{1/2}\exp\left(\frac{i}{\hbar}S_n^{(3)}\right)\\ &+\sum_{n=1}^{\infty}\left(\frac{1}{2\pi i\hbar}\cdot\frac{-m}{T}\right)^{1/2}\exp\left(\frac{i}{\hbar}S_n^{(4)}\right).\end{aligned} \tag{3.30}$$

We can factor this expression, substitute the expression for action for each case (replacing d_1 and d_2

with the variable necessary for the case) above to get

$$\langle x_b|\exp\left(-i\hat{H}t/\hbar\right)|x_a\rangle = \left(\frac{m}{2\pi i\hbar T}\right)^{1/2}$$
$$\left(\sum_{n=0}^{\infty}\exp\left(\frac{im}{2\hbar T}\left((2nL_0-x_a+x_b)^2+4nu((-x_at_b+x_bt_a)+nL_0(t_a+t_b))+4n^2u^2t_at_b\right)\right)+\right.$$
$$\sum_{n=0}^{\infty} i\exp\left(\frac{im}{2\hbar T}\left((2nL_0+x_a+x_b)^2+4nu((x_at_b+x_bt_a)+nL_0(t_a+t_b))+4n^2u^2t_at_b\right)\right)+$$
$$\sum_{n=1}^{\infty}\exp\left(\frac{im}{2\hbar T}\left((2nL_0+x_a-x_b)^2+4nu((x_at_b-x_bt_a)+nL_0(t_a+t_b))+4n^2u^2t_at_b\right)\right)+$$
$$\left.\sum_{n=1}^{\infty} i\exp\left(\frac{im}{2\hbar T}\left((2nL_0-x_a-x_b)^2+4nu((-x_at_b-x_bt_a)+nL_0(t_a+t_b))+4n^2u^2t_at_b\right)\right)\right).$$

This is a convoluted expression, and showcases the difficulty in evaluating path integrals , even with a semi-classical method. However, this can be simplified to a closed form expression using the 3rd Jacobi Theta Function, which can be found in (Gradshteyn & Ryzhik 2007). The Jacobi Theta Function is a function used in the theory of elliptic functions. To get the above equation, we evaluate the $n=0$ term of the action to ensure all of the sums have the same starting index. This gives

$$\langle x_b|\exp\left(-i\hat{H}t/\hbar\right)|x_a\rangle = \left(\frac{m}{2\pi i\hbar T}\right)^{1/2}$$
$$\left(\exp\left(\frac{im}{2\hbar T}(x_b-x_a)^2\right)\right.$$
$$+\sum_{n=1}^{\infty}\exp\left(\frac{im}{2\hbar T}\left((2nL_0-x_a+x_b)^2+4nu((-x_at_b+x_bt_a)+nL_0(t_a+t_b))+4n^2u^2t_at_b\right)\right)$$
$$-\exp\left(\frac{im}{2\hbar T}(x_a+x_b)^2\right)$$
$$+\sum_{n=1}^{\infty} i\exp\left(\frac{im}{2\hbar T}\left((2nL_0+x_a+x_b)^2+4nu((x_at_b+x_bt_a)+nL_0(t_a+t_b))+4n^2u^2t_at_b\right)\right)$$
$$+\sum_{n=1}^{\infty}\exp\left(\frac{im}{2\hbar T}\left((2nL_0+x_a-x_b)^2+4nu((x_at_b-x_bt_a)+nL_0(t_a+t_b))+4n^2u^2t_at_b\right)\right)$$
$$\left.+\sum_{n=1}^{\infty} i\exp\left(\frac{im}{2\hbar T}\left((2nL_0-x_a-x_b)^2+4nu((-x_at_b-x_bt_a)+nL_0(t_a+t_b))+4n^2u^2t_at_b\right)\right)\right).$$

We can now use the Jacobi Theta function to express the propagator as

$$\langle x_b|\exp\left(-i\hat{H}t/\hbar\right)|x_a\rangle = \left(\frac{m}{2\pi i\hbar T}\right)^{1/2}\left[\exp\left(\frac{im(x_b-x_a)^2}{2\hbar T}\right)\theta_3\left(\frac{m(x_bL_a-x_aL_b)}{\hbar T},\frac{2mL_aL_b}{\pi\hbar T}\right)\right.$$
$$\left.-\exp\left(\frac{im(x_a+x_b)^2}{2\hbar T}\right)\theta_3\left(\frac{m(x_bL_a+x_aL_b)}{\hbar T},\frac{2mL_aL_b}{\pi\hbar T}\right)\right].$$

This gives us a closed form expression for the propagator. However, I will rewrite the propagator one more time using an identity of the theta function to express the propagator in terms of the eigenstates of the infinite square well, a well-known solution to the Schrödinger equation. Using the identity, we get

$$\langle x_b|\exp\left(-i\hat{H}(\lambda_t)t/\hbar\right)|x_a\rangle =$$
$$\frac{2}{\sqrt{L_aL_b}}\exp\left[\frac{imu}{2\hbar}\left(\frac{x_b^2}{L_b}-\frac{x_a^2}{L_a}\right)\right]\sum_{n=1}^{\infty}\exp\left[\frac{in^2\pi^2\hbar}{2mu}\left(\frac{1}{L_b}-\frac{1}{L_a}\right)\right]\sin\left(\frac{n\pi x_b}{L_b}\right)\sin\left(\frac{n\pi x_a}{L_a}\right). \tag{3.31}$$

This is the final form of the propagator that we will use in our calculation of the work statistics .

To find the propagator for the time period when the wall is not moving, we set $u=0$ in the action, and follow the same solution pattern to get

$$\langle x_b|\exp\left(-i\hat{H}(\lambda_0)t/\hbar\right)|x_a\rangle = \frac{2}{L_0}\sum_{n=1}^{\infty}\exp\left(-\frac{n^2\pi^2\hbar^2}{2mL_0^2}\nu\right)\sin\left(\frac{n\pi x_a}{L_0}\right)\sin\left(\frac{n\pi x_m}{L_0}\right).$$

This propagator can be found by taking the outer product of the eigenstates found when solving the Schrödinger equation.

Just as in Problem 1, we can find the propagator for the entire propagation by introducing an intermediate point. The entire forward propagator will then be

$$\langle x_b|\exp\left(-i\hat{H}(\lambda_0)t/\hbar\right)|x_a\rangle = \frac{1}{l_a}\sqrt{\frac{\pi\hbar}{2mul_b}}(-1)^(5/4)\sum_{n_1,n_2=1}^{\infty}\times$$
$$\exp(-\frac{n_1^2\pi^2\hbar^2\nu}{2ml_0^2}+\frac{imux_b^2}{2\hbar l_b}+\frac{i\pi^2\hbar}{2mu}\left(\frac{n_2^2}{l_b}+\frac{n_1^2}{l_a}\right)\times \tag{3.32}$$
$$\sin\left(\frac{n_1\pi x_a}{l_a}\right)\sin\left(\frac{n_2\pi x_b}{l_b}\right)A(n_1,n_2),$$

where $A(n_1,n_2)$ is a constant defined in Appendix A.

3.3 Calculating the Initial Density Matrix for Problem 1

From this point forward, we will only talk about Problem 2, as the results from problem 1 are still being discussed.

The density matrix was defined in Eq. (1.11) in more detail in chapter 1, where we included a definition. Using the eigenstates of the infinite square well, we can find the density matrix. We use these eigenstates because the system originally starts with a stationary wall, which is the infinite square well. These eigenstates are

$$\psi_n(x) = \sqrt{\frac{2}{L_0}} \sin\left(\frac{n\pi x}{L_0}\right)$$

and the quantization of the energy is given by

$$E_n^0 = \frac{n^2\pi^2\hbar^2}{2mL_0^2}.$$

These results can be found in quantum mechanics textbooks. We insert these equations into the definition of the initial density matrix to get

$$\rho(x_i, y_i) = \frac{2}{Z_0 L_0} \sum_{n=1}^{\infty} \exp\left(-\frac{\beta n^2\pi^2\hbar^2}{2mL_0^2}\right) \sin\left(\frac{n\pi x_i}{L_0}\right) \sin\left(\frac{n\pi y_i}{L_0}\right), \tag{3.33}$$

where $\beta = 1/k_B T$ is the standard inverse temperature and Z_0 is the partition function, as discussed in Chapter 1.

3.4 Calculation of Work Statistics for Problem 1

At this point, we have found the forward propagator, the backward propagator, and the initial density matrix, which are the three components in the expression for the characteristic work function , which was discussed in Chapter 2. All that remains is to multiply the three factors together, perform

the integral, and simplify the result. The final result is

$$\chi_W(\nu) = \frac{\pi^2\hbar^2}{64m^2u^2L_0L_fZ_0} \sum_{n_1,n_2,n_3,n_4,=1}^{\infty} \exp\left(-\frac{in_1^2\pi^2\hbar^2\nu}{2mL_0^2} + \frac{in_3^2\pi^2\hbar^2\nu}{2mL_f^2} - \frac{\beta n_1^2\pi^2\hbar^2}{2mL_0^2}\right) A_1(n_1,n_2)A_2(n_3,n_4)A_3(n_4,n_1)A_4(n_2,n_3). \tag{3.34}$$

In this formula, each n is an arbitrary quantum number, introduced to keep track of the summations. We will see shortly what the physical interpretation of these quantum numbers are. In addition, A_1, A_2, A_3, A_4 are all constants. These constants are quite lengthy and not particularly enlightening and are not included here (these are included in Appendix A).

This solution is the analytic solution for the characteristic function of work, found by using a path integral approach . It does not have a closed form expression (to our knowledge), but was found using a path integral approach.

From the characteristic function of work, we can take an inverse Fourier Transform to get the work distribution for the process. This was discussed in Chapter 1. By taking the Fourier Transform, we can recover the work variable W. Doing this, we get

$$P(W) = \frac{\pi^2\hbar^2}{64m^2u^2L_0L_fZ_0} \sum_{n_1,n_2,n_3,n_4=1}^{\infty} \delta\left[W - \frac{\pi^2\hbar^2}{2m}\left(\frac{n_3^2}{L_f^2} - \frac{n_1^2}{L_0^2}\right)\right] \exp\left(-\frac{\beta n_1^2\pi^2\hbar^2}{2mL_0^2}\right) A_1(n_1,n_2)A_2(n_3,n_4)A_3(n_4,n_1)A_4(n_2,n_3). \tag{3.35}$$

This formula is also unwieldy, but we can get some meaning out of the formula by focusing on the argument inside the Dirac Delta Functions. We see the work variable W, but also the expression for the energy level n_1 when the box is at the initial length L_0, and the expression for the energy level n_3 when the box is at the final length L_f. Because of that, we can assume that the probability distribution that we have found here is the probability that the work done by the system will increase the energy level of the particle from n_1 to n_3.

This makes intuitive sense because work is traditional thermodynamics changes the energy of the system, and that is what we have found here. These results are exact, and can be found by

solving the Schrodinger equation.

3.5 Conclusion and Future Work

By finding the work statistics by using a path integral approach and verifying the validity against results obtained using the the traditional formalism of quantum mechanics, We have shown that the path integral is an alternative approach to calculating the work statistics. The path integral approach can be useful for calculating the work statistics in open systems (systems that can transfer heat and energy out in an environment), and so future work needs to be done to further explore those possibilities [1]. This will no doubt improve our understanding of quantum thermodynamics, which will hopefully lead to a better understanding of quantum technology.

There is also further work to be done exploring the quantum to classical relationship, and whether the path integral expression for work can be shown to find work in a classical system. This is a necessary step to better understand how quantum thermodynamics and classical thermodynamics are related, and whether or not classical thermodynamics emerges from a fundamentally quantum description of fluctuating thermal phenomena.

Appendix A

Definition of Constants

The constants $A_1(n_1,n_2)$, $A_2(n_3,n_4)$, $A_3(n_4,n_1)$, $A_4(n_2,n_3)$ are defined as follows:

$$A_1 = \frac{(-1)^{3/4}\sqrt{\hbar l_a \pi}}{4\sqrt{2mu}} \exp\left(\frac{i\hbar\pi^2 n_1^2}{2l_a mu}\right) \exp\left(\frac{i\hbar\pi^2 n_2^2}{2l_a mu}\right)$$
$$\left(\exp\left(-\frac{in_1 n_2 \hbar\pi^2}{l_a mu}\right)\left(\text{Erfi}\left(\frac{(1/2-i/2)(\hbar\pi(n1-n2)-l_a mu)}{\sqrt{\hbar l_a mu}}\right) - \text{Erfi}\left(\frac{(1/2-i/2)(\hbar\pi(n_1-n_2)+l_a mu)}{\sqrt{\hbar l_a mu}}\right)\right)\right.$$
$$\left.-\exp\left(\frac{in_1 n_2 \hbar\pi^2}{l_a mu}\right)\left(\text{Erfi}\left(\frac{(1/2-i/2)(\hbar\pi(n_1+n_2)-l_a mu)}{\sqrt{\hbar l_a mu}}\right) - \text{Erfi}\left(\frac{(1/2-i/2)(\hbar\pi(n_1+n_2)+l_a mu)}{\sqrt{\hbar l_a mu}}\right)\right)\right) \tag{A.1}$$

$$A_2 = \frac{(-1)^{3/4}\sqrt{\hbar l_b \pi}}{4\sqrt{2mu}} \exp\left(-\frac{i\hbar\pi^2 n_2^2}{2l_b mu}\right) \exp\left(\frac{i\hbar\pi^2 n_3^2}{2l_b mu}\right)$$
$$\left(\exp\left(-\frac{in_2 n_3 \hbar\pi^2}{l_b mu}\right)\left(\text{Erfi}\left(\frac{(1/2+i/2)(\hbar\pi(n2-n3)-l_b mu)}{\sqrt{\hbar l_b mu}}\right) - \text{Erfi}\left(\frac{(1/2+i/2)(\hbar\pi(n_2-n_3)+l_b mu)}{\sqrt{\hbar l_b mu}}\right)\right)\right.$$
$$\left.-\exp\left(-\frac{in_2 n_3 \hbar\pi^2}{l_b mu}\right)\left(\text{Erfi}\left(\frac{(1/2+i/2)(\hbar\pi(n_2+n_3)-l_b mu)}{\sqrt{\hbar l_b mu}}\right) - \text{Erfi}\left(\frac{(1/2+i/2)(\hbar\pi(n_2+n_3)+l_b mu)}{\sqrt{\hbar l_b mu}}\right)\right)\right)$$

$$A_3 = \frac{(-1)^{3/4}\sqrt{\hbar l_a \pi}}{4\sqrt{2mu}} \exp\left(-\frac{i\hbar\pi^2 n_1^2}{2l_a mu}\right) \exp\left(-\frac{i\hbar\pi^2 n_4^2}{2l_a mu}\right)$$
$$\left(\exp\left(-\frac{in_1 n_4 \hbar\pi^2}{l_a mu}\right)\left(\text{Erfi}\left(\frac{(1/2+i/2)(\hbar\pi(n1-n4)-l_a mu)}{\sqrt{\hbar l_a mu}}\right) - \text{Erfi}\left(\frac{(1/2+i/2)(\hbar\pi(n_1-n_4)+l_a mu)}{\sqrt{\hbar l_a mu}}\right)\right)\right.$$
$$\left. -\exp\left(\frac{in_1 n_4 \hbar\pi^2}{l_a mu}\right)\left(\text{Erfi}\left(\frac{(1/2+i/2)(\hbar\pi(n_1+n_4)-l_a mu)}{\sqrt{\hbar l_a mu}}\right) - \text{Erfi}\left(\frac{(1/2+i/2)(\hbar\pi(n_1+n_4)+l_a mu)}{\sqrt{\hbar l_a mu}}\right)\right)\right) \tag{A.2}$$

and

$$A_4 = \frac{(-1)^{3/4}\sqrt{\hbar l_b \pi}}{4\sqrt{2mu}} \exp\left(\frac{i\hbar\pi^2 n_3^2}{2l_b mu}\right) \exp\left(\frac{i\hbar\pi^2 n_4^2}{2l_b mu}\right)$$
$$\left(-\exp\left(-\frac{in_3 n_4 \hbar\pi^2}{l_b mu}\right)\left(\text{Erfi}\left(\frac{(1/2-i/2)(\hbar\pi(n3-n4)-l_b mu)}{\sqrt{\hbar l_b mu}}\right) - \text{Erfi}\left(\frac{(1/2-i/2)(\hbar\pi(n_3-n_4)+l_b mu)}{\sqrt{\hbar l_b mu}}\right)\right)\right.$$
$$\left. -\exp\left(\frac{in_1 n_2 \hbar\pi^2}{l_b mu}\right)\left(\text{Erfi}\left(\frac{(1/2-i/2)(\hbar\pi(n_1+n_2)-l_b mu)}{\sqrt{\hbar l_b mu}}\right) - \text{Erfi}\left(\frac{(1/2-i/2)(\hbar\pi(n_1+n_2)+l_b mu)}{\sqrt{\hbar l_b mu}}\right)\right)\right). \tag{A.3}$$

All of these are defined in terms of the imaginary error function, which is defined as

$$\text{Erfi}(x) = -i\,\text{Erfi}(ix) = -\frac{2i}{\sqrt{\pi}}\int_0^{ix} \exp\left(-t^2\right)dt\Big) \tag{A.4}$$

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