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Mori Projected Dynamics On A Quantum System

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ABSTRACT

In this thesis we discuss Mori Projected Time Dynamics in a quantum mechanical system. As a precursor to calculating the time derivative of a mixed state of the system we examine the derivation of the Mori-Zwanzig formalism and different ways of calculating the time dynamics of various quantum systems. We consider the exact calculation of the time derivative of a mixed state. We then calculate the same time evolution using Mori Theory and compare the two results. From the general calculation of the Mori Equation we were able to perform a series of simple tests to compare Mori Theory to the known result. We discovered that in each of the three simple cases the Mori Equation and the direct calculation of the derivative give the same result, but in the more complicated situations the two calculations differed. This result leads us to believe that the Mori Equation is an accurate way of calculating the derivative of a mechanical variable in a quantum system.

1.0 INTRODUCTION

In this thesis we discuss Mori Projected Time Dynamics in a quantum mechanical system. Mori theory is a way of calculating the time dynamics of any variable of a system in statistical mechanics. The Mori theory allows a person to: (1) know the full solution of the time evolution of a system; (2) see the random force and the memory kernel calculations allowing the reader to more clearly understand how the function evolves in time; (3) use the projection operator to understand how a system evolves in time without a particular mechanical variable; (4) isolate one mechanical variable of the system and analyze its time dynamics; and (5) reduce the likelihood that any category of effect will be overlooked during the calculation and keep track of possible classes of effect[12].

As a precursor to calculating the time derivative of a mixed state of the system we will look at the derivation of the Mori-Zwanzig formalism and different ways of calculating the time dynamics of various quantum mechanical systems. After determining the best calculation of the time dynamics of a mixed state we will calculate the time dynamics using Mori Theory and compare the two results. In this case the "best calculation" of the time dynamics of the system will be the one which presents the least complicated form so it is easier to compare the two calculations.

We will look at two distinct types of quantum systems, the perturbed harmonic oscillator and the two level perturbed spin system. We will calculate the time dependence of the eigenstates of the perturbed harmonic oscillator in two ways: first, using classic perturbation theory, and, second, applying the Hamiltonian to the wave equation to propagate the expression forward in time. We also calculated the time dependence of a perturbed two particle spin system using classic perturbation theory. After looking at the results of these two calculations we decided that it would be best to use a mixed state of an unperturbed system and take the direct time derivative of the state.

We will then try a test calculation of a projection operator on a two state Hamiltonian by projecting out a pure eigenstate of the system. After determining that the projection operator performs in the way expected and projects out the state from the system with no other complications, we do a second calculation on the system with a mixed state as the state to be projected out. Using this information we will calculate the rest of the Mori expression and compare our results to the actual time dependence of the system. One of the complications we have in this system is the

exponentials. To determine how the operators act on the quantum system we will use a first order Taylor Expansion for $e^{-\frac{itE_n}{\hbar}}$, which will cause our Mori theory result to differ at least slightly, in some cases, from the exact answer.

2.0 LITERATURE REVIEW

During the literature review portion of this thesis we looked at various papers. The papers described below are a representative sample of those looked at and what we were looking for. Our main goal was to find someone who had done a calculation of the Mori Projection Operator and the Mori Theory in a quantum mechanical system. We unfortunately were unable to find anyone who had looked at this problem to our satisfaction.

2.1 Elementary Lectures in Statistical Mechanics

Phillies[12] discusses many of the elementary and more advanced concepts in Statistical Mechanics. Our objective was to learn Gibbsian statistical mechanics well enough to use Mori projected dynamics to determine the behavior of a Mori Projection Operator on a quantum system. During this portion of the research we covered many of the chapters and questions of this book to make sure I had a firm grasp on all of the concepts we would need to solve this problem. This particular portion of my research also helped me to read and understand many of the finer points of Mori's paper[7], "Transport, Collective Motion, and Brownian Motion paper.

2.2 "Transport, Collective Motion, and Brownian Motion"

Mori[7] discussed his formulation of the Mori Projection Operator and the Mori equations for calculating a Brownian system using a classical mechanical system. This paper was the motivation for our research. Mori discusses a classical system of particles but does not discuss a quantum system of particles. Our goal was to apply Mori's theory to a quantum system to determine what happens when you project out a part of the system.

2.3 "Relaxation In Interacting Arrays of Oscillators"

Tsang and Ngai[13] discussed a system of interacting arrays of globally coupled nonlinear oscillators and are primarily focused on the decay of the phase coherence[13]. Our objective was to find an

explanation of Ngai's Random Hamiltonian. The paper did prove to be useful to our study because it gives an example of the treatment of a system of a perturbed system. Since we are using a system of weakly coupled harmonic oscillators it is important to know all of the different possible behaviors of the system. One of the most useful conclusions is that the coupling of the interacting arrays slows down the relaxation of any one of the interacting oscillators[13]. This paper allows us to look at the time dependent relaxation behavior of the system we have chosen and confirm how it relaxes. While this paper is not quite along the lines of our paper its general treatment of the system was extremely helpful in getting started.

2.4 "Basic Physics of the Coupling Model: Direct Experimental Evidences"

Ngai and Rendell [8] treat a system of coupled harmonic oscillators and crystal systems. Our objective was to find an example of the Ngai Random Hamiltonian but we did not find an example in this paper. One of the large differences between crystal systems and the one we are looking at is that this paper treats large classical systems while we would like to treat a quantum system. This paper was mainly useful because it detailed the behavior of various different coupled systems, giving us an overall view of the coupled model and how the relaxation time is affected by different conditions (i.e. high temperature limit, low frequency, etc.). From this paper we were able to see that even though many systems can be modeled by coupled harmonic oscillators their behavior can be radically different depending upon their individual properties.

2.5 "Dynamics of Relaxing Systems Subjected to Nonlinear Interactions"

Ngai and White[11] treat a system of coupled particles. This paper addresses relaxation of the Fermi-stadium map with different R's[10]. While this topic diverges significantly from the topic of study in this paper, our objective was to find an example of a random Hamiltonian or something else about this system of coupled harmonic oscillators would help with our model. Unfortunately we were unable to find any aspect of the paper that would assist us in our analysis.

3.0 BACKGROUND RESEARCH

3.1 Proving the Mori-Zwanzig Identity From the Langevin Equation

To study the Mori Projected Time Dynamics proving the Mori-Zwanzig Identity is the first step. The Mori-Zwanzig formalism systemizes non-equilibrium calculations in a way that reduces the likelihood that any physical effect will be overlooked. The formalism keeps track of possible classes of effect[12]. Understanding this particular identity and the steps leading to it are crucial to applying the projected time dynamics to a simple quantum mechanic harmonic oscillator or any oscillation system. We first provide a calculation that motivates the Mori-Zwanzig Identity's derivation:

$$\frac{d\vec{p}(t)}{dt} = -f\frac{\vec{p}(t)}{m} + F(t), \tag{3.1.1}$$

simplified,

$$\frac{d\vec{p}(t)}{dt} = -\left[\int_0^t ds\ f(t-s)\frac{\vec{p}(t)}{m}\right] + F(t), \tag{3.1.2}$$

where p is the momentum, m is the mass, t is the time, $f(t-s)$ is the memory function, f is the friction factor, and $F(t)$ is the random force. The reason that we use the Mori-Zwanzig equation instead of the Langevin equation is two fold: First, the Langevin equation has a lot of ad-hoc assumptions, while we want to do something that has more concrete assumptions. Second the Langevin equation is not derived from the Louiville operator or the Hamiltonian. We would like to look at something that begins with exact dynamics and resembles the Brownian equations of motion more closely when we are finished with our calculation.

To further explain the variables f and $F(t)$ we must make two assumptions: **Assumption 1:** $f(t-s)$ must be the memory function and have the form $f\ \delta(t-s)$; and **Assumption 2:** The equilibrium result $\langle v^2(t)\rangle = \frac{3k_BT}{m}$ is true regardless of the time at which $\langle v^2(t)\rangle$ is determined. Using the assumption that the equilibrium result is true regardless of the time at which it is determined, f and $F(t)$ can be shown to be related by

$$f = \frac{\beta}{3}\int_0^\infty \langle F(0)\cdot F(t)\rangle dt. \tag{3.1.3}$$

That is, f is the time-correlation function of F.

We will now begin our derivation of the Mori-Zwanzig Theorem by defining the projection operator, normalized autocorrelation function, frequency matrix, part of $A(t)$ not correlated with $A(0)$, and part of $\dot{A}(t)$ not correlated with $A(0)$ to be:

Projection Operator

$$P_A = \frac{\langle A^*(0),\ \ \rangle A(0)}{\langle A^*(0), A(0)\rangle}. \tag{3.1.4}$$

Normalized Autocorrelation Function

$$\Xi(t) = \frac{\langle A^*(0), A(t)\rangle}{\langle A^*(0), A(0)\rangle}. \tag{3.1.5}$$

Frequency Matrix

$$i\Omega(t) = \frac{\langle A^*(0), \dot{A}(0)\rangle}{\langle A^*(0), A(0)\rangle}. \tag{3.1.6}$$

Part of $A(t)$ Not Correlated with $A(0)$

$$A'(t) = (I - P_A)\, A(t). \tag{3.1.7}$$

Part of $\dot{A}(t)$ Not Correlated with $A(0)$

$$K(t) = (I - P_A)\, \dot{A}(t). \tag{3.1.8}$$

Now it is possible to re-define $A(t)$ and $A'(t)$ using (3.1.5)-(3.1.8)

$$A(t) = (P_A + I - P_A)\, A(t), \tag{3.1.9}$$

which gives us

$$A(t) = \Xi A(0) + A'(t). \tag{3.1.10}$$

We now define the relationship between $\dot{A}(t)$ and L, the Louiville Operator:

$$\frac{dA}{dt} = LA(t). \tag{3.1.11}$$

Multiplying both sides of (3.1.11) by $I - P_A$, where I is the identity matrix,

$$(I - P_A)\, \frac{dA}{dt} = (I - P_A)\, LA(t). \tag{3.1.12}$$

Using (3.1.10) in (3.1.12) we replace $A(t)$ with $\Xi A(0) + A'(t)$

$$(I - P_A)\, \frac{dA}{dt} = \Xi\, (I - P_A)\, LA(0) + (I - P_A)\, LA'(t). \tag{3.1.13}$$

Simplifying the first term of (3.1.13), $\Xi\, (I - P_A)\, LA(0)$, by using the definition $\frac{dA}{dt} = LA(t)$, (3.1.13) becomes

$$(I - P_A)\, \frac{dA}{dt} = \Xi\, (I - P_A)\, \dot{A}(0) + (I - P_A)\, LA'(t). \tag{3.1.14}$$

We then use (3.1.8) to replace $(I - P_A)\dot{A}(t)$ with $K(t)$ in (3.1.14), such that

$$(I - P_A)\frac{dA}{dt} = \Xi K(0) + (I - P_A)\,LA'(t). \tag{3.1.15}$$

Rearranging the left hand side of (3.1.15) by applying the derivative in $\frac{dA}{dt}$ to the entire term $\frac{d}{dt}(I - P_A)\,A$, yields

$$\frac{d}{dt}(I - P_A)\,A = \Xi K(0) + (I - P_A)\,LA'(t). \tag{3.1.16}$$

We now see from (3.1.7) that $\frac{d}{dt}(I - P_A)\,A = \frac{dA'}{dt}$. Using this result on the left hand side of (3.1.16) and rearranging gives

$$\Xi K(0) = \frac{dA'}{dt} - (I - P_A)\,LA'(t). \tag{3.1.17}$$

Now that we have a simplified differential equation for $\frac{d}{dt}(I - P_A)\,A$, we can solve (3.1.17) by applying simple differential calculus

$$A'(t) = \exp\left[t\,(I - P_A)\,L\right]A'(0) + \int_0^t ds\;\Xi(s)\exp\left[(t-s)\,(I - P_A)\,L\right]K(0). \tag{3.1.18}$$

The first term on the right hand side of (3.1.18) is 0, because $A'(0) = 0$. To confirm this we start with the expression $(I - P_A)\,A(0)$

$$A'(0) = (I - P_A)\,A(0). \tag{3.1.19}$$

We expand $I - P_A$ in (3.1.19), obtaining

$$A'(0) = A(0) - \frac{\langle A^*(0), A(0)\rangle}{\langle A^*(0), A(0)\rangle}A(0). \tag{3.1.20}$$

Now it becomes clear that $A'(0) = 0$, because $\frac{\langle A^*(0),A(0)\rangle}{\langle A^*(0),A(0)\rangle} = 1$ and therefore (3.1.20) becomes $A'(0) = A(0) - A(0)$. Eliminating the first term of the left side of (3.1.18) gives

$$A'(t) = \int_0^t ds\;\Xi(s)\exp\left[(t-s)\,(I - P_A)\,L\right]K(0). \tag{3.1.21}$$

Now it will be helpful to define a variable f such that

$$f(0) = K(0), \tag{3.1.22}$$

and

$$f(t-s) = \exp\left[(t-s)\,(I - P)\,L\right]K(0). \tag{3.1.23}$$

Using the newly defined $f(t-s)$ it is possible to simplify (3.1.21) to

$$A(t) = \Xi(t)A(0) + \int_0^t ds\;\Xi(s)f(t-s). \tag{3.1.24}$$

Now we must make another assumption: **Assumption 3:** The system is time reversal invariant, because the Louiville operator e^{tL} has time reversal invariance. By assuming that $A(t)$ is time reversal invariant we can rearrange convolutions of $A(t)$ without changing the core of the expression. In the next steps we will use this assumption repeatedly.

Time reversal invariance guarantees that

$$A(-t) = \Xi(-t)A(0) + \int_0^{-t} ds\ \Xi(s)f(-t-s). \tag{3.1.25}$$

is also true. The convolution of the integral makes it possible to rearrange (3.1.24) to

$$A(t) = \Xi(t)A(0) + \int_0^{t} ds\ \Xi(t-s)f(s). \tag{3.1.26}$$

Taking the derivative of (3.1.26) with respect to t yields

$$\frac{dA(t)}{dt} = \frac{d\Xi(t)}{dt}A(0) + \left[\int_0^t ds\ \frac{d\Xi(t-s)}{dt}f(s)\right] + f(t). \tag{3.1.27}$$

There are two distinct portions of (3.1.27): the portion dependent upon the random force $f(s)$; and the portion not dependent upon the random force. The two portions of this expression are, respectively,

$$\left[\int_0^t ds\ \frac{d\Xi(t-s)}{dt}f(s)\right] + f(t), \tag{3.1.28}$$

$$\frac{d\Xi(t)}{dt}A(0). \tag{3.1.29}$$

The ability to separate (3.1.27) into two different portions allows us to confirm that (3.1.3) is a proper definition of the Langevin random force.

To proceed in further interpreting (3.1.27) it is necessary to explicitly determine $\frac{d\Xi(t)}{dt}$. Using (3.1.5) we find

$$\frac{d\Xi(t)}{dt} = \frac{\left\langle A^*(0), \frac{dA(t)}{dt}\right\rangle}{\langle A^*(0), A(0)\rangle}, \tag{3.1.30}$$

In (3.1.30) we replace $\frac{dA(t)}{dt}$ with $\dot{A}(t)$

$$\frac{d\Xi(t)}{dt} = \frac{\left\langle A^*(0), \dot{A}(t)\right\rangle}{\langle A^*(0), A(0)\rangle}. \tag{3.1.31}$$

The projection operator $P_{A(t)}$ with respect to $A(t)$ is

$$P_{A(t)} = \frac{\langle A^*(t),\quad\rangle A(t)}{\langle A^*(t), A(t)\rangle}. \tag{3.1.32}$$

We apply the projection operator in the form $I = P_{A(t)} + I - P_{A(t)}$ to (3.1.31), gaining

$$\frac{d\Xi(t)}{dt} = P_{A(t)}\frac{\left\langle A^*(0), \dot{A}(t)\right\rangle}{\langle A^*(0), A(0)\rangle} + \left(I - P_{A(t)}\right)\frac{\left\langle A^*(0), \dot{A}(t)\right\rangle}{\langle A^*(0), A(0)\rangle}, \tag{3.1.33}$$

Expanding $P_{A(t)}$, as seen in (3.1.32), the expression in (3.1.33) becomes

$$\frac{d\Xi(t)}{dt} = \frac{\langle A^*(t), \dot{A}(t)\rangle}{\langle A^*(t), A(t)\rangle}\frac{\langle A^*(0), A(t)\rangle}{\langle A^*(0), A(0)\rangle} + \frac{\left\langle A^*(0), \left(I - P_{A(t)}\right)\dot{A}(t)\right\rangle}{\langle A^*(0), A(0)\rangle}. \tag{3.1.34}$$

Using the property $(I - P_A)\frac{dA}{dt} = (I - P_A)\,LA(t)$ from (3.1.8) we replace $(I - P_A)\dot{A}(t)$ with $K(t)$ such that (3.1.34) is

$$\frac{d\Xi(t)}{dt} = \frac{\langle A^*(t), \dot{A}(t)\rangle}{\langle A^*(t), A(t)\rangle}\frac{\langle A^*(0), A(t)\rangle}{\langle A^*(0), A(0)\rangle} + \frac{\langle A^*(0), K(t)\rangle}{\langle A^*(0), A(0)\rangle}. \tag{3.1.35}$$

We then use (3.1.5) to replace $\frac{\langle A^*(0), A(t)\rangle}{\langle A^*(0), A(0)\rangle}$ with $\Xi(t)$, so that (3.1.35) becomes

$$\frac{d\Xi(t)}{dt} = \frac{\langle A^*(t), \dot{A}(t)\rangle}{\langle A^*(t), A(t)\rangle}\Xi(t) + \frac{\langle A^*(0), K(t)\rangle}{\langle A^*(0), A(0)\rangle}. \tag{3.1.36}$$

At this point we must make one more assumption: **Assumption 4:** Ω is time invariant. Since Ω is time invariant (3.1.6) can be expressed as

$$i\Omega = \frac{\langle A^*(0)\dot{A}(0)\rangle}{\langle A^*(0)A(0)\rangle} = \frac{\langle A^*(t)\dot{A}(t)\rangle}{\langle A^*(t)A(t)\rangle}. \tag{3.1.37}$$

Using (3.1.34), we can replace $\frac{\langle A^*(t), \dot{A}(t)\rangle}{\langle A^*(t), A(t)\rangle}\Xi(t)$ with $i\Omega\Xi(t)$ in (3.1.36) such that

$$\frac{d\Xi(t)}{dt} = i\Omega \cdot \Xi(t) + \frac{\langle A^*(0), K(t)\rangle}{\langle A^*(0), A(0)\rangle}. \tag{3.1.38}$$

Because $A(t)$ is time translation invariant, we write

$$\langle A^*(0)K(t)\rangle = \langle A^*(-t)K(0)\rangle, \tag{3.1.39}$$

and thus

$$A^*(-t) = \Xi^*(-t)A^*(0) + \int_0^{-t} ds\ \Xi^*(s)f^*(-t-s). \tag{3.1.40}$$

Using (3.1.39) and (3.1.40), in (3.1.38) we replace $\langle A^*(0)K(t)\rangle$ with
$\left\langle \left[\Xi^*(-t)A^*(0) + \int_0^{-t} ds\ \Xi^*(s)f^*(-t-s)\right], K(0)\right\rangle$

$$\frac{d\Xi}{dt} = \frac{\left\langle \left[\Xi^*(-t)A^*(0) + \int_0^{-t} ds\ \Xi^*(s)f^*(-t-s)\right], K(0)\right\rangle}{\langle A^*(0), A(0)\rangle} + i\Omega \cdot \Xi(t). \tag{3.1.41}$$

Again using the assumption that $A(t)$ is time reversal invariant

$$\Xi(-t) = \frac{\langle A^*(0), A(-t)\rangle}{\langle A^*(0), A(0)\rangle}\langle A^*(0), A(0)\rangle = \frac{\langle A^*(t), A(0)\rangle}{\langle A^*(0), A(0)\rangle}\langle A^*(0), A(0)\rangle = \Xi^*(t). \tag{3.1.42}$$

Looking at the interaction of $\langle K(0)\Xi^*(0)A^*(0)\rangle$ we see that

$$\langle K(0)\Xi^*(-t)A^*(0)\rangle = \Xi(t)\left\langle A^*(0), (I - P_A)\frac{dA}{dt}\right\rangle = 0. \tag{3.1.43}$$

Inserting (3.1.43) into (3.1.41) we get the simplified expression

$$\frac{d\Xi}{dt} = \int_0^{-t} ds\ \frac{\langle \Xi(-s) f^*(-t-s), K(0)\rangle}{\langle A^*(0), A(0)\rangle} + i\Omega \cdot \Xi(t). \tag{3.1.44}$$

Using (3.1.22) to replace $f(0)$ in (3.1.44)

$$\frac{d\Xi}{dt} = \left[\int_0^{-t} ds\ \frac{\langle \Xi(-s) f^*(-t-s), f(0)\rangle}{\langle A^*(0), A(0)\rangle}\right] + i\Omega \cdot \Xi(t). \tag{3.1.45}$$

Since $\Xi(-t)$ is constant it can be pulled out of the brackets and so (3.1.45) becomes

$$\frac{d\Xi}{dt} = \left[\int_0^{-t} ds\ \Xi(-s)\frac{\langle f^*(-t-s) f(0)\rangle}{\langle A^*(0), A(0)\rangle}\right] + i\Omega \cdot \Xi(t). \tag{3.1.46}$$

We now change variables from $-s$ to s, use time reversal invariance, and replace $\langle f^*(-t-s), f(0)\rangle \rightarrow \langle f^*(0), f(t-s)\rangle$ so (3.1.46) becomes

$$\frac{d\Xi}{dt} = \left[-\int_0^{t} ds\ \Xi(s)\frac{\langle f^*(0) f(t-s)\rangle}{\langle A^*(0), A(0)\rangle}\right] + i\Omega \cdot \Xi(t). \tag{3.1.47}$$

Since the integral is a convolution it is possible to exchange $t-s$ and s, so (3.1.47) becomes

$$\frac{d\Xi}{dt} = \left[-\int_0^{t} ds\ \Xi(t-s)\frac{\langle f^*(0) f(s)\rangle}{\langle A^*(0), A(0)\rangle}\right] + i\Omega \cdot \Xi(t). \tag{3.1.48}$$

At this point we must define a function $\phi(s)$, the Mori-Zwanzig memory kernel, to be

$$\phi(s) = \frac{\langle f^*(0), f(s)\rangle}{\langle A^*(0), A(0)\rangle}. \tag{3.1.49}$$

Using the memory kernel in (3.1.48) $\frac{d\Xi}{dt}$ becomes

$$\frac{d\Xi}{dt} = i\Omega\Xi(t) - \int_0^{t} ds\ \Xi(t-s)\phi(s). \tag{3.1.50}$$

Exchanging $\frac{d\Xi}{dt}$ in (3.1.27) with the expression in (3.1.50) to obtain

$$\frac{dA(t)}{dt} = \left[i\Omega\Xi(t) - \int_0^{t} ds\ \Xi(t-s)\phi(s)\right] A(0) + \left\{\int_0^{t} ds \left[i\Omega\Xi(t) - \int_0^{t} ds\ \Xi(t-s)\phi(s)\right] f(s)\right\} + f(t). \tag{3.1.51}$$

Rearrange (3.1.51) and apply (3.1.40) such that $i\Omega\Xi(t)A(0) + \int_0^t ds i\Omega\Xi(t)\ f(s)$ is replaced with $i\Omega A(t)$, and $-\int_0^t ds \Xi(t-s)\phi(s)A(0) - \int_0^t ds \int_0^t ds \Xi(t-s)\phi(s)\ f(s)$ is replaced with $\int_0^t ds\phi(s)\ A(t-s)$, yielding

$$\frac{dA(t)}{dt} = i\Omega A(t) + \left[\int_0^{t} ds\ \phi(s)A(t-s)\right] + f(t), \tag{3.1.52}$$

which is the Mori-Zwanzig identity[12].

3.2 One Harmonic Oscillator With Perturbation

The perturbed harmonic oscillator and its time propagation will be the foundation on which our Mori-Zwanzig formalism is based. Later in this paper we will take a perturbed quantum system, attempt to project out a random mixed state, and then calculate the time derivative from the Mori-Zwanzig formalism. To do this, however, we will first outline how the perturbed wave function propagates in time using a more well known method. A system of weakly coupled, perturbed harmonic oscillators is examined to demonstrate how the second order perturbed wave function can be found on a system that is directly coupled to its neighbor states. After determining the time evolution of the perturbed wave function using perturbation theory we will calculate the time evolution of the perturbed wave function by applying the Hamiltonian to the wave function two times, to propagate the wave function forward two time steps. We calculate the time dependent wave function in the two methods described above in order to determine which method will be best for looking at the time dependent behavior of our final system, and comparing to the Mori-Zwanzig Equation.

The particular Hamiltonian chosen for this system is:

$$H_{OP} = \begin{bmatrix} \frac{1}{2}\hbar\omega & b & 0 & 0 & 0 & \cdots \\ b & \frac{3}{2}\hbar\omega & b & 0 & 0 & \cdots \\ 0 & b & \frac{5}{2}\hbar\omega & b & 0 & \cdots \\ 0 & 0 & b & \frac{7}{2}\hbar\omega & b & \cdots \\ 0 & 0 & 0 & b & \frac{9}{2}\hbar\omega & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & b \\ 0 & 0 & 0 & \cdots & b & \frac{17}{2}\hbar\omega \end{bmatrix} \tag{3.2.1}$$

where H_{OP} is the Hamiltonian, $\hbar$ is Planck's Constant, ω is the oscillation frequency of the system, and b is a small perturbation. This particular Hamiltonian only extends to $n = 9$ because we wanted a Hamiltonian that was large enough to represent the system, but small enough that our calculations could be analyzed without "blowing up" to unmanageable proportions.

Some of the properties of this Hamiltonian are:

$$\langle n|H_{OP}|n\rangle = \left(n + \frac{1}{2}\right)\hbar\omega, \tag{3.2.2}$$

$$\langle n|H_{OP}|n+1\rangle = b, \qquad \langle n|H_{OP}|n-1\rangle = b, \tag{3.2.3}$$

$$\langle n+1|H_{OP}|n\rangle = b, \qquad \langle n-1|H_{OP}|n\rangle = b, \tag{3.2.4}$$

$$\langle n|H_{OP}|m\rangle = 0 \quad m \neq \{n,\ n+1,\ n-1\}, \tag{3.2.5}$$

$$\langle m|H_{OP}|n\rangle = 0 \quad m \neq \{n,\ n+1,\ n-1\}\,. \tag{3.2.6}$$

where $|n\rangle$ is the eigenstate of the system. $|m\rangle$ and $|n\rangle$ are energy levels. In this case the couplings between n and $n-1$ or $n+1$ represent stepping down or up an energy level. When the highest energy level $|n_{max}\rangle$ is evaluated, $\langle n_{max}+1|H_{OP}|n_{max}\rangle$ and $\langle n_{max}|H_{OP}|n_{max}+1\rangle$ are 0, not b, because an energy level n_{max+1} does not exist. Also when evaluating the lowest energy level of this system, $\langle -1|H_{OP}|0\rangle$ and $\langle 0|H_{OP}|-1\rangle$ vanish because the energy level -1 does not exist.

Here we calculate the second-order perturbed wave function and then we will take the original wave function and apply it to the Hamiltonian two times to see what advancing the wave function forward two time steps yields. In the case of a perturbed system one of the first fundamental calculations is that of the perturbed wave function. The second calculation moves the unperturbed wave function forward two time steps and is less conventional in quantum mechanics.

To calculate the second-order perturbed energy one must first calculate the perturbed energy, and the first-order perturbed wave function. Calculating the perturbed energy starts with the general formulation[2]:

$$E'_n = E_n + \langle n|v|n\rangle + \sum_{m=0}^{\infty} \frac{|\langle n|v|m\rangle|^2}{E_n - E_m}, \tag{3.2.7}$$

where E'_n is the energy of the perturbed system, E_n is the energy associated with level n, E_m is associated with level m, and v is the perturbation, b, in our system. From the Hamiltonian, H_{OP}, we know that only the directly off diagonal terms have energy values so in general we can say that

$$\sum_{m=0}^{\infty} \frac{|\langle n|v|m\rangle|^2}{E_n - E_m} = \frac{|\langle n|v|n-1\rangle|^2}{E_n - E_{n-1}} + \frac{|\langle n|v|n+1\rangle|^2}{E_n - E_{n+1}} \tag{3.2.8}$$

The unperturbed energies are calculated as

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \tag{3.2.9}$$

$$E_{n-1} = \left(n - \frac{1}{2}\right)\hbar\omega, \tag{3.2.10}$$

$$E_{n+1} = \left(n + \frac{3}{2}\right)\hbar\omega, \tag{3.2.11}$$

We also know from our Hamiltonian matrix

$$\langle n|v|n\rangle = 0, \tag{3.2.12}$$

because the perturbation does not affect the diagonal terms of H_{OP}. Using (3.2.9), (3.2.10), and (3.2.11), when $n \neq \{0, n_{max}\}$ we find

$$\sum_{m=0}^{\infty} \frac{|\langle n|v|m\rangle|^2}{E_n - E_m} = \frac{b^2}{\hbar\omega} - \frac{b^2}{\hbar\omega} = 0. \tag{3.2.13}$$

When $n = 0$, E' does not vanish because $|n-1\rangle$ does not exist. For $n = 0$, (3.2.8) is evaluated as

$$\sum_{m=0}^{\infty} \frac{|\langle 0|v|m\rangle|^2}{E_n - E_m} = 0 - \frac{|\langle 0|v|1\rangle|^2}{E_0 - E_1}, \tag{3.2.14}$$

which becomes

$$\sum_{m=0}^{\infty} \frac{|\langle 0|v|m\rangle|^2}{E_n - E_m} = -\frac{b^2}{\hbar\omega}. \tag{3.2.15}$$

If n is the maximum state $\sum_{m=0}^{\infty} \frac{|\langle n_{max}|\nu|m\rangle|^2}{E_n - E_m} = \frac{b^2}{\hbar\omega}$. Looking back to (3.2.7) and using the calculated properties from (3.2.12), (3.2.13), and (3.2.16) the total perturbed energy is

$$E_n = \begin{cases} \frac{\hbar\omega}{2} - \frac{b^2}{\hbar\omega} & n = 0 \\ \left(n + \frac{1}{2}\right)\hbar\omega & n \neq \{0, n_{max}\} \\ \left(n_{max} + \frac{1}{2}\right)\hbar\omega + \frac{b^2}{\hbar\omega} & n = n_{max} \end{cases}.$$

Now that we have calculated the first-order perturbed energy we calculate the first-order perturbed wave function. The first-order perturbed wave function[2] is

$$|\Psi_{1^{st}\ order}\rangle = |\Psi^{(0)}\rangle + |\Psi^{(1)}\rangle, \tag{3.2.16}$$

where $|\Psi(t)\rangle$ represents the wave function and $|\Psi^{(n)}\rangle$ represents the change in the wave function at the n^{th} time cycle (i.e. $|\Psi^{(1)}\rangle$: first-order, $|\Psi^{(2)}\rangle$: second-order, etc.) more specifically[2]

$$|\Psi_{1^{st}\ order}\rangle = |n\rangle + \sum_{m \neq n} |m\rangle \frac{\langle m|v|n\rangle}{E_n - E_m}. \tag{3.2.17}$$

Using (3.2.17) and the energy values found in (3.2.9)-(3.2.11), we find for the perturbed wave function

$$|\Psi_{1^{st}\ order}\rangle = \begin{cases} |0\rangle - \frac{b}{\hbar\omega}|1\rangle & n = 0 \\ |n\rangle + \frac{b}{\hbar\omega}\left(|n-1\rangle - |n+1\rangle\right) & n \neq 0 \\ |n_{max}\rangle + \frac{b}{\hbar\omega}|n_{max} - 1\rangle & n = n_{max} \end{cases}.$$

The second-order perturbed wave function [1]

$$|\Psi_{2^{nd}\ order}\rangle = |\Psi^{(0)}\rangle + |\Psi^{(1)}\rangle + |\Psi^{(2)}\rangle \tag{3.2.18}$$

To simplify the calculation, $|\Psi^{(2)}\rangle$ is calculated first and then incorporated into $|\Psi\rangle$. The expression used for calculating $|\Psi^{(2)}\rangle$ is

$$|\Psi^{(2)}\rangle = \sum_{l \neq n} \left[\sum_{k \neq n} \frac{\langle l|v|k\rangle\langle k|v|n\rangle}{(E_n - E_l)(E_n - E_k)} - \frac{\langle n|v|n\rangle\langle l|v|n\rangle}{(E_n - E_l)^2} \right] |l\rangle - \frac{1}{2} \sum_{k \neq n} \frac{|\langle k|v|n\rangle|^2}{(E_n - E_k)} |n\rangle. \tag{3.2.19}$$

where k labels the energy levels[1]. Using (3.2.12) we eliminated the second term of (3.2.19), leading to

$$|\Psi^{(2)}\rangle = \sum_{l\neq n}\sum_{k\neq n}\frac{\langle l|v|k\rangle\langle k|v|n\rangle}{(E_n-E_l)(E_n-E_k)}|l\rangle - \frac{1}{2}\sum_{k\neq n}\frac{|\langle k|v|n\rangle|^2}{(E_n-E_k)}|n\rangle. \tag{3.2.20}$$

In the first term on the right hand side of (3.2.20), k can only be $k=\{n-1,n+1\}$ for $\langle k|v|n\rangle \neq 0$. Using the limitations for k, l also is restricted to $l=\{n-2,n+2\}$. Evaluating the energies for each value of n,k, and m the associated energies are

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega, \tag{3.2.21}$$

$$E_{n-1} = \left(n-\frac{1}{2}\right)\hbar\omega, \tag{3.2.22}$$

$$E_{n+1} = \left(n+\frac{3}{2}\right)\hbar\omega, \tag{3.2.23}$$

$$E_{n-2} = \left(n-\frac{3}{2}\right)\hbar\omega, \tag{3.2.24}$$

$$E_{n+2} = \left(n+\frac{5}{2}\right)\hbar\omega. \tag{3.2.25}$$

To calculate $|\Psi^{(2)}\rangle$ we use the properties of our Hamiltonian, shown above, to eliminate terms in which k and m are not n, $n-1$, $n+1$, $n-2$, and $n+2$. Applying equation (3.2.20) and the above rules for k and m

$$\begin{aligned}|\Psi^{(2)}\rangle &= \frac{\langle n-2|v|n-1\rangle\langle n-1|v|n\rangle}{(\hbar\omega)^2}|n-2\rangle + \frac{\langle n+2|v|n+1\rangle\langle n+1|v|n\rangle}{(\hbar\omega)^2}|n+2\rangle - \\ &- \frac{1}{2}\left[\frac{|\langle n-1|v|n\rangle|^2}{(\hbar\omega)^2}+\frac{|\langle n+1|v|n\rangle|^2}{(\hbar\omega)^2}\right]|n\rangle.\end{aligned} \tag{3.2.26}$$

Using the energies calculated in (3.2.21)-(3.2.25), we replace the off-diagonal expectation values with b such that

$$|\Psi^{(2)}\rangle = \frac{b^2}{(\hbar\omega)^2}\left[|n-2\rangle + |n+2\rangle - |n\rangle\right]. \tag{3.2.27}$$

As before there are four special cases. Since there is no value for $|n-2\rangle$ or $|n-1\rangle$, when $n=0$

$$|\Psi_{n=0\ 2^{nd}\ order}\rangle = \left(1-\frac{b^2}{(\hbar\omega)^2}\right)|0\rangle + \frac{b^2}{(\hbar\omega)^2}|2\rangle. \tag{3.2.28}$$

When $n=1$, there is no value for $|n-2\rangle$ and

$$|\Psi_{n=1\ 2^{nd}\ order}\rangle = \frac{b}{\hbar\omega}|0\rangle + \left(1-\frac{b^2}{(\hbar\omega)^2}\right)|1\rangle - \frac{b}{\hbar\omega}|2\rangle + \frac{b^2}{(\hbar\omega)^2}|3\rangle. \tag{3.2.29}$$

On the other end of the energy spectrum, when $n = n_{max} - 1$ there is no eigenstate for $n = n + 2$

$$|\Psi_{n=n_{max}-1\ 2^{nd}\ order}\rangle = \left(1 - \frac{b^2}{(\hbar\omega)^2}\right)|n_{max} - 1\rangle + \frac{b}{\hbar\omega}\left(|n_{max} - 2\rangle - |n_{max}\rangle\right) + \frac{b^2}{(\hbar\omega)^2}|n_{max} - 3\rangle. \tag{3.2.30}$$

Our last special case is when $n = n_{max}$. In this case there is no eigenstate for $n = n+2$ and $n = n+1$ so $|\Psi_{n=n_{max}\ 2^{nd}\ order}\rangle$ is

$$|\Psi_{n=n_{max}\ 2^{nd}\ order}\rangle = \left(1 - \frac{b^2}{(\hbar\omega)^2}\right)|n_{max}\rangle + \frac{b}{\hbar\omega}|n_{max} - 1\rangle + \frac{b^2}{(\hbar\omega)^2}|n_{max} - 2\rangle. \tag{3.2.31}$$

Inserting (3.2.27) and (3.2.28)-(3.2.31) back into (3.2.26) the second-order perturbed wave function becomes

$$|\Psi_{2^{nd}\ order}\rangle = \begin{cases} \left(1 - \frac{b^2}{(\hbar\omega)^2}\right)|0\rangle - \frac{b}{\hbar\omega}|1\rangle + \frac{b^2}{(\hbar\omega)^2}|2\rangle & n = 0 \\ \frac{b}{\hbar\omega}|0\rangle + \left(1 - \frac{b^2}{(\hbar\omega)^2}\right)|1\rangle - \frac{b}{\hbar\omega}|2\rangle + \frac{b^2}{(\hbar\omega)^2}|3\rangle & n = 1 \\ \left(1 - \frac{b^2}{(\hbar\omega)^2}\right)|n\rangle + \frac{b}{\hbar\omega}\left(|n-1\rangle - |n+1\rangle\right) + \frac{b^2}{(\hbar\omega)^2}\left(|n-2\rangle + |n+2\rangle\right) & n \neq \{0, 1, n_{max} - 1, n_{max}\} \\ \left(1 - \frac{b^2}{(\hbar\omega)^2}\right)|n_{max} - 1\rangle + \frac{b}{\hbar\omega}\left(|n_{max} - 2\rangle - |n_{max}\rangle\right) + \frac{b^2}{(\hbar\omega)^2}|n_{max} - 3\rangle & n = n_{max} - 1 \\ \left(1 - \frac{b^2}{(\hbar\omega)^2}\right)|n_{max}\rangle + \frac{b}{\hbar\omega}|n_{max} - 1\rangle + \frac{b^2}{(\hbar\omega)^2}|n_{max} - 2\rangle & n = n_{max} \end{cases}. \tag{3.2.32}$$

The most interesting part of this calculation is that using the same small perturbation for each off diagonal matrix element causes the perturbed energy to be the same as the unperturbed energy with the exception of the first and last state of the system.

Now that the time independent perturbed wave function has been calculated, we evaluate the time dependent perturbed wave function using the form from[3]

$$|\Psi(t)\rangle = \sum_{n=0}^{\infty} c_n |\Psi_n\rangle \exp\left(-\frac{iE_n t}{\hbar}\right). \tag{3.2.33}$$

Here $|\Psi(t)\rangle$ must be evaluated for five distinct cases: $n = 0$, $n = 1$, $n \neq \{0, 1, n_{max} - 1, n_{max}\}$, $n_{max} - 1$, and n_{max}. We will start with the case where $n = 0$.

$$|\Psi_{2^{nd}\ order}\rangle = \left(1 - \frac{b^2}{(\hbar\omega)^2}\right)|0\rangle - \frac{b}{\hbar\omega}|1\rangle + \frac{b^2}{(\hbar\omega)^2}|2\rangle \tag{3.2.34}$$

The perturbed energies for the coupled harmonic oscillator are

$$E_0 = \frac{1}{2}\hbar\omega - \left(\frac{b}{\hbar\omega}\right)^2 \tag{3.2.35}$$

Using the energy from (3.2.35)we calculated the time dependent wave function

$$|\Psi(t)_{2^{nd}\ order\ n=0}\rangle = \left[\left(1-\left(\frac{b}{\hbar\omega}\right)^2\right)|0\rangle - \frac{b}{\hbar\omega}|1\rangle + \left(\frac{b}{\hbar\omega}\right)^2|2\rangle\right]\exp\left(-\frac{it}{\hbar}\left(\frac{\hbar\omega}{2}-\frac{b^2}{\hbar\omega}\right)\right) \tag{3.2.36}$$

To calculate the $n = 1$ case we will use the same procedure as for the $n = 0$ case.

$$|\Psi_{2^{nd}\ order\ n=1}\rangle = \frac{b}{\hbar\omega}|0\rangle + \left(1-\frac{b^2}{(\hbar\omega)^2}\right)|1\rangle - \frac{b}{\hbar\omega}|2\rangle + \frac{b^2}{(\hbar\omega)^2}|3\rangle \tag{3.2.37}$$

The perturbed energies for this wave function are

$$E_1 = \frac{3}{2}\hbar\omega \tag{3.2.38}$$

Using the energy from (3.2.38)we calculated the time dependent wave function

$$|\Psi(t)_{2^{nd}\ order\ n=1}\rangle = \left[\frac{b}{\hbar\omega}|0\rangle + \left(1-\frac{b^2}{(\hbar\omega)^2}\right)|1\rangle - \frac{b}{\hbar\omega}|2\rangle + \left(\frac{b}{\hbar\omega}\right)^2|3\rangle\right]\exp\left(-\frac{3it\omega}{2}\right) \tag{3.2.39}$$

In general the time dependent wave function is

$$\begin{aligned}|\Psi(t)_{2^{nd}\ order}\rangle &= \left[\left(1-\frac{b^2}{(\hbar\omega)^2}\right)|n\rangle\frac{b}{\hbar\omega}\left(|n-1\rangle - |n+1\rangle\right) + \right.\\ &+ \left.\frac{b^2}{(\hbar\omega)^2}\left(|n-2\rangle + \exp\left(-\frac{iE'_{n+2}t}{\hbar}\right)|n+2\rangle\right)\right]\exp\left(-\frac{iE'_n t}{\hbar}\right)\end{aligned} \tag{3.2.40}$$

Remembering that $|n+2\rangle$ does not exist when $n = n_{max}-1$, to calculate the value of the second-order wave function one must amend (3.2.40) such that all terms with $n+2$ are eliminated.

$$\begin{aligned}|\Psi(t)_{2^{nd}\ order\ n_{max}-1}\rangle &= \left[\left(1-\frac{b^2}{(\hbar\omega)^2}\right)|n_{max}-1\rangle + \frac{b}{\hbar\omega}\left(|n_{max}-2\rangle - |n_{max}\rangle\right) + \right.\\ &+ \left.\frac{b^2}{(\hbar\omega)^2}|n_{max}-3\rangle\right]\exp\left(-\frac{iE'_{n_{max}-1}t}{\hbar}\right)\end{aligned} \tag{3.2.41}$$

Similarly to (3.2.41) above $n+2$ and $n+1$ do not exist when $n = n_{max}$ so (3.2.40) then becomes

$$|\Psi(t)_{2^{nd}\ order\ n=n_{max}}\rangle = \left[\left(1-\frac{b^2}{(\hbar\omega)^2}\right)|n_{max}\rangle + \frac{b}{\hbar\omega}|n_{max}-1\rangle + \frac{b^2}{(\hbar\omega)^2}|n_{max}-2\rangle\right]\exp\left(-\frac{iE'_{n_{max}}t}{\hbar}\right) \tag{3.2.42}$$

Using (3.2.33), (3.2.39), (3.2.40), (3.2.41), and (3.2.42) we constructed the time dependent wave function

$$|\Psi(t)_{2^{nd}\ order}\rangle = \begin{cases} \left[\left(1-\left(\frac{b}{\hbar\omega}\right)^2\right)|0\rangle - \frac{b}{\hbar\omega}|1\rangle + \left(\frac{b}{\hbar\omega}\right)^2|2\rangle\right]\exp\left(-\frac{it}{\hbar}\left(\frac{\hbar\omega}{2}-\frac{b^2}{\hbar\omega}\right)\right) & n=0 \\ \left[\frac{b}{\hbar\omega}|0\rangle + \left(1-\frac{b^2}{(\hbar\omega)^2}\right)|1\rangle - \frac{b}{\hbar\omega}|2\rangle + \left(\frac{b}{\hbar\omega}\right)^2|3\rangle\right]\exp\left(-\frac{3it\omega}{2}\right) & n=1 \\ \left[\left(1-\frac{b^2}{(\hbar\omega)^2}\right)|n\rangle\frac{b}{\hbar\omega}\left(|n-1\rangle - |n+1\rangle\right) + \right. & \\ \left. + \frac{b^2}{(\hbar\omega)^2}\left(|n-2\rangle + \exp\left(-\frac{iE'_{n+2}t}{\hbar}\right)|n+2\rangle\right)\right]\exp\left(-\frac{iE'_n t}{\hbar}\right) & n\neq\{0,1,n_{max}-1,n_{max}\} \\ \left[\left(1-\frac{b^2}{(\hbar\omega)^2}\right)|n_{max}-1\rangle + \frac{b}{\hbar\omega}\left(|n_{max}-2\rangle - |n_{max}\rangle\right) + \right. & \\ \left. + \frac{b^2}{(\hbar\omega)^2}|n_{max}-3\rangle\right]\exp\left(-\frac{iE'_{n_{max}-1}t}{\hbar}\right) & n=n_{max}-1 \\ \left[\left(1-\frac{b^2}{(\hbar\omega)^2}\right)|n_{max}\rangle + \frac{b}{\hbar\omega}|n_{max}-1\rangle + \right. & \\ \left. + \frac{b^2}{(\hbar\omega)^2}|n_{max}-2\rangle\right]\exp\left(-\frac{iE'_{n_{max}}t}{\hbar}\right) & n=n_{max} \end{cases} \tag{3.2.43}$$

Now that the perturbed wave function has been found, it is useful to expand the original time independent wave function to be able to more quickly see the trends that depend upon n or the energy level of the system. Initially we had expanded this wave function, replacing $\exp(-\frac{iE_n t}{\hbar})$ with its Taylor series, to see if this calculated form of the wave function will be comparable to the above calculation and then iteratively applying the Hamiltonian to the wave function. This particular calculation turned out to be different from our iterative calculation. The reason will be explained later in the paper. Using Mathematica to expand (3.2.40) we see that $|\Psi(t)_{expanded}\rangle$ becomes

$$
\begin{aligned}
|\Psi(t)_{expanded}\rangle \quad = \quad & \left(\frac{b}{\hbar\omega}\right)^2\left[1+it\omega\left(\frac{3}{2}-n\right)-\frac{t^2\omega^2}{2}\left(\frac{3}{2}-n\right)^2\right]|n-2\rangle+ \\
& +\frac{b}{\hbar\omega}\left[1+it\omega\left(\frac{1}{2}-n\right)-\frac{t^2\omega^2}{2}\left(\frac{1}{2}-n\right)^2\right]|n-1\rangle+ \\
& +\left[1-\left(\frac{b}{\hbar\omega}\right)^2\right]\left[1-it\omega\left(\frac{1}{2}+n\right)+\frac{t^2\omega^2}{2}\left(\frac{1}{2}+n\right)^2\right]|n\rangle+ \\
& +\frac{b}{\hbar\omega}\left[1+it\omega\left(\frac{3}{2}+n\right)-\frac{t^2\omega^2}{2}\left(\frac{3}{2}+n\right)^2\right]|n+1\rangle+ \\
& +\left(\frac{b}{\hbar\omega}\right)^2\left[it\omega\left(\frac{5}{2}+n\right)-\frac{t^2\omega^2}{2}\left(\frac{5}{2}+n\right)^2-1\right]|n+2\rangle
\end{aligned}
\tag{3.2.44}
$$

It is useful to keep in mind that, there are truly 5 cases for the wave function, $n = 0$, $n = 1$, $n \neq \{0, 1, n_{max} - 1, n_{max}\}$, $n = n_{max} - 1$, and $n = n_{max}$ and each has to be evaluated slightly differently.

We may evaluate the perturbed system in the numerical way described above, by taking the calculated perturbed wave function $|\Psi(t)\rangle$ and advancing it forward two time steps, by iteratively applying the Hamiltonian to $|\Psi(t)\rangle$. In this case we see that the first iterated wave function is

$$
|\Psi_{1\ iteration}\rangle = \left[|\Psi^{(0)}\rangle + \left(\frac{iH}{\hbar}\right)|\Psi^{0}\rangle\right]\Delta t \tag{3.2.45}
$$

where $|\Psi^{'}\rangle$ is the wave function that will be iterated against the Hamiltonian and Δt is one time step for the wave function. The second perturbation is

$$
|\Psi_{2\ iterations}\rangle = \left[|\Psi^{(0)}\rangle + \left(\frac{iH}{\hbar}\right)|\Psi^{(0)}\rangle - \frac{H^2}{\hbar^2}|\Psi^{(0)}\rangle\Delta t\right]\Delta t \tag{3.2.46}
$$

The successive perturbed wave functions were calculated use Mathematica. The first perturbation was calculated in parts, first calculating only $H|\Psi^{(0)}\rangle$ and then adding it to the initial wave function. Applying the Hamiltonian to the iterated wave function

$$
|\Psi_{1\ iteration}\rangle = \begin{bmatrix}
\frac{1}{2}\hbar\omega & b & 0 & 0 & 0 & \cdots \\
b & \frac{3}{2}\hbar\omega & b & 0 & 0 & \cdots \\
0 & b & \frac{5}{2}\hbar\omega & b & 0 & \cdots \\
0 & 0 & b & \frac{7}{2}\hbar\omega & b & \cdots \\
0 & 0 & 0 & b & \frac{9}{2}\hbar\omega & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots
\end{bmatrix}\begin{bmatrix} 0 \\ 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{bmatrix} \tag{3.2.47}
$$

The result in general is

$$|\Psi_{1\ iteration}\rangle = \frac{i\Delta tb}{\hbar}|n-1\rangle + \left[\frac{1}{\hbar} + i\Delta t\omega\left(n+\frac{1}{2}\right)\right]|n\rangle + \frac{i\Delta tb}{\hbar}|n+1\rangle \tag{3.2.48}$$

Again there are two special cases, $n = 0$ and $n = n_{max}$

$$|\Psi_{1\ iteration}\rangle = \begin{cases} \left(\frac{i\Delta t\omega}{2}+1\right)|0\rangle + \frac{i\Delta tb}{\hbar}|1\rangle & n=0 \\ \frac{i\Delta tb}{\hbar}|n-1\rangle + \left[\frac{1}{\hbar} + i\Delta t\omega\left(n+\frac{1}{2}\right)\right]|n\rangle + \frac{i\Delta tb}{\hbar}|n+1\rangle & n\neq 0 \\ \frac{i\Delta tb}{\hbar}|n_{max}-1\rangle + \left[\frac{1}{\hbar} + i\Delta t\omega\left(n_{max}+\frac{1}{2}\right)\right]|n_{max}\rangle & n=n_{max} \end{cases} \tag{3.2.49}$$

For the second perturbation

$$|\Psi_{2\ iterations}\rangle = \left[|\Psi^{(0)}\rangle + \left(\frac{iH}{\hbar}\right)|\Psi^{(0)}\rangle - \frac{H^2}{\hbar^2}|\Psi^{(0)}\rangle\Delta t\right]\Delta t \tag{3.2.50}$$

Using matrix multiplication as above it is possible to calculate the last portion of the perturbation $H^2|\Psi^{(0)}\rangle$

$$|\Psi_{2\ iterations}\rangle = \begin{bmatrix} \frac{(\hbar\omega)^2}{4}+b^2 & 2\hbar\omega b & b^2 & 0 & \cdots \\ 2\hbar\omega b & 2b^2+\frac{9(\hbar\omega)^2}{4} & 4\hbar\omega b & b^2 & \cdots \\ b^2 & 4\hbar\omega b & 2b^2+\frac{25(\hbar\omega)^2}{4} & 6\hbar\omega b & \cdots \\ 0 & b^2 & 6\hbar\omega b & 2b^2+\frac{49(\hbar\omega)^2}{4} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \\ \cdots & b^2 & 2n\hbar\omega b & 2b^2+\left[\left(n+\frac{1}{2}\right)\hbar\omega\right]^2 & (2n+2)\,\hbar\omega b \end{bmatrix}\begin{bmatrix} 0 \\ \vdots \\ 0 \\ 1 \\ \vdots \\ 0 \end{bmatrix} \tag{3.2.51}$$

$$\begin{aligned} |\Psi_{2\ iterations}\rangle &= -(\Delta t)^2\left(b^2|n-2\rangle + (n-1)\,b\hbar\omega|n-1\rangle + \left(2b^2+\left(\left(n+\frac{1}{2}\right)\hbar\omega\right)^2\right)|n\rangle + \right. \\ &+ \left.(n+1)\,b\hbar\omega|n+1\rangle + b^2|n+2\rangle\right) \end{aligned} \tag{3.2.52}$$

Using (3.2.52) to replace $\left(\frac{i\Delta t}{\hbar}H\right)^2|\Psi^{(0)}\rangle$ (3.2.50) becomes

$$\begin{aligned} |\Psi_{2\ iterations}\rangle &= -\left(\frac{\Delta tb}{\hbar}\right)^2(|n-2\rangle + |n+2\rangle) + \frac{i\Delta tb - (\Delta t)^2 b\omega\,(n-1)}{\hbar}|n-1\rangle + \\ &+ \left(1-\left(2b^2-\left(n+\frac{1}{2}\right)\hbar\omega\right)^2\left(\frac{\Delta t}{\hbar}\right)^2 + i\Delta t\omega\left(n+\frac{1}{2}\right)\right)|n\rangle + \\ &+ \frac{i\Delta tb - (\Delta t)^2 b\omega\,(n+1)}{\hbar}|n+1\rangle \end{aligned} \tag{3.2.53}$$

In this case we have to analyze this function for $n = 0$, $n = 1$, $n \neq \{0,1\}$, $n = n_{max} - 1$, and $n = n_{max}$ so (3.2.53) is

$$|\Psi_{2\ iterations}\rangle = \begin{cases} -\left(\frac{\Delta tb}{\hbar}\right)^2|2\rangle + \left(1 - \left(2b^2 - \frac{\hbar\omega}{2}\right)^2\left(\frac{\Delta t}{\hbar}\right)^2 + \frac{i\Delta t\omega}{2}\right)|0\rangle + \\ +\frac{i\Delta tb - (\Delta t)^2 b\omega}{\hbar}|1\rangle & n = 0 \\ \\ -\left(\frac{\Delta tb}{\hbar}\right)^2|3\rangle + \frac{i\Delta tb}{\hbar}|0\rangle + \left(1 - \left(2b^2 - \frac{3\hbar\omega}{2}\right)^2\left(\frac{\Delta t}{\hbar}\right)^2 + \frac{3i\Delta t\omega}{2}\right)|1\rangle + \\ +\frac{i\Delta tb - 2(\Delta t)^2 b\omega}{\hbar}|2\rangle & n = 1 \\ \\ -\left(\frac{\Delta tb}{\hbar}\right)^2(|n-2\rangle + |n+2\rangle) + \frac{i\Delta tb - (\Delta t)^2 b\omega(n-1)}{\hbar}|n-1\rangle + \\ +\left(1 - \left(2b^2 - \left(\left(n+\frac{1}{2}\right)\hbar\omega\right)^2\right)\left(\frac{\Delta t}{\hbar}\right)^2 + i\Delta t\omega\left(n+\frac{1}{2}\right)\right)|n\rangle + \\ +\frac{i\Delta tb - (\Delta t)^2 b\omega(n+1)}{\hbar}|n+1\rangle & n \neq \{0,1\} \\ \\ -\left(\frac{\Delta tb}{\hbar}\right)^2|n-2\rangle + \frac{i\Delta tb - (\Delta t)^2 b\omega(n-1)}{\hbar}|n-1\rangle + \\ +\left(1 - \left(2b^2 - \left(\left(n+\frac{1}{2}\right)\hbar\omega\right)^2\right)\left(\frac{\Delta t}{\hbar}\right)^2 + i\Delta t\omega\left(n+\frac{1}{2}\right)\right)|n\rangle + \\ +\frac{i\Delta tb - (\Delta t)^2 b\omega(n+1)}{\hbar}|n+1\rangle & n = n_{max} - 1 \\ \\ -\left(\frac{\Delta tb}{\hbar}\right)^2|n_{max}-2\rangle + \frac{i\Delta tb - (\Delta t)^2 b\omega(n_{max}-1)}{\hbar}|n_{max}-1\rangle + \\ +\left(1 - \left(2b^2 - \left(\left(n_{max}+\frac{1}{2}\right)\hbar\omega\right)^2\right)\left(\frac{\Delta t}{\hbar}\right)^2 + i\Delta t\omega\left(n_{max}+\frac{1}{2}\right)\right)|n_{max}\rangle & n = n_{max} \end{cases} \tag{3.2.54}$$

Comparing $|\Psi(t)\rangle$ and $|\Psi_{2\ itterations}\rangle$ it becomes clear that our hypothesis that they should be the same or similar is completely incorrect. The reason that these two wave functions are completely different is $|\Psi(t)\rangle$ is calculated based on the perturbation both of the system and the total energy of each level while the iterated version of the wave function is calculated based on the initial state $|n\rangle$ propagated forward in time two steps using the Hamilonian. Each of these calculations turned out to be very useful, though.

The first wave function calculated showed that with a weakly coupled system that only has a measurable perturbation on the immediate off diagonal elements of the Hamiltonian, will only perturb the lowest energy level. All of the other energy levels have been left untouched. Also in calculating the second-order perturbed wave function we see that the wave will spread out over the other energy levels of the system if given enough time and perturbation to do so. In this case we have only calculated the second-order perturbation and the wave function has spread out to the two nearest energy levels on each side of $|n\rangle$; $|n-2\rangle$, $|n-1\rangle$, $|n+1\rangle$, and $|n+2\rangle$. This "leaking" of the wave function shows that when $|\Psi(t)\rangle$ is perturbed even an extremely small amount the wave

function is still noticeably affected. For our particular calculation we decided to use the original wave function as opposed to the calculated perturbed wave function.

The second calculation shows a wave propagated forward two time steps. This calculation revealed what would happen to our original wave function if we were to push it forward in time. We see that in this case as well as in the first case a wave function slowly spreads out over an energy level. After two time steps we are, as in the first calculation, spread out to the two nearest energy levels on each side of $|n\rangle$. For our particular calculation we decided that this calculation would be a more appropriate representation of the wave function since it preserves the wave function but also shows us what happens at later times.

3.3 Two Coupled Spins

We now look at the case where the wave function is initially only a single basis vector. We use $|\phi_1\rangle = |\uparrow\uparrow\rangle$ and $|\phi_2\rangle = |\uparrow\downarrow\rangle$, which gives us a representative sample of possible perturbed wave function behaviors. This calculation shows how a wave function disperses across its neighbor eigenstates when the first and second order perturbed wave functions are calculated.

We will use the same Hamiltonian as in section 2.3.1. The perturbed Hamiltonian is

$$H_{perturbed} = \frac{\hbar}{2}\begin{bmatrix} \omega_1+\omega_2 & b & 0 & 0 \\ b & \omega_1-\omega_2 & b & 0 \\ 0 & b & -\omega_1+\omega_2 & b \\ 0 & 0 & b & -(\omega_1+\omega_2) \end{bmatrix} \tag{3.3.1}$$

We now apply two different wave functions to our Hamiltonian. The first calculation will be made using $|\phi_1\rangle$

$$|\phi_1\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{3.3.2}$$

To calculate the first and second order perturbed wave functions we first determine the first order perturbed energy. The general form of the perturbed energy is[2] $E'_n = E_n + \langle n|\nu|n\rangle + \sum_{m\neq n}^{\infty} \frac{|\langle n|\nu|n\rangle|^2}{E_n - E_m}$. For $|\phi_1\rangle$ the only available value of m is $m = n+1$, since the $n-1$ state does not exist. The perturbed energy is found to be

$$E'_{\uparrow\uparrow} = \frac{\hbar}{2}(\omega_1+\omega_2) + \frac{b^2}{\hbar\omega_1} \tag{3.3.3}$$

Now we calculate the first and second order perturbed wave function, using the information from (3.3.3). The general form for the first order perturbed wave function is [2]

$$|\phi_{1^{st}\ order}\rangle = |n\rangle + \sum_{m\neq n} |m\rangle \frac{\langle m|\nu|n\rangle}{E_n - E_m}. \tag{3.3.4}$$

For $|\phi_1\rangle = |\uparrow\uparrow\rangle$ the first order perturbed wave function is

$$|\phi_{1\ 1^{st}\ order}\rangle = \begin{bmatrix} 1 \\ \frac{b}{\hbar\omega_1} \\ 0 \\ 0 \end{bmatrix} \tag{3.3.5}$$

The perturbed wave function the perturbation has already dispersed wave function out over two eigenstates instead of the single eigenstate it initially occupied.

We now calculate the second order perturbation. The general form is [2]

$$\begin{aligned} |\phi_{2^{nd}\ order}\rangle &= |n\rangle + \sum_{m\neq n} |m\rangle \frac{\langle m|\nu|n\rangle}{E_n - E_m} + \sum_{l\neq n} \left[\sum_{k\neq n} \frac{\langle l|\nu|k\rangle\langle k|\nu|n\rangle}{(E_n - E_m)(E_n - E_k)} - \frac{\langle n|\nu n\rangle\langle l|\nu|n\rangle}{(E_n - E_m)^2} \right] |m\rangle - \\ &- \frac{1}{2} \sum_{k\neq n} \frac{|\langle k|\nu|n\rangle|^2}{(E_n - E_k)^2} |n\rangle \end{aligned} \tag{3.3.6}$$

We have already calculated the first two terms on the right hand side of $|\phi_{2^{nd}\ order}\rangle$. We now calculate one extra set of terms to complete the second order perturbed wave function. These terms of $|\phi_{2^{nd}\ order}\rangle$ are

$$|\phi^{(2)}\rangle = \sum_{l\neq n} \left[\sum_{k\neq n} \frac{\langle l|\nu|k\rangle\langle k|\nu|n\rangle}{(E_n - E_m)(E_n - E_k)} - \frac{\langle n|\nu n\rangle\langle l|\nu|n\rangle}{(E_n - E_m)^2} \right] |m\rangle - \frac{1}{2} \sum_{k\neq n} \frac{|\langle k|\nu|n\rangle|^2}{(E_n - E_k)^2} |n\rangle \tag{3.3.7}$$

In our case the perturbation vanishes for $\langle n|\nu|n\rangle$, so the second term on the right hand side of (3.3.6) is 0.

$$|\phi_{2^{nd}\ order}\rangle = |n\rangle + \sum_{m\neq n} |m\rangle \frac{\langle m|\nu|n\rangle}{E_n - E_m} - \frac{1}{2} \sum_{k\neq n} \frac{|\langle k|\nu|n\rangle|^2}{(E_n - E_k)} |n\rangle + \sum_{m\neq n} \sum_{k\neq n} \frac{\langle m|\nu|k\rangle\langle k|\nu|n\rangle}{(E_n - E_m)(E_n - E_k)} |m\rangle \tag{3.3.8}$$

Rearranging (3.3.7)

$$|\phi_{2^{nd}\ order}\rangle = \left[1 - \frac{1}{2} \sum_{k\neq n} \frac{|\langle k|\nu|n\rangle|^2}{(E_n - E_k)} \right] |n\rangle + \sum_{m\neq n} |m\rangle \frac{\langle m|\nu|n\rangle}{E_n - E_m} + \sum_{m\neq n} \sum_{k\neq n} \frac{\langle m|\nu|k\rangle\langle k|\nu|n\rangle}{(E_n - E_m)(E_n - E_k)} |m\rangle \tag{3.3.9}$$

For $|\phi_{1\ 2^{nd}\ order}\rangle$ the second order perturbed wave function in vector form

$$|\phi_{1\ 2^{nd}\ order}\rangle = \begin{bmatrix} 1 - \frac{b^2}{2\hbar\omega_1} \\ \frac{b}{\hbar\omega_1} \\ \frac{b^2}{\hbar^2\omega_1\omega_2} \\ 0 \end{bmatrix} \tag{3.3.10}$$

Again the wave function has spread out over the neighboring eigenstates. Since this wave function started out in the first energy level it can not expand as much as function $|n\rangle$ that had eigenstates $|m\rangle$ for $m < n$, where m would be any other eigenstate.

Our of $|\phi_2\rangle$ will be much the same as the first, our initial wave function will be

$$|\phi_2\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} \tag{3.3.11}$$

The Hamiltonian used in this calculation will be the same one shown above . To calculate the first and second order perturbed wave functions we first determine the first order perturbed energy. In general this energy is represented as $E'_n = E_n + \langle n|\nu|n\rangle + \sum_{m\neq n}^{\infty} \frac{|\langle m|\nu|n\rangle|^2}{E_n - E_m}$. The non-zero values of $\langle m|\nu|n\rangle$ for $|\phi_2\rangle$ are $m = \{n-1, n+1\}$ so the perturbed energy is

$$E_{\uparrow\downarrow} = \frac{\hbar}{2}(\omega_1 - \omega_2) - \frac{b^2}{\hbar\omega_2} + \frac{b^2}{\hbar(\omega_1 - \omega_2)} \tag{3.3.12}$$

Now that we have calculated the first order perturbed energy we will calculate the first and second order perturbed wave function. To calculate the first order perturbed wave function, we use the general expression $|\phi_{1^{st}\ order}\rangle = |n\rangle + \sum_{m\neq n} |m\rangle \frac{\langle m|\nu|n\rangle}{E_n - E_m}$. The first order perturbed wave function for $|\phi_2\rangle$ is

$$|\phi_{2\ 1^{st}\ order}\rangle = \begin{bmatrix} \frac{b}{\hbar(\omega_1 - \omega_2)} \\ 1 \\ -\frac{b}{\hbar\omega_2} \\ 0 \end{bmatrix} \tag{3.3.13}$$

Here we see that the wave function spreads out over its two nearest neighbor eigenstates, in contrast to $|\phi_{1\ 1^{st}\ order}\rangle$ which only had one nearest neighbor eigen state to disperse over.

The second order perturbed wave function has as its general form

$$\begin{aligned}|\phi_{2^{nd}\ order}\rangle &= |n\rangle + \sum_{m\neq n}|m\rangle\frac{\langle m|\nu|n\rangle}{E_n - E_m} + \sum_{l\neq n}\left[\sum_{k\neq n}\frac{\langle l|\nu|k\rangle\langle k|\nu|n\rangle}{(E_n - E_m)(E_n - E_k)} - \frac{\langle n|\nu n\rangle\langle l|\nu|n\rangle}{(E_n - E_m)^2}\right]|m\rangle - \\ &- \frac{1}{2}\sum_{k\neq n}\frac{|\langle k|\nu|n\rangle|^2}{(E_n - E_k)^2}|n\rangle\end{aligned} \tag{3.3.14}$$

For $|\phi_{2\ 2^{nd}\ order}(t)\rangle$

$$|\phi_{2\ 2^{nd}\ order}\rangle = \begin{bmatrix} \frac{b}{\hbar(\omega_1-\omega_2)} \\ 1 - \frac{b^2(\omega_1-2\omega_1\omega_2)}{\hbar\omega_2^2(\omega_1-\omega_2)^2} \\ -\frac{b}{\hbar\omega_2} \\ -\frac{b^2}{\hbar^2\omega_1\omega_2} \end{bmatrix} \exp\left(-\frac{it}{\hbar}\left(\frac{\hbar}{2}(\omega_1-\omega_2) - \frac{b^2}{\hbar\omega_2} + \frac{b^2}{\hbar(\omega_1-\omega_2)}\right)\right) \tag{3.3.15}$$

which has spread over all of the available basis states.

3.4 The Thermal Average in Classical and Quantum Mechanics

In this section we would like consider an example of the projection operator acts on the mechanical variable F. The model system is a Brownian particle in a sea of other particles. The Brownian particle feels a force from all other particles of the system. We will project with respect to the operator p_k

$$p_k = \sum_{i=1}^{N}\exp\left(i\vec{k}\cdot\vec{r}_{1i}\right), \tag{3.4.1}$$

where $\vec{k}$ is a constant $\vec{r}_{1i}$ is the vector from the Brownian particle to each of the other particles. The projection operator with respect to p_k is [12]

$$P_{p_k} = \frac{\langle p_k^*,\ \ \rangle}{\langle p_k^*, p_k\rangle}p_k. \tag{3.4.2}$$

The force on a Brownian particle is

$$F = \sum_j -\frac{\partial}{\partial r_j}U_{ij}, \tag{3.4.3}$$

where F is the total force and U_{1j} is the energy of the pair of particles $(1, j)$. The function we would like to examine is $P_{p_k}F$ [12]

$$P_{p_k}F = \frac{\langle p_k^*, F\rangle}{\langle p_k^*, p_k\rangle}p_k. \tag{3.4.4}$$

Working from this expression, we convert this thermal average into a set of integrals to determine the value of $P_{p_k}F$. The thermal average in integral form is [12]

$$P_{p_k}F = \left[\frac{\int d\Gamma\ p_k^* F \exp\left(-\beta\sum_j U_{ij}\right)}{\int d\Gamma\ p_k^* p_k \exp\left(-\beta U\right)}\right] p_k. \tag{3.4.5}$$

where $d\Gamma$ is the integral over phase space, and $\exp\left(-\beta\sum_j U_{1j}\right)$ is the last component of the thermal average in a statistical mechanical system where β is a constant and $\sum_j U_{1j}$ is the total energy of the system, when looking at the interaction of one particle with the rest of the system. Inserting (3.4.1) and (3.4.3) into (3.4.5)

$$P_{p_k}F = \left[\frac{\int d\mathbf{r}^N\ \sum_{i=1}^N \exp\left(-i\vec{k}\cdot\vec{r}_{1i}\right)\left(\sum_j -\frac{\partial}{\partial r}U_{1j}\right)\exp\left(-\beta\sum_j U_{ij}\right)}{\int d\mathbf{r}^N\ \sum_{i=1}^N \exp\left(-i\vec{k}\cdot\vec{r}_{1i}\right)\sum_{j=1}^N \exp\left(i\vec{k}\cdot\vec{r}_{1j}\right)\exp\left(-\beta\sum_j U_{1j}\right)}\right]\sum_{i=1}^N \exp\left(i\vec{k}\cdot\vec{r}_{1i}\right). \tag{3.4.6}$$

Simplifying,

$$P_{p_k}F = \left[\frac{\int d\mathbf{r}^N\ \sum_{i=1}^N \exp\left(-i\vec{k}\cdot\vec{r}_{1i}\right)\left(\sum_j -\frac{\partial}{\partial r_j}U_{1j}\right)\exp\left(-\beta\sum_j U_{ij}\right)}{\int d\mathbf{r}^N\ \sum_{i,j=1} \exp\left(ik\left(r_{1j}-r_{1i}\right)\right)\exp\left(-\beta\sum_j U_{ij}\right)}\right]\sum_{i=1}^N \exp\left(i\vec{k}\cdot\vec{r}_{1i}\right). \tag{3.4.7}$$

We know that each $\exp\left(-i\vec{k}\cdot\vec{r}_{1i}\right)$ is the same so the sum in (3.4.7) will be replaced by the term N. We also see that $\left(\sum_j -\frac{\partial}{\partial r_j}U_{ij}\right)\exp\left(-\beta\sum_j U_{ij}\right) = \frac{1}{\beta}\frac{\partial}{\partial r_j}\exp\left(-\beta\sum_j U_{ij}\right)$

$$P_{p_k}F = \frac{N^2}{\beta}\left[\frac{\int d\mathbf{r}^N\ \exp\left(-i\vec{k}\cdot\vec{r}_{1i}\right)\frac{\partial}{\partial r_j}\exp\left(-\beta\sum_j U_{ij}\right)}{\int d\mathbf{r}^N\ \sum_{i,j=1} \exp\left(ik\left(r_{1j}-r_{1i}\right)\right)\exp\left(-\beta\sum_j U_{ij}\right)}\right]\exp\left(i\vec{k}\cdot\vec{r}_{1i}\right). \tag{3.4.8}$$

To simplify (3.4.14) we use the method of integration by parts. In general

$$\int_a^b u(x)v'(x)\ dx = [u(x)v(x)]_a^b - \int_a^b u'(x)v(x)\ dx) \tag{3.4.9}$$

For (3.4.14)

$$u(r) = \exp\left(-i\vec{k}\cdot\vec{r}_{1i}\right) \qquad u'(r) = -i\vec{k}\exp\left(-i\vec{k}\cdot\vec{r}_{1i}\right)) \tag{3.4.10}$$

$$v(r) = \exp\left(-\beta\sum_j U_{1j}\right) \qquad v'(r) = \frac{\partial}{\partial r_j}\exp\left(-\beta\sum_j U_{1j}\right) \tag{3.4.11}$$

So our integration by parts on r_1 for (3.4.14) is

$$P_{p_k}F = \left[\frac{\left\{\left[\exp\left(-i\vec{k}\cdot\vec{r_{1i}}\right)\exp\left(-\beta\sum_j U_{ij}\right)\right]_0^\infty + i\vec{k}\int \mathbf{r}^N\ \exp\left(-\beta\sum_j U_{ij}\right)\exp\left(-i\vec{k}\cdot\vec{r_{1j}}\right)\right\}}{\int d\mathbf{r}^N\ \sum_{i,j=1} \exp\left(ik\left(r_{1j}-r_{1i}\right)\right)\exp\left(-\beta\sum_j U_{ij}\right)}\right]\exp\left(i\vec{k}\cdot\vec{r}_{1i}\right). \tag{3.4.12}$$

The term $\left[\exp\left(-i\vec{k}\cdot\vec{r_{1i}}\right)\exp\left(-\beta\sum_j U_{ij}\right)\right]_0^\infty = 0$, so

$$P_{p_k}F = \frac{i\vec{k}N^2}{\beta}\left[\frac{\int dr\ \exp\left(-\beta\sum_j U_{ij}\right)\exp\left(-i\vec{k}\cdot\vec{r_{1j}}\right)}{\int d\mathbf{r}^N\ \sum_{i,j=1}\exp\left(ik\left(r_{1j}-r_{1i}\right)\right)\exp\left(-\beta\sum_j U_{ij}\right)}\right]\exp\left(i\vec{k}\cdot\vec{r}_{1i}\right). \tag{3.4.13}$$

We can go no further until we know what U_{1j} is.

Now that we have determined how the projection operator would work on a classical system, we consider how that calculation would change if we treated a quantum system. We start with the expression (3.4.4) for the projection operator. In the case of a quantum system we must treat the projection operator slightly differently than the classical system. The projection operator takes the form $P_A = \frac{\langle A|G\rangle}{\langle A|A\rangle}A$ where A is a classical operator and $\langle\ |\ \rangle$ is the thermal average. The reason we can use this form is because we are taking the thermal average of two classical quantities so the specific order does not matter. The true form of the projection operator is $P_A = \frac{G,A^*}{A,A^*}A$ [7] which is the form we have used in (3.4.14). In a quantum system, the order of the operators matters, because we will be dealing with matrices, in matrix multiplication order holds great importance. In quantum mechanics an expectation value is taken with respect to the eigenstates involved. (3.4.4) becomes

$$P_{p_k}F = \frac{\sum_n^{all\ states}\langle n|F,p_k^*|n\rangle}{\sum_n^{all\ states}\langle n|p_k^*,p_k|n\rangle}p_k. \tag{3.4.14}$$

This is also the thermal average, so we add our extra function $\exp\left(-\beta U\right)$ and must sum over all states leading to

$$P_{p_k}F = \frac{\sum_n^{all\ states}\langle n|F,p_k^*\exp\left(-\beta\sum_j U_{1j}\right)|n\rangle}{\sum_n^{all\ states}\langle n|p_k^*,p_k\exp\left(-\beta\sum_j U_{1j}\right)|n\rangle}p_k. \tag{3.4.15}$$

Inserting (3.4.1) and (3.4.3) into (3.4.10)

$$P_{p_k}F = \frac{\sum_n^{all\ states}\langle n|\sum_{i=1}^N\exp\left(-i\vec{k}\cdot\vec{r}_{1i}\right)\left(\sum_j-\frac{\partial}{\partial r_j}U_{ij}\right)\exp\left(-\beta H\right)|n\rangle}{\sum_n^{all\ states}\langle n|p_k^*p_k\exp\left(-\beta H\right)|n\rangle}\sum_{i=1}^N\exp\left(-i\vec{k}\cdot\vec{r}_{1i}\right). \tag{3.4.16}$$

4.0 THE EFFECT OF MORI THEORY ON A QUANTUM SYSTEM

4.1 The Projection Operator On a Perturbed Quantum Harmonic Oscillator

To determine the effect of the projection operator on a perturbed quantum system we will first need to choose a perturbed Hamiltonian. To do this calculation in its most easily understood form we will choose the perturbed basis, this will make our calculation easier because we may use a diagonalize Hamiltonian instead of a tri-diagonal hamiltonian, as used in earlier sections. The Hamiltonian chosen is

$$H = \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix}. \tag{4.1.1}$$

We will to see how projecting out one of the basis states from H will affect the system. If we project out the basis state $|a\rangle$ the general projection operator is represented as

$$P_{|a\rangle}G = \frac{\langle G|a\rangle}{\langle a|a\rangle}|a\rangle, \tag{4.1.2}$$

where G is the quantity the projection operator is being applied to. In the case of a quantum system we must treat the projection operator slightly differently than the classical system. In section **3.1** the projection operator takes the form $P_A = \frac{\langle A|G\rangle}{\langle A|A\rangle}A$ where A is a classical operator and $\langle\ |\ \rangle$ is the thermal average. We express the quantities H and $|a\rangle$ as the thermal average in quantum mechanics

$$P_{|a\rangle}H = \frac{\sum_n \langle n|H|a\rangle e^{-\beta H}|n\rangle}{\sum_n \langle n|\langle a|a\rangle e^{-\beta H}|n\rangle} \otimes |a\rangle \tag{4.1.3}$$

In this case we can insert $\sum_m |m\rangle\langle m|$ into (4.1.3) and isolate the term $e^{-\beta H}$

$$P_{|a\rangle}H = \frac{\sum_n \langle n|H|a\rangle \sum_m |m\rangle\langle m|e^{-\beta H}|n\rangle}{\sum_n \langle n|\langle a|a\rangle \sum_m |m\rangle\langle m|e^{-\beta H}|n\rangle} \otimes |a\rangle, \tag{4.1.4}$$

since only the on diagonal matrix elements have value other than 0 for this system

$$P_{|a\rangle}H = \frac{\sum_n \langle n|H|a\rangle|n\rangle\langle n|e^{-\beta H}|n\rangle}{\sum_n \langle n|\langle a|a\rangle|n\rangle\langle n|e^{-\beta H}|n\rangle} \otimes |a\rangle, \tag{4.1.5}$$

so

$$P_{|a\rangle}H = \frac{\sum_n \langle n|H|a\rangle|n\rangle e^{-\beta E_n}}{\sum_n \langle n|\langle a|a\rangle|n\rangle e^{-\beta E_n}} \otimes |a\rangle, \tag{4.1.6}$$

since $|a\rangle$ and $|n\rangle$ are properly normalized $\langle a|a\rangle = 1$ and $\sum_n \langle n|n\rangle = 1$

$$P_{|a\rangle}H = \frac{\sum_n \langle n|H|a\rangle|n\rangle e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \otimes |a\rangle, \tag{4.1.7}$$

Now that we have the full expression we will make our calculation easier by expressing each term in its matrix form

$$\begin{aligned} P_{|a\rangle}H &= \tfrac{1}{e^{-\beta a}+e^{-\beta b}} \left\{ \begin{bmatrix} 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix} \cdot \begin{bmatrix} 1 \\ 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \right\} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} e^{-\beta a} + \\ &+ \tfrac{1}{e^{-\beta a}+e^{-\beta b}} \left\{ \begin{bmatrix} 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix} \cdot \begin{bmatrix} 1 \\ 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \right\} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} e^{-\beta b}. \end{aligned} \tag{4.1.8}$$

This expression can be evaluated as

$$P_{|a\rangle}H = \begin{bmatrix} \frac{ae^{-\beta a}}{e^{-\beta a}+e^{-\beta b}} & 0 \\ 0 & 0 \end{bmatrix}. \tag{4.1.9}$$

To project out the basis state $|a\rangle$ we use the expression $(1 - P_{|a\rangle})H$ so

$$\left(1 - P_{|a\rangle}\right) H = \begin{bmatrix} \frac{ae^{-\beta b}}{e^{-\beta a}+e^{-\beta b}} & 0 \\ 0 & b \end{bmatrix}. \tag{4.1.10}$$

We see that if we project a basis state out of the Hamiltonian it does not project an eigenvalue out of the system but its thermal average.

Now that we have seen that the projection operator is able to project out one state of the system in a quantum mechanical system properly we see what projecting out a random state of the system does. In this case we will choose a vector p_k for our random vector.

$$p_k = \begin{bmatrix} \alpha \\ \delta \end{bmatrix} \tag{4.1.11}$$

We perform the same calculation as above starting from scratch. We know that the general expression is

$$P_{p_k}H = \frac{\sum_n \langle n|H \cdot p_k e^{-\beta H}|n\rangle}{\sum_n \langle n|p_k^* p_k e^{-\beta H}|n\rangle} \otimes p_k. \tag{4.1.12}$$

Again we insert $\sum_m |m\rangle\langle m|$ into (4.1.12) such that

$$P_{p_k}H = \frac{\sum_n \langle n|H \cdot p_k \sum_m |m\rangle\langle m|e^{-\beta H}|n\rangle}{\sum_n \langle n|p_k^* \cdot p_k \sum_m |m\rangle\langle m|e^{-\beta H}|n\rangle} \otimes p_k. \tag{4.1.13}$$

since only the diagonal matrix elements have value other than 0 for this system

$$P_{p_k}H = \frac{\sum_n \langle n|H \cdot p_k|n\rangle}{\sum_n \langle n|p_k^* \cdot p_k|n\rangle e^{-\beta E_n}} e^{-\beta E_n} \otimes p_k. \tag{4.1.14}$$

In this case p_k and $|n\rangle$ are properly normalized

$$P_{p_k}H = \frac{\sum_n \langle n|H \cdot p_k|n\rangle}{\sum_n e^{-\beta E_n}} e^{-\beta E_n} \otimes p_k. \tag{4.1.15}$$

We can now insert our matrix representation for each of the variables in this system

$$\begin{aligned} P_{p_k}H &= \tfrac{1}{e^{-\beta a}+e^{-\beta b}} \left\{ \begin{bmatrix} 1 & 0 \end{bmatrix} \left\{ \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix} \cdot \begin{bmatrix} \alpha \\ \delta \end{bmatrix} \right\} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \right\} \otimes \begin{bmatrix} \alpha \\ \delta \end{bmatrix} e^{-\beta a} + \\ &+ \tfrac{1}{e^{-\beta a}+e^{-\beta b}} \left\{ \begin{bmatrix} 0 & 1 \end{bmatrix} \left\{ \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix} \cdot \begin{bmatrix} \alpha \\ \delta \end{bmatrix} \right\} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \right\} \otimes \begin{bmatrix} \alpha \\ \delta \end{bmatrix} e^{-\beta b} \end{aligned}, \tag{4.1.16}$$

simplifying this calculation

$$P_{p_k}H = \frac{1}{e^{-\beta a}+e^{-\beta b}} \begin{bmatrix} \alpha^2 a e^{-\beta a} & \alpha\delta a e^{-\beta a} \\ \alpha\delta b e^{-\beta b} & \delta^2 b e^{-\beta b} \end{bmatrix}. \tag{4.1.17}$$

This calculation will be used in later sections.

4.2 The Mori Projection Operator on A Quantum Mechanical System

Now that we have calculated the effect of a projection operator and thermal average on the Hamiltonian of a system we would like to use the Mori Projection Operator to look at the time evolution of a quantum system. We compare the projected and non-projected dynamics of a two level system. First we look at $\langle A| \exp\left[it\left(1-P_{p_k}\right)\frac{H}{\hbar}\right]|A\rangle$ and then we look at $\langle A| \exp\left(\frac{itH}{\hbar}\right)|A(t)\rangle$ and see how the two calculations compare. We defined the quantities P_{p_k}, H, and $|A\rangle$ in the above section. In this case

$$|A(t)\rangle = \begin{bmatrix} f \exp\left(\frac{-iat}{\hbar}\right) \\ g \exp\left(\frac{-ibt}{\hbar}\right) \end{bmatrix}. \tag{4.2.1}$$

and t will represent time.

To do the first calculation $\langle A| \exp\left[it\left(1-P_{p_k}\right)\frac{H}{\hbar}\right]|A\rangle$ we make a couple space saving replacements, $\Delta = \langle A| \exp\left[it\left(1-P_{p_k}\right)\frac{H}{\hbar}\right]|A\rangle$ and $\gamma = \exp\left[it\left(1-P_{p_k}\right)\frac{H}{\hbar}\right]$. We also need to use some properties of the e^x. We know that for an expression e^{A+B}, unless A and B do not commute, we use the replacement $e^{A+B} = e^A e^B e^{[A,B]}$ to simplify the exponential[2]. In our calculation P_{p_k} and H are not guaranteed to commute so

$$\gamma = \exp\left[\frac{it}{\hbar}H\right] \exp\left[-\frac{it}{\hbar}P_{p_k}H\right] \exp\left[-\frac{t^2}{2\hbar^2}\left(H - P_{p_k}H\right)\right], \tag{4.2.2}$$

where the commutator can be written as

$$\gamma = \exp\left[\frac{it}{\hbar}H\right] \exp\left[-\frac{it}{\hbar}P_{p_k}H\right] \exp\left[\frac{t^2}{2\hbar^2}\left(HP_{p_k}H - P_{p_k}HH\right)\right]. \tag{4.2.3}$$

We now calculate $HP_{p_k}H$ and $P_{p_k}HH$. From section **4.1** we know

$$P_{p_k}H = \frac{1}{e^{-\beta a}+e^{-\beta b}} \begin{bmatrix} \alpha^2 a e^{-\beta a} & \alpha\delta a e^{-\beta a} \\ \alpha\delta b e^{-\beta b} & \delta^2 b e^{-\beta b} \end{bmatrix}. \tag{4.2.4}$$

Using the value for $P_{p_k}H$, $HP_{p_k}H$ is

$$HP_{p_k}H = \frac{1}{e^{-\beta a}+e^{-\beta b}} \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix} \cdot \begin{bmatrix} \alpha^2 a e^{-\beta a} & \alpha\delta a e^{-\beta a} \\ \alpha\delta b e^{-\beta b} & \delta^2 b e^{-\beta b} \end{bmatrix}. \tag{4.2.5}$$

Doing the matrix multiplication,

$$HP_{p_k}H = \frac{1}{e^{-\beta a}+e^{-\beta b}} \begin{bmatrix} \alpha^2 a^2 e^{-\beta a} & \alpha\delta a^2 e^{-\beta a} \\ \alpha\delta b^2 e^{-\beta b} & \delta^2 b^2 e^{-\beta b} \end{bmatrix}. \tag{4.2.6}$$

Using the same process we calculate $P_{p_k}H_pH_p$

$$P_{p_k}HH = \frac{1}{e^{-\beta a}+e^{-\beta b}} \begin{bmatrix} \alpha^2 a e^{-\beta a} & \alpha\delta a e^{-\beta a} \\ \alpha\delta b e^{-\beta b} & \delta^2 b e^{-\beta b} \end{bmatrix} \cdot \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix}. \tag{4.2.7}$$

Doing the multiplication,

$$P_{p_k}HH = \frac{1}{e^{-\beta a}+e^{-\beta b}} \begin{bmatrix} \alpha^2 a^2 e^{-\beta a} & \alpha\delta a b e^{-\beta a} \\ \alpha\delta a b e^{-\beta b} & \delta^2 b^2 e^{-\beta b} \end{bmatrix}. \tag{4.2.8}$$

Now that we know $HP_{p_k}H$ and $P_{p_k}HH$ we can calculate $HP_{p_k}H - P_{p_k}HH$

$$HP_{p_k}H - P_{p_k}HH = \frac{(a-b)\,\alpha\delta}{e^{-\beta a}+e^{-\beta b}} \begin{bmatrix} 0 & a e^{-\beta a} \\ -b e^{-\beta b} & 0 \end{bmatrix} \tag{4.2.9}$$

(4.2.3) is found to be

$$\begin{aligned} \gamma &= \exp\left[\tfrac{it}{\hbar}\begin{pmatrix} a & 0 \\ 0 & b \end{pmatrix}\right] \exp\left[-\tfrac{it}{\hbar(e^{-\beta a}+e^{-\beta b})}\begin{pmatrix} \alpha^2 a e^{-\beta a} & \alpha\delta a e^{-\beta a} \\ \alpha\delta b e^{-\beta b} & \delta^2 b e^{-\beta b} \end{pmatrix}\right] \cdot \\ &\cdot \exp\left[\tfrac{(a-b)\alpha\delta t^2}{2\hbar^2(e^{-\beta a}+e^{-\beta b})}\begin{pmatrix} 0 & a e^{-\beta a} \\ -b e^{-\beta b} & 0 \end{pmatrix}\right] \end{aligned}. \tag{4.2.10}$$

It would be quite difficult to apply any of these operators to an arbitrary vector A so we will use the Taylor Series Expansion $e^x \approx 1 + x$, finding

$$\begin{aligned} \gamma &= \left[1 + \tfrac{it}{\hbar}\begin{pmatrix} a & 0 \\ 0 & b \end{pmatrix}\right] \left[1 - \tfrac{it}{\hbar(e^{-\beta a}+e^{-\beta b})}\begin{pmatrix} \alpha^2 a e^{-\beta a} & \alpha\delta a e^{-\beta a} \\ \alpha\delta b e^{-\beta b} & \delta^2 b e^{-\beta b} \end{pmatrix}\right] \cdot \\ &\cdot \left[1 + \tfrac{(a-b)\alpha\delta t^2}{2\hbar^2(e^{-\beta a}+e^{-\beta b})}\begin{pmatrix} 0 & a e^{-\beta a} \\ -b e^{-\beta b} & 0 \end{pmatrix}\right] \end{aligned}, \tag{4.2.11}$$

simplifying

$$\gamma = \begin{bmatrix} 1+\frac{iat}{\hbar} & 0 \\ 0 & 1+\frac{ibt}{\hbar} \end{bmatrix} \begin{bmatrix} 1-\frac{iat\alpha^2 e^{-\beta a}}{\hbar(e^{-\beta a}+e^{-\beta b})} & -\frac{iat\alpha\delta e^{-\beta a}}{\hbar(e^{-\beta a}+e^{-\beta b})} \\ -\frac{ibt\alpha\delta e^{-\beta b}}{\hbar(e^{-\beta a}+e^{-\beta b})} & 1-\frac{ibt\delta^2 e^{-\beta b}}{\hbar(e^{-\beta a}+e^{-\beta b})} \end{bmatrix} \begin{bmatrix} 1 & \frac{(a-b)a\alpha\delta t^2 e^{-\beta a}}{2\hbar^2(e^{-\beta a}+e^{-\beta b})} \\ -\frac{(a-b)b\alpha\delta t^2 e^{-\beta b}}{2\hbar^2(e^{-\beta a}+e^{-\beta b})} & 1 \end{bmatrix}, \tag{4.2.12}$$

after completing the multiplication

$$\gamma = \frac{1}{\hbar\left(e^{-\beta a}+e^{-\beta b}\right)} \begin{bmatrix} \left(\hbar+iat-iat\alpha^2\right)e^{-\beta a}+(\hbar+iat)\,e^{-\beta b} & -iat\alpha\delta e^{-\beta a} \\ -ibt\alpha\delta e^{-\beta b} & (\hbar+ibt)\,e^{-\beta a}+\left(\hbar+ibt-ibt\delta^2\right)e^{-\beta b} \end{bmatrix}. \tag{4.2.13}$$

We now continue with our calculation of $\langle A|\exp\left[it\left(1-P_{p_k}\right)\frac{H}{\hbar}\right]|A\rangle$ using the matrix representations for $|A\rangle$ and γ to write

$$\langle A|\exp\left[it\left(1-P_{p_k}\right)\frac{H}{\hbar}\right]|A\rangle = \begin{bmatrix} f & g \end{bmatrix} \begin{bmatrix} \frac{\left(\hbar+iat-iat\alpha^2\right)e^{-\beta a}+(\hbar+iat)e^{-\beta b}}{\hbar(e^{-\beta a}+e^{-\beta b})} & -\frac{iat\alpha\delta e^{-\beta a}}{\hbar(e^{-\beta a}+e^{-\beta b})} \\ -\frac{ibt\alpha\delta e^{-\beta b}}{\hbar(e^{-\beta a}+e^{-\beta b})} & \frac{(\hbar+ibt)e^{-\beta a}+\left(\hbar+ibt-ibt\delta^2\right)e^{-\beta b}}{\hbar(e^{-\beta a}+e^{-\beta b})} \end{bmatrix} \cdot \begin{bmatrix} f \\ g \end{bmatrix}, \tag{4.2.14}$$

which, after the multiplication, is

$$\begin{aligned} \langle A|\exp\left[it\left(1-P_{p_k}\right)\frac{H}{\hbar}\right]|A\rangle &= \frac{1}{\hbar\left(e^{-\beta a}+e^{-\beta b}\right)}\left\{f^2\left[\left(\hbar+iat-iat\alpha^2\right)e^{-\beta a}+(\hbar+iat)\,e^{-\beta b}\right]+\right. \\ &+ \left. g^2\left[(\hbar+ibt)\,e^{-\beta a}+\left(\hbar+ibt-ibt\delta^2\right)e^{-\beta b}\right]-it\alpha\delta fg\left[ae^{-\beta a}+be^{-\beta b}\right]\right\} \end{aligned} \tag{4.2.15}$$

Here we see that the the original amplitude is included in the formula and after applying the projection operator and projecting out some arbitrary vector p_k the amplitude is affected by the perturbation. In this case the calculation is based on the Taylor Series Approximation, so it is possible to carry this calculation out to higher orders of magnitude.

4.3 Calculating the Mori Quantities

Now that we have seen how a Mori Projection operator acts on a quantum system we calculate each of the Mori quantities looks in our system. The quantities are the normalized autocorrelation function (3.1.5), the frequency matrix (3.1.6), part of $p_k(t)$ not correlated with $p_k(0)$ (3.1.7), part of $\dot{p}_k(t)$ not correlated with $p_k(0)$ (3.1.8), and random force (3.1.23). The reason we would like to calculate these quantities is that they will be necessary when calculating the Mori Equation later on in this paper.

For this section we will be using the quantities

$$H = \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix} \qquad p_k(0) = \begin{bmatrix} \alpha \\ \delta \end{bmatrix} \tag{4.3.1}$$

$$p_k(t) = \begin{bmatrix} \alpha \exp\left(-\frac{iat}{\hbar}\right) \\ \delta \exp\left(-\frac{ibt}{\hbar}\right) \end{bmatrix} \qquad \dot{p}_k(t) = \begin{bmatrix} -\frac{ia\alpha}{\hbar} \exp\left(-\frac{iat}{\hbar}\right) \\ -\frac{ib\delta}{\hbar} \exp\left(-\frac{ibt}{\hbar}\right) \end{bmatrix} \qquad \dot{p}_k(0) = \begin{bmatrix} -\frac{i\alpha a}{\hbar} \\ -\frac{i\delta b}{\hbar} \end{bmatrix} \tag{4.3.2}$$

The first quantity, the normalized autocorrelation function, is generally represented as

$$\Xi(t) = \frac{\langle p_k^*(0) \cdot p_k(t) \rangle}{\langle p_k^*(0) \cdot p_k(0) \rangle}, \tag{4.3.3}$$

remembering, in statistical mechanics $\langle \ | \ \rangle$ is the thermal average of the system, not the typical quantum average. As discussed above the system is normalized so $\langle p_k^* \cdot (0), p_k(0) \rangle = e^{-\beta a} + e^{-\beta b}$

$$\Xi(t) = \frac{\langle p_k^*(0) \cdot p_k(t) \rangle.}{e^{-\beta a} + e^{-\beta b}} \tag{4.3.4}$$

In quantum mechanics the expression is modified slightly to represent all of the basis states and the thermal average requires the addition of an $\exp(-\beta H)$

$$\Xi(t) = \frac{\sum_n \langle n | p_k^*(0) \cdot p_k(t) \exp(-\beta H) | n \rangle}{e^{-\beta a} + e^{-\beta b}}. \tag{4.3.5}$$

As in the above sections we add $\sum_m |m\rangle\langle m|$ into the expression to isolate $\exp(-\beta H)$

$$\Xi(t) = \frac{\sum_n \sum_m \langle n | p_k^*(0) \cdot p_k(t) | m \rangle \langle m | \exp(-\beta H) | n \rangle}{e^{-\beta a} + e^{-\beta b}}, \tag{4.3.6}$$

since only the diagonal terms of the matrix have a value other than 0 we eliminate $\sum_m$ from (4.3.6)

$$\Xi(t) = \frac{\sum_n \langle n | p_k^*(0) \cdot p_k(t) | n \rangle \langle n | \exp(-\beta H) | n \rangle}{e^{-\beta a} + e^{-\beta b}}. \tag{4.3.7}$$

Now that the value of each of the quantities in (4.3.7) are known

$$\begin{aligned} \Xi(t) &= \frac{1}{e^{-\beta a} + e^{-\beta b}} \left\{ \begin{bmatrix} 1 & 0 \end{bmatrix} \left(\begin{bmatrix} \alpha & \delta \end{bmatrix} \cdot \begin{bmatrix} \alpha \exp\left(-\frac{iat}{\hbar}\right) \\ \delta \exp\left(-\frac{ibt}{\hbar}\right) \end{bmatrix} \right) \begin{bmatrix} 1 \\ 0 \end{bmatrix} \exp(-\beta a) \right\} + \\ &+ \frac{1}{e^{-\beta a} + e^{-\beta b}} \left\{ \begin{bmatrix} 0 & 1 \end{bmatrix} \left(\begin{bmatrix} \alpha & \delta \end{bmatrix} \cdot \begin{bmatrix} \alpha \exp\left(-\frac{iat}{\hbar}\right) \\ \delta \exp\left(-\frac{ibt}{\hbar}\right) \end{bmatrix} \right) \begin{bmatrix} 0 \\ 1 \end{bmatrix} \exp(-\beta b) \right\}, \end{aligned} \tag{4.3.8}$$

which simplifies to

$$\Xi(t) = \left[\alpha^2 \exp\left(-\frac{iat}{\hbar}\right) + \delta^2 \exp\left(-\frac{ibt}{\hbar}\right) \right] \tag{4.3.9}$$

The second quantity, the frequency matrix $i\Omega$ is generally represented as

$$i\Omega = \frac{\langle p_k^*(0) \cdot \dot{p}_k(0) \rangle}{\langle p_k^*(0) \cdot p_k(0) \rangle}, \tag{4.3.10}$$

again we use the property that our system is normalized and $\langle p_k^*(0) \cdot p_k(0) \rangle = e^{-\beta a} + e^{-\beta b}$ and (4.3.2)

$$i\Omega = \frac{\langle p_k^*(0) \cdot \dot{p}_k(0) \rangle}{e^{-\beta a} + e^{-\beta b}}. \tag{4.3.11}$$

Since this is a quantum mechanics system the thermal average will be modified to represent all of the basis states, and since this is a thermal average an $\exp(-\beta H)$ will be added as well

$$i\Omega = \frac{\sum_n \langle n|p_k^*(0)\cdot \dot{p}_k(0)\exp(-\beta H)|n\rangle}{e^{-\beta a}+e^{-\beta b}}. \tag{4.3.12}$$

Again it is best to input $\sum_n |n\rangle\langle n|$ into the expression such that $\sum_n \langle n|\exp(-\beta H)|n\rangle = \sum_n \exp(-\beta E_n)$

$$\begin{aligned} i\Omega &= \tfrac{1}{e^{-\beta a}+e^{-\beta b}}\left\{\begin{bmatrix}1 & 0\end{bmatrix}\left(\begin{bmatrix}\alpha & \delta\end{bmatrix}\cdot\begin{bmatrix}-\frac{ia\alpha}{\hbar}\\ -\frac{ib\delta}{\hbar}\end{bmatrix}\right)\begin{bmatrix}1\\0\end{bmatrix}\exp(-\beta a)\right\}+ \\ &+ \tfrac{1}{e^{-\beta a}+e^{-\beta b}}\left\{\begin{bmatrix}0 & 1\end{bmatrix}\left(\begin{bmatrix}\alpha & \delta\end{bmatrix}\cdot\begin{bmatrix}-\frac{ia\alpha}{\hbar}\\ -\frac{ib\delta}{\hbar}\end{bmatrix}\right)\begin{bmatrix}0\\1\end{bmatrix}\exp(-\beta b)\right\}, \end{aligned} \tag{4.3.13}$$

which simplifies to

$$i\Omega = -\frac{i}{\hbar}\left[\alpha^2 a+\delta^2 b\right]. \tag{4.3.14}$$

The third quantity, the part of $p_k(t)$ not correlated with $p_k(0)$ is generally represented as

$$p_k'(t) = (I - P_{p_k})\,p_k(t). \tag{4.3.15}$$

In this case all of the values necessary to calculate $p_k'(t)$ are already available

$$p_k'(t) = \begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}\cdot\begin{bmatrix}\alpha\exp\left(-\frac{iat}{\hbar}\right)\\ \delta\exp\left(-\frac{ibt}{\hbar}\right)\end{bmatrix} - \sum_n \frac{\langle n|p_k(t)\cdot p_k^*(0)\exp(-\beta H)|n\rangle}{\langle p_k(0)\cdot p_k^*(0)\rangle}\otimes p_k(0), \tag{4.3.16}$$

the system is normalized so $\langle p_k(0)p_k^*(0)\rangle = e^{-\beta a}+e^{-\beta b}$ and if we insert $\sum_n |n\rangle\langle n|$ into the expression

$$p_k'(t) = \begin{bmatrix}\alpha\exp\left(-\frac{iat}{\hbar}\right)\\ \delta\exp\left(-\frac{ibt}{\hbar}\right)\end{bmatrix} - \frac{\sum_n\langle n|p_k(t)\cdot p_k^*(0)|n\rangle}{e^{-\beta a}+e^{-\beta b}}\exp(-\beta E_n)\otimes p_k(0). \tag{4.3.17}$$

Inserting the values of each matrix into the equation

$$\begin{aligned} p_k'(t) &= \begin{bmatrix}\alpha\exp\left(-\frac{iat}{\hbar}\right)\\ \delta\exp\left(-\frac{ibt}{\hbar}\right)\end{bmatrix} - \\ &- \begin{bmatrix}1 & 0\end{bmatrix}\left(\frac{\begin{bmatrix}\alpha\exp\left(-\frac{iat}{\hbar}\right) & \delta\exp\left(-\frac{ibt}{\hbar}\right)\end{bmatrix}}{e^{-\beta a}+e^{-\beta b}}\cdot\begin{bmatrix}\alpha\\ \delta\end{bmatrix}\right)\begin{bmatrix}1\\0\end{bmatrix}\exp(-\beta a)\begin{bmatrix}\alpha\\ \delta\end{bmatrix} - , \\ &- \begin{bmatrix}0\\1\end{bmatrix}\left(\frac{\begin{bmatrix}\alpha\exp\left(-\frac{iat}{\hbar}\right) & \delta\exp\left(-\frac{ibt}{\hbar}\right)\end{bmatrix}}{e^{-\beta a}+e^{-\beta b}}\cdot\begin{bmatrix}\alpha\\ \delta\end{bmatrix}\right)\begin{bmatrix}0\\1\end{bmatrix}\exp(-\beta b)\begin{bmatrix}\alpha\\ \delta\end{bmatrix} \end{aligned}$$

simplifying the expression

$$p_k'(t) = \begin{bmatrix}\alpha\exp\left(-\frac{iat}{\hbar}\right)\\ \delta\exp\left(-\frac{ibt}{\hbar}\right)\end{bmatrix} - \left[\alpha^2\exp\left(-\frac{iat}{\hbar}\right)+\delta^2\exp\left(-\frac{ibt}{\hbar}\right)\right]\begin{bmatrix}\alpha\\ \delta\end{bmatrix}. \tag{4.3.18}$$

The fourth quantity we are calculating is the part of $\dot{p}_k(t)$ not correlated with $p_k(0)$, which is generally represented as

$$K(t) = (I - P_{p_k})\,\dot{p}_k(t), \tag{4.3.19}$$

substituting the expression for P_{p_k}

$$K(t) = \begin{bmatrix} -\frac{ia\alpha}{\hbar}\exp\left(-\frac{iat}{\hbar}\right) \\ -\frac{ib\delta}{\hbar}\exp\left(-\frac{ibt}{\hbar}\right) \end{bmatrix} - \sum_n \frac{\langle n|\dot{p}_k(t)\cdot p_k(0)\exp\left(-\beta H\right)|n\rangle}{\langle p_k^*(0)\cdot p_k(0)\rangle} p_k(0) \tag{4.3.20}$$

from above, $\langle p_k^*(0)p_k(0)\rangle = e^{-\beta a} + e^{-\beta b}$, and we can insert $\sum_n |n\rangle\langle n|$ into the equation such that

$$K(t) = \begin{bmatrix} -\frac{ia\alpha}{\hbar}\exp\left(-\frac{iat}{\hbar}\right) \\ -\frac{ib\delta}{\hbar}\exp\left(-\frac{ibt}{\hbar}\right) \end{bmatrix} - \frac{\sum_n \langle n|\dot{p}_k(t)\cdot p_k(0)|n\rangle p_k(0)\exp\left(-\beta E_n\right)}{e^{-\beta a} + e^{-\beta b}}. \tag{4.3.21}$$

Inserting our values for each of the quantities

$$\begin{aligned} K(t) \;=\; & \begin{bmatrix} -\frac{ia\alpha}{\hbar}e^{-\frac{iat}{\hbar}} \\ -\frac{ib\delta}{\hbar}e^{-\frac{ibt}{\hbar}} \end{bmatrix} - \begin{bmatrix} 1 & 0 \end{bmatrix} \left(\frac{\begin{bmatrix} -\frac{ia\alpha}{\hbar}e^{-\frac{iat}{\hbar}} & -\frac{ib\delta}{\hbar}e^{-\frac{ibt}{\hbar}} \end{bmatrix}}{e^{-\beta a}+e^{-\beta b}} \cdot \begin{bmatrix} \alpha \\ \delta \end{bmatrix} \right) \begin{bmatrix} 1 \\ 0 \end{bmatrix} e^{-\beta a} \begin{bmatrix} \alpha \\ \delta \end{bmatrix} - \\ & - \begin{bmatrix} 0 & 1 \end{bmatrix} \left(\frac{\begin{bmatrix} -\frac{ia\alpha}{\hbar}e^{-\frac{iat}{\hbar}} & -\frac{ib\delta}{\hbar}e^{-\frac{ibt}{\hbar}} \end{bmatrix}}{e^{-\beta a}+e^{-\beta b}} \cdot \begin{bmatrix} \alpha \\ \delta \end{bmatrix} \right) \begin{bmatrix} 0 \\ 1 \end{bmatrix} \exp\left(-\beta b\right) \begin{bmatrix} \alpha \\ \delta \end{bmatrix} \end{aligned} \tag{4.3.22}$$

simplifying

$$K(t) = \begin{bmatrix} -\frac{ia\alpha}{\hbar}\exp\left(\frac{iat}{\hbar}\right) \\ -\frac{ib\delta}{\hbar}\exp\left(\frac{ibt}{\hbar}\right) \end{bmatrix} + \frac{i}{\hbar}\left[a\alpha^2\exp\left(\frac{iat}{\hbar}\right) + b\delta^2\exp\left(\frac{ibt}{\hbar}\right)\right] \begin{bmatrix} \alpha \\ \delta \end{bmatrix}. \tag{4.3.23}$$

The last quantity we are calculating is the random force f which is generally represented as

$$f(t-s) = \exp\left[i\,(t-s)\,(I-P)\,\frac{H}{\hbar}\right] K(0). \tag{4.3.24}$$

In this case we will first calculate $K(0)$ from the above expression for $K(t)$

$$K(0) = \begin{bmatrix} \frac{i\alpha}{\hbar}\left[\left(a\alpha^2 + b\delta^2\right) - a\right] \\ \frac{i\delta}{\hbar}\left[\left(a\alpha^2 + b\delta^2\right) - b\right] \end{bmatrix}, \tag{4.3.25}$$

and from section **4.2** we know that $\exp\left[i\,(t-s)\,(I-P)\,H\right]$ is

$$\gamma = \frac{1}{\hbar\left(e^{-\beta a} + e^{-\beta b}\right)} \begin{bmatrix} \left(\hbar + iat - iat\alpha^2\right)e^{-\beta a} + (\hbar + iat)\,e^{-\beta b} & -iat\alpha\delta e^{-\beta a} \\ -ibt\alpha\delta e^{-\beta b} & (\hbar + ibt)\,e^{-\beta a} + \left(\hbar + ibt - ibt\delta^2\right)e^{-\beta b} \end{bmatrix} \tag{4.3.26}$$

Now we calculate $f(t-s)$

$$f(t-s)=\left[\begin{array}{cc}\frac{\left(\hbar+iat-iat\alpha^2\right)e^{-\beta a}+(\hbar+iat)e^{-\beta b}}{\hbar(e^{-\beta a}+e^{-\beta b})} & -\frac{iat\alpha\delta e^{-\beta a}}{\hbar(e^{-\beta a}+e^{-\beta b})}\\ -\frac{ibt\alpha\delta e^{-\beta b}}{\hbar(e^{-\beta a}+e^{-\beta b})} & \frac{(\hbar+ibt)e^{-\beta a}+\left(\hbar+ibt-ibt\delta^2\right)e^{-\beta b}}{\hbar(e^{-\beta a}+e^{-\beta b})}\end{array}\right].\left[\begin{array}{c}\frac{i\alpha}{\hbar}\left[\left(a\alpha^2+b\delta^2\right)-a\right]\\ \frac{i\delta}{\hbar}\left[\left(a\alpha^2+b\delta^2\right)-b\right]\end{array}\right] \tag{4.3.27}$$

simplifying

$$f(t)=\left[\begin{array}{c}\frac{i\alpha}{\hbar^2(e^{-\beta a}+e^{-\beta b})}\left[\left(\left(a\alpha^2+b\delta^2\right)-a\right)\left((\hbar+iat)\left(e^{-\beta a}+e^{-\beta b}\right)-iat\alpha^2e^{-\beta a}\right)-\right.\\ \left.-\,iat\delta^2e^{-\beta a}\left(\left(a\alpha^2+b\delta^2\right)-b\right)\right]\\ \\ \frac{i\delta}{\hbar^2(e^{-\beta a}+e^{-\beta b})}\left[\left((\hbar+ibt)\left(e^{-\beta a}+e^{-\beta b}\right)-ibt\delta^2e^{-\beta b}\right)\left(\left(a\alpha^2+b\delta^2\right)-b\right)-\right.\\ \left.-\,ibt\alpha^2e^{-\beta b}\left(\left(a\alpha^2+b\delta^2\right)-a\right)\right]\end{array}\right], \tag{4.3.28}$$

and

$$f(0)=\left[\begin{array}{c}\frac{i\alpha}{\hbar}\left(\left(a\alpha^2+b\delta^2\right)-a\right)\\ \frac{i\delta}{\hbar}\left(\left(a\alpha^2+b\delta^2\right)-b\right)\end{array}\right], \tag{4.3.29}$$

Now that we have calculated the random force we calculate the Mori-Zwanzig memory kernel[12]

$$\phi(s)=\frac{\langle f^*(0)\cdot f(s)\rangle}{\langle p_k^*(0)\cdot p_k(0)\rangle}, \tag{4.3.30}$$

in the quantum representation

$$\phi(s)=\frac{\sum_n\langle n|f^*(0)\cdot f(s)e^{-\beta H}|n\rangle}{\langle n|p_k^*(0)\cdot p_k(0)e^{-\beta H}|n\rangle}. \tag{4.3.31}$$

We know that $\sum_n\langle n|p_k^*(0)p_k(0)e^{-\beta H}|n\rangle=e^{-\beta a}+e^{-\beta b}$ so (4.3.31) becomes

$$\phi(s)=\frac{\sum_n\langle n|f^*(0)\cdot f(s)|n\rangle e^{-\beta E_n}}{e^{-\beta a}+e^{-\beta b}}. \tag{4.3.32}$$

Since the expressions for $f(0)$ and $f(t-s)$ are both fairly large we will just give the result of the multiplication

$$\begin{aligned}f^*(0)f(t) &= -\frac{1}{\hbar^3\left(e^{-\beta a}+e^{-\beta b}\right)}\left\{\alpha^2\left[\left(\left(a\alpha^2+b\delta^2\right)-a\right)^2\left((\hbar+iat)\left(e^{-\beta a}+e^{-\beta b}\right)-iat\alpha^2e^{-\beta a}\right)-\right.\right.\\ &- \left.\left(\left(a\alpha^2+b\delta^2\right)-a\right)\left(\left(a\alpha^2+b\delta^2\right)-b\right)iat\delta^2e^{-\beta a}\right]+\\ &+ \delta^2\left[\left(\left(a\alpha^2+b\delta^2\right)-b\right)^2\left((\hbar+ibt)\left(e^{-\beta a}+e^{-\beta b}\right)-ibt\delta^2e^{-\beta b}\right)-\right.\\ &- \left.\left.\left(\left(a\alpha^2+b\delta^2\right)-a\right)\left(\left(a\alpha^2+b\delta^2\right)-b\right)ibt\alpha^2e^{-\beta b}\right)\right]\right\}\end{aligned} \tag{4.3.33}$$

Using (4.3.33) in (4.3.32)

$$\begin{aligned}\phi(s) &= -\frac{1}{\hbar^3\left(e^{-\beta a}+e^{-\beta b}\right)}\left\{\alpha^2\left[\left(\left(a\alpha^2+b\delta^2\right)-a\right)^2\left((\hbar+ias)\left(e^{-\beta a}+e^{-\beta b}\right)-ias\alpha^2e^{-\beta a}\right)-\right.\right.\\ &- \left.\left(\left(a\alpha^2+b\delta^2\right)-a\right)\left(\left(a\alpha^2+b\delta^2\right)-b\right)ias\delta^2e^{-\beta a}\right]+\\ &+ \delta^2\left[\left(\left(a\alpha^2+b\delta^2\right)-b\right)^2\left((\hbar+ibs)\left(e^{-\beta a}+e^{-\beta b}\right)-ibs\delta^2e^{-\beta b}\right)-\right.\\ &- \left.\left.\left(\left(a\alpha^2+b\delta^2\right)-a\right)\left(\left(a\alpha^2+b\delta^2\right)-b\right)ibs\alpha^2e^{-\beta b}\right)\right]\right\}.\end{aligned} \tag{4.3.34}$$

Which are all of the quantities necessary to calculate the Mori Equation.

4.4 Calculating the Mori Equation

With all of the Mori Quantities calculated and the knowledge of how a projection operator works on a quantum mechanical system we will calculate $\frac{dp_k(t)}{dt}$ using the Mori Equation. We have chosen one harmonic oscillator as our system because we already know what the time derivative is, since Mori Theory calculates the time derivative of a particular quantity we can check the result of Mori theory against the known result. The general Mori Equation is written as

$$\frac{dp_k(t)}{dt} = i\Omega p_k(t) + \int_0^t \phi(s) p_k(t-s)\, ds + f(t) \tag{4.4.1}$$

In section **4.3** we calculated, $i\Omega$, $\phi(s)$, and $f(t)$

$$i\Omega = -\frac{i}{\hbar}\left[\alpha^2 a + \delta^2 b\right]; \tag{4.4.2}$$

$$\begin{aligned}
\phi(s) &= -\frac{1}{\hbar^3\left(e^{-\beta a}+e^{-\beta b}\right)}\Big\{\alpha^2\Big[\left(\left(a\alpha^2+b\delta^2\right)-a\right)^2\left((\hbar+ias)\left(e^{-\beta a}+e^{-\beta b}\right)-ias\alpha^2e^{-\beta a}\right)- \\
&- \left(\left(a\alpha^2+b\delta^2\right)-a\right)\left(\left(a\alpha^2+b\delta^2\right)-b\right)ias\delta^2e^{-\beta a}\Big]+ \\
&+ \delta^2\Big[\left(\left(a\alpha^2+b\delta^2\right)-b\right)^2\left((\hbar+ibs)\left(e^{-\beta a}+e^{-\beta b}\right)-ibs\delta^2e^{-\beta b}\right)- \\
&- \left(\left(a\alpha^2+b\delta^2\right)-a\right)\left(\left(a\alpha^2+b\delta^2\right)-b\right)ibs\alpha^2e^{-\beta b}\Big]\Big\},
\end{aligned} \tag{4.4.3}$$

$$f(t) = \begin{bmatrix}
\frac{i\alpha}{\hbar^2\left(e^{-\beta a}+e^{-\beta b}\right)}\Big[\left(\left(a\alpha^2+b\delta^2\right)-a\right)\left((\hbar+iat)\left(e^{-\beta a}+e^{-\beta b}\right)-iat\alpha^2e^{-\beta a}\right)- \\
-\, iat\delta^2e^{-\beta a}\left(\left(a\alpha^2+b\delta^2\right)-b\right)\Big] \\
\\
\frac{i\delta}{\hbar^2\left(e^{-\beta a}+e^{-\beta b}\right)}\Big[\left((\hbar+ibt)\left(e^{-\beta a}+e^{-\beta b}\right)-ibt\delta^2e^{-\beta b}\right)\left(\left(a\alpha^2+b\delta^2\right)-b\right)- \\
-\, ibt\alpha^2e^{-\beta b}\left(\left(a\alpha^2+b\delta^2\right)-a\right)\Big]
\end{bmatrix}. \tag{4.4.4}$$

Using the random vector used in the previous sections

$$p_k(t) = \begin{bmatrix} \alpha e^{\left(\frac{ia t}{\hbar}\right)} \\ \delta e^{\left(\frac{ibt}{\hbar}\right)} \end{bmatrix} \qquad p_k(t-s) = \begin{bmatrix} \alpha e^{\left(\frac{ia(t-s)}{\hbar}\right)} \\ \delta e^{\left(\frac{ib(t-s)}{\hbar}\right)} \end{bmatrix}. \tag{4.4.5}$$

To make the calculation of $\frac{dp_k(t)}{dt}$ easier we do two independent calculations and then add them together to give the result. The two calculations are $i\Omega p_k(t)$ and $\int_0^t \phi(s)p_k(t-s)\,ds$. The first calculation is $i\Omega p_k(t)$ multiplying (4.4.2) and (4.4.5)

$$i\Omega p_k(t) = -\frac{i}{\hbar}\left[\alpha^2 a + \delta^2 b\right]\begin{bmatrix} \alpha e^{-\left(\frac{ia t}{\hbar}\right)} \\ \delta e^{-\left(\frac{ibt}{\hbar}\right)} \end{bmatrix}, \tag{4.4.6}$$

simplifying the multiplication

$$i\Omega p_k(t) = \begin{bmatrix} -\frac{i\alpha e^{-\left(\frac{iat}{\hbar}\right)}}{\hbar}\left[\alpha^2 a + \delta^2 b\right] \\ -\frac{i\delta e^{-\left(\frac{ibt}{\hbar}\right)}}{\hbar}\left[\alpha^2 a + \delta^2 b\right] \end{bmatrix}. \tag{4.4.7}$$

Since $i\Omega p_k(t)$ has been found the second quantity to calculate is $\nu = \int_0^t \phi(s) p_k(t-s)\, ds$ multiplying (4.4.3) with (4.4.5) and integrating

$$\nu = -\begin{bmatrix} \int_0^t \left\{ \frac{\alpha e^{\frac{ia(t-s)}{\hbar}}}{\hbar^3(e^{-\beta a}+e^{-\beta b})} \left\{ \alpha^2 \left[\left(\left(a\alpha^2 + b\delta^2\right) - a \right)^2 \left((\hbar + ias)\left(e^{-\beta a} + e^{-\beta b}\right) - ias\alpha^2 e^{-\beta a} \right) - \right.\right. \right. \\ \left. - \left(\left(a\alpha^2 + b\delta^2\right) - a \right) \left(\left(a\alpha^2 + b\delta^2\right) - b \right) ias\delta^2 e^{-\beta a} \right] + \\ +\delta^2 \left[\left(\left(a\alpha^2 + b\delta^2\right) - b \right)^2 \left((\hbar + ibs)\left(e^{-\beta a} + e^{-\beta b}\right) - ibs\delta^2 e^{-\beta b} \right) - \\ \left. \left. - \left(\left(a\alpha^2 + b\delta^2\right) - a \right) \left(\left(a\alpha^2 + b\delta^2\right) - b \right) ibs\alpha^2 e^{-\beta b} \right) \right] \right\} \right\} \, ds \\ \\ \int_0^t \left\{ \frac{\delta e^{\frac{ib(t-s)}{\hbar}}}{\hbar^3(e^{-\beta a}+e^{-\beta b})} \left\{ \alpha^2 \left[\left(\left(a\alpha^2 + b\delta^2\right) - a \right)^2 \left((\hbar + ias)\left(e^{-\beta a} + e^{-\beta b}\right) - ias\alpha^2 e^{-\beta a} \right) - \right.\right. \right. \\ \left. - \left(\left(a\alpha^2 + b\delta^2\right) - a \right) \left(\left(a\alpha^2 + b\delta^2\right) - b \right) ias\delta^2 e^{-\beta a} \right] + \\ +\delta^2 \left[\left(\left(a\alpha^2 + b\delta^2\right) - b \right)^2 \left((\hbar + ibs)\left(e^{-\beta a} + e^{-\beta b}\right) - ibs\delta^2 e^{-\beta b} \right) - \\ \left. \left. - \left(\left(a\alpha^2 + b\delta^2\right) - a \right) \left(\left(a\alpha^2 + b\delta^2\right) - b \right) ibs\alpha^2 e^{-\beta b} \right) \right] \right\} \right\} \, ds \end{bmatrix}. \tag{4.4.8}$$

Performing the integral

$$\nu = -\begin{bmatrix} \frac{\alpha}{a\hbar^2(e^{-\beta a}+e^{-\beta b})} \left\{ \alpha^2 \left(a\alpha^2 + b\delta^2 - a\right)^2 \left[at\left(e^{-\beta a} + e^{-\beta b}\right) - i\alpha^2 e^{-\beta a}\left(\hbar\left(1 - e^{-\frac{iat}{\hbar}}\right) - iat\right)\right] + \right. \\ +\delta^2 \left(a\alpha^2 + b\delta^2 - b\right)^2 \left[\left(e^{-\beta a} + e^{-\beta b}\right)\left[i\hbar\left(\frac{b}{a} - 1\right)\left(1 - e^{-\frac{iat}{\hbar}}\right) + bt\right] - \frac{ib\delta^2}{a} e^{-\beta b}\left(\hbar\left(1 - e^{-\frac{iat}{\hbar}}\right) - iat\right)\right] - \\ \left. - \frac{i\alpha^2\delta^2}{a}\left(a\alpha^2 + b\delta^2 - a\right)\left(a\alpha^2 + b\delta^2 - b\right)\left(ae^{-\beta a} + be^{-\beta b}\right)\left(\hbar\left(1 - e^{-\frac{iat}{\hbar}}\right) - iat\right)\right\} \\ \\ \frac{\delta}{b\hbar^2(e^{-\beta a}+e^{-\beta b})} \left\{ \delta^2 \left(a\alpha^2 + b\delta^2 - b\right)^2 \left[bt\left(e^{-\beta a} + e^{-\beta b}\right) - i\delta^2 e^{-\beta b}\left(\hbar\left(1 - e^{-\frac{ibt}{\hbar}}\right) - ibt\right)\right] + \right. \\ +\alpha^2 \left(a\alpha^2 + b\delta^2 - a\right)^2 \left[\left(e^{-\beta a} + e^{-\beta b}\right)\left[i\hbar\left(\frac{a}{b} - 1\right)\left(1 - e^{-\frac{ibt}{\hbar}}\right) + at\right] - \frac{ia\alpha^2}{b} e^{-\beta a}\left(\hbar\left(1 - e^{-\frac{ibt}{\hbar}}\right) - iat\right)\right] - \\ \left. - \frac{i\alpha^2\delta^2}{b}\left(a\alpha^2 + b\delta^2 - a\right)\left(a\alpha^2 + b\delta^2 - b\right)\left(ae^{-\beta a} + be^{-\beta b}\right)\left(\hbar\left(1 - e^{-\frac{ibt}{\hbar}}\right) - ibt\right)\right\} \end{bmatrix}. \tag{4.4.9}$$

Now that we have found $i\Omega p_k(t)$ and $\int_0^t \phi(s) p_k(t-s)\, ds$ we may add them together with the random force, $f(t)$, using (4.4.7), (4.4.9), and (4.4.4). Since the expression for $\int_0^t \phi(s) p_k(t-s)\, ds$ is so complicated and long we will leave the answer in its raw form, three matrices added together, because any further simplification would complicate the viewing of the expression.

$$\frac{dp_k(t)}{dt} = \begin{bmatrix} -\frac{i\alpha e^{-\left(\frac{iat}{\hbar}\right)}}{\hbar}\left[\alpha^2 a + \delta^2 b\right] \\ -\frac{i\delta e^{-\left(\frac{ibt}{\hbar}\right)}}{\hbar}\left[\alpha^2 a + \delta^2 b\right] \end{bmatrix} -$$

$$- \begin{bmatrix} \frac{\alpha}{a\hbar^2(e^{-\beta a}+e^{-\beta b})}\left\{\alpha^2\left(a\alpha^2+b\delta^2-a\right)^2\left[at\left(e^{-\beta a}+e^{-\beta b}\right)-i\alpha^2 e^{-\beta a}\left(\hbar\left(1-e^{-\frac{iat}{\hbar}}\right)-iat\right)\right]+\right. \\ +\delta^2\left(a\alpha^2+b\delta^2-b\right)^2\left[\left(e^{-\beta a}+e^{-\beta b}\right)\left[i\hbar\left(\frac{b}{a}-1\right)\left(1-e^{-\frac{iat}{\hbar}}\right)+bt\right]-\frac{ib\delta^2}{a}e^{-\beta b}\left(\hbar\left(1-e^{-\frac{iat}{\hbar}}\right)-iat\right)\right]- \\ \left.-\frac{i\alpha^2\delta^2}{a}\left(a\alpha^2+b\delta^2-a\right)\left(a\alpha^2+b\delta^2-b\right)\left(ae^{-\beta a}+be^{-\beta b}\right)\left(\hbar\left(1-e^{-\frac{iat}{\hbar}}\right)-iat\right)\right\} \\ \\ \frac{\delta}{b\hbar^2(e^{-\beta a}+e^{-\beta b})}\left\{\delta^2\left(a\alpha^2+b\delta^2-b\right)^2\left[bt\left(e^{-\beta a}+e^{-\beta b}\right)-i\delta^2 e^{-\beta b}\left(\hbar\left(1-e^{-\frac{ibt}{\hbar}}\right)-ibt\right)\right]+\right. \\ \alpha^2\left(a\alpha^2+b\delta^2-a\right)^2\left[\left(e^{-\beta a}+e^{-\beta b}\right)\left[i\hbar\left(\frac{a}{b}-1\right)\left(1-e^{-\frac{ibt}{\hbar}}\right)+at\right]-\frac{ia\alpha^2}{b}e^{-\beta a}\left(\hbar\left(1-e^{-\frac{ibt}{\hbar}}\right)-iat\right)\right]- \\ \left.-\frac{i\alpha^2\delta^2}{b}\left(a\alpha^2+b\delta^2-a\right)\left(a\alpha^2+b\delta^2-b\right)\left(ae^{-\beta a}+be^{-\beta b}\right)\left(\hbar\left(1-e^{-\frac{ibt}{\hbar}}\right)-ibt\right)\right\} \end{bmatrix} +$$

$$+ \begin{bmatrix} \frac{i\alpha}{\hbar^2(e^{-\beta a}+e^{-\beta b})}\left[\left(\left(a\alpha^2+b\delta^2\right)-a\right)\left(\left(\hbar+iat\right)\left(e^{-\beta a}+e^{-\beta b}\right)-iat\alpha^2 e^{-\beta a}\right)-\right. \\ \left.-iat\delta^2 e^{-\beta a}\left(\left(a\alpha^2+b\delta^2\right)-b\right)\right] \\ \\ \frac{i\delta}{\hbar^2(e^{-\beta a}+e^{-\beta b})}\left[\left(\left(\hbar+ibt\right)\left(e^{-\beta a}+e^{-\beta b}\right)-ibt\delta^2 e^{-\beta b}\right)\left(\left(a\alpha^2+b\delta^2\right)-b\right)-\right. \\ \left.-ibt\alpha^2 e^{-\beta b}\left(\left(a\alpha^2+b\delta^2\right)-a\right)\right] \end{bmatrix}. \tag{4.4.10}$$

If we do another Taylor series expansion on $e^{-\frac{iat}{\hbar}}$ and $e^{-\frac{ibt}{\hbar}}$ in the second matrix of (4.4.10), there are multiple cancelations, leading to

$$\frac{dp_k(t)}{dt} = \begin{bmatrix} -\frac{i\alpha}{\hbar}\left[\alpha^2 a+\delta^2 b\right]e^{-\left(\frac{iat}{\hbar}\right)}-\frac{t\alpha}{\hbar^2}\left\{\alpha^2\left(a\alpha^2+b\delta^2-a\right)^2+\delta^2\left(a\alpha^2+b\delta^2-b\right)^2\right\} \\ \\ -\frac{i\delta}{\hbar}\left[\alpha^2 a+\delta^2 b\right]e^{\left(-\frac{ibt}{\hbar}\right)}-\frac{t\delta}{\hbar^2}\left\{\alpha^2\left(a\alpha^2+b\delta^2-a\right)^2+\delta^2\left(a\alpha^2+b\delta^2-b\right)^2\right\} \end{bmatrix} +$$

$$+ \begin{bmatrix} \frac{i\alpha}{\hbar^2(e^{-\beta a}+e^{-\beta b})}\left[\left(\left(a\alpha^2+b\delta^2\right)-a\right)\left(\left(\hbar+iat\right)\left(e^{-\beta a}+e^{-\beta b}\right)-iat\alpha^2 e^{-\beta a}\right)-\right. \\ \left.-iat\delta^2 e^{-\beta a}\left(\left(a\alpha^2+b\delta^2\right)-b\right)\right] \\ \\ \frac{i\delta}{\hbar^2(e^{-\beta a}+e^{-\beta b})}\left[\left(\left(\hbar+ibt\right)\left(e^{-\beta a}+e^{-\beta b}\right)-ibt\delta^2 e^{-\beta b}\right)\left(\left(a\alpha^2+b\delta^2\right)-b\right)-\right. \\ \left.-ibt\alpha^2 e^{-\beta b}\left(\left(a\alpha^2+b\delta^2\right)-a\right)\right] \end{bmatrix}. \tag{4.4.11}$$

Using the same Taylor Series expansion for $e^{-\frac{i\alpha t}{\hbar}}$ and $e^{-\frac{ibt}{\hbar}}$ on the first term we can isolate the time dependent and the time independent terms.

$$\frac{dp_k(t)}{dt} = \begin{bmatrix} -\frac{i\alpha a}{\hbar} - \frac{\alpha a t}{\hbar^2}\left[\alpha^2 a + \delta^2 b\right] - \frac{t\alpha}{\hbar^2}\left\{\alpha^2\left(a\alpha^2 + b\delta^2 - a\right)^2 + \delta^2\left(a\alpha^2 + b\delta^2 - b\right)^2\right\} \\ \\ -\frac{i\delta b}{\hbar} - \frac{\delta b t}{\hbar^2}\left[\alpha^2 a + \delta^2 b\right] - \frac{t\delta}{\hbar^2}\left\{\alpha^2\left(a\alpha^2 + b\delta^2 - a\right)^2 + \delta^2\left(a\alpha^2 + b\delta^2 - b\right)^2\right\} \end{bmatrix} +$$

$$+ \begin{bmatrix} \frac{a\alpha t}{\hbar^2(e^{-\beta a}+e^{-\beta b})}\left[\left(\left(a\alpha^2 + b\delta^2\right) - a\right)\left(\left(e^{-\beta a} + e^{-\beta b}\right) - \alpha^2 e^{-\beta a}\right) - \delta^2 e^{-\beta a}\left(\left(a\alpha^2 + b\delta^2\right) - b\right)\right] \\ \\ \frac{b\delta t}{\hbar^2(e^{-\beta a}+e^{-\beta b})}\left[\left(\left(e^{-\beta a} + e^{-\beta b}\right) - \delta^2 e^{-\beta b}\right)\left(\left(a\alpha^2 + b\delta^2\right) - b\right) - \alpha^2 e^{-\beta b}\left(\left(a\alpha^2 + b\delta^2\right) - a\right)\right] \end{bmatrix}. \tag{4.4.12}$$

From this form of the time derivative it is unclear whether the answer from the Mori Equation is the same as taking the time derivative of the known exact solution. Looking at the expression we see that the first term $i\Omega p_k(t)$ gives the average frequency $\alpha^2 a + \delta^2 b$. The second and third term $\int_0^t ds\ \phi(s) p_k(t-s)$ and the random force have terms that involve the difference between the average frequency and the actual frequency $\alpha^2 a + \delta^2 b - a$ or $\alpha^2 a + \delta^2 b - b$. In this case we have an expression that is not the same as the exact calculation of $\frac{dp_k(t)}{dt}$ because we took the Taylor Series expansion for $\exp\left[it\left(I-P\right)H\right]$, $e^{-\frac{i\alpha t}{\hbar}}$, and $e^{-\frac{ibt}{\hbar}}$.

In quantum mechanics we would express the time derivative of the function as

$$\dot{p}_k(t) = \begin{bmatrix} -\frac{ia\alpha}{\hbar}e^{-\frac{i\alpha t}{\hbar}} \\ -\frac{ib\delta}{\hbar}e^{-\frac{ibt}{\hbar}} \end{bmatrix}. \tag{4.4.13}$$

To determine if (4.4.10) and (4.4.13) are the same we will perform some simple tests. The first one will be to set $\alpha = 1$ and $\delta = 0$. In this case the second matrix element (21) of each of the matrices in (4.4.10) is 0. For the last two matrices of (4.4.10) the matrix element (11) is also 0 because of the term $a\alpha^2 - a$ if $\alpha = 1$ then this term is also 0 eliminating those terms as well. The last portion of (4.4.10) to evaluate is the first matrix

$$\frac{dp_k(t)}{dt} = \begin{bmatrix} -\frac{i\alpha^3 a}{\hbar}e^{-\frac{i\alpha t}{\hbar}} \\ 0 \end{bmatrix}, \tag{4.4.14}$$

When $\alpha = 1$ (4.4.14) becomes

$$\frac{dp_k(t)}{dt} = \begin{bmatrix} -\frac{ia}{\hbar}e^{-\frac{i\alpha t}{\hbar}} \\ 0 \end{bmatrix}, \tag{4.4.15}$$

This is the same as when $\alpha = 1$ and $\delta = 0$ for the equation (4.4.13) the typical calculation of the

time derivative of the wave function

$$\dot{p}_k(t) = \begin{bmatrix} -\frac{ia}{\hbar}e^{-\frac{iat}{\hbar}} \\ 0 \end{bmatrix}. \tag{4.4.16}$$

Now that we have done this first calculation we can easily see that if we were to set $\alpha = 0$ and $\delta = 1$ that the both results would, again, be the same. The simple test has worked, but this does not definitively prove that the results are always the same.

Another simple test we can perform is to ask what happens when a and b are equal to one another. In this case we look at the memory kernel and the random force terms first. We find that any term with an $a\alpha^2 + b\delta^2 - a$ or $a\alpha^2 + b\delta^2 - b$ becomes 0 when a and b are set equal. This will eliminate both the memory kernel and the random force, leaving only the $i\Omega p_k(t)$ term in our expression.

$$\frac{dp_k(t)}{dt} = \begin{bmatrix} -\frac{i\alpha}{\hbar}\left[a\alpha^2 + b\delta^2\right]e^{-\frac{iat}{\hbar}} \\ -\frac{i\delta}{\hbar}\left[a\alpha^2 + b\delta^2\right]e^{-\frac{ibt}{\hbar}} \end{bmatrix}. \tag{4.4.17}$$

We know that $\alpha^2 + \delta^2 = 1$ so

$$\frac{dp_k(t)}{dt} = \begin{bmatrix} -\frac{ia\alpha}{\hbar}e^{-\frac{iat}{\hbar}} \\ -\frac{ib\delta}{\hbar}e^{-\frac{ibt}{\hbar}} \end{bmatrix}. \tag{4.4.18}$$

Which again is the same result as the classic calculation of the time derivative of our state.

The last simple test we performed was to set $t = 0$ for both (4.3.19) and (4.3.15). For (4.3.19) the result is

$$\frac{dp_k(t)}{dt} = \begin{bmatrix} -\frac{i\alpha a}{\hbar} \\ -\frac{i\delta b}{\hbar} \end{bmatrix}. \tag{4.4.19}$$

For (4.3.15) our result is a bit harder to calculate.

$$\frac{dp_k(t)}{dt} = \begin{bmatrix} -\frac{i\alpha}{\hbar}\left[a\alpha^2 + b\delta^2\right] + \frac{i\alpha}{\hbar}\left(a\alpha^2 + b\delta^2 - a\right) \\ -\frac{i\delta}{\hbar}\left[a\alpha^2 + b\delta^2\right] + \frac{i\delta}{\hbar}\left(a\alpha^2 + b\delta^2 - b\right) \end{bmatrix}, \tag{4.4.20}$$

which simplifies to

$$\frac{dp_k(t)}{dt} = \begin{bmatrix} -\frac{ia\alpha}{\hbar} \\ -\frac{ib\delta}{\hbar} \end{bmatrix}, \tag{4.4.21}$$

which is the same result as the direct calculation.

After performing these three simple tests on the system and confirming that it agreed there we decided to perform a more complicated test. In this case we set $\alpha = \frac{1}{\sqrt{2}}$ and $\delta = \frac{1}{\sqrt{2}}$, we found that while the Mori Theory calculation and the classic calculation started out the same at $t = 0$ as proven in the last test they started to differ at later times. This difference can mostly be attributed to the Taylor Series Approximation we took of e^x in the earlier calculations, since we only looked

at the first order terms we did not get the benefit of the later order corrections to our equations. It is unclear at this stage whether or not adding higher order terms would completely resolve the divergence we have in the terms.

5.0 CONCLUSION

Mori theory is a way of calculating the time dynamics of any variable of a system in statistical mechanics. The Mori theory allows a person to: (1) know the full solution of the time evolution of a system; (2) see the random force and the memory kernel calculations allowing the reader to more clearly understand how the function evolves in time; (3) use the projection operator to understand how a system evolves in time without a particular mechanical variable or state; (4) isolate one mechanical variable of the system and analyze its time dynamics; and (5) reduce the likelihood that any category of effect will be overlooked during the calculation and keep track of possible classes of effect[12]. This theory is based on four main assumptions: (1) the system is time reversal invariant, because the Louiville operator e^{tL} has time reversal invariance and (2) Ω is time invariant.

The Mori Theory also depends upon the calculation of the projection operator. The projection operator shows up both is statistical and a quantum mechanics. The Mori projection operator, $P_A = \frac{\sum_n \langle n| \cdot A|n\rangle}{\sum_n \langle n|A^* \cdot A|n\rangle} \otimes A$, takes on a very different form from the quantum projection operator, $P = |n\rangle\langle n|$. In section **4.1** we prove that the Mori projection operator not only works on a statistical mechanical system but also works on a quantum mechanical system. The ability to apply the Mori projection operator to a quantum system has many possible applications. For example, we may calculate the full Mori Theory, look at the system dynamics without one variable of the system, or isolate one mechanical variable of the system to analyze its qualities.

Having confirmed the Mori projection operator works on a quantum mechanical system we calculated the time dependence of the wave equation using a direct calculation. The system had a completely diagonalized Hamiltonian and a straightforward calculation of the basis states. We decided to use a diagonalized Hamiltonian because the complications to the expressions would be minimal, therefore comparing Mori Theory to the direct calculation would be much easier. We chose a mixed basis state $p_k(t)$, (4.4.5), and calculated its time derivative using both the direct calculation and the Mori Theory calculation. Having computed the Mori Equation for this system we were able to perform a series of tests by changing the amplitudes of $p_k(t)$, α and δ, to represent different states of the system.

From the general calculation of the Mori Equation, we were able to perform a series of simple tests

to compare Mori Theory and the known result. We discovered that in each of the three simple cases: $\alpha = 1$ and $\delta = 0$, $\alpha = 0$ and $\delta = 1$, $b = a$, and $t = 0$ the Mori Equation and the direct calculation of the time dynamics were the same. This result leads us to believe that the Mori Equation is an accurate way of calculating the time dynamics of a mechanical variable in a quantum system.

Some possible extensions of this analysis would be to try extending the Taylor Series expansion from first order in t to second or higher or trying a Fourier Series expansion of e^x instead of the Taylor Series expansion. I predict that if a higher order of Taylor series is used that the more complex solution will not differ as much from the exact calculation, but from the Mori result that we obtained it is unclear what the true answer is.

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