QUANTUM-CLASSICAL AND SEMICLASSICAL PATH INTEGRAL METHODS
FOR CONDENSED PHASE DYNAMICS

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DISSERTATION
Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Chemistry
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2018

Urbana, Illinois

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ABSTRACT

Chemical dynamics are essentially quantum mechanical processes. A great variety of chemical processes such as electron transfer and energy relaxation occur in condensed phase, reactants and products embedding in a non-reactive solution/environment. Therefore, quantum dynamics in condensed phase is the study of the behavior of the quantum system coupled to an interacting bath. The development of robust methodologies and efficient computational tools for condensed phase dynamics remains central to theoretical chemistry.

Since the full quantum treatment only limits to a system with a few degrees of freedom, the partition of the entire system into a subsystem for which quantum mechanical description is necessary and the bath which can be modeled by the less expensive classical dynamics, is a common strategy.

Due to the decoherence nature of the bath on the system, the quantum dynamics of the system is often described by the density matrix. Path integral formulation of the density matrix provides a versatile tool for studying quantum dynamics in condensed phase. Unlike the Schrödinger equation in which the wavefunction is central, Feynman’s path integral formulation is trajectory based, and therefore offers a natural connection between quantum mechanics and classical mechanics. This work will investigate path integral formulation in treating a quantum system coupled to anharmonic environment and the semiclassical formulation of path integral.

A big achievement in using Feynman’s path integral to study condensed phase dynamics is the development of quantum-classical path integral (QCPI) methodology.
Taking advantage that the non-reactive environment can be modeled accurately by classical mechanics, a great reduction of computational cost is achieved. Previous studies have been largely focusing on a quantum system interacting with harmonic environment, mainly because the analytical expressions of harmonic oscillator can be obtained. In this work, we extend the QCPI method to anharmonic environment by making numerically accurate approximations.

Semiclassical approach reduces all the possible quantum paths into one or several classical trajectories, therefore automatically eliminates the exponential growth of paths with time evolution. The distinct forward and backward trajectories in the density matrix allows quantum interference. This work explores the semiclassical-system classical-bath formulation of path integral. The stationary phase condition makes the phase smooth and makes Monte Carlo sampling very efficient with respect to the bath initial phase space distribution. The continuous coordinate formulation offers a potential utility of the method to treating multi-level systems.
ACKNOWLEDGEMENTS

First and foremost, I’d like to give sincere gratitude to my advisor, professor Nancy Makri, who has always been supportive and encouraging, and a true model for a great scientist. Her great insight, extensive knowledge and never-ending passion for science are my constant inspirations. You will not find such an advisor common who would guide you through equations step by step and analyze data down to details. Beyond academics, she would often make cakes and cookies that foster a very friendly and warm atmosphere within the group.

I would like to give big thanks to Prof. Martin Gruebele. During my first two years of coursework, he has been extremely patient in answering every question I had. Among those answers are great insight you’ll never find in any textbooks or journal articles. His enthusiasm and achievement as an educator, a research and in other pursuits in life constantly impress and inspire me and everyone around him. There’s so much you can learn from him, and he has lent numerous supports in my years at University of Illinois.

I’d also like to give my special thanks to Prof. Michael Stone with whom I enjoyed the math course so much and who had shown me the unceasing beauty of math again and again.

I’d like to extend my gratitude to Prof. Taras Pogorelov for his prompt and nice response for my late notice and a long-term friendship with our group.

I’d like to thank Dr. Peter Walters, Dr. Thomas Allen and Dr. Amartya Bose for helping me with my project and programming. Without them, I would not be able to initiate my research.
I’d also like to thank Connie, Beth, Karen and Katie for making every new step of the process a smooth transition.

In addition, I’d like to thank my friend Qiong Zhang, Shujian Liu and Junwen He for their generous support and wonderful discussions during up and down times.

I’d like to give big thanks to a special girl in my life for her timeless companion and consistent support. Her love makes me move forward. Peiyu Yang, I can’t wait to start my new chapter of life with you.

Lastly, I’d like to thank my parents and my family for their unconditional and unending love. I owe my everything to them.
To my parents and grandparents
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CHAPTER 1: INTRODUCTION

Condensed phase dynamics form an important class of chemical dynamics, such as proton/electron transfer processes in solutions\(^1\)\(^-\)\(^3\) and energy relaxation and dissipation\(^4\)\(^-\)\(^6\). The quantum nature of chemical reactions invites quantum mechanics to be used to investigate such phenomena. Due to the enormous degrees of freedom involved and the exponential scaling of quantum mechanics, the partition of the global system into subsystem and the environment is necessary. The subsystem is the dissipative system of interest and the environment or the bath applies a fluctuating force to alter the state of the system, the detailed dynamics of which is insignificant. On its own, the study of quantum dynamics in condensed phase is essential in understanding quantum dissipation and decoherence\(^7\),\(^8\).

Since the system is coupled to the environment, i.e. an open system, which leads to the destruction of the phase, density matrix is used to describe the system dynamics. The diagonal elements of the density matrix give information to the probability distribution of different quantum states. The off diagonal describes coherence/decoherence. To be precise, it is the reduced density matrix, which the bath degrees of freedom are integrated out, that is used to calculate any real observables of interest.

There have been many attempts and rich theories on quantum dynamics in condensed phase, such as Redfield theory\(^9\),\(^10\) and Lindblad theory\(^11\),\(^12\) that cast the density matrix into a master equation form \(\frac{d\rho(t)}{dt}\). Since the Born-Markov approximations are generally imposed, they only work well in the weak coupling cases\(^13\).
The path integral influence functional approach, first derived by Feynman\textsuperscript{14,15} and later applied to the celebrated Caldeira and Leggett model, or the spin-boson model\textsuperscript{7,16}, has been extensively investigated\textsuperscript{17,18}. It is shown that in the case of a system linearly coupled to a harmonic bath, an analytical expression can be obtained\textsuperscript{7,15} and it captures the complete non-Markovian dynamics of the system without any approximations. Numerically exact methods are available, and they often serve as benchmark calculations\textsuperscript{17,19}.

In this thesis, I will focus on using the harmonic back reaction approximation to extend path integral methods to anharmonic environment and the semiclassical-system classical-environment path integral methodology.

1.1 Harmonic and Anharmonic Environment

Harmonic bath model was proposed in the early attempt to model the environment in condensed phase, and has led fruitful success in the theoretical development, such as Marcus electron transfer theory\textsuperscript{20} and Caldeira and Leggett Hamiltonian\textsuperscript{16}. The great advantage is that analytical expressions can be obtained for harmonic oscillators. It might come with surprise that such a simple model can describe a plethora of dynamical processes with great accuracy, such as electron transfer process and energy relaxation in condensed phase environment. The deep reason lies in the central limit theorem\textsuperscript{21}. With sufficient amount of bath modes, no matter how complicated the bath potential might be, as long as the system bath interaction is well dispersed into a large number of degrees of freedom, the bath can be mapped into a harmonic environment\textsuperscript{22}, each one of the harmonic oscillator being the fictitious mode. The collective effect of those fictitious harmonic oscillators
mimics exactly a generic bath. It is often said the within the harmonic limit, linear response theory is valid.

However, there are cases where the bath is intrinsically anharmonic$^{23,24}$ and is not able to reduce to a harmonic bath due to limited numbers of bath degrees of freedom coupled to the system. In this case, there’s no analytical expression for a generic anharmonic bath, and the calculations will be either tedious with perturbation theory assuming the interaction can be treated perturbatively or very computationally expensive for numerical non-perturbative method.

We propose a harmonic back reaction method to resolve this problem based on the observation that the most expensive part of the influence functional computation is the time non-local term. This term is the so called the “back reaction” that describes the system’s influence on the bath. The back reaction has the origin of spontaneous emission, which is a zero-point energy effect at the bottom of the potential well$^{25}$. As every realistic potential energy surface almost always mimics a harmonic potential at the bottom of the potential well, the true back reaction part in the influence functional, which is expensive to calculate numerically, could be well approximated with the analytical harmonic expression, which is trivial to evaluate. In this way, the computational cost is greatly reduced while still preserving great precision. For the calculation of a system interacting with a complicated environment/bath using quantum-classical scheme$^2$, $^{26}$, this method may offer great computation savings in an otherwise a tough case.
1.2 Semiclassical-Classical Path Integral (SCPI)

Path integral methods offer a natural way to merge quantum and classical mechanics through the action, which is a phase factor. In quantum mechanics, the different trajectories comprising the different actions add together to count for constructive and destructive interference, which is characteristic of quantum mechanics. In classical mechanics, the action follows the stationary phase trajectories. Both schemes, quantum and classical mechanics, are trajectory-based in the Feynman’s path integral formulation.

A recently developed methodology, quantum-classical path integral (QCPI), is a successful and efficient method in treating a quantum system coupled to a non-reactive environment. The system takes on all possible trajectories in the forward and backward time propagation whereas the environment follows a particular classical trajectory under the average force (from a specific forward and backward path) of the system. It can be argued that although the environment is quantum mechanical in nature as well, as long as it is not undergoing some intrinsically quantum mechanical process, such as electron/proton transfers and tunneling, it can be well modeled using classical mechanics, for example, the non-bond-breaking vibrations of the bath. This is the simple justification of the QCPI method. It is different from Feynman-Vernon’s influence functional approach, in that the latter integrated out the initial bath distribution to get a close form for harmonic bath, whereas QCPI uses Monte Carlo method to generate the bath initial phase space distribution and propagate them under a given potential. This potential can be any potential, not only limited to the harmonic case. When employing a harmonic bath, QCPI reduced to Feynman-Vernon’s influence functional. Another great advantage of QCPI is that the different Monte Carlo trajectories can be computed on a parallel computing platform and...
the classical trajectory propagation can be obtained from molecular dynamics simulation for real systems\(^1\).

The semiclassical-classical path integral (SCPI) goes one step further based on QCPI to collapse the all possible quantum path of the system onto one single classical trajectory in the forward/bathward propagation. This is done through the stationary phase condition with respect to the system coordinate. This automatically eliminates the exponential scaling of the quantum path. In the real calculation, there will still be \(O(N^3)\) scaling due to the determinant evaluation of the Jacobian matrix in the semiclassical expression and \(O(N^2)\) of the time nonlocal term in the quantum influence function. However, it is still a much better situation than exponential scaling, especially in long time dynamics. In addition, since the trajectories obey stationary phase, the sign problem can be circumvented and allow efficient Monte Carlo integration with limited number of sampling points\(^3^1\).

Our proposed semiclassical-classical path integral is formulated in terms of boundary value problem of the system, i.e. \(\langle s|U|s_1\rangle\langle s_1|\rho_s(0)|s_2\rangle\langle s_2|U^+|s\rangle\), where in the forward propagation, the system starts with \(s_1\) and ends in \(s\), and in the backward propagation, it starts in \(s_2\) and ends up in \(s\). The system trajectory evolves under the force exerted by the bath. We discovered that the system equations of motion not only involve past time, a time nonlocal term as in generalized Langevin equation\(^3^2,3^3\), but also a future time. This does not violate causality after careful examination. Since the problem is formulated as a boundary value problem, the end point in the trajectory should determine its past path. The future-involved term in the equations of motion is a manifestation of the
fact that the current trajectory is predetermined by the future end point. The main computational cost of this semiclassical-classical method is devoted to finding the stationary phase trajectories in the root search algorithm.

Although semiclassical theory propagate trajectories solely on classical dynamics, it captures quantum mechanical behavior because the action from the classical trajectory becomes a phase factor in the influence function, hence adding different classical trajectories with fixed end points allows interference in quantum mechanics. Semiclassical theory is exact for harmonic oscillator and is an excellent approximation as long as the system is not extremely quantum in nature, such as in deep tunneling\textsuperscript{34}. 
1.3 References

27. R. P. Feynman, A. R. Hibbs, and D. F. Styer, Quantum mechanics and path integrals (Dover Publications, Mineola, N.Y., 2010), Emended edn., Dover books on physics,
This chapter briefly describes the path integral methodology that is developed in the Makri group, which the subsequent chapters are based on.

2.1 Path Integral Formulation

Consider a Cartesian Hamiltonian with \( n \) degrees of freedom

\[
H(x, p) = \sum_{j=1}^{n} \frac{p_j^2}{2m_j} + V(x_1, \ldots, x_n) \tag{2.1}
\]

Breaking up the propagator into short time propagators,

\[
e^{-iH\Delta t/\hbar} = e^{-iH\Delta t/\hbar} e^{-iH\Delta t/\hbar} \ldots e^{-iH\Delta t/\hbar} \tag{2.2}
\]

Inserting the complete states of position,

\[
\int dx_k |x_k \rangle \langle x_k| = 1 \tag{2.3}
\]

the time propagator in the position representation becomes,

\[
\langle x_f | e^{-iH\Delta t/\hbar} | x_0 \rangle = \int dx_1 \ldots \int dx_N \prod_{k=1}^{N} \langle x_k | e^{-iH\Delta t/\hbar} | x_{k-1} \rangle \tag{2.4}
\]

The Trotter splitting\(^3\), the symmetric splitting of the potential energy term,

\[
e^{-iH\Delta t/\hbar} \approx e^{-iV\Delta t/2\hbar} e^{-iT\Delta t/\hbar} e^{-iV\Delta t/2\hbar} \tag{2.5}
\]

renders better convergence. Therefore, the time propagator becomes,

\[
\langle x_k | e^{-iH\Delta t/\hbar} | x_{k-1} \rangle \approx \langle x_k | e^{-iT\Delta t/\hbar} | x_{k-1} \rangle e^{-i\Delta t/2\hbar[V(x_k) + V(x_{k-1})]} \tag{2.6}
\]

The kinetic energy part can be evaluated analytically,
\[ \langle x_k | e^{-itH_0/\hbar} | x_{k-1} \rangle = \prod_{j=1}^{n} \left( \frac{m_j}{2\pi i\hbar} \right)^{1/2} \exp \left[ \frac{i}{\hbar} \frac{m_j}{2\Delta t} (x_{j,k} - x_{j,k-1})^2 \right] \]  

(2.7)

\[ \langle x_j | e^{-i\hbar t/\hbar} | x_0 \rangle = \prod_{j=1}^{n} \left( \frac{m_j N}{2\pi i\hbar t} \right)^{1/2} \int d^n x_i \int d^n x_{N-1} \exp \left\{ \frac{i}{\hbar} \sum_{k=1}^{N} \left[ \sum_{j=1}^{n} \frac{m_j N}{2t} (x_{j,k} - x_{j,k-1})^2 - \frac{t}{2N} \left[ V(x_j) + V(x_{N-1}) \right] \right] \right\} \]  

(2.8)

As \( N \to \infty \),

\[ \langle x_j | e^{-i\hbar t/\hbar} | x_0 \rangle = \int D x_t \left( \exp \frac{i}{\hbar} \int_0^t L(x, \dot{x}) \, dt' \right) = \int D x_t \left( \exp \frac{i}{\hbar} S[x_t] \right) \]  

(2.9)

where \( \int D x_t \) stands for integration over all the possible trajectories.

This brings to the celebrated form which the classical action enters in the phase. Different paths will give different values of action, thus different phase factors, and when adding them up, allow interference that is characteristic of quantum mechanics. The stationary phase condition, \( \delta S[x_t] = 0 \), gives Euler-Lagrange equations of motion, \( \frac{\partial L}{\partial x} = \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{x}} \right) \), which is the classical equation of motion. Hence in the Feynman’s path integral formulation, there’s a natural transition between quantum and classical mechanics, and this is the starting point for developing quantum (system)-classical (bath) path integral\(^4-6\) and semiclassical (system)-classical (bath) path integral methodology\(^7\) in condensed phase quantum dynamics. It should be pointed out that even when a classical trajectory is plugged into the phase, it still captures significant quantum effect and the classical trajectory phase is exact for harmonic oscillator.
2.2 Reduced Density Matrix\(^2,8\)

When studying condensed phase dynamics, the dynamics of the system is of our interest and we don’t explicitly concern about the dynamics of the environment. Therefore, the reduced density matrix is used, which integrates over all the environment degrees of freedom and leaves only the system degrees of freedom for consideration, analogous to the probability distribution, \(P(x) = \int p(x, y) dy\). Any real observables can be calculated from the reduced density matrix, \(\langle A \rangle = Tr(\hat{A})\).

Letting \(s\) denote the position of the system, the reduced density matrix is defined as

\[
\rho_{\text{red}}(s', s; t) = Tr_h \left( s' \int e^{\frac{ih}{\hbar}} \rho(0) e^{\frac{ih}{\hbar}} s \right)
\]

where \(s\) and \(s'\) are the system coordinates and \(H\) is the total Hamiltonian.

The time evolution of the reduced density matrix is given by

\[
\rho_{\text{red}}(s', s; t) = \int ds_0^+ \int ds_1^+ \cdots \int ds_{N-1}^+ \int ds_0^- \int ds_1^- \cdots \int ds_{N-1}^- \left( s' \int e^{\frac{-iH_b \Delta t}{\hbar}} s \right) \times IF(s_0^+, s_1^+, \ldots, s_{N-1}^+, s_0^-, s_1^-, \ldots, s_{N-1}^-, s; \Delta t)
\]

where the influence functional \(IF\) has the expression

\[
IF(s_0^+, s_1^+, \ldots, s_{N-1}^+, s_0^-, s_1^-, \ldots, s_{N-1}^-, s; \Delta t)
\]

\[
= Tr_{\text{bath}} \left[ e^{\frac{-iH_{\text{m}}(s') \Delta t}{2\hbar}} e^{\frac{-iH_{\text{m}}(s^-) \Delta t}{2\hbar}} \cdots e^{\frac{-iH_{\text{m}}(s) \Delta t}{2\hbar}} \rho_{\text{bath}}(0) e^{\frac{iH_{\text{m}}(s') \Delta t}{2\hbar}} e^{\frac{iH_{\text{m}}(s^-) \Delta t}{2\hbar}} \cdots e^{\frac{iH_{\text{m}}(s) \Delta t}{2\hbar}} \right]
\]
with \( s^+_k \), \( s^-_k \) being the system’s forward and backward paths respectively. The role of the influence functional is to include nonadiabatic corrections to the exact dynamics along the system’s adiabatic path\(^9\).

Because of the Trotter splitting, the discretized system coordinate varies with time in the following manner

\[
s_0 \left( 0 \rightarrow \frac{1}{2} \Delta t \right), s_1 \left( \frac{1}{2} \Delta t \rightarrow \frac{3}{2} \Delta t \right), \ldots,
\]

\[
s_{N-1} \left( \left( N - \frac{3}{2} \right) \Delta t \rightarrow \left( N - \frac{1}{2} \right) \Delta t \right), s_N \left( \left( N - \frac{1}{2} \right) \Delta t \rightarrow N \Delta t \right)
\]

(2.13)

2.3 DVR (Discrete Variable Representation) State\(^2,10,11\)

The path integral formulation in terms of classical action is expressed in position coordinate. The number of paths for the system can be enormous, especially in long time dynamics. When we study the electron or proton transfer process in solutions, the quantum system is essentially a two-state system with a donor and an acceptor. For other real systems, a multi-state model may be used\(^12,13\). This suggests that for many cases we intend to study, e.g. population change, the continuous coordinate representation is not a good choice. This motivates the utility of DVR (discrete variable representation) states\(^14-16\). It is a site representation which guarantees the structure of the path integral formulation in the position representation using the classical action as the phase, in the meantime having the same number as the quantum states. In other words, the DVR states diagonalize the potential energy operator or equivalently, the position operator.
Assuming that $|\Phi\rangle$ is a basis set, the DVR state $|\mu\rangle$ can be obtained by expanding it in the $|\Phi\rangle$ basis

$$
|u_i\rangle = \sum_{r=1}^{M} L_{ir}^\dagger |\Phi_r\rangle
$$

such that

$$
\langle u_i | s | u_r \rangle = s_i \delta_{ir}
$$

In the case of two-level systems, there are only two DVR states.

2.4 Quantum-Classical Path Integral (QCPI)\textsuperscript{4-6,17}

When we have little information about the bath a priori, we cannot assume the Feynman-Vernon type influence functional for the reduced density. One way to extract the information of the bath is the run molecular dynamics (MD) simulation\textsuperscript{18,19}. In the MD simulation, each bath degree of freedom is propagated classically from a certain initial condition. The QCPI formulation is well suited to couple MD to obtain the dynamics of the classical bath which acts on the quantum system.

In the QCPI formulation, a Hamiltonian is partitioned into a quantum system Hamiltonian $H_0(\hat{s},\hat{p}_s)$ and the rest $H_b(\hat{s},\hat{x},\hat{p})$ that comprises the bath Hamiltonian and the system-bath interaction potential.

$$
\hat{H} = H_0(\hat{s},\hat{p}_s) + H_b(\hat{s},\hat{x},\hat{p}) = H_0(\hat{s},\hat{p}_s) + T_b(\hat{p}) + V(\hat{s},\hat{x})
$$

The reduced density matrix is given by the form

$$
\rho_{\text{red}}(s^\pm_N;N\Delta) = \int dx_0 \int dp_0 P(x_0, p_0) Q(x_0, p_0; s^\pm_N)
$$
In the above expression, \( P(x_0, p_0) \) is the phase space distribution of the bath and the initial conditions can be obtained by Monte Carlo sampling\(^{\text{20, 21}} \). \( Q \) is the quantum influence function given by

\[
Q(x_0, p_0; s_N^\pm) = \int ds_0^\pm \ldots \int ds_{N-1}^\pm \left< s_N^+ \left| e^{-\frac{i\hat{H}_0\Delta t}{\hbar}} \right| s_{N-1}^+ \right> \ldots \left< s_1^+ \left| e^{-\frac{i\hat{H}_0\Delta t}{\hbar}} \right| s_0^+ \right>
\]

\[
\rho_{\text{red}}(s_0^\pm, 0) \left< s_0^- \left| e^{\frac{i\hat{H}_0\Delta t}{\hbar}} \right| s_1^- \right> \ldots \left< s_{N-1}^- \left| e^{\frac{i\hat{H}_0\Delta t}{\hbar}} \right| s_N^- \right> e^{i\varphi(x_0, p_0; x_0^\pm, \ldots, x_N^\pm)\hbar} \tag{2.18}
\]

where

\[
\Phi = -\left[ \frac{1}{2\hbar} \left( \int_0^{\frac{1}{2}\Delta t} V(s_0^-, x(t')) dt' \right) + \sum_{k=1}^{N-1} \int_{\frac{k-1}{2}\Delta t}^{\frac{k+1}{2}\Delta t} V(s_k^-, x(t')) dt' + \int_{\frac{N-1}{2}\Delta t}^{\frac{N+1}{2}\Delta t} V(s_N^-, x(t')) dt' \right] \left( \int_0^{\frac{1}{2}\Delta t} V(s_0^+, x(t')) dt' \right) + \sum_{k=1}^{N-1} \int_{\frac{k-1}{2}\Delta t}^{\frac{k+1}{2}\Delta t} V(s_k^+, x(t')) dt' + \int_{\frac{N-1}{2}\Delta t}^{\frac{N+1}{2}\Delta t} V(s_N^+, x(t')) dt' \right] \right] \tag{2.19}
\]

The bath trajectory \( x(t) \) is moving under the average force of the forward and backward system trajectory. Therefore, for a specific system forward backward path, there’s only one bath trajectory starting from a specific initial condition.

In the same spirit as the Feynman-Vernon influence functional, the influence function incorporates the effect the bath has on the system.
2.5 Solvent-Driven Reference Propagator

The above is the primitive version of QCPI. Convergence with large time steps is always the central strive for a better theoretical frame. Observe that for a given Hamiltonian partitioning into $H_0$ and $H_1$

$$H(\hat{x}, \hat{p}) = \hat{H}_0(\hat{x}, \hat{p}) + \hat{H}_1(\hat{x})$$

(2.20)

The propagator converges with time complexity

$$\Delta t^3 \left[ \hat{H}_0, \left[ \hat{H}_0, \hat{H}_1 \right] \right]$$

(2.21)

which means the closer $H_0$ is to $H$, the larger the quantum time step can be. This is the motivation for a better choice of the system propagator.

The bath free trajectory is altered by the system state due to the system bath interaction. In a mathematical term, the differential equation for the bath is an inhomogeneous one containing a source term that is the system-bath coupling force. Thus the solution to the bath trajectory will have a source free term that represents the free propagation of the bath, plus a source dependent term that counts the alteration of the bath trajectory through the force exerted by the system.

A harmonic oscillator case will serve as a nice illustration of the above argument since it has analytical expressions. Suppose the harmonic bath is linearly coupled to the system,

$$V(s, x) = \frac{1}{2} m_b \omega^2 x^2 - c s x$$

(2.22)

where $c$ is the coupling strength.

The bath follows the following trajectory
The phase in the influence function

\[ \Phi = c \int_0^t dt' \left[ s^+(t') - s^-(t') \right] x(t') \]

\[ = cx_0 \int_0^t dt' \left[ s^+(t') - s^-(t') \right] \cos \omega t' + c \frac{p_0}{m\omega} \int_0^t dt' \left[ s^+(t') - s^-(t') \right] \sin \omega t' \]

\[ + \frac{e^2}{2m\omega} \int_0^t dt' dt'' \left[ s^+(t') - s^-(t') \right] \left[ s^+(t'') + s^-(t'') \right] \sin \omega (t - t'') \]

\[ = \Phi_{\text{ref}} + \Delta \Phi \tag{2.24} \]

The free term in the phase can be incorporated in the system propagator, thus allowing larger quantum time steps. This is analogous to a system interacting with classical light which the system is evolving under a time dependent Hamiltonian.

Hence

\[ i\hbar \frac{\partial}{\partial t} \langle s^1 | \hat{U}_{\text{ref}} (t) | s^n \rangle = \langle s^1 | \hat{H}_{\text{ref}} (t) \hat{U}_{\text{ref}} (t) | s^n \rangle \tag{2.25} \]

This first order differential equation can be solved numerically\textsuperscript{24}.

With

\[ \Delta V = H - H_{\text{ref}} \tag{2.26} \]

\[ \Delta \Phi = - \left[ \frac{1}{2} \Delta V \left( s_0^+, x(t') \right) dt' + \sum_{k=1}^{N-1} \left( \frac{k+1}{2} \right) \Delta V \left( s_k^+, x(t') \right) dt' + \left( \frac{N}{2} \right) \Delta V \left( s_N^+, x(t') \right) dt' \right] \]
The influence function becomes

\[
Q(x_0, p_0; s_{N}^{\pm}) = \int ds_{0}^{\pm} \ldots \int ds_{N-1}^{\pm} \langle s_{N}^{\pm} | \hat{U}_{\text{ref}} (N \Delta t, (N-1) \Delta t; x_0, p_0) | s_{N-1}^{\pm} \rangle \ldots \\
\langle s_{1}^{\pm} | \hat{U}_{\text{ref}} (\Delta t, 0; x_0, p_0) | s_{0}^{\pm} \rangle \rho_{\text{red}} (s_{0}^{\pm}, 0) \langle s_{0}^{\pm} | \hat{U}_{\text{ref}}^{\dagger} (0, \Delta t; x_0, p_0) | s_{1}^{\pm} \rangle \ldots \\
\langle s_{N-1}^{\pm} | \hat{U}_{\text{ref}}^{\dagger} ((N-1) \Delta t, N \Delta t; x_0, p_0) | s_{N}^{\pm} \rangle e^{i \Delta \Phi (s_{m}, p_{m}; s_{m-1}, \ldots, s_{0})} / h 
\]

(2.28)

2.6 Finite Memory and the Iterative Procedure\textsuperscript{2, 25, 26}

The phase that is left out to go into the influence function, \(\Delta \Phi\), couples the current quantum state with all the previous ones and the forward and backward paths are also coupled. In a two-level system case, the number of paths grows with \(4^N\) where \(N\) is the number of time steps.

In a condensed phase setting, the bath has finite memory due to phase cancellation and this is manifested in the finite width of the time autocorrelation function of the bath. Hence the trajectory coupling of the system expands only on finite time interval and allows an effective iterative procedure that renders the computation cost to grow only linearly in time.

Assume the memory span is \(\tau = m \Delta t\), a \(2m\)-rank tensor can be created

\[
R_{m-1} (s_{0}^{\pm}, s_{1}^{\pm}, \ldots, s_{m-1}^{\pm}; x_0, p_0) = \langle s_{m-1}^{\pm} | \hat{U}_{\text{ref}} ((m-1) \Delta t, (m-2) \Delta t; x_0, p_0) | s_{m-2}^{\pm} \rangle \ldots \langle s_{1}^{\pm} | \hat{U}_{\text{ref}} (\Delta t, 0; x_0, p_0) | s_{0}^{\pm} \rangle 
\]

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To propagate through the next step, a propagator tensor of rank $2(m+1)$ is constructed,

$$T_m \left(x_0, p_0, s_0^+, s_1^+, \ldots, s_m^+ \right) = \langle s_m^+ | \hat{U}_{\text{ref}} \left( m \Delta t, (m-1) \Delta t; x_0, p_0 \right) | s_{m-1}^+ \rangle$$

$$\times \langle s_{m-2}^- | \hat{U}_{\text{ref}} \left( (m-2) \Delta t, (m-1) \Delta t; x_0, p_0 \right) | s_{m-1}^- \rangle e^{i \Delta \phi \left(s_m^+, p_0; s_m^+ \ldots s_{m-1}^+ \right)}$$

(2.29)

In this way, the next step $2m$-rank tensor can be created.

$$R_m \left(s_0^+, \ldots, s_m^+, x_0, p_0 \right) = \int ds_0^+ T_m \left(s_0^+, \ldots, s_m^+, x_0, p_0 \right) R_{m-1} \left(s_0^+, \ldots, s_{m-1}^+, x_0, p_0 \right)$$

(2.30)

At each time step, the influence function can be obtained

$$Q \left(s_N^+, x_0, p_0; N \Delta t \right) = \int ds_N^+ \cdots \int ds_1^+ R_N \left(s_N^+, \ldots, s_1^+, x_0, p_0 \right)$$

(2.31)

as well as the density matrix

$$\rho_{\text{rad}} \left(s_N^+, N \Delta t \right) = \int dx_0 \int dp_0 Q \left(s_N^+, x_0, p_0; N \Delta t \right), N = m, m+1, \ldots$$

(2.32)

This procedure is repeated until the end time point of interest is reached.

2.7 Discretization of the Bath$^{18, 27, 28}$

The bath is characterized by a spectral density function

$$J(\omega) = \frac{\pi}{2} \sum_{k=1}^{N} \frac{e_k^2}{m \omega_k} \delta(\omega - \omega_k)$$

(2.33)

For example, the Ohmic spectral density has the form

$$J(\omega) = \gamma \omega \exp \left( -\omega / \omega_c \right)$$

(2.34)

where $\gamma$ is related to the Kondo parameter $\xi$ as $\xi = 2\gamma / \pi \hbar$. 

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In any practical calculation the spectral density is discretized into finite modes. There is a cutoff frequency $\omega_N = \omega_f$. There are various ways to discretize the bath through which the number of modes, the frequency of each modes and the coupling constant $c_k$ are determined. The number of oscillators needs to be enough so that the recurrence time $2\pi / \Delta \omega$ is larger than any other time scale of interest. In the following chapter, we will specify how the bath is discretized in each of the applications.
2.8 References

CHAPTER 3: HARMONIC BACK-REACTION APPROXIMATION IN ANHARMONIC ENVIRONMENT

This chapter is based on the paper [Fei Wang and Nancy Makri. “Using harmonic back-reaction approximation in quantum influence functional for anharmonic environment” (in preparation)].

3.1 Anharmonic Environment Path Integral

Understanding dissipative dynamics of a quantum system embedded in a polyatomic environment is important in many areas of physics and chemistry\(^1\)\(^-\)\(^5\). The most celebrated spin-boson model has been investigated extensively over the decades\(^6\)\(^-\)\(^10\). The bosonic bath is composed of non-interacting harmonic oscillators and its influence on the system is characterized by the spectral density. The widespread utility of the spin-boson model lies in the fact that the system-bath coupling typically scales as \(1/\sqrt{N}\), with \(N\) being the number of bath modes, and in the thermodynamic limit, all the higher order contributions vanish and only the Gaussian character remains\(^11\). This form the basis of Marcus electron transfer theory\(^12\)\(^-\)\(^14\). In addition to the above merit, the harmonic bath can be evaluated analytically, and the spectral density can be extracted from molecular dynamics simulation\(^15\).

However, there are situations where the harmonic bath approximation is not valid, for instance intramolecular vibrational energy relaxation and donor-acceptor complex strongly coupled to low frequency or nonpolar solvents. Several authors\(^16\)\(^-\)\(^20\) have used independent Morse oscillators or quartic oscillators to study such anharmonic effect. The common ways to incorporate the anharmonic effect would be to include the multi-time
correlation functions of the bath beyond second order or to numerically calculate the
dynamics of bath explicitly.

The formulation of path integral for anharmonic environment, formally speaking,
will bear no difference from what was described in the previous section. The free bath
propagation can be incorporated into the reference propagator and the inhomogeneous
driven term goes into the phase factor $\Delta \Phi^{21}$. The technical difference is, for the
anharmonic potential, analytical expressions cannot be obtained, thus the bath trajectories
are propagated numerically, e.g. Verlet algorithm$^{22, 23}$. It is this numerical integration of
Newton’s equation that becomes computationally expensive for many bath degrees of
freedom in long time dynamics. Usually for one quantum step, multiple classical steps need
to be taken$^{24}$, meaning solving the differential equation numerically multiple times within
each quantum time step. Assuming the quantum system is of $M$ levels, the memory length
is $L$, and the quantum time step is $N$ times larger than the classical time step, then within
each quantum time step, $N \times M^{2L}$ differential equations need to be solved numerically to
get all the trajectories, $p(t)$ and $q(t)$. And since $\Delta \Phi$ involves current time step coupling to
previous time steps, the trajectory grows exponentially within memory span, so the
calculation of all these classical trajectories can be very costly. A good strategy to
approximate $\Delta \Phi$ is necessary in order to make the calculations efficient.

3.2 Harmonic Back-Reaction

Since the bath trajectory evolves under the force of the system, i.e. the bath equation
of motion is an inhomogeneous one, the solution of the bath trajectory inevitably contains
a free propagation term (solution to the homogeneous differential equation) and a “back
reaction” term (integration of the inhomogeneous term with the Green’s function), a term that counts for the influence of the system to the bath, “react back”. These two terms are directly carried to the phase of the path integral expression.

For a harmonic bath linearly coupled to the system, the interaction potential is given by the following\(^{25}\),

\[
V(s,x) = \frac{1}{2} m\omega^2 x^2 - csx
\]  

(3.1)

where \(c\) is the coupling strength, \(s\) and \(x\) are system and bath coordinates respectively.

The bath trajectory has an analytical expression, which is a forced harmonic oscillator\(^{26}\).

\[
x(t) = x_0 \cos \omega t + \frac{P_0}{m\omega} \sin \omega t + \frac{c}{2m\omega} \int_0^t dt' \left[ s^+ (t') + s^- (t') \right] \sin \omega (t - t')
\]  

(3.2)

It is composed of a free propagation term and a back-reaction term.

\[
x_{\text{free}}(t) = x_0 \cos \omega t + \frac{P_0}{m\omega} \sin \omega t
\]  

(3.3)

\[
x_{\text{br}}(t) = \frac{c}{2m\omega} \int_0^t dt' \left[ s^+ (t') + s^- (t') \right] \sin \omega (t - t')
\]  

(3.4)

It is shown that these two terms give two different contributions to the Feynman-Vernon influence functional\(^{27}\). Below is a sketch of this.

\[
\Phi_{\text{free}} = cx_0 \int_0^t dt' \left[ s^+ (t') - s^- (t') \right] \cos \omega t' + c \frac{P_0}{m\omega} \int_0^t dt' \left[ s^+ (t') - s^- (t') \right] \sin \omega t'
\]  

(3.5)

\[
\Phi_{\text{br}} = \frac{c^2}{2m\omega} \int_0^t dt' \int_0^t dt'' \left[ s^+ (t') - s^- (t') \right] \left[ s^+ (t'') + s^- (t'') \right] \sin \omega (t - t'')
\]  

(3.6)

\[
\Phi = \Phi_{\text{free}} + \Phi_{\text{br}}
\]  

(3.7)
They can be cast into the standard influence functional form with minimal algebraic manipulation,

\[ IF = \exp \left[ -\frac{1}{\hbar} \int_0^t dt' \int_0^{t''} dt'' \left( \alpha(t' - t'')s^+(t'') - \alpha^*(t' - t'')s^-(t'') \right) \right] \]

Plugging this phase factor into the influence function and integrate with respect to the Wigner distribution\(^{28}\),

\[ Q(x_0, p_0; S^+) = \int ds_0^+ \cdots \int ds_{N-1}^+ \left\langle s_0^+ \left| e^{-iH_0 t'/\hbar} \right| s_0^- \right\rangle \cdots \left\langle s_N^+ \left| e^{-iH_0 t'/\hbar} \right| s_N^- \right\rangle \rho_{\text{red}} (s_0^+, 0) \]

\[ \times \left\langle s_0^- \left| e^{iH_0 t'/\hbar} \right| s_1^- \right\rangle \cdots \left\langle s_{N-1}^- \left| e^{iH_0 t'/\hbar} \right| s_N^- \right\rangle e^{i\phi(x_0, p_0; s_0^+, \cdots; s_N^+)} \]

\[ P(x_0, p_0) = \frac{1}{\pi \hbar} \tanh \left( \frac{1}{2} \hbar \omega \beta \right) e^{-\tanh \left( \frac{1}{2} \hbar \omega \beta \right) (\Delta s^2 + p_0^2) / 2 \hbar} \]

we get the Feynman-Vernon influence functional from these two contributions,

\[ \rho_{\text{red}} (S^+_N; t) = \int ds_0^+ \cdots \int ds_{N-1}^+ \left\langle s_0^+ \left| e^{-iH_0 t'/\hbar} \right| s_0^- \right\rangle \cdots \left\langle s_N^+ \left| e^{-iH_0 t'/\hbar} \right| s_N^- \right\rangle \rho (s_0^+, 0) \]

\[ \times \left\langle s_0^- \left| e^{-iH_0 t'/\hbar} \right| s_1^- \right\rangle \cdots \left\langle s_{N-1}^- \left| e^{-iH_0 t'/\hbar} \right| s_N^- \right\rangle \times IF \]

with

\[ IF = IF_{\text{free}} \times IF_{\text{br}} \]
It is more transparent from this correlation function expression to see that the first term in the sum is temperature dependent, and the second term is temperature independent and looks exactly like a free oscillator at zero-point energy. The first term derives from the free bath trajectory part and the second term comes from the back-reaction part. Drawing the analogy from light, the first term represents the physical process of the stimulated emission and absorption of the phonon, and the second term the stimulated emission. In the solvent driven propagator scheme, the first term has already been incorporated into the reference propagator.

Since the back-reaction term is of spontaneous emission origin, which is a zero-point energy effect at the bottom of the well, plus the fact that every potential energy surface resembles a harmonic potential at the bottom of the well, any back-reaction contribution can be approximated by a harmonic one, if the anharmonicity is not exceedingly large. This is the basis for the harmonic back reaction approximation.

Therefore, for any type of anharmonic bath, the trajectory can be approximated by

$$x(t) \equiv x_{\text{free}}(t) + \frac{c}{2m\omega} \int_0^t dt' \left[ s^+(t') + s^-(t') \right] \sin \omega(t-t')$$  \hspace{1cm} (3.16)

from which
Therefore, with the back-reaction part approximated by the analytical harmonic back reaction, the calculation can be expected to be both fast and accurate. Together with the free propagation incorporated in the reference propagator, large quantum steps can be taken, and the interrogation of long-time dynamics is possible in anharmonic environment.

3.3 Discretization of Harmonic Back-Reaction Phase

The system coordinate varies with time in the fashion consistent with symmetric trotter splitting:

\[
\Delta \Phi \equiv \frac{e^2}{2m\omega^3} \int_0^t dt' \int_0^{t'} dt'' \left[ s^+(t') - s^-(t') \right] \left[ s^+(t'') + s^-(t'') \right] \sin \omega (t' - t'')
\] (3.17)

Thus, corresponding to the discretized version of the system trajectories, the \textit{Sine} function in \( \Delta \Phi \) can be integrated out analytically in each time segment\(^{29}\), therefore reducing to a number trivial to calculate for the computer. The discretized \( \Delta \Phi \) is given as follows:

\[
\Delta \Phi_{00} = \frac{e^2}{2m\omega^3} \left( s^+_0 - s^-_0 \right) \left( s^+_0 + s^-_0 \right) \left( \frac{1}{2} \omega \Delta t - \sin \frac{1}{2} \omega \Delta t \right)
\] (3.19)

\[
\Delta \Phi_{k0} = \frac{e^2}{2m\omega^3} \left( s^+_k - s^-_k \right) \left( s^+_0 + s^-_0 \right) \left[ \sin k \omega \Delta t - \sin (k - 1) \omega \Delta t - \sin \left( k + \frac{1}{2} \right) \omega \Delta t \right]
\] (3.20)

\[+ \sin \left( k - \frac{1}{2} \right) \omega \Delta t \], \( k = 1, \ldots, N - 1 \)
Due to the finite memory length of the bath correlation function in condensed phase, these terms only span the length up to $k_{\text{max}}$.

3.4 Choice of the Back-Reaction Harmonic Frequency

We propose two ways to choose the harmonic back reaction frequency for each harmonic mode. The first one is to choose the frequency matching the bottom of the anharmonic potential well, essentially the quadratic truncation of the potential. The second one is the harmonic mapping of the anharmonic bath and use the effective harmonic modes as the frequencies$^{11,15}$. It will be shown from the numerical calculations that the effective modes through harmonic mapping offers better approximation, and in fact with great accuracy.
3.5 Harmonic Mapping

It is well known from linear response theory\textsuperscript{30,31} that if there are infinite number (in practice large enough) of oscillators and the coupling is well distributed among all the modes, the effect of the environment can be described in terms a harmonic bath linearly coupled to the system\textsuperscript{11,15}. Such a fictitious harmonic bath has a simple form

\[ H_b = \sum_{i=1}^{M} \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 x_i^2 - c_i f_i(s) x_i \]  

(3.26)

where \( M \) is the number of fictitious harmonic oscillators, \( s \) is the system coordinate, \( x \) the bath coordinate and \( c \) the coupling constant.

The bath can be fully characterized by the spectral density\textsuperscript{6}

\[ J(\omega) = \frac{\pi}{2} \sum_{j} \frac{c_j^2}{m_j \omega_j} \delta(\omega - \omega_j) \]  

(3.27)

The harmonic mapping is achieved by matching the environment’s force-force autocorrelation function \( \alpha(t) \) with that of the harmonic bath\textsuperscript{15}.

\[ \alpha(t) = f(x(0)) \cdot f(x(t)) = Tr \left[ \rho e^{-iHt/\hbar} f e^{iHt/\hbar} f \right] \]

\[ = \sum_{i=1}^{n} c_i^2 x_i(0) x_i(t) \beta = \frac{\hbar}{\pi} \int_{0}^{\infty} d\omega J(\omega) \left( \coth \left( \frac{1}{2} \hbar \omega \beta \right) \cos \omega t + i \sin \omega t \right) \]  

(3.28)

In practice, the environment’s classical correlation function can be obtained from molecular dynamic simulation, which corresponds to the high temperature limit of the quantum correlation function

\[ \alpha_{ct}(t) = \lim_{\hbar \to 0} \alpha(t) = \frac{2}{\pi \beta} \int_{0}^{\infty} \frac{J(\omega)}{\omega} \cos \omega t \, d\omega \]  

(3.29)

Therefore, by reversing the relation,
The reorganization energy $\lambda$ is

$$\lambda = \frac{4}{\pi} \int_{0}^{\infty} \frac{J(\omega)}{\omega} d\omega = 2 \sum_{j=1}^{M} \frac{c_{j}^{2}}{m_{j} \omega_{j}^{2}}$$  \hspace{1cm} (3.31)$$

The autocorrelation function at time zero can be given by the reorganization energy

$$\alpha_{c_{j}}(0) = \frac{2}{\beta \pi} \int_{0}^{\infty} \frac{J(\omega)}{\omega} d\omega = \frac{\lambda}{2\beta}$$  \hspace{1cm} (3.32)$$

There can be different ways to obtain the discretized modes. We prefer a physically motivated one, in which the discretization divides the frequency into intervals that correspond to equal fractions of the reorganization energy and places the discrete frequencies at the center of these intervals$^{15}$,

$$\frac{4}{\pi} \int_{0}^{\infty} \frac{J(\omega)}{\omega} d\omega = \frac{j - \frac{1}{2}}{M} \lambda$$ \hspace{1cm} (3.33)$$

$$\frac{4\beta}{\pi} \int_{0}^{\infty} d\omega \int_{0}^{\infty} \alpha_{c_{j}}(t) \cos \omega t \, dt = \frac{j - \frac{1}{2}}{M} \lambda$$ \hspace{1cm} (3.34)$$

Integrating out $\cos \omega t$, we get

$$\frac{2M \omega_{j}}{\pi \alpha_{c_{j}}(0)} \int_{0}^{\infty} dt \frac{\alpha_{c_{j}}(t)}{\omega_{j} t} \sin \omega_{j} t = j - \frac{1}{2}$$ \hspace{1cm} (3.35)$$

This equation has the form of $f(\omega_{j}) = j - \frac{1}{2}$ and finding $\omega_{j}$ can be achieved by root searching algorithm, such as the secant method.
3.6 Model System

The system is a two-level system with the Hamiltonian

\[ H_0 = -\hbar \Omega \sigma_x + \hbar \epsilon \sigma_z \]  

(3.36)

The discrete system states are represented by the two DVR states, denoted by \( s \) and in our case take the value 0 and 2. We choose \( \Omega = 1 \) and system mass \( M = 1 \). \( \epsilon \) denotes asymmetry of the system potential.

To construct an anharmonic bath, we modify the spin-boson model by adding a quartic term to the harmonic potential,

\[
H_b = \sum_j \left( \frac{1}{2} m \omega_j^2 \left( x_j - \frac{c_j s}{m \omega_j^2} \right)^2 + b_j \left( x_j - \frac{c_j s}{m \omega_j^2} \right)^4 \right)
\]

(3.37)

\( H_b \) depicts the interactive anharmonic bath. The parameter \( b \) quantifies the anharmonicity. \( b \) is calculated through first order perturbation theory such that the zero-point energy of the quartic potential is 10% larger than the harmonic one, i.e.

\[
\langle \psi_0 | b_j x^4 | \psi_0 \rangle = 10\% \times \frac{1}{2} \hbar \omega_j
\]

(3.38)

where \( \psi_0 \) is the harmonic oscillator ground state wavefunction

\[
\psi_0(x) = \left( \frac{m \omega}{\pi \hbar} \right)^{1/4} e^{-m x^2 / 2 \hbar}
\]

(3.39)

Then

\[
b_j = 10\% \times \frac{2}{3} \omega_j^3 m_j / \hbar
\]

(3.40)

We choose \( m_j = 1 \) for all bath oscillators.
Figure 1. Illustration of anharmonic potential (red) compared to harmonic potential (black). The anharmonicity is 10%. The frequency in this figure is chosen to be $\omega = 4$. The first two horizontal lines are the ground state energies of the harmonic and anharmonic potentials (purple: harmonic; yellow: anharmonic). The next two horizontal lines on the top are energies of the first excited state (purple: harmonic; yellow: anharmonic). The anharmonic potential eigen energies are calculated through harmonic oscillator eigenfunctions.

This graph shows a comparison of a harmonic oscillator and an anharmonic oscillator potential used in the bath. The frequency $\omega = 4$. The steeper potential is the
anharmonic potential. The lines represent the ground and first excited energy level, with the anharmonic ones larger than the harmonic ones.

The bath modes are characterized by the spectral density. We use Ohmic spectral density for the bath

\[ J(\omega) = \frac{\pi}{2} h \xi \omega e^{-\omega^2/\omega_c^2} \]  \hspace{1cm} (3.41)

where \( \xi \) is the Kondo parameter.

Following this equation, the classical autocorrelation function is

\[ \alpha_{cl}(t) = \frac{h \xi}{\beta} \left( \frac{\omega_c}{1 + \omega_c^2 t^2} \right) \]  \hspace{1cm} (3.42)

Therefore

\[ \omega_j = \omega_c \ln \left( \frac{M}{M - j + 0.5} \right) \]  \hspace{1cm} (3.43)

\[ c_j = \sqrt{\xi m \omega_c / M \omega_j} \]  \hspace{1cm} (3.44)

The number of oscillators is chosen to be 20-30 such that the bath shows enough dissipation before reoccurrence, but not too many to approach the harmonic limit.

The bath initial condition is taken to be Boltzmann distribution

\[ P_{cl}(q_0, p_0) = \prod_j \frac{\omega_j \beta}{2\pi} \exp \left( -\frac{1}{2} \beta m \omega_j^2 q_{0,j}^2 - \beta b \beta q_{0,j}^4 - \frac{\beta p_{0,j}^2}{2m_j} \right) \]  \hspace{1cm} (3.45)

With the system in \( s = 0 \) state, the bath is initially in equilibrium with this localized state\(^{32}\).

The effective harmonic bath is constructed by calculating the force-force autocorrelation function

\[ \alpha(t) = \langle f(x(0)) \cdot f(x(t)) \rangle_\beta \]  \hspace{1cm} (3.46)
where the force is

\[ f_j(t) = c_j x_j(t) + 4bc_j x_j^3(t)/m_j \omega_j^3 \]  \hspace{1cm} (3.47)

The discretized effective bath modes are given by \(^{33}\)

\[ \frac{2Mj\omega_j}{\pi \alpha(0)} \int_0^\infty dt \frac{\alpha(t)}{\omega_j} \sin \omega_j t = j - \frac{1}{2} \]  \hspace{1cm} (3.48)

Below we show calculations of a two-level system coupled to an anharmonic bath. The system of both symmetric \((\epsilon = 0)\) and asymmetric \((\epsilon \neq 0)\) cases will be demonstrated. In each graph, there are four curves. The black line is the accurate calculation for anharmonic potential, bath trajectories propagated through Verlet algorithm. The black dot is the harmonic back reaction frequency with the effective bath modes. The bath reference trajectories in the reference propagator are obtained by Verlet. The effective bath modes are constructed by harmonic mapping and enter into the \(\Delta \Phi\). The blue line is the harmonic back reaction frequency chosen to be the frequency at the bottom of the well, essentially \(\omega_j\), which is just the first order truncation of the anharmonic potential. The red line is obtained by assuming that the anharmonic bath is an effective harmonic bath and the bath modes are constructed through harmonic mapping, essentially assuming the problem can be reduced to a two-level system coupled to a harmonic bath.
3.7 Numerical Results and Discussions

Figure 2. Population of state 1 for a symmetric two level system coupled to an anharmonic bath with 10% anharmonicity. 25 oscillators, $\beta = 3, \xi = 0.3, \omega_c = 3$.

Black line: accurate calculation for anharmonic potential.

Black dot: the harmonic back reaction frequency with the effective bath modes.

Blue line: the harmonic back reaction frequency chosen to be the frequency at the bottom of the well.

Red line: assuming the anharmonic bath is an effective harmonic bath, the bath modes constructed through harmonic mapping.
Figure 3. Population of state 1 for a symmetric two level system coupled to an anharmonic bath with 10% anharmonicity. 25 oscillators, $\beta = 1$, $\xi = 0.3$, $\omega_c = 3$.

Black line: accurate calculation for anharmonic potential.

Black dot: the harmonic back reaction frequency with the effective bath modes.

Blue line: the harmonic back reaction frequency chosen to be the frequency at the bottom of the well.

Red line: assuming the anharmonic bath is an effective harmonic bath, the bath modes constructed through harmonic mapping.
Figure 4. Population of state 1 for a symmetric two level system coupled to an anharmonic bath with 10% anharmonicity. 25 oscillators, $\beta = 0.2, \xi = 0.3, \omega_c = 3$.

Black line: accurate calculation for anharmonic potential.

Black dot: the harmonic back reaction frequency with the effective bath modes.

Blue line: the harmonic back reaction frequency chosen to be the frequency at the bottom of the well.

Red line: assuming the anharmonic bath is an effective harmonic bath, the bath modes constructed through harmonic mapping.

First, we show results at different temperatures with other parameters fixed (Figure 2-4). Notice that the harmonic back reaction substitution with the effective modes gives excellent approximations to the accurate dynamics across temperatures. Although the
harmonic back reaction in theory is an approximation to the true back reaction, the effective bath modes encode some of the anharmonicity collectively. With finite bath, if the anharmonicity is not huge, the collective harmonic effect dominates the bath dynamics. From an influence functional point of view, the quadratic term in the influence functional expansion dominates. In addition, as mentioned in the previous section, since the harmonic back reaction is a zero-point energy effect, we expect the anharmonicity is small at the bottom of the potential well and thus can be approximated by a harmonic potential. Also, in the reference propagator, some degree of anharmonicity is automatically accounted for. Thus, the harmonic back reaction is an excellent approximation with minimal computational cost.

Second, the harmonic mapping does not match exactly the accurate results, meaning the anharmonic bath has not reached the central limit, hence not quite harmonic, which also indicates that the harmonic back reaction method is necessary in that it is able to deal with regimes where the full harmonic bath model is not valid.

Third, the harmonic back reaction with the frequency to be the bottom of the well does not offer a good approximation. It is just the quadratic truncation of the anharmonic potential. As mentioned above, the effective bath modes have already incorporated some or most of the anharmonicity whereas the quadratic truncation does not.

The following plots (Figure 5-7) will show bath with larger \( \omega_c \) where the system is very off-resonant with the bath, and at different temperatures. They show similar trends. It is observed that the harmonic bath approximation is better than the quadratic truncation, which reiterates the point that the effective modes have already incorporated some degree
of anharmonicity, thus additionally justify the legitimacy of the back-reaction approximation.

Figure 5. Population of state 1 for a symmetric two level system coupled to an anharmonic bath with 10% anharmonicity. 20 oscillators, $\beta = 1$, $\xi = 0.1$, $\omega_c = 10$.

Black line: accurate calculation for anharmonic potential.

Black dot: the harmonic back reaction frequency with the effective bath modes.

Blue line: the harmonic back reaction frequency chosen to be the frequency at the bottom of the well.

Red line: assuming the anharmonic bath is an effective harmonic bath, the bath modes constructed through harmonic mapping.
Figure 6. Population of state 1 for a symmetric two level system coupled to an anharmonic bath with 10% anharmonicity. 20 oscillators, $\beta = 0.2$, $\xi = 0.1$, $\omega_c = 8$.

Black line: accurate calculation for anharmonic potential.

Black dot: the harmonic back reaction frequency with the effective bath modes.

Blue line: the harmonic back reaction frequency chosen to be the frequency at the bottom of the well.

Red line: assuming the anharmonic bath is an effective harmonic bath, the bath modes constructed through harmonic mapping.
Figure 7. Population of state 1 for a symmetric two level system coupled to an anharmonic bath with 10% anharmonicity. 30 oscillators, $\beta = 0.2$, $\xi = 0.15$, $\omega_c = 6$.

Black line: accurate calculation for anharmonic potential.

Black dot: the harmonic back reaction frequency with the effective bath modes.

Blue line: the harmonic back reaction frequency chosen to be the frequency at the bottom of the well.

Red line: assuming the anharmonic bath is an effective harmonic bath, the bath modes constructed through harmonic mapping.
It is expected that as the number of oscillators increases, the harmonic mapping becomes a better approximation, which is an obvious outcome of linear response theory and central limit theorem. The following plot (Figure 8) shows this outcome. As we increase the number of oscillators from 20 to 35, the bath is approaching the harmonic limit thus both the back reaction and the harmonic bath give excellent agreement with the accurate one.

Figure 8. Population of state 1 for a symmetric two level system coupled to an anharmonic bath with 10% anharmonicity. 35 oscillators, $\beta = 1, \xi = 0.1, \omega_c = 8$.

Black line: accurate calculation for anharmonic potential.

Black dot: the harmonic back reaction frequency with the effective bath modes.

Blue line: the harmonic back reaction frequency chosen to be the frequency at the bottom of the well.

Red line: assuming the anharmonic bath is an effective harmonic bath, the bath modes constructed through harmonic mapping.
The rest (Figure 9-10) show asymmetric cases at different temperatures. The harmonic back reaction is in excellent agreement with the accurate calculation.

Figure 9. Population of state 1 for an asymmetric (asymmetry denoted by $\epsilon$) two level system coupled to an anharmonic bath with 10% anharmonicity. 20 oscillators, $\beta = 0.5$, $\epsilon = 1$, $\xi = 0.1$, $\omega_c = 8$.

Black line: accurate calculation for anharmonic potential.

Black dot: the harmonic back reaction frequency with the effective bath modes.

Blue line: the harmonic back reaction frequency chosen to be the frequency at the bottom of the well.

Red line: assuming that the anharmonic bath is an effective harmonic bath, the bath modes constructed through harmonic mapping.
Figure 10. Population of state 1 for an asymmetric (asymmetry denoted by \( \epsilon \)) two level system coupled to an anharmonic bath with 10% anharmonicity. 20 oscillators, \( \beta = 0.2, \epsilon = 3, \xi = 0.1, \omega_c = 8 \).

- Black line: accurate calculation for anharmonic potential.
- Black dot: the harmonic back reaction frequency with the effective bath modes.
- Blue line: the harmonic back reaction frequency chosen to be the frequency at the bottom of the well.
- Red line: assuming that the anharmonic bath is an effective harmonic bath, the bath modes constructed through harmonic mapping.
3.8 Conclusion

In situations where the environment is intrinsically anharmonic and cannot be reduced to a harmonic bath, anharmonic effect needs to be accounted for. Instead of including higher order terms of the bath response function in terms of multi-time correlation functions, or directly calculate the bath dynamics explicitly, we proposed a harmonic back reaction approximation within the QCPI framework to effectively incorporate the anharmonic effect. We pointed out that the back reaction has the origin of spontaneous emission which is a zero-point energy effect. This forms the basis for the validity of the harmonic back reaction approximation, as any potential at the bottom of the well can be expanded accurately up to a quadratic term.

We derived the discretized expression of the harmonic back reaction consistent with Trotter splitting of the time segment of the quantum system and used the modified spin-boson model adding a quartic term to test the accuracy of this approximation. Through various temperature ranges, coupling strength, bath frequencies and system symmetry character, we demonstrated that the harmonic back reaction approximation is a very efficient and accurate method for treating non-harmonic environment with varying parameters. Since the harmonic back reaction expressions are analytical, it is a huge computational saving, which is its biggest merit. It is also amenable to merging with molecular dynamics to calculate real systems within an anharmonic environment.
3.9 References

29 P. L. Waters, A. Bose, and N. Makri, Iterative evaluation of the quantum-classical path integral within a quadratic treatment of the back-reaction (in preparation)
CHAPTER 4: SEMICLASSICAL-CLASSICAL PATH INTEGRAL (SCPI)

This chapter is based on the paper [Fei Wang and Nancy Makri, “Semiclassical-classical path integral of system coupled to a harmonic bath” (in preparation)].

4.1 Introduction

The development of robust methodologies and efficient computational tools for simulating quantum dynamics in condensed phase remains central to theoretical chemistry. *Ab initio* quantum mechanical treatment of the entire system is not possible except for a few degrees of freedom. The main limitation lies in the exponential growth of the dimensionality, thus basis set, of the Schrödinger equation and the analogous exponential proliferation of the paths in Feynman path integral formulation of quantum dynamics. The most common strategy is to split the entire system into a subsystem and the environment. The subsystem receives the quantum treatment whereas the environment is simulated by approximate classical methods.

There are a variety of methods for embracing this idea of quantum-classical system-bath dynamics. One approach is based on the Ehrenfest model\(^1, 2\), in which one simultaneously integrates the time-dependent Schrödinger equation for the system and the classical equation of motion for the bath. Another common method is surface hopping\(^3, 4\), where the quantum system is assumed to be time-evolving on an adiabatic surface except for localized hopping between surfaces. Besides the above approaches, the Makri group have developed a systematic methodology and effective numerical methods based on Feynman path integral formulation. The system of a few degrees of freedom receives the
full quantum mechanical treatment and the environment is treated either classically (QCPI)\(^5, 6\) or semiclassically (FBSD)\(^7, 8\). Except the condition that the environment can be simulated by classical mechanics, QCPI or FBSD make no \textit{ad hoc} assumptions, and the system and bath dynamics are all trajectory-based in path integral formulation. The exponential growth of the quantum paths is ameliorated by the finite memory span of the environment\(^9-11\).

In this section, we present an alternative method in which we treat the system semiclassically and the environment classically. The semiclassical treatment of the system collapses all the quantum paths onto only classical trajectories, therefore automatically eliminates the problem of the exponential growth of the quantum paths. The phase factor is smooth under stationary phase conditions, therefore bypassing the issue of the sign problem in Monte Carlo sampling. Unlike QCPI which is suitable for modeling quantum systems with a few discrete levels, SCPI is natural to work with continuous coordinate and thus multi-level systems.

4.2 Semiclassical Propagator

Semiclassical mechanics is an elegant theory. Conceptually, it offers great insight into the connection between quantum mechanics and classical mechanics. Computationally, it reduces the many quantum paths onto classical trajectories. From the early stage of Van Vleck propagator\(^12\), WKB theory, to the more recent development by Herman-Kluk-Kay\(^13, 14\), Miller\(^15-18\) and Heller\(^19-21\), semiclassical theory has become a rich subject and seen applications in many areas of physics and chemistry\(^7, 8, 17, 18, 22-25\).
The essence of semiclassical theory is the stationary phase condition, i.e. expanding the action around classical trajectories in a power series, and then truncating to the second order\(^2\). Consider the path

\[ x(t) = x_0(t) + \delta x(t) \]  \hspace{1cm} (4.1)

where \(x_0(t)\) corresponds to a classical trajectory. The action \(S\) can be expanded in orders of \(\delta x(t)\) with fixed endpoints \((x', t'; x, t)\)

\[ S = S_0 + \delta S_0 + \frac{1}{2} \delta^2 S_0 + \ldots \]  \hspace{1cm} (4.2)

where

\[ S_0 = \int_0^t L(x_0, \dot{x}_0, t') dt' \]  \hspace{1cm} (4.3)

\[ \delta S_0 = 0 \]  \hspace{1cm} (4.4)

\[ \langle x'| e^{-iHt/\hbar} | x \rangle^{SC} = \left( \frac{m}{2\pi i\hbar} \right)^{1/2} \sum_{\text{classical paths}} \int D\delta x_0 e^{i \left( S_0 + \frac{1}{2} \delta^2 S_0 \right) / \hbar} \]  \hspace{1cm} (4.5)

With some algebra, the second variation in the phase will turn into a Gaussian integral and can be integrated out, which brings to the form

\[ \langle x'| e^{-iHt/\hbar} | x \rangle^{SC} = \sum_{\text{classical paths}} \left( \frac{-\partial^2 S / \partial x \partial x'}{2\pi i\hbar} \right)^{1/2} e^{iS/\hbar} \]  \hspace{1cm} (4.6)

Equation (4.6) is the boundary value representation of the semiclassical propagator. There are other forms of semiclassical expressions such as initial value representation\(^1\) or coherent state representation\(^2\).
4.3 Semiclassical-Classic Path Integral (SCPI)

The idea of semiclassical-classical path integral (SCPI) is to enforce the bath to propagate classically on the average force of the system trajectories while maintaining separate forward and backward system trajectories following classical dynamics. We proceed with the QCPI formulation⁵,⁶ where the bath has already assumed a classical path while maintaining all possible paths of the system, then apply stationary phase condition to the system coordinate which reduce the many system trajectories to one trajectory for the forward propagation and one for the backward propagation under one bath initial condition. These separate forward and backward trajectories are the basis for quantum interference.

We start with a system Hamiltonian $H_0$ couple to a harmonic bath, assuming the bath is linearly coupled to the system. This Hamiltonian can be quite general as the system potential can assume any form and the bath in many cases can be mapped into a harmonic bath.

$$H = \frac{p^2}{2M} + V_0(s) + \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} x_i^2 - \sum_{i=1}^{N} c_i f_i(s) x_i + \frac{c_i^2 f_i^2(s)}{2m_i \omega_i^2} \quad (4.7)$$

The last term is the counter term added to counter balance the distortion of the system potential by the system bath interaction.

The density matrix is

$$\rho_{red}(s_N^+; N\Delta t) = \int dx_0 \int dp_0 P(x_0, p_0) Q(x_0, p_0; s_N^+) \quad (4.8)$$

with
\[
Q(x_0, p_0; s^+_N) = \int ds_0^+ \ldots \int ds^+_N \left\langle s^+_N \left| e^{\frac{-iH_{\mu}t}{\hbar}} \right| s^+_0 \right\rangle \ldots \left\langle s^+_1 \left| e^{\frac{-iH_{\mu}t}{\hbar}} \right| s^+_0 \right\rangle \rho_{\text{red}}(s^+_0; 0)
\]  
(4.9)

Denoting

\[
V(s, \bar{x}) = \sum_i -c_i f_i(s)x_i + \frac{c^2_i f_i^2(s)}{2m_i \omega_i^2},
\]
(4.10)

then

\[
\Phi = -\left[ \int_0^{\frac{1}{2}\Delta t} V(s^+_0, x(t'))dt' + \sum_{k=1}^{N-1} \int_{(k-\frac{1}{2})\Delta t}^{(k+\frac{1}{2})\Delta t} V(s^+_k, x(t'))dt' + \int_{(N-\frac{1}{2})\Delta t}^{N\Delta t} V(s^+_N, x(t'))dt' \right] + \left[ \int_0^{\frac{1}{2}\Delta t} V(s^-_0, x(t'))dt' + \sum_{k=1}^{N-1} \int_{(k-\frac{1}{2})\Delta t}^{(k+\frac{1}{2})\Delta t} V(s^-_k, x(t'))dt' + \int_{(N-\frac{1}{2})\Delta t}^{N\Delta t} V(s^-_N, x(t'))dt' \right]
\]
(4.11)

The bath degree of freedom behaves like a forced oscillator with the equation of motion

\[
m\ddot{x} + m\omega^2 x = cf(s)
\]
(4.12)

The solution of \(x(t)\) can be obtained by the standard Green’s function technique,

\[
x(t) = x_0 \cos \omega t + \frac{p_0}{m\omega} \sin \omega t + \frac{c}{2m\omega} \int_0^t dt' \left[ f^+(t') \right] \left( f^+(t') + f^-(t') \right) \sin \omega (t - t')
\]
(4.13)

Plugging the above in the phase \(\Phi\), the integral in the potential can be evaluated analytically as they only involve \(sine\) and \(cosine\) functions, and we get the influence function \(Q\) only in terms of the system coordinate.

With the system propagator, we use symmetric trotter splitting to bring it to an analytical form

\[
e^{-iH_{\mu}t/h} = e^{-iH_{\mu}t/2h} e^{-iH_{\mu}t/2h} e^{-iH_{\mu}t/2h}
\]
(4.14)
\[
\left\langle s_k \left| e^{\frac{-i[H_M]}{\hbar}} \right| s_{k-1} \right\rangle = \left\langle s_k \left| e^{-\frac{iV_o}{2}} e^{-\frac{iP}{\hbar}} e^{-\frac{iV_o}{2}} \right| s_{k-1} \right\rangle = \left\langle s_k \left| e^{\frac{-i[H_M]}{\hbar}} \right| s_{k-1} \right\rangle e^{\left(\frac{iN}{2\hbar}\right)\left[V_0(t_k)+V_0(t_{k-1})\right]}
\]

\[
= \left(\frac{M}{2\pi\hbar\Delta t}\right)^{\frac{1}{2}} \exp\left\{ \frac{i}{\hbar} \frac{M}{2\Delta t} (s_k - s_{k-1})^2 - \frac{i\hbar\Delta t}{2} \left[ V_0(s_k) + V_0(s_{k-1}) \right] \right\}
\]

The influence function becomes

\[
Q(x_0, p_0; s^+_N) = \int ds_0^+ \cdots \int ds_{N-1}^+ \left(\frac{M}{2\pi\hbar\Delta t}\right)^N \exp\left(\frac{i}{\hbar} \phi \right)
\]

where

\[
\phi = -\frac{1}{2} V_0(s_0^+) \Delta t - \sum_{k=1}^{N-1} V_0(s_k^+) \Delta t - \frac{1}{2} V_0(s_N^+) \Delta t + \frac{1}{2} V_0(s_0^-) \Delta t + \sum_{k=1}^{N-1} V_0(s_k^-) \Delta t + \frac{1}{2} V_0(s_N^-) \Delta t
\]

\[
+ \sum_{k=1}^{N} \frac{M}{2\Delta t} (s_k^+ - s_{k-1}^+)^2 - \sum_{k=1}^{N} \frac{M}{2\Delta t} (s_k^- - s_{k-1}^-)^2 + \frac{c\gamma}{\omega} \left( f(s_0^+) - f(s_0^-) \right) \sin\left(\frac{1}{2} \omega \Delta t\right)
\]

\[
+ \frac{c\gamma}{\omega} \sum_{k=1}^{N-1} \left( f(s_k^+) - f(s_k^-) \right) \left[ \sin \omega \left( k + \frac{1}{2} \right) \Delta t - \sin \omega \left( k - \frac{1}{2} \right) \Delta t \right]
\]

\[
+ \frac{c\gamma}{\omega} \left( f(s_N^+) - f(s_N^-) \right) \left[ \sin \omega N \Delta t - \sin \omega \left( N - \frac{1}{2} \right) \Delta t \right]
\]

\[
+ \frac{c\gamma}{\omega} \left( f(s_0^+) - f(s_0^-) \right) \left( 1 - \cos \frac{1}{2} \omega \Delta t \right)
\]

\[
+ \frac{c\gamma}{\omega} \sum_{k=1}^{N-1} \left( f(s_k^+) - f(s_k^-) \right) \left[ \cos \omega \left( k - \frac{1}{2} \right) \Delta t - \cos \omega \left( k + \frac{1}{2} \right) \Delta t \right]
\]
\[ + \frac{c p_o}{m \omega^2} \left( f(s_N^+) - f(s_N^-) \right) \left[ \cos \omega \left( N - \frac{1}{2} \right) \Delta t - \cos \omega N \Delta t \right] \]
\[ + \frac{c^2}{2m \omega^2} \left( f(s_0^+) - f(s_0^-) \right) \left( f(s_0^+) + f(s_0^-) \right) \left( \frac{1}{2} \omega \Delta t - \sin \frac{1}{2} \omega \Delta t \right) \]
\[ + \frac{c^2}{2m \omega^2} \sum_{k=1}^{N-1} \left( f(s_k^+) - f(s_k^-) \right) \left( f(s_k^+) + f(s_k^-) \right) \left[ \sin k \omega \Delta t - \sin (k-1) \omega \Delta t \right. \]
\[ - \sin \left( k + \frac{1}{2} \right) \omega \Delta t + \sin \left( k - \frac{1}{2} \right) \omega \Delta t \]
\[ + \frac{c^2}{2m \omega^2} \sum_{k=2}^{N-1} \sum_{k'=1}^{N-1} \left( f(s_k^+) - f(s_{k'}^-) \right) \left( f(s_{k'}^+) + f(s_{k'}^-) \right) \times \]
\[ \left[ 2 \sin (k - k') \omega \Delta t - \sin (k - k' - 1) \omega \Delta t - \sin (k - k' + 1) \omega \Delta t \right] \]
\[ + \frac{c^2}{2m \omega^2} \sum_{k=1}^{N-1} \left( f(s_N^+) - f(s_n^-) \right) \left( f(s_N^+) + f(s_n^-) \right) \left( \omega \Delta t - \sin \omega \Delta t \right) \]
\[ + \frac{c^2}{2m \omega^2} \left( f(s_0^+) - f(s_0^-) \right) \left( f(s_0^+) + f(s_0^-) \right) \left[ 2 \sin \left( N - \frac{1}{2} \right) \omega \Delta t - \sin (N - 1) \omega \Delta t - \sin N \omega \Delta t \right] \]
\[ + \frac{c^2}{2m \omega^2} \sum_{k=1}^{N-1} \left( f(s_N^+) - f(s_k^-) \right) \left( f(s_k^+) + f(s_k^-) \right) \left[ \sin \left( N - k - \frac{1}{2} \right) \omega \Delta t - \sin (N - k - 1) \omega \Delta t \right. \]
\[ - \sin \left( N - k + \frac{1}{2} \right) \omega \Delta t + \sin (N - k) \omega \Delta t \]
\[ + \frac{c^2}{2m \omega^2} \left( f(s_N^+) - f(s_N^-) \right) \left( f(s_N^+) - f(s_N^-) \right) \left( \frac{1}{2} \omega \Delta t - \sin \frac{1}{2} \omega \Delta t \right) \]
\[ - \frac{c^2}{2m \omega^2} \left( f^2(s_0^+) - f^2(s_0^-) \right) \frac{1}{2} \Delta t - \frac{c^2}{2m \omega^2} \sum_{k=1}^{N-1} \left( f^2(s_k^+) - f^2(s_k^-) \right) \Delta t \]
\[ - \frac{c^2}{2m \omega^2} \left( f^2(s_N^+) - f^2(s_N^-) \right) \frac{1}{2} \Delta t \quad (4.17) \]
The stationary phase condition is achieved by varying all the intermediate coordinates $s_i^+, s_i^-, s_{N-1}^+, s_{N-1}^-$, while $s_0^+, s_0^-, s_N^+, s_N^-$ are not varying since they are fixed endpoints.

When we take the stationary phase condition and truncate the phase up to second order, the zero-order has the phase value taken along the classical trajectory. The first order is zero. The second order becomes a Gaussian form and, together with the integration variables, can be evaluated as a Gaussian integral, therefore producing a Jacobian as a prefactor. Therefore, the semiclassical influence function is

\[
Q^{\text{SC}}(x_0, p_0; s_{N,sc}) = \int d\delta s_0^+ \cdots \int d\delta s_{N-1}^+ \left( \frac{M}{2\pi\hbar\Delta t} \right)^N \exp\left( \frac{i}{\hbar} \phi \right) \exp\left( \frac{i}{2\hbar} \frac{\delta^2 \varphi}{\delta s_m^+ \delta s_n^\pm} \delta s_m^+ \delta s_n^\pm \right)
\]

where $\delta s_m^+ \delta s_n^\pm$ denotes all possible combinations of forward and backward coordinate combinations.

The stationary phase conditions are given by setting the derivative of $\varphi$ with respect to system coordinates to zero.

\[
\frac{\partial \varphi}{\partial s_k^+} = -\Delta t V_0^t(s_k^+) + \frac{M}{\Delta t} (2s_k^+ - s_{k-1}^+ - s_{k+1}^+) + \frac{c}{\omega} f'(s_k^+) \left[ \sin\left( k + \frac{1}{2} \right) \omega \Delta t - \sin\left( k - \frac{1}{2} \right) \omega \Delta t \right]
\]

\[
+ \frac{c^2 p_0}{m \omega^2} f'(s_k^+) \left[ \cos\left( k - \frac{1}{2} \right) \omega \Delta t - \cos\left( k + \frac{1}{2} \right) \omega \Delta t \right]
\]

\[
+ \frac{c^2}{2m \omega^3} f''(s_0^+) \left[ f'(s_0^+) + f'(s_0^+) \right] \times
\]

\[
\sin k \omega \Delta t - \sin(k - 1) \omega \Delta t - \sin\left( k + \frac{1}{2} \right) \omega \Delta t + \sin\left( k - \frac{1}{2} \right) \omega \Delta t
\]
\[ + \frac{c^2}{2m\omega^3} f''(s_i^+ \sum_{k=1}^{k-1} (f(s_k^+) + f(s_{k-}^+)) \times 
\]
\[ 2\sin(k-k')\Delta t - \sin(k-k'-1)\Delta t - \sin(k-k'+1)\Delta t \]
\[ + \frac{c^2}{m\omega} f(s_i^+) f'(s_i^+) (\Delta t - \sin \Delta t) \]
\[ + \frac{c^2}{2m\omega^3} f''(s_i^+) \sum_{k=k+1}^{N-1} (f(s_k^+) - f(s_{k-}^+)) \times 
\]
\[ 2\sin(k'-k)\Delta t - \sin(k'-k-1)\Delta t - \sin(k'-k+1)\Delta t \]
\[ + \frac{c^2}{2m\omega^3} f''(s_i^+) (f(s_N^+) - f(s_{N-}^+)) \times 
\]
\[ \left[ \sin \left( N - k - \frac{1}{2} \right) \Delta t - \sin \left( N - k - 1 \right) \Delta t - \sin \left( N - k + \frac{1}{2} \right) \Delta t + \sin \left( N - k \right) \Delta t \right] \]
\[- \frac{c^2}{m\omega^3} f(s_i^+) f'(s_i^+) \Delta t = 0 \quad (4.19) \]

and

\[ \frac{\partial \phi}{\partial s_k} = \Delta t V_0 f'(s_i^+) - \frac{M}{\Delta t} (2s_i^+ - s_{k-1}^- - s_{k+1}^-) - \frac{c_0}{\omega} f'(s_i^-) \left[ \sin \left( k + \frac{1}{2} \right) \Delta t - \sin \left( k - \frac{1}{2} \right) \Delta t \right] \]
\[- \frac{c_0}{m\omega^3} f'(s_i^-) \left[ \cos \left( k - \frac{1}{2} \right) \Delta t - \cos \left( k + \frac{1}{2} \right) \Delta t \right] \]
\[- \frac{c^2}{2m\omega^3} f''(s_i^-) \left( f(s_0^+) + f(s_0^-) \right) \times \]
These are, in general, coupled nonlinear algebraic equations. The solution must be obtained by root searching algorithms such as globally convergent Newton’s method or Broyden’s method. Although it might be tempting to think that the stationary phase trajectories can be obtained through minimization of the phase \( \phi \) directly by some minimization algorithms, the stationary phase trajectories are neither the minimum or maximum in the value of phase \( \phi \), as \( \phi \) is the sum of forward and backward propagators. Take free propagation as an example. For the forward propagator, the stationary phase trajectory gives the maximum value of phase \( \phi \), whereas for backward propagator that has
a negative sign, the stationary phase trajectory gives a minimum of \( \phi \). Therefore, we anticipate that the stationary phase trajectory for this semiclassical classical phase is a saddle point.

The second derivatives of \( \phi \) are given by the following

\[
\frac{\partial^2 \phi}{\partial s_k^2} = -\Delta V_0''(s_k^+) + \frac{2M}{\Delta t} + \frac{c\omega}{\omega} f''(s_k^+) \left[ \sin \left( k + \frac{1}{2} \right) \omega \Delta t - \sin \left( k - \frac{1}{2} \right) \omega \Delta t \right]
\]

\[
+ \frac{c^2}{m \omega^3} f''(s_k^+) \left[ \cos \left( k - \frac{1}{2} \right) \omega \Delta t - \cos \left( k + \frac{1}{2} \right) \omega \Delta t \right]
\]

\[
+ \frac{c^2}{2m \omega^3} f''(s_k^+) \left[ f\left( s_k^+ \right) + f\left( s_k^- \right) \right] \sin k \omega \Delta t - \sin \left( k - 1 \right) \omega \Delta t - \sin \left( k + 1 \right) \omega \Delta t + \sin \omega \Delta t
\]

\[
+ \frac{c^2}{2m \omega^3} f''(s_k^+) \left( f\left( s_k^+ \right) + f\left( s_k^- \right) \right) \sum_{k=1}^{k'=1} \left( f\left( s_k^+ \right) + f\left( s_k^- \right) \right) \times
\]

\[
\left[ 2 \sin \left( k - k' \right) \omega \Delta t - \sin \left( k - k' - 1 \right) \omega \Delta t - \sin \left( k - k' + 1 \right) \omega \Delta t \right]
\]

\[
+ \frac{c^2}{m \omega} f\left( s_k^+ \right) f''\left( s_k^+ \right) \left( \omega \Delta t - \sin \omega \Delta t \right) + \frac{c^2}{m \omega} f''\left( s_k^+ \right) f''\left( s_k^- \right) \left( \omega \Delta t - \sin \omega \Delta t \right)
\]

\[
+ \frac{c^2}{2m \omega^3} f''(s_k^+) \sum_{k'=1}^{k'=N-1} \left( f\left( s_k^+ \right) - f\left( s_k^- \right) \right) \times
\]

\[
\left[ 2 \sin \left( k' - k \right) \omega \Delta t - \sin \left( k' - k - 1 \right) \omega \Delta t - \sin \left( k' - k + 1 \right) \omega \Delta t \right]
\]

\[
+ \frac{c^2}{2m \omega^3} f''(s_k^+) \left( f\left( s_N^+ \right) - f\left( s_N^- \right) \right) \times
\]

\[
\left[ \sin \left( N - k - \frac{1}{2} \right) \omega \Delta t - \sin \left( N - k - 1 \right) \omega \Delta t - \sin \left( N - k + \frac{1}{2} \right) \omega \Delta t + \sin \left( N - k \right) \omega \Delta t \right]
\]

\[- \frac{c^2}{m \omega} f\left( s_k^+ \right) f''\left( s_k^+ \right) \Delta t - \frac{c^2}{m \omega^2} f''\left( s_k^+ \right) f''\left( s_k^+ \right) \Delta t, \quad k = 1, \ldots, N - 1 \quad (4.21)
\]
\[
\frac{\partial^2 \phi}{\partial s_k^* \partial s_{k+1}^*} = -\frac{M}{\Delta t} + \frac{c^2}{2m\omega^3} f''(s_k^*) f''(s_{k+1}^*) \left(2 \sin \omega \Delta t - 2 \sin 2\omega \Delta t\right), \quad k = 2, \ldots, N - 1
\]

\[
\frac{\partial^2 \phi}{\partial s_k^* \partial s_{k+1}^*} = -\frac{M}{\Delta t} + \frac{c^2}{2m\omega^3} f''(s_k^*) f''(s_{k+1}^*) \left(2 \sin \omega \Delta t - 2 \sin 2\omega \Delta t\right), \quad k = 1, \ldots, N - 2
\]

\[
\frac{\partial^2 \phi}{\partial s_k^* \partial s_{k+1}^*} = \frac{c^2}{2m\omega^3} f''(s_k^*) f''(s_{k+1}^*) \left[2 \sin (k-k') \omega \Delta t - \sin (k-k' - 1) \omega \Delta t\right] - \sin (k-k' + 1) \omega \Delta t, \quad 1 \ll k' < k \ll N - 1, \quad k \neq k' + 1
\]

\[
\frac{\partial^2 \phi}{\partial s_k^* \partial s_{k+1}^*} = \frac{c^2}{2m\omega^3} f''(s_k^*) f''(s_{k+1}^*) \left[2 \sin (k'-k) \omega \Delta t - \sin (k'-k - 1) \omega \Delta t\right] - \sin (k' - k + 1) \omega \Delta t, \quad 1 \ll k' < k \ll N - 1, \quad k' \neq k + 1
\]

\[
\frac{\partial^2 \phi}{\partial s_k^* \partial s_{k+1}^*} = \frac{c^2}{2m\omega^3} f''(s_k^*) f''(s_{k+1}^*) \left[2 \sin (k-k') \omega \Delta t - \sin (k-k' - 1) \omega \Delta t\right] - \sin (k-k' + 1) \omega \Delta t, \quad 1 \ll k' < k \ll N - 1
\]

\[
\frac{\partial^2 \phi}{\partial s_k^* \partial s_{k+1}^*} = -\frac{c^2}{2m\omega^3} f''(s_k^*) f''(s_{k+1}^*) \left[2 \sin (k'-k) \omega \Delta t - \sin (k'-k - 1) \omega \Delta t\right] - \sin (k' - k + 1) \omega \Delta t, \quad 1 \ll k' < k \ll N - 1
\]

\[
\frac{\partial^2 \phi}{\partial s_k^* \partial s_{k-1}^*} = 0, \quad k = 1, \ldots, N - 1
\]

\[
\frac{\partial^2 \phi}{\partial s_k^* \partial s_{k-1}^*} = \Delta t V_0''(s_k^*) - \frac{2M}{\Delta t} - Cx_k^* f''(s_k^*) \left[\sin \left(k + \frac{1}{2}\right) \omega \Delta t - \sin \left(k - \frac{1}{2}\right) \omega \Delta t\right]
\]

\[
- \frac{cp_0}{m\omega^3} f''(s_k^*) \left[\cos \left(k - \frac{1}{2}\right) \omega \Delta t - \cos \left(k + \frac{1}{2}\right) \omega \Delta t\right]
\]
\[-\frac{c^2}{2m\omega^3} f''(s_k^-)(f(s_k^+) - f(s_k^-)) \sin k\omega\Delta t - \sin(k-1)\omega\Delta t - \sin\left(k + \frac{1}{2}\right)\omega\Delta t + \sin\omega\Delta t\]

\[-\frac{c^2}{2m\omega^3} f''(s_k^-) \sum_{k=1}^{K-1} (f(s_k^+) - f(s_k^-)) \times
\left[2\sin(k-k')\omega\Delta t - \sin(k-k' - 1)\omega\Delta t - \sin(k-k' + 1)\omega\Delta t\right]\]

\[-\frac{c^2}{m\omega^3} f(s_k^-) f''(s_k^-)(\omega\Delta t - \sin \omega\Delta t) - \frac{c^2}{m\omega^3} f'(s_k^-) f'(s_k^-)(\omega\Delta t - \sin \omega\Delta t)\]

\[+\frac{c^2}{2m\omega^3} f''(s_k^-) \sum_{N=1}^{K'=k+1} (f(s_k^+) - f(s_k^-)) \times
\left[2\sin(k'-k)\omega\Delta t - \sin(k'-k - 1)\omega\Delta t - \sin(k'-k + 1)\omega\Delta t\right]\]

\[+\frac{c^2}{2m\omega^3} f''(s_k^-)(f(s_N^+) - f(s_N^-)) \times
\left[\sin\left(N-k-\frac{1}{2}\right)\omega\Delta t - \sin(N-k-1)\omega\Delta t - \sin\left(N-k+\frac{1}{2}\right)\omega\Delta t + \sin(N-k)\omega\Delta t\right]\]

\[+\frac{c^2}{m\omega^3} f(s_k^-) f''(s_k^-)\Delta t + \frac{c^2}{m\omega^3} f'(s_k^-) f'(s_k^-)\Delta t, \quad k = 1, \ldots, N-1 \quad (4.29)\]

\[\frac{\partial^2 \varphi}{\partial s_k^- \partial s_{k-1}^+} = \frac{M}{\Delta t} - \frac{c^2}{2m\omega^3} f'(s_k^-) f'(s_k^-)(2\sin \omega\Delta t - \sin 2\omega\Delta t), \quad k = 2, \ldots, N-1 \quad (4.30)\]

\[\frac{\partial^2 \varphi}{\partial s_k^- \partial s_{k+1}^-} = \frac{M}{\Delta t} - \frac{c^2}{2m\omega^3} f'(s_k^-) f'(s_k^-)(2\sin \omega\Delta t - \sin 2\omega\Delta t), \quad k = 1, \ldots, N-2 \quad (4.31)\]

\[\frac{\partial^2 \varphi}{\partial s_k^- \partial s_{k'}^-} = -\frac{c^2}{2m\omega^3} f'(s_k^-) f'(s_k^-)[2\sin(k-k')\omega\Delta t - \sin(k-k' - 1)\omega\Delta t]
- \sin(k-k' + 1)\omega\Delta t], \quad 1 \ll k < k' \ll N-1, \quad k \neq k' + 1 \quad (4.32)\]
The determinant of this \(2N-2\) dimensional Jacobian can be evaluated numerically, e.g. through LU decomposition. This operation is \(O(N^3)\). This Jacobian matrix is symmetric and can be divided into four square blocks corresponding to forward-forward, forward-backward, backward-forward, backward-backward combinations. The upper left block is positive definite, and the lower right block is negative definite. They represent the coupling between the forward system trajectories and backward trajectories, respectively. The upper right and the bottom left quadrans represent the correlations between the forward and backward system paths.

The continuous version of the phase is

\[
S = \int_0^t dt' \left[ \frac{1}{2} M s^+(t')^2 - V_0(s^+(t')) - \frac{1}{2} M s^-(t')^2 + V_0(s^-(t')) \right]
\]
\[ + c x \int_{t'}^t dt' \left[ f \left( s' \left( t' \right) \right) - f \left( s' \left( t'' \right) \right) \right] \cos \omega t' + \frac{cp_o}{m o} \int_{t'}^t dt' \left[ f \left( s' \left( t' \right) \right) - f \left( s' \left( t'' \right) \right) \right] \sin \omega t' \]

\[ + \frac{c^2}{2 m o} \int_{t'}^t dt' \int_{t''}^{t'} dt'' \left[ f \left( s' \left( t' \right) \right) - f \left( s' \left( t'' \right) \right) \right] \left[ f \left( s' \left( t'' \right) \right) + f \left( s' \left( t''' \right) \right) \right] \sin \omega (t' - t'') \]

\[ - \int_{t'}^t dt' \left[ \frac{c^2}{2 m o} \right] \left[ f^{2} \left( s' \left( t' \right) \right) - f^{2} \left( s' \left( t'' \right) \right) \right] \]

(4.37)

The variation with respect to the system coordinate \( s \) involves structure like this

\[ \int_{t'}^t dt' \int_{t''}^{t'} dt'' f \left( s \left( t' \right) \right) f \left( s \left( t'' \right) \right) \sin \omega (t' - t'') \]

(4.38)

The variation of the above yields

\[ \delta \int_{t'}^t dt' \int_{t''}^{t'} dt'' f \left( s \left( t' \right) \right) f \left( s \left( t'' \right) \right) \sin \omega (t' - t'') \]

\[ = \int_{t'}^t dt' \int_{t''}^{t'} dt'' \delta f \left( s \left( t' \right) \right) f \left( s \left( t'' \right) \right) \sin \omega (t' - t'') \]

\[ + \int_{0}^{t'} dt' \int_{t''}^{t'} dt'' \delta f \left( s \left( t' \right) \right) f \left( s \left( t'' \right) \right) \sin \omega (t' - t'') \]

\[ = \int_{0}^{t} dt' \delta s \left( t' \right) f' \left( s \left( t'' \right) \right) \int_{t'}^{t''} dt'' f \left( s \left( t'' \right) \right) \sin \omega (t' - t'') \]

\[ + \int_{t'}^{t} dt' \int_{t''}^{t'} dt'' f \left( s \left( t' \right) \right) \delta s \left( t'' \right) f' \left( s \left( t'' \right) \right) \sin \omega (t' - t'') \]

(4.39)

The second term can be manipulated into the variation of \( \delta s \left( t' \right) \) instead of \( \delta s \left( t'' \right) \)

by switching the integration order of \( dt' \) and \( dt'' \)

\[ \int_{t'}^{t} dt' \int_{t''}^{t'} dt'' f \left( s \left( t' \right) \right) \delta s \left( t'' \right) f' \left( s \left( t'' \right) \right) \sin \omega (t' - t'') \]

\[ = \int_{0}^{t} dt'' \int_{t'}^{t} dt' \delta s \left( t' \right) f' \left( s \left( t'' \right) \right) \sin \omega (t' - t'') \]

\[ = \int_{t'}^{t} dt'' \delta s \left( t'' \right) f' \left( s \left( t'' \right) \right) \int_{t'}^{t} dt' f \left( s \left( t' \right) \right) \sin \omega (t' - t'') \]

(4.40)
Switch the label of \(t'\) and \(t''\), the above equation becomes

\[
\int_0^t dt' \delta s(t') \frac{\dot{f}(s(t'))}{\int_0^t dt'' f(s(t''))} \sin \omega (t'' - t') \\
= -\int_0^t dt' \delta s(t') \frac{\dot{f}(s(t'))}{\int_0^t dt'' f(s(t''))} \sin \omega (t' - t'') \\
\]  

(4.41)

So, equation (3.33) becomes,

\[
\delta \int_0^t dt' \int_0^t dt'' f(s(t')) f(s(t'')) \sin \omega (t' - t'') \\
= \int_0^t dt' \delta s(t') \frac{\dot{f}(s(t'))}{\int_0^t dt'' f(s(t''))} \sin \omega (t' - t'') \\
- \int_0^t dt' \delta s(t') \frac{\dot{f}(s(t'))}{\int_0^t dt'' f(s(t''))} \sin \omega (t' - t'') \\
\]  

(4.42)

Therefore, the variation of the action can be written as,

\[
\delta S = \int_0^t dt' \delta s^+(t') \left[ -M \dot{s}^+(t') - V_0 \left( \dot{s}^+(t') \right) \right] - \int_0^t dt' \delta s^-(t') \left[ -M \dot{s}^- (t') - V_0 \left( \dot{s}^- (t') \right) \right] \\
+ cx_0 \int_0^t dt' \left[ \delta s^+(t') f' \left( s^+(t') \right) - \delta s^-(t') f' \left( s^-(t') \right) \right] \cos \omega t' \\
+ \frac{cp_0}{m \omega} \int_0^t dt' \left[ \delta s^+(t') f' \left( s^+(t') \right) - \delta s^-(t') f' \left( s^-(t') \right) \right] \sin \omega t' \\
+ \frac{e^2}{2m \omega} \int_0^t dt' \delta s^+(t') f' \left( s^+(t') \right) \int_0^t dt'' f \left( s^+ (t'') \right) \sin \omega (t' - t'') \\
- \frac{e^2}{2m \omega} \int_0^t dt' \delta s^+(t') f' \left( s^+(t') \right) \int_0^t dt'' f \left( s^- (t'') \right) \sin \omega (t' - t'') \\
+ \frac{e^2}{2m \omega} \int_0^t dt' \delta s^-(t') f' \left( s^- (t') \right) \int_0^t dt'' f \left( s^- (t'') \right) \sin \omega (t' - t'') \\
- \frac{e^2}{2m \omega} \int_0^t dt' \delta s^-(t') f' \left( s^- (t') \right) \int_0^t dt'' f \left( s^+ (t'') \right) \sin \omega (t' - t'') \\
\]
\[-\frac{e^2}{2m\omega} \int_0^t dt' \delta s^+ (t') f' (s^+ (t')) \int_0^t dt'' f (s^+(t'')) \sin \omega (t' - t'') \]

\[+ \frac{e^2}{2m\omega} \int_0^t dt' \delta s^+ (t') f' (s^+ (t')) \int_0^t dt'' f (s^+(t'')) \sin \omega (t' - t'') \]

\[-\frac{e^2}{2m\omega} \int_0^t dt' \delta s^- (t') f' (s^- (t')) \int_0^t dt'' f (s^- (t'')) \sin \omega (t' - t'') \]

\[+ \frac{e^2}{2m\omega} \int_0^t dt' \delta s^- (t') f' (s^- (t')) \int_0^t dt'' f (s^- (t'')) \sin \omega (t' - t'') \]

\[-\frac{e^2}{m\omega} \int_0^t dt \left[ \delta s^+ (t') f (s^+ (t')) f' (s^+ (t')) - \delta s^- (t') f (s^- (t')) f' (s^- (t')) \right] \]

By setting the first variation to zero, we can immediately get the equations of motion for the system in the forward and backward propagation.

The forward trajectory is given by,

\[\delta s^+ (t') : \]

\[-M \dot{s}^+ (t') - V (s^+ (t')) + c x_0 f' (s^+ (t')) \cos \omega t' + \frac{e^2}{m\omega} f' (s^+ (t')) \sin \omega t' \]

\[+ \frac{e^2}{2m\omega} f' (s^+ (t')) \int_0^t dt'' f (s^+ (t'')) \sin \omega (t' - t'') \]

\[-\frac{e^2}{2m\omega} f' (s^+ (t')) \int_0^t dt'' f (s^+ (t'')) \sin \omega (t' - t'') \]

\[+ \frac{e^2}{2m\omega} f' (s^+ (t')) \int_0^t dt'' f (s^- (t'')) \sin \omega (t' - t'') \]

\[+ \frac{e^2}{2m\omega} f' (s^+ (t')) \int_0^t dt'' f (s^- (t'')) \sin \omega (t' - t'') - \frac{e^2}{m\omega} f (s^+ (t')) f' (s^+ (t')) = 0 \]

The backward propagation is given by,

\[\delta s^- (t') : \]

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Note that these equations of motion not only couple the present time with the past, as in the generalized Langevin equation \(^{29,30}\), but also couple the present time with future times. This is because the problem is formulated as a boundary value problem instead of an initial value problem, such that the intermediate positions are predetermined by the endpoints\(^{31}\).

The time-discretized algebraic equations (4.13) and (4.14) reduce to the time-continuous differential equations in the \(\lim \Delta t \to 0\). The following is the proof of this.

Let \(t'\) denotes the time at \(k\text{'th time step, meaning } k\Delta t = t', \lim_{\Delta t \to 0} \frac{\partial \psi}{\partial s^+_k} = 0\) will reduce to the continuous equation of motion.

Take the time limit of equation (3.13) term by term, we get

\[
\lim_{\Delta t \to 0} \frac{-\Delta t V_0(s^+_k)}{\Delta t} = -M\Omega^2 V(s^+_k) = -M\Omega^2 V_0(s^+(t'))
\]  

\[\text{(4.46)}\]
\[
\lim_{\Delta t \to 0} \frac{M}{(\Delta t)^2} \left( 2s_k^+ - s_{k-1}^+ - s_{k+1}^+ \right) = \lim_{\Delta t \to 0} \frac{-M \left( \frac{s_{k+1}^+ - s_k^+}{\Delta t} - \frac{s_k^+ - s_{k-1}^+}{\Delta t} \right)}{\Delta t} = -M \dot{s}^+ (t')
\]  
(4.47)

\[
\lim_{\Delta t \to 0} \frac{c_0}{\omega \Delta t} f'(s_k^+) \left[ \sin \left( k + \frac{1}{2} \right) \omega \Delta t - \sin \left( k - \frac{1}{2} \right) \omega \Delta t \right] = \frac{c_0}{\omega} f'(s_k^+) \frac{2 \cos k \omega \Delta t}{\Delta t} \lim_{\Delta t \to 0} \frac{\sin \frac{1}{2} \omega \Delta t}{\Delta t}
\]

\[
= c_0 f'(s_k^+) \cos k \omega \Delta t \lim_{\Delta t \to 0} \frac{\sin \frac{1}{2} \omega \Delta t}{\Delta t} = c_0 f'(s_k^+) \cos k \omega \Delta t = c_0 f'(s_k^+) \cos \omega t' 
\]  
(4.48)

\[
\lim_{\Delta t \to 0} \frac{c_0}{\omega \Delta t} f'(s_k^+) \left[ \cos \left( k - \frac{1}{2} \right) \omega \Delta t - \cos \left( k + \frac{1}{2} \right) \omega \Delta t \right]
\]

\[
= \frac{c_0}{\omega \Delta t} f'(s_k^+) \frac{2 \sin k \omega \Delta t}{\Delta t} \lim_{\Delta t \to 0} \frac{1}{\Delta t} \sin \frac{1}{2} \omega \Delta t = \frac{c_0}{\omega \Delta t} f'(s_k^+) \sin k \omega \Delta t \lim_{\Delta t \to 0} \frac{\sin \frac{1}{2} \omega \Delta t}{\Delta t}
\]

\[
= \frac{c_0}{\omega \Delta t} f'(s_k^+) \sin k \omega \Delta t = \frac{c_0}{\omega \Delta t} f'(s_k^+) \sin \omega t' 
\]  
(4.49)

\[
\lim_{\Delta t \to 0} \frac{c^2}{2\omega^3} \left( f(s_k^+) + f(s_k^-) \right) \frac{1}{\Delta t} \left[ \sin k \omega \Delta t - \sin \left( k - 1 \right) \omega \Delta t - \sin \left( k + \frac{1}{2} \right) \omega \Delta t + \sin \omega \Delta t \right]
\]

\[
= \lim_{\Delta t \to 0} \frac{c^2}{2\omega^3} \left( s_k^+ + s_k^- \right) \frac{1}{\Delta t} \left[ 2 \sin k \omega \Delta t \left( \cos k \omega \Delta t + \cos k \omega \Delta t \right) + \cos k \omega \Delta t \left( \sin \omega \Delta t - 2 \sin \frac{1}{2} \omega \Delta t \right) \right]
\]

\[
= \frac{c^2}{2\omega^3} \left( s_k^+ + s_k^- \right) \lim_{\Delta t \to 0} \frac{2 \sin k \omega \Delta t}{\Delta t} \frac{1}{\Delta t} \left( \frac{2 \sin \frac{1}{2} \omega \Delta t}{\Delta t} \right)
\]

\[
+ \cos k \omega \Delta t \left( \cos k \Delta t \right) \frac{1}{\Delta t} \left( \frac{\omega \Delta t}{3} \right)^3 + \ldots - 2 \left( \frac{1}{2} \omega \Delta t \right)^3 \frac{3!}{3!} + \ldots
\]
\[
\frac{c^2}{2m\omega} \left( f(s^+_0) + f(s^-_0) \right) \sin k\omega\Delta t = \frac{c^2}{2m\omega} \left[ f(s^+(0)) + f(s^-(0)) \right] \sin \omega t' \tag{4.50}
\]

\[
\lim_{\Delta t \to 0} \frac{c^2}{2m\omega^3} \left( f(s^+_k) + f(s^-_k) \right) \frac{1}{\Delta t} \frac{1}{\Delta t} \left[ 2\sin(k-k')\omega\Delta t - \sin(k-k'-1)\omega\Delta t \right] = \sin(k-k'+1)\omega\Delta t
\]

\[
= \frac{c^2}{2m\omega^3} \left( f(s^+_k) + f(s^-_k) \right) 2\sin(k-k')\omega\Delta t \lim_{\Delta t \to 0} \frac{1}{\Delta t} \frac{1}{\Delta t} \left( 1 - \cos \omega\Delta t \right)
\]

\[
= \frac{c^2}{2m\omega^3} \left( f(s^+_k) + f(s^-_k) \right) 2\sin(k-k')\omega\Delta t \lim_{\Delta t \to 0} \frac{1}{\Delta t} \frac{2\sin^2 \frac{1}{2}\omega\Delta t}{\Delta t}
\]

\[
= \frac{c^2}{2m\omega^3} \left( f(s^+_k) + f(s^-_k) \right) \sin(k-k')\omega\Delta t
\]

\[
= \frac{c^2}{2m\omega^3} \left[ f(s^+(t')) + f(s^-(t')) \right] \sin \omega (t-t') \tag{4.51}
\]

\[
\lim_{\Delta t \to 0} \frac{c^2}{m\omega^3} s_k' \frac{1}{\Delta t} \frac{1}{\Delta t} \left( \omega\Delta t - \sin \omega\Delta t \right) = 0 \tag{4.52}
\]

\[
\lim_{\Delta t \to 0} \frac{c^2}{2m\omega^3} \left( f(s^+_k) - f(s^-_k) \right) \frac{1}{\Delta t} \frac{1}{\Delta t} \left[ \sin \left( N - k - \frac{1}{2} \right)\omega\Delta t - \sin(N - k - 1)\omega\Delta t \right.
\]

\[
- \sin \left( N - k + \frac{1}{2} \right)\omega\Delta t + \sin(N - k)\omega\Delta t \right] = \frac{2^2}{2m\omega^3} \left( f(s^+_k) - f(s^-_k) \right) \lim_{\Delta t \to 0} \frac{1}{\Delta t} \frac{1}{\Delta t} \left[ 2\sin(N - k)\omega\Delta t \left( 1 - \cos \omega\Delta t \right) \right.
\]

\[
+ \cos(N - k)\omega\Delta t \left( \sin \omega\Delta t - 2\sin \frac{1}{2}\omega\Delta t \right] \tag{4.53}
\]
Thus, (4.13) is the discretized version of (4.38). For $s^{-}_k$, the same derivation applies.

On the other hand, the continuous-time differential equation (4.38) and (4.39) after performing the time segment integral would recover the discrete equation $\frac{\partial \phi}{\partial s^+_k} = 0$ and $\frac{\partial \phi}{\partial s^-_k} = 0$ exactly.

4.4 Memory Kernel

In the harmonic bath situation, the memory kernel is

$$\alpha(t' - t'') = \sum_i \frac{e^2}{2m_i\omega_i} \sin \omega_i (t' - t'')$$

and we are not aware of any further simplification of the further-time-containing differential equation.
For a special memory kernel, Drude friction, that arises from the Fourier transform of a Lorentzian spectral density,

\[
\alpha(t' - t") = \begin{cases} 
\tilde{k} \gamma e^{-\gamma |t'|}, & t' > t" \\
0, & t' = t" \\
-\tilde{k} \gamma e^{-\gamma |t'|}, & t' < t"
\end{cases}
\]  

(4.56)

the second order differential equation that involves a future term can be turned into a fourth order differential equation that does not involve a future term. In addition, the forward and backward path decouple. If the kernel is not zero at time 0, then the fourth order equation is still local in time, but the forward and backward paths are still coupled. Below is the demonstration of the above argument using forward system path.

For \( s^+(t') \), the second order equation becomes (not including the counter term)

\[
-Ms^+(t') - V_0'(s^+(t')) + c_0 f'(s^+(t')) \cos \omega t' + \frac{C_0}{m \omega} f'(s^+(t')) \sin \omega t' \\
+f'(s^+(t')) \tilde{k} \gamma \int_0^t dt" [f(s^+(t")) + f(s^-(t"))] e^{-\gamma (t' - t")} \\
-f'(s^+(t')) \tilde{k} \gamma \int_t^\infty dt" [f(s^+(t")) - f(s^+(t"))] e^{-\gamma (t'-t")} = 0
\]

(4.57)

Take the derivative again, the above equation becomes

\[
-Ms^+(t') - V_0''(s^+(t')) \ddot{s}^+(t') + c_0 f''(s^+(t')) \dot{s}^+(t') \cos \omega t' + \frac{C_0}{m \omega} f''(s^+(t')) \dot{s}^+(t') \sin \omega t' \\
-c_0 \omega f'(s^+(t')) \sin \omega t' + \frac{C_0}{m} f'(s^+(t')) \cos \omega t' \\
+f''(s^+(t')) \tilde{k} \gamma \ddot{s}^+(t') \int_0^t dt" [f(s^+(t")) + f(s^-(t"))] e^{-\gamma (t' - t")} \\
-f''(s^+(t')) \tilde{k} \gamma \ddot{s}^+(t') \int_t^\infty dt" [f(s^+(t")) - f(s^+(t"))] e^{-\gamma (t' - t")}
\]
\[ -f'(s^+(t')) \tilde{k} \gamma^2 \int_0^t dt'' \left[ f(s^+(t'')) + f(s^-(t'')) \right] e^{-\gamma(t'-r)} \]

\[ -f'(s^+(t')) \tilde{k} \gamma^2 \int_r^t dt'' \left[ f(s^-(t'')) - f(s^+(t'')) \right] e^{-\gamma(t'-r)} = 0 \quad (4.58) \]

Take the fourth order derivative,

\[ -M s^{(4)}(t') - V_0'' \left( s^+(t') \right) \dot{s}^2(t') - V_0'' \left( s^+(t') \right) s^+(t') + c \omega^2 s^+(t') \dot{s}^2(t') \cos \omega t' \]

\[ + c \omega f''(s^+(t')) \dot{s}^+(t') \cos \omega t' - 2c \omega f''(s^+(t')) \dot{s}^+(t') \sin \omega t' \]

\[ + \frac{c_0}{m_0} f''(s^+(t')) \dot{s}^+(t') \sin \omega t' + \frac{c_0}{m_0} f''(s^+(t')) \dot{s}^+(t') \sin \omega t' \]

\[ + f'''(s^+(t')) \tilde{k} \gamma s^2(t') \int_0^t dt'' \left[ f(s^+(t'')) + f(s^-(t'')) \right] e^{-\gamma(t'-r)} \]

\[ -f'''(s^+(t')) \tilde{k} \gamma s^2(t') \int_r^t dt'' \left[ f(s^-(t'')) - f(s^+(t'')) \right] e^{-\gamma(t'-r)} \]

\[ + f''(s^+(t')) \tilde{k} \gamma \dot{s}^+(t') \int_0^t dt'' \left[ f(s^+(t'')) + f(s^-(t'')) \right] e^{-\gamma(t'-r)} \]

\[ -f''(s^+(t')) \tilde{k} \gamma \dot{s}^+(t') \int_r^t dt'' \left[ f(s^-(t'')) - f(s^+(t'')) \right] e^{-\gamma(t'-r)} \]

\[ -2 f''(s^+(t')) \tilde{k} \gamma \ddot{s}^+(t') \int_0^t dt'' \left[ f(s^+(t'')) + f(s^-(t'')) \right] e^{-\gamma(t'-r)} \]

\[ -2 f''(s^+(t')) \tilde{k} \gamma \ddot{s}^+(t') \int_r^t dt'' \left[ f(s^-(t'')) - f(s^+(t'')) \right] e^{-\gamma(t'-r)} \]

\[ + f'(s^+(t')) \tilde{k} \gamma \int_0^t dt'' \left[ f(s^+(t'')) + f(s^-(t'')) \right] e^{-\gamma(t'-r)} \]

\[ - f'(s^+(t')) \tilde{k} \gamma \int_r^t dt'' \left[ f(s^-(t'')) - f(s^+(t'')) \right] e^{-\gamma(t'-r)} = 0 \quad (4.59) \]
Note, the time non-local functions are equal to the time local terms, from the second order (4.51) and third order (4.52) differential equations.

With the time non-local functions expressed as time local terms

\[
\int_0^t dt'' \left[ f^+(t'') + f^-(t'') \right] e^{-\gamma(t'-t)} - \int_0^t dt'' \left[ f^-(t'') - f^+(t'') \right] e^{-\gamma(t'-t)}
\]

\[
= \frac{1}{f'(s^+(t''))} \left[ M \dddot{s}^+(t') + V_0' \dddot{s}^+(t') - c \dot{\omega} f''(s^+(t')) \cos \omega t' - \frac{c \dot{\omega}}{m \omega} f'(s^+(t')) \sin \omega t' \right]
\]

\[
- \int_0^t dt'' \left[ f^+(t'') + f^-(t'') \right] e^{-\gamma(t'-t)} - \int_0^t dt'' \left[ f^-(t'') - f^+(t'') \right] e^{-\gamma(t'-t)}
\]

\[
= \frac{1}{f'(s^+(t''))} \left[ M \dddot{s}^+(t') + V_0'' \dddot{s}^+(t') \dddot{s}^+(t') - c \dot{\omega} f'''(s^+(t')) \dddot{s}^+(t') \cos \omega t' \right]
\]

\[
- \frac{c \dot{\omega}}{m \omega} f'''(s^+(t')) \dddot{s}^+(t') \sin \omega t' + c \dot{\omega} f''(s^+(t')) \sin \omega t' - \frac{c \dot{\omega}}{m} f'(s^+(t')) \cos \omega t'
\]

\[
= \frac{f''(s^+(t')) \dddot{s}^+(t')}{[f'(s^+(t'))]^2} \left[ M \dddot{s}^+(t') + V_0' \dddot{s}^+(t') - c \dot{\omega} f''(s^+(t')) \cos \omega t' - \frac{c \dot{\omega}}{m \omega} f'(s^+(t')) \sin \omega t' \right]
\]

(4.60)

the fourth order differential equation becomes

\[
-M s^{(4)} + \dddot{s}^2 [-V'' + c \dot{\omega} f''' \cos \omega t' + \frac{c \dot{\omega}}{m \omega} f''' \sin \omega t']
\]

\[
+ \frac{f'''}{f'} \left( V' - c \dot{\omega} f' \cos \omega t' - \frac{c \dot{\omega}}{m \omega} f' \sin \omega t' \right)
\]

\[
+ \frac{2 f''}{f'} \left( V'' - c \dot{\omega} f'' \cos \omega t' - \frac{c \dot{\omega}}{m \omega} f'' \sin \omega t' \right) - \frac{2 f'''}{f'} \left( V' - c \dot{\omega} f' \cos \omega t' - \frac{c \dot{\omega}}{m \omega} f' \sin \omega t' \right)
\]

\[
+ \frac{M f'''}{f'} \dddot{s}^2 + \frac{2 f'' M}{f'} \dddot{s}^2 \dddot{s}^2 + \frac{M}{f'} \left( f''' \dddot{s}^2 - \frac{2 f'''}{f'} \right) \dddot{s}^2 \dddot{s}^2
\]

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For backward trajectories, similar results can be obtained.

Expressed in fourth order, the forward and backward paths decouple. The above equation needs four initial/boundary (or the combination of both) conditions to get a unique solution. The first two are $s^+(0)$ and $s^+(t)$, i.e. boundary conditions, which could be converted to $s^+(0)$ and $s^+(0)$. The last two are achieved by evaluate the second order and third order equation at $t' = 0$ and $t' = t$, and match all terms that are equal.\textsuperscript{31}

The following derivations give the expressions for the last two constraints.

With

$$
\int_0^t dt'' \left[ f(s^-(t'')) - f(s^+(t'')) \right] e^{-\eta''} = \frac{1}{f'(s^+(0))} k' \gamma \left[ M s^+ (0) + V_0' \left( s^+(0) \right) - c x_0 f'(s^+(0)) \right]
$$

(4.62)

and

$$
\int_0^t dt'' \left[ f(s^+(t'')) + f(s^-(t'')) \right] e^{-\eta(t-t'')}
$$

$$
= -\frac{1}{f'(s^+(t))} k' \gamma \left[ M s^+ (t) + V_0' \left( s^+(t) \right) - c x_0 f'(s^+(t)) \cos \omega t - \frac{c p_0}{m \omega} f'(s^+(t)) \sin \omega t \right]
$$

(4.63)

we get the last two constraints,
\[ M \ddot{s}^{(+)} + V_0'' s^{(+)} \dot{s}^{(+)}(0) - c x_0 f''(s^{(+)}(0)) \dot{s}^{(+)}(0) - \frac{c p_0}{m} f'(s^{(+)}(0)) \]

\[ = \frac{f''(s^{(+)}(0)) \dot{s}^{(+)}(0)}{f'(s^{(+)}(0))} \left[ M \ddot{s}^{(+)} + V_0' \dot{s}^{(+)}(0) - c x_0 f'(s^{(+)}(0)) \right] + \gamma M \ddot{s}^{(+)}(0) + V_0' \dot{s}^{(+)}(0) - c x_0 f'(s^{(+)}(0)) \]

(4.64)

and

\[ M \ddot{s}^{(t)} + V_0' \dot{s}^{(t)}(t) - c x_0 f''(s^{(t)}(t)) \dot{s}^{(t)}(t) \cos \omega t - \frac{c p_0}{m} f''(s^{(t)}(t)) \dot{s}^{(t)}(t) \sin \omega t \]

\[ + c x_0 \omega f'(s^{(t)}(t)) \sin \omega t - \frac{c p_0}{m} f'(s^{(t)}(t)) \cos \omega t \]

\[ = \frac{f''(s^{(t)}(t)) \dot{s}^{(t)}(t)}{f'(s^{(t)}(t))} \left[ M \ddot{s}^{(t)} + V_0' \dot{s}^{(t)}(t) - c x_0 f'(s^{(t)}(t)) \cos \omega t - \frac{c p_0}{m} f'(s^{(t)}(t)) \sin \omega t \right] - \gamma M \ddot{s}^{(t)}(t) + V_0' \dot{s}^{(t)}(t) - c x_0 f'(s^{(t)}(t)) \cos \omega t - \frac{c p_0}{m} f'(s^{(t)}(t)) \sin \omega t \]

(4.65)

For a harmonic system linearly coupled to the bath, the equation of motion (4.55) is greatly simplified,

\[ M \ddot{s}^{(t)}(t) + \left( \Omega^2 - \gamma^2 \right) \ddot{s}^{(t)} + \gamma^2 \Omega^2 \dot{s}^{(t)} + \gamma^2 \left( c x_0 \cos \omega t' + \frac{c p_0}{m} \sin \omega t' \right) \]

\[ = c x_0 \omega^2 \cos \omega t' + \frac{c p_0}{m} \omega \sin \omega t' = 0 \]

(4.66)

where \( \Omega \) is the frequency of the system. The constraints (4.58) and (4.59) simplify to

\[ M \ddot{s}^{(0)}(0) + M \Omega^2 \dot{s}^{(0)}(0) - \frac{c p_0}{m} = \gamma \left[ M \ddot{s}^{(0)} + M \Omega^2 \dot{s}^{(0)} - c x_0 \right] \]

(4.67)
The last constraint (4.62) is expressed in terms of the end point. Therefore, it is not possible to completely cast the equation into an initial value problem. However, this opens up an alternative way to get the stationary phase trajectory, under this specific Drude memory kernel, i.e. solve the fourth order ordinary differential equation with four boundary/initial conditions.

4.5 Numerical Results

A. Harmonic oscillator coupled to harmonic bath

We first use the simplest case to test the validity of SCPI which we know the exact result and which is easy to obtain. We study a harmonic system linearly coupled to a harmonic bath. The Hamiltonian is

\[ H = \frac{P^2}{2M} + \frac{1}{2} M \Omega^2 s^2 + \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} x_i^2 = \sum_{i=1}^{N} c_i s_n + \frac{c_i^2 s_i^2}{2 m_i \omega_i^2} \]  

(4.69)

Using the above results, setting \( f(s) = s, \ f'(s) = 1, \ f''(s) = 0, \) we immediately get all the ingredients we need for the calculation. What simplifies greatly is the second derivative since \( f''(s) = 0. \) In this special case, the second derivatives are

\[ \frac{\partial^2 \varphi}{\partial s_k^2} = -\Delta t V' \left( s_k^+ \right) + \frac{2M}{\Delta t} + \frac{c^2}{m \omega^3} \left( \omega \Delta t - \sin \omega \Delta t \right) - \frac{c^2}{m \omega^2} \Delta t, \ k = 1, \ldots, N-1 \]  

(4.70)

\[ \frac{\partial^2 \varphi}{\partial s_k^+ \partial s_{k-1}^+} = -\frac{M}{\Delta t} + \frac{c^2}{2 m \omega^3} \left( 2 \sin \omega \Delta t - \sin 2 \omega \Delta t \right), \ k = 2, \ldots, N-1 \]  

(4.71)
\[
\frac{\partial^2 \varphi}{\partial s_k^+ \partial s_{k+1}^-} = -\frac{M}{\Delta t} + \frac{c^2}{2m\omega^3} (2\sin \omega \Delta t - \sin 2\omega \Delta t), \quad k = 1, \ldots, N-2
\]  
(4.72)

\[
\frac{\partial^2 \varphi}{\partial s_k^+ \partial s_{k'}^+} = \frac{c^2}{2m\omega^3} \left[ 2\sin (k-k') \omega \Delta t - \sin (k-k'-1) \omega \Delta t - \sin (k-k'+1) \omega \Delta t \right],
\]
(4.73)

\[
1 \ll k' < k \ll N-1, \quad k \neq k'+1
\]

\[
\frac{\partial^2 \varphi}{\partial s_k^+ \partial s_{k'}^-} = \frac{c^2}{2m\omega^3} \left[ 2\sin (k-k') \omega \Delta t - \sin (k-k'-1) \omega \Delta t - \sin (k-k'+1) \omega \Delta t \right],
\]
(4.74)

\[
1 \ll k < k' \ll N-1, \quad k' \neq k+1
\]

\[
\frac{\partial^2 \varphi}{\partial s_k^- \partial s_{k'}^-} = \frac{c^2}{2m\omega^3} \left[ 2\sin (k-k') \omega \Delta t - \sin (k-k'-1) \omega \Delta t - \sin (k-k'+1) \omega \Delta t \right],
\]
(4.75)

\[
1 \ll k' < k \ll N-1
\]

\[
\frac{\partial^2 \varphi}{\partial s_k^- \partial s_{k'}^+} = -\frac{c^2}{2m\omega^3} \left[ 2\sin (k-k') \omega \Delta t - \sin (k-k'-1) \omega \Delta t - \sin (k-k'+1) \omega \Delta t \right],
\]
(4.76)

\[
1 \ll k < k' \ll N-1
\]

\[
\frac{\partial^2 \varphi}{\partial s_k^- \partial s_k^-} = 0, \quad k = 1, \ldots, N-1
\]  
(4.77)

\[
\frac{\partial^2 \varphi}{\partial s_k^-} = \Delta t V_0 \left( s_k^- \right) - \frac{2M}{\Delta t} - \frac{c^2}{m\omega^3} (\alpha \omega \Delta t - \sin \alpha \omega \Delta t) + \frac{c^2}{m\omega^3} \Delta t, \quad k = 1, \ldots, N-1
\]  
(4.78)

\[
\frac{\partial^2 \varphi}{\partial s_k^- \partial s_{k-1}^-} = \frac{M}{\Delta t} - \frac{c^2}{2m\omega^3} (2\sin \omega \Delta t - \sin 2\omega \Delta t), \quad k = 2, \ldots, N-1
\]  
(4.79)

\[
\frac{\partial^2 \varphi}{\partial s_k^- \partial s_{k+1}^-} = \frac{M}{\Delta t} - \frac{c^2}{2m\omega^3} (2\sin \omega \Delta t - \sin 2\omega \Delta t), \quad k = 1, \ldots, N-2
\]  
(4.80)

\[
\frac{\partial^2 \varphi}{\partial s_k^- \partial s_{k'}^-} = -\frac{c^2}{2m\omega^3} \left[ 2\sin (k-k') \omega \Delta t - \sin (k-k'-1) \omega \Delta t - \sin (k-k'+1) \omega \Delta t \right],
\]
(4.81)

\[
1 \ll k' < k \ll N-1, \quad k \neq k'+1
\]
These terms are independent of the bath initial conditions, thus remaining constant for a fixed quantum time step. This is great computationally saving as it only needs to be evaluated once throughout the calculation.

Also, the coupled algebraic equations derived from the first derivative responsible for stationary phase condition, (4.13) and (4.14), become a set of linearly coupled algebraic equations. The solution to it can be easily obtained through standard algorithms, such as LU decomposition\(^{28}\). In fact, if we write it in a matrix form

\[
A x = b
\]

The A matrix is exactly the same as the Jacobian matrix, and b contains terms dependent on the bath initial conditions \(x_0, p_0\).

We will calculate the expectation value of the position operator \(\langle \hat{s} \rangle\) of the system initially prepared to have the ground state wave function of the harmonic oscillator, displaced away from the equilibrium position.
\[ \psi_0(s) = \left( \frac{M\Omega}{\pi\hbar} \right)^{\frac{1}{4}} e^{-\frac{M\Omega(s-a)^2}{2\hbar}} \]  

(4.87)

The bath is at thermal equilibrium. The system frequency \( \Omega = 1 \), mass \( M = 1 \) and starts with the density

\[ \langle s_0^+ | \rho_s(0) | s_0^- \rangle = \sqrt{\frac{M\Omega}{\pi\hbar}} e^{-\frac{M\Omega(s_a^0-a)^2}{2\hbar}} e^{-\frac{M\Omega(s_0-a)^2}{2\hbar}} \]  

(4.88)

The bath starts with Wigner distribution

\[ W(x_0, p_0) = \frac{1}{\hbar\pi} \tanh \left( \frac{1}{2} \hbar \omega \beta \right) e^{-\frac{1}{2} \hbar \omega \beta \left( \frac{\max^2}{\hbar} \frac{p^2}{m\omega} \right)} \]  

(4.89)

The bath assumes Ohmic spectral density

\[ J(\omega) = \frac{\pi}{2} \hbar \xi \omega e^{-\omega/\omega_c} \]  

(4.90)

The discretization of the bath follows the logarithm procedure\(^ {32} \), which gives the coupling strength \( c_i \) and the harmonic modes \( \omega_j \). We choose \( \omega_{\max} = 4\omega_c \).

\[ \omega_j = -\omega_c \ln \left( 1 - \frac{\omega_j}{\omega_c} \right) \]  

(4.91)

\[ c_i = \sqrt{\xi \hbar \omega_0 m_i \omega_i} \]  

(4.92)

Since the problem at hand is a harmonic oscillator bilinearly coupled to a harmonic bath, the exact result can be achieved through normal mode transformation of the system and bath coordinate combined, then propagate the free oscillators, and in the end transform them back.

Below (Figure 11) shows the average position of a harmonic oscillator linearly coupled to a harmonic bath. The initial state of the harmonic oscillator is a displaced
Gaussian. We use parameters of system frequency $\Omega = 1$, system displacement $a = 1$, bah parameters $\omega_c = 6$, $\xi = 2$, $\beta = 1$. The black curve is from the accurate calculation and the dots are from the stationary phase condition. The matching of the two confirms that the stationary phase differential equation does involve a future term.

Figure 11. Average position of a displaced harmonic oscillator coupled to a harmonic bath.

Initial state of the harmonic oscillator is a displaced Gaussian.

$\Omega = 1$, $a = 1$, $\omega_c = 6$, $\xi = 2$, $\beta = 1$. Black curve: accurate result; Black dots: SCPI result.

B. Morse oscillator coupled to harmonic bath

We are trying to extend the method to a non-harmonic system. The model we are using is adopted from MCTDH (multi-configurational time-dependent Hartree) calculation from H.D. Meyer. 33
The Hamiltonian is a Morse oscillator nonlinearly coupled to a harmonic bath.

\[
H = \frac{p^2}{2M} + D\left(e^{-2as} - 2e^{-as}\right) - \sum_{i=1}^{N} c_i \frac{1-e^{-as}}{a} x_i + \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{m\omega_i^2}{2} x_i^2
\]  

(4.93)

The harmonic frequency associated with the Morse potential is given by

\[
\Omega = a \sqrt{\frac{2D}{M}}
\]  

(4.94)

Characteristic length scale of Morse oscillator is:

\( \bar{s} = 0.09129, \ D = 0.018, \ a = 2, \ M = 10^5, \ m = 10^4. \)

The system initial state is a displaced Gaussian wave packet with displacement \( s_0 = 2\bar{s} \) and width \( \sigma = \bar{s}. \)

The spectral density uses Ohmic spectral density

\[
J(\omega) = M\gamma\omega
\]  

(4.95)

with the following discretization, i.e. the modes are equally spaced.

\[
\omega_i = i\frac{\omega_f}{N} = i\Delta \omega
\]  

(4.96)

\[
c_i = i\sqrt{\frac{2mM\gamma \Delta \omega^3}{\pi}}
\]  

(4.97)

20 oscillators are sufficient to converge the result. \( \gamma = \frac{1}{50 \text{fs}}. \)

The bath is at zero temperature and the oscillators are initially placed at the equilibrium position with respect to the system

\[
\frac{\partial V}{\partial x_i} = 0
\]  

(4.98)
We use root search algorithm to perform the calculation of the expectation value of the system position. The initial guess positions are taken from the corresponding harmonic system linearly coupled to the harmonic bath. Below (Figure 12) shows the semiclassical result compared with the accurate one obtained from MCTDH.

\[
x_{i}^{eq} = \frac{c_{i} - e^{-as}}{m\omega^{2}}
\]

(4.99)

Figure 12. Average position of a Morse oscillator coupled to a harmonic bath. System initial state is a displaced Gaussian on the flatter side of the Morse potential.

\[\bar{s} = 0.09129, \; D = 0.018, \; a = 2, \; M = 10^{5}, \; m = 10^{4}, \; s_{0} = 2\bar{s}, \; \sigma = \bar{s}, \; \gamma = 1/50 \text{ fs}\]

Black dots are the root search result; black curve is adopted from MCTDH.
The calculation matches the exact result initially and then is becoming harder to converge due to the following speculated reasons. First of all, when the wave packet hits the hard wall of the Morse potential, the wave function can break up into several packets and become highly oscillatory, making the numerical integration with respect to positions difficult. Second, there might be multiple classical trajectories at longer times whereas the root search algorithm can only capture one. Another issue we noticed is, for certain boundary values, the derivatives of the phase never goes to zero. This is also confirmed by running calculations with a softer system potential, i.e. take the flatter side of the Morse potential and symmetrically reflected to the other side. This could be the situations where there’s no solution with a specific boundary condition.

4.6 Conclusion

We derived the semiclassical-classical path integral (SCPI) expression using a general quantum system coupled to a harmonic bath. In this SCPI scheme, the system’s paths have separate and distinct forward and backward trajectories. These trajectories follow classical dynamics under the influence of the system. The different forward and backward system classical paths contribute to different values in the phase, thus allowing quantum interference on this classical skeleton. The quantum effect is also being taken into account by the second variation of the action, which ultimately becomes a prefactor. The bath is time-evolving under the average force from the system’s forward and backward paths, and the bath’s forward and backward trajectories are collapsed into one.

In this SCPI scheme, the system paths no longer grow exponentially with time. For a specific boundary condition, there is only one or a few unique forward backward system
paths. This is a huge computational saving. But the evaluation of the entire path integral is not linear in time because the prefactor is a determinant that goes as $O(N^3)$, where $N$ is the number of time steps. However, this still has a great advantage especially at long time.

By taking the stationary phase condition, the integrand in the path integral expression becomes a smooth function, which automatically eliminates the sign problem plagued by Monte Carlo sampling. In fact, the Monte Carlo sampling is so efficient that for all the above calculations, less than 1000 points is needed for each bath degree of freedom.

By performing the derivation, we discovered that the classical equation of motion for the system has a future-involved term that originates from the boundary value problem. This future term cannot be made to disappear unless in special cases as shown in the Drude friction. Even in this special case, the fourth order differential equation cannot be completely cast into an initial value problem. Therefore, the root searching algorithms become the essential techniques for solving classical trajectories. We have demonstrated in the harmonic oscillator coupled to a harmonic bath case that this future term is necessary.

The SCPI method can be very efficient at evaluating quantum systems with continuous coordinates. Besides assuming the system can be treated semiclassically and the bath classically, the method does not impose any other approximations. However, the method itself is not free from drawbacks. As illustrated in the last numerical test, the multiple roots or no root situations offer challenges to root searching algorithms. Active research is under way in our group to investigate this problem.
4.7 References

CHAPTER 5: CONCLUSION

Path integral formulation of the density matrix provides an excellent tool for studying quantum dynamics in condensed phase. The trajectory-based structure allows a natural connection between quantum and classical mechanics, therefore a consistent treatment of system-bath dynamics free from \textit{ad hoc} approximations.

The classical trajectory evaluation of the an anharmonic environment can be computationally expensive. The majority of the computational cost resides in the evaluation of the back-reaction term. It is non-local in time and the number of terms grow exponentially with time. The harmonic back-reaction offers an excellent approximation to the time-nonlocal term in the influence function. Combined with the reference propagator and the iterative approach, it provides a very fast and accurate way of calculating the properties of a two (or several discrete) level system embedded in an anharmonic environment. It has the potential to couple with molecular dynamics to study real systems.

Semiclassical-classical path integral (SCPI), based on the skeleton of quantum-classical path integral (QCPI), further reduces the many system paths to one or several classical paths. Therefore, in the SCPI scheme, both the system and the bath follow classical trajectories, which greatly saves the computational cost. Due to the stationary phase condition, the phase is no longer plagued by the sign problem thus allows very effective Monte Carlo sampling of the bath initial phase space distribution. Because this method is formulated in a continue coordinate manner, it has the potential to apply to multi-level systems in which many DVR (discrete variable representation) states need to be used. However, it is not free from its own drawbacks due to the future term that arises from the
boundary value formulation, which prevents from solving the dynamics in a time-local manner. It can be tough for the root search algorithms to capture multiple roots solutions. It is shown that even with the Drude friction with which the fourth order differential equation becomes local in time, the problem cannot be cast into an initial value problem completely. Further research needs to be done to resolve this issue.