DYNAMICAL PATH INTEGRAL CALCULATIONS
FOR CONDENSED PHASE PROCESSES

BY

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DISSERTATION
Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Physics
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2013

Urbana, Illinois

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Abstract

As is well known, the computational effort in quantum mechanics grows exponentially with system size. Thus a typical computation of an interesting many-body problem quickly becomes prohibitive. In this work, we try to circumvent this exponential scaling by treating a few degrees of freedom explicitly (i.e. the system) while integrating out the rest of the degrees of freedom (i.e. the bath). For a bath of harmonic oscillators, this integration procedure is well known and we apply this result to problems of charge transfer across molecules by summing over statistically significant system paths. If we have a generic bath composed of classical like particles interacting with the system of interest, the classical behavior of the bath influences the quantum mechanical behavior of the system. Thus we arrive at a rigorous quantum-classical path integral formulation which we believe has very promising applications in chemistry and biology.
Acknowledgements

I am very grateful to my advisor, Dr. Nancy Makri, for her support, patience, and guidance. The work presented here would have been impossible without her vision, insightfulness, and expertise. In my many years as a graduate student, I have come across many people who have made graduate student life a bit easier. I am indebted to Aruna, Héctor, Matias, Angel, Ana Lia, and Varsha. I also cannot forget about the lasting friendships I established as an undergraduate. I want to thank especially Avon, Jessie, Advay, and Nathan for their friendship even after all these years. I also want to show my gratitude to my family. They have given me unconditional love and support. This work is dedicated to my mother, who although is not here with us, still resides in my heart. Finally, I would like to mention a very special girl in my life. She has been there for me with her support and boundless love. Sasha, thank you.
# Table of Contents

Chapter 1  
Introduction .................................................................................................................. 1

Chapter 2  
Overview of the Iterative Path Integral Methodology for Dissipative Systems ........................................... 9

Chapter 3  
Filtering Scheme for Path Integral Calculations ................................................. 18

3.1  
Introduction ........................................................................................................... 18

3.2  
Methodology ............................................................................................................. 19

3.3  
Application: Tight-binding model for long range charge transport ....... 23

3.4  
Concluding Remarks ................................................................................................. 25

3.5  
Figures ........................................................................................................................ 27

Chapter 4  
Molecular Wires ........................................................................................................ 35

4.1  
Introduction ............................................................................................................. 35

4.2  
The Molecular Wire Hamiltonian ............................................................................... 36

4.3  
The Recharging Model .............................................................................................. 39

4.4  
Dissipation .................................................................................................................. 43

4.5  
Results ....................................................................................................................... 45

4.5.1  
Recharging Method I ................................................................................................. 46

4.5.1.1  
Resonant Regime ............................................................................................... 46

4.5.1.2  
Nonresonant Regime ............................................................................................ 47

4.5.2  
Recharging Method II ............................................................................................... 48
4.5.2.1  Resonant Regime ................................................................. 48

4.5.2.2  Nonresonant Regime ............................................................ 49

4.6  Concluding Remarks ................................................................. 50

4.7  Figures .......................................................................................... 52

Chapter 5  Quantum-Classical Path Integral: Classical Memory and Weak Quantum Nonlocality ................................................................. 74

5.1  Introduction .................................................................................. 74

5.2  Quantum-Semiclassical and Quantum-Classical Path Integral .......... 77

5.3  Classical Memory, Quantum Nonlocality and Near-Classical Conditions ... 84

5.4  Numerical Illustrations ................................................................. 91

5.5  Concluding Remarks ................................................................. 94

5.6  Figures .......................................................................................... 96

Chapter 6  Quantum-Classical Path Integral: Numerical Methodology .......... 107

6.1  Introduction ................................................................................. 107

6.2  Discretized Quantum-Classical Path Integral .................................. 109

6.3  Hopping penalty and solvent reorganization .................................. 117

6.4  Iterative Evaluation of the Quantum-Classical Path Integral ............. 119

6.5  Numerical Examples ................................................................. 125

6.6  Concluding Remarks ................................................................. 127

6.7  Figures .......................................................................................... 130
Chapter 1 Introduction

Feynman’s path integral formulation of quantum mechanics provides an insightful picture of the behavior of quantum systems. Namely, the probability amplitude of a particle starting at point $A$ at $t=0$ and ending at point $B$ at a later time $t$ (or equivalently, the matrix element $\langle B|e^{-i\hbar H/\hbar}|A\rangle$) is given by a sum over all possible paths that connect points $A$ and $B$. The probability is then the squared modulus of this sum. To be more precise, this path sum is given by

$$\text{Probability Amplitude}(A,B,t) = \sum_{\text{paths}} e^{iS[\text{path}]/\hbar}.$$  \hspace{1cm} (1.1)

In Equation (1.1), each path included satisfies the boundary conditions specified above and has weight given by the exponential of its corresponding action, $S[\text{path}].times \frac{i}{\hbar}$ [1]. We can see right away that, in the limit of $\hbar \rightarrow 0$, only those paths for which the action functional is stationary contribute to the sum. These paths are exactly those obeying Newton’s laws [2]. Thus, we have clear relationship between quantum and classical regimes.

As is well known, quantum mechanics was formulated to address the strange behavior of particles at the smallest length and time scales. Phenomena such as particle interference, tunneling into classically forbidden regions, and zero-point energy effects cannot be explained by Newton’s laws. Unfortunately, given a system of many particles, calculations within the framework of quantum mechanics are more computationally challenging than classical ones. This is simply because we need to work on a grid of points that scales exponentially with the number of particles, and on this grid we need to perform some type of integration over some function defined on this space. Metropolis Monte Carlo algorithms do away with this exponential growth of grid size by randomly selecting points that are statistically significant [3]. However, the function to be integrated must be positive and smooth enough for Monte Carlo to produce an
average result that is much bigger than its error bar (i.e. a high signal to noise ratio is desired, otherwise the answer is meaningless). The integrand that is present in quantum dynamics involves the quantum evolution operator (a complex exponential of the Hamiltonian), and unfortunately it is a highly oscillatory function of the coordinate system, with the phase evolving at an ever increasing rate with the distance between any two grid points [4, 5]. Thus it seems that we have no choice but to work with a dense grid that grows exponentially with system size. Moreover, since the number of possible paths in Equation (1.1) scales exponentially with the final time $t$, the path integral formulation results in an exponential scaling in time as well. In classical mechanics, on the other hand, we would specify for a system of $N$ particles $N$ initial positions and $N$ initial momenta. These initial conditions are propagated in time utilizing Hamilton’s equations of motions, a set of $2N$ coupled first order ordinary differential equations [2]. Thus, the effort in classical mechanics is linear in both system size and propagation time.

For many situations, one is interested in the dynamics of a few degrees of freedom with the rest of the system (called the bath) being integrated out. This greatly reduces the computational cost as we only need to specify a grid that spans the system degrees of freedom. For concreteness, we look at the dynamics of the reduced density matrix which is defined as,

$$\hat{\rho}_{\text{red}}(t) = \text{Tr}_{\text{bath}} \left( \hat{U}(t) \hat{\rho}(0) \hat{U}^\dagger(t) \right).$$

Here, we start with an initial density matrix defined in the full space of the system-bath; propagate it to time $t$ using the time evolution operator, $\hat{U}(t) = e^{-i\hat{H}t/\hbar}$ (and its adjoint, $\hat{U}^\dagger(t)$); and finally trace the propagated density matrix over the states spanning the bath coordinates. Note that the evolution operator is defined by the Hamiltonian, $\hat{H}$, of the entire system-bath Hilbert space. The end result is a density matrix which lives in the subspace of the system degrees of freedom. In the limit of zero bath coupling, the density matrix is trivially propagated in iterative fashion as a series of matrix vector operations, where the vector stores the elements of the density
matrix and the matrix includes the elements of the evolution operators. In this case, the computational effort is linear with propagation time, unlike the exponential effort required in the path integral expression in Equation (1.1).

Using path integrals, Feynman and Vernon have done exactly the procedure of Equation (1.2) for a bath of simple harmonic oscillators, each coupled linearly to the system [6]. The evolution operators in Equation (1.2) are expressed as path integrals over the system coordinates only (an integral over forward/backward paths, \( s^+ / s^- \), for the propagator \( \hat{U}(t)/\hat{U}^*(t) \), respectively). The effect of the bath comes in as an additional influence functional factor, \( F[s^+, s^-] \), which is analytical for the case of harmonic oscillators. For clarity, the path integral expression of Equation (1.2) is equal to

\[
\rho_t \left( s_0^+, s_0^- \right) = \int Ds^\pm \exp \left( i S[s^+] - S[s^-] \right) F[s^+, s^-],
\]

where we include all forward/backward paths, \( s^\pm \), that start at \( s_0^\pm \) and end at \( s_t^\pm \) at some later time \( t \). Note that the symbol \( Ds^\pm \) represents a sum or functional integral over forward/backward paths. The influence functional includes interactions amongst different points of time \( t', t'' \) along a forward/backward path pair whose strength is proportional to the bath’s position autocorrelation function \( \alpha(t' - t'') \). In other words, the bath introduces memory that is specific to what forward/backward path the particle took to get to a certain point in space at the present time \( t \). Since we now need to specify all possible paths up to a certain propagation time and this set of paths grows exponentially in time, the computational effort scales exponentially with time, making this procedure unrealistic for long time dynamics. However, for a macroscopic bath, the autocorrelation function \( \alpha(\tau) \) decays to zero and thus all nonlocal interactions are negligible beyond a finite decoherence time. The destructive interference amongst all bath’s modes and the makeup of the bath’s frequency spectrum are the source of this finite memory. If the bath’s frequency spectrum is composed of mostly fast modes, then the memory length is on the order of
a few time steps. On the other hand, if the bath is rather sluggish, the bath’s memory is significant
over a couple of tens of time steps. Makri used this fact to formulate an iterative matrix vector
procedure which propagates the reduced density matrix forward in time. In this method, the size
of this vector is equal to the set of all possible forward/backward system paths that span a time
equal to a memory cutoff. It is assumed that nonlocal interactions beyond the cutoff are small.
This memory cutoff is increased until results converge within a prescribed accuracy [7, 8].

If the memory cutoff spans $\Delta k_{\text{max}}$ time steps and the number of discretized position states
is $M$, the set of all possible forward/backward paths is $M^{2\Delta k_{\text{max}}}$. Usually, the number of time
steps $N$ required for a typical simulation is much greater than the memory cutoff, $\Delta k_{\text{max}}$, so that
$M^{2\Delta k_{\text{max}}} \ll M^{2N}$. Thus, taking advantage of the finite bath induced memory greatly reduces the
computational burden associated with long time dynamics. Still if $M$ and/or $\Delta k_{\text{max}}$ is large
enough, we again need to deal with a very large set of system paths.

Propagators living in an infinite dimensional Hilbert space (for example, the free particle
propagator) have matrix elements in position space which are simple phase factors. In other
words, a particle localized at a certain point in space is equally likely to be anywhere in space at
an infinitesimally small time later. This makes sense since the particle is initially localized to a
point and thus its momentum space spectrum is uniform. However, when we work in a Hilbert
space of finite dimension (for example, by only including those energy eigenstates below a given
temperature) and diagonalize the position operator, the off-diagonal matrix elements of the
propagator in this basis (known as the discrete variable representation (DVR) basis) decrease in
magnitude as the difference between their position eigenvalues increases [9, 10]. Thus path
segments composed of many transitions (a path with many kinks) has weight much smaller than a
path composed of a few transitions (a smooth path) [11]. Furthermore, the presence of a bath
reduces the weight of a transition even further since the particle hop is now accompanied by a
change in the system-bath potential energy (known in the literature as the bath’s reorganization energy; see Section 6.3). In Chapter 2, we review in more detail the propagation of the reduced density matrix and talk about the influence functional form for a collection of harmonic oscillators. In Chapter 3, we introduce a simple filtering scheme which throws out paths of diminishing weight. This filtering algorithm is applied to a model describing long range electron transfer in the presence of slow baths.

For about sixty years, computer chip designers have been able to pack an exponentially increasing number of transistors on a small surface leading to faster, cheaper, and more portable computing systems. The latest CPUs have transistor components on the order of tens of nanometers and in order to maintain this miniaturization trend, it is important to study the conductance properties of small molecules which will serve as the electronic components of future integrated circuits. Molecular wires possess a rich dynamical behavior due to the interplay of multiple timescales (those of the electronic transitions and the molecular vibrations) [12]. Usually for these systems, the molecular vibrations are rather slow compared to the system’s timescale necessitating the use of a large memory cutoff, $\Delta k_{\text{max}}$. For this reason and the fact that the number $M$ of discretized position states grows with molecule size, we apply the path filtering ideas of Chapter 3 in Chapter 4 to study the conductance of molecular wires, focusing on the conductance dependence on both the molecule length and the strength of the system-bath interaction.

In Chapter 5 and Chapter 6, we take a look at systems composed of light and heavy particles. The goal is to treat the light particles quantum mechanically and the heavier particles classically. This is a typical situation in chemical and biological systems (for example, proton transfer across a large molecule). Furthermore, we are interested in the construction of influence functionals stemming from anharmonic baths whose degrees of freedom are treated within a classical framework. By linearizing the path integral expression over the classical degrees of freedom, we
derive Newton’s equations for these particles where the equations of motion contain a driving force term stemming from the interaction with the quantum particles. In turn, the response of the classical degrees of freedom is fed back to dynamics of the quantum system which evolves via a Hamiltonian that depends parametrically on the classical trajectory. This analysis sheds light on the source of the nonlocal memory present in any influence functional. We also point out in Chapter 5 that the classical limit, where the bath-system interaction is negligible on the classical dynamics, is an excellent starting point for calculations of interest and requires minimal effort since there is no memory involved. In this approximation, the bulk of the bath’s decoherence and relaxation effects are present. Corrections away from this limit are easily included with modest effort by summing over the set of all classical path segments spanning the bath’s memory. This procedure is discussed in detail in Chapter 6. Furthermore, we point out in Chapter 5 that the reduced density matrix (or say some correlation function of two system operators) is a smooth, mostly positive function of the initial position and momenta of the classical particles. This allows efficient integration of the classical particles using Monte Carlo methods whose effort is independent of the number of variables to be integrated. Finally we end with an overview of our work in Chapter 7.
References


Chapter 2  Overview of the Iterative Path Integral Methodology for Dissipative Systems

In a series of papers [1-10], our group has introduced an iterative algorithm for evaluating the real-time path integral of systems interacting with a dissipative environment [11-13]. The latter is often referred to as the bath or solvent, and even though it is typically composed of atoms or molecules interacting with one another via nonlinear many-body forces, the simple model of a harmonic bath is known to capture the essential characteristics of condensed phase environments. With proper parameterization, harmonic baths can in some cases capture the effects of complex molecular environments very accurately [14]. To the extent that the (harmonic or anharmonic) bath can be integrated out, being replaced by an influence functional [15], our earlier work has shown [1-3] that the path integral representation of the reduced density matrix (or a time correlation function) of the system can be decomposed into a series of successive matrix-vector multiplications. This is possible because of decoherence induced by the bath, which leads to the quenching of memory in the influence functional beyond a finite number of time steps.

The conventional system-bath Hamiltonian has the form

\[ \hat{H} = \hat{H}_{\text{sys}} + \sum_j \left( \frac{\hat{p}_j^2}{2m_j} + \frac{1}{2} m\omega_j^2 \hat{x}_j^2 - f_j(s)\hat{\hat{x}}_j \right), \]

(2.1)

Here \( s \) denotes the coordinate(s) of the system of interest, described by the Hamiltonian \( H_{\text{sys}} \), and \( x_j \) are harmonic “bath” degrees of freedom representing phonons or molecular vibrations of the environment. Interaction between system and bath is described through the coupling functions \( f_j(s) \) and is assumed linear in the bath coordinates.

The time evolution of observables pertaining to the system can be obtained from the reduced density operator,
\[ \dot{\rho}(t) = \text{Tr}_{\text{bath}} \left( e^{-i\hat{H}_t/\hbar} \rho(0)e^{i\hat{H}_t/\hbar} \right) \]  

(2.2)

Here \( \rho(0) \) is the initial density operator and the trace is evaluated with respect to all the bath degrees of freedom. It is often assumed that the system and bath are uncorrelated at \( t = 0 \), such that the density operator factorizes \[12\], and that the bath is initially at thermal equilibrium, such that

\[ \dot{\rho}(0) = \dot{\rho}_{\text{sys}}(0) \dot{\rho}_{\text{bath}}(0) = \dot{\rho}_{\text{sys}}(0) \exp(-\beta \hat{H}_{\text{bath}}) / Z_{\text{bath}}, \]

(2.3)

where \( \hat{H}_{\text{bath}} \) is the Hamiltonian for the isolated bath. Below we adopt this form for convenience. Equilibrium initial conditions, where \( \rho(0) \propto \exp(-\beta \hat{H}) \), can also be treated via a generalization of the iterative path integral methodology \[9, 10\]. We adopt the quasiadiabatic splitting of the Hamiltonian \[16\], rewriting Eq. (2.1) in the form

\[ \hat{H} = \hat{H}_0 + \sum_j \frac{p_j^2}{2m_j} + \frac{1}{2} \sum_j \frac{1}{m_j \omega^2_j} \left( \dot{x}_j - \frac{f_j(\xi)}{m_j \omega^2_j} \right)^2 \]  

(2.4)

where

\[ \hat{H}_0 = \hat{H}_{\text{sys}} - \sum_j \frac{f_j(\xi)}{2m_j \omega^2_j}. \]

(2.5)

In many applications the coupling functions \( f_j \) are assumed linear in the system coordinate, i.e.,

\[ f_j(s) = c_j s. \]  

(2.6)

The effect of the bath on the dynamics of the system reduced density matrix is captured in the spectral density function

\[ J(\omega) = \frac{\pi}{2} \sum_j \frac{c^2_j}{m_j \omega_j} \delta(\omega - \omega_j). \]  

(2.7)

A discrete variable representation \[17-20\] (DVR) derived from the eigenstates of the bare system Hamiltonian provides the optimal representation for the discretized path integral \[21\].
These system-specific DVR states are expressed in terms of the $M$ lowest energy eigenstates $\Phi_n$ of $H_0$.

$$|\sigma_n\rangle = \sum_{n'=1}^M I_{nn'}|\Phi_{n'}\rangle,$$

(2.8)

where the transformation coefficients are specified by the requirement

$$\langle \sigma_n|\delta|\sigma_{n'}\rangle = \delta_{nn'}.$$

(2.9)

Because the position operator is diagonal in this finite basis, the DVR states $|\sigma_n\rangle$ act as discretized position states and the $M$ eigenvalues $\sigma_n$ form the relevant coordinate grid.

The DVR-discretized path integral representation of the reduced density matrix is obtained by splitting the time into $N$ increments of length $\Delta t = t/N$, replacing the exponential of the sum by the product of exponentials, and inserting $2(N-1)$ sets of DVR states. This leads to the expression [3]

$$\langle \sigma_N^+|\hat{\rho}(N\Delta t)|\sigma_N^-\rangle = \text{Tr}_\text{bath} \sum_{\sigma_0}^{M} \sum_{\sigma_1}^{M} \cdots \sum_{\sigma_{N-1}}^{M} \sum_{\sigma_0}^{M} \sum_{\sigma_1}^{M} \cdots \sum_{\sigma_{N-1}}^{M} \langle \sigma_N^+ | e^{-iH\Delta t/\hbar} | \sigma_{N-1}^- \rangle$$

$$\times \langle \sigma_{N-1}^- | e^{-iH\Delta t/\hbar} | \sigma_{N-2}^- \rangle \cdots \langle \sigma_1^- | e^{-iH\Delta t/\hbar} | \sigma_0^- \rangle \langle \sigma_0^- | \rho(0) | \sigma_0^- \rangle$$

$$\times \langle \sigma_0^- | e^{iH\Delta t/\hbar} | \sigma_1^- \rangle \langle \sigma_1^- | e^{iH\Delta t/\hbar} | \sigma_2^- \rangle \cdots \langle \sigma_{N-1}^- | e^{iH\Delta t/\hbar} | \sigma_N^- \rangle.$$  

(2.10)

Substitution of the factorized initial density, Eq. (2.3), and use of the quasi-adiabatic splitting of the time evolution operator [16] according to the terms in Eq. (2.4), brings the reduced density matrix in the following form [7]:

$$\langle \sigma_N^+|\hat{\rho}(N\Delta t)|\sigma_N^-\rangle = \text{Tr}_\text{bath} \sum_{\sigma_0}^{M} \sum_{\sigma_1}^{M} \cdots \sum_{\sigma_{N-1}}^{M} \sum_{\sigma_0}^{M} \sum_{\sigma_1}^{M} \cdots \sum_{\sigma_{N-1}}^{M} \langle \sigma_N^+ | e^{-i\hat{H}_0\Delta t/\hbar} | \sigma_{N-1}^- \rangle$$

$$\times \langle \sigma_{N-1}^- | e^{-i\hat{H}_0\Delta t/\hbar} | \sigma_{N-2}^- \rangle \cdots \langle \sigma_1^- | e^{-i\hat{H}_0\Delta t/\hbar} | \sigma_0^- \rangle \langle \sigma_0^- | \hat{\rho}_\text{sys}(0) | \sigma_0^- \rangle$$

$$\times \langle \sigma_0^- | e^{i\hat{H}_0\Delta t/\hbar} | \sigma_1^- \rangle \langle \sigma_1^- | e^{i\hat{H}_0\Delta t/\hbar} | \sigma_2^- \rangle \cdots \langle \sigma_{N-1}^- | e^{i\hat{H}_0\Delta t/\hbar} | \sigma_N^- \rangle$$

$$\times F(\sigma_0^+, \sigma_1^+, \ldots, \sigma_N^+, \sigma_0^-, \sigma_1^-, \ldots, \sigma_N^-).$$

(2.11)
Here $F$ is the DVR-discretized influence functional, given by the expression

$$F\left(\sigma_0^+, \sigma_1^+, \ldots, \sigma_N^+, \sigma_0^-, \sigma_1^-, \ldots, \sigma_N^-\right) = \exp\left(-\frac{1}{\hbar} \sum_{k=0}^{N} \sum_{k=0}^{k} \left(\sigma_k^+ - \sigma_k^-\right)\left(\eta_{kk^*}^+ \sigma_k^+ + \eta_{kk^*}^- \sigma_k^-\right)\right)$$  \hspace{1cm} (2.12)

where $\eta_{kk^*}$ are complex-valued coefficients which are the discrete analogs of the force autocorrelation function of the bath and have been given explicitly in [2]. The double sum in this expression constitutes nonlocal “memory” interactions, introduced to the system dynamics by its coupling to the bath. The strength of the memory terms is given by the magnitude of the bath correlation function, or equivalently the coefficients $\eta_{kk^*}$.

As argued in earlier papers by our group [1-6], the correlation function of a dissipative bath decays to zero and thus its magnitude is smaller than any chosen threshold beyond a "memory" time interval $\tau_m = \Delta k_{\text{max}} \Delta t$. This feature is a consequence of decoherence in media with broad spectra and implies that "long memory" terms make negligible contribution to the dynamics. As a result, the coefficients $\eta_{kk^*}$ drop below a threshold value when $k - k' > \Delta k_{\text{max}}$. This fact implies that the second summation index in Eq. (2.12) can be restricted to the $\Delta k_{\text{max}}$ time points preceding the first summation index, leading to quasi-Markovian dynamics for the probed system that forms the basis of an iterative decomposition [1-3]. Specifically, a multi-time reduced density matrix $R$ (a tensor of rank $\Delta k_{\text{max}}$) can be constructed whose evolution is obtained via the iterative procedure [2]

$$R\left(\sigma^+_{k+1}, \ldots, \sigma^+_{k+\Delta k_{\text{max}}}; (k+1)\Delta t\right) = \sum_{\sigma_r^+ = 1}^{M} \Lambda\left(\sigma_{k+1}^+, \ldots, \sigma_{k+\Delta k_{\text{max}}}^+\right)R\left(\sigma_{k+1}^+, \ldots, \sigma_{k+\Delta k_{\text{max}}-1}^+; k\Delta t\right),$$  \hspace{1cm} (2.13)

where $\Lambda$ is a multi-time propagator matrix (a tensor of rank $\Delta k_{\text{max}} + 1$) with elements given by the expression
Another propagator matrix $T$, whose elements contain all propagators and influence functional terms up to the chosen memory length $\Delta k_{\text{max}}$ and thus are given by the expression

$$T(\sigma_k^+,\ldots,\sigma_{k+\Delta k_{\text{max}}}^+) = \prod_{l=1}^{\Delta k_{\text{max}}} \left\langle \sigma_{k+l}^+ \left| e^{-iH_0\Delta t/h} \sigma_{k+l-1}^+ \right| \sigma_{k+l}^- \right\rangle e^{iH_0\Delta t/h} \sigma_{k+l}^- \right\rangle \times \exp \left\{ -\frac{1}{\hbar} \sum_{l=0}^{k+\Delta k_{\text{max}}} \sum_{l'=0}^{k+\Delta k_{\text{max}}} \left( \sigma_{l+l'}^+ - \sigma_{l+l'}^- \right) \left( \eta_{l\bar{l}} \sigma_{l+l'}^+ - \eta_{l\bar{l}} \sigma_{l+l'}^- \right) \right\}.$$  

(2.15)

(with appropriate endpoint values for the coefficients), is used to terminate the iteration, yielding the system reduced density matrix according to the multiplication/contraction procedure

$$\rho(\sigma_{N}^+, N\Delta t) = \sum_{\sigma_{k-\Delta k_{\text{max}}}^k} \sum_{\sigma_{k+\Delta k_{\text{max}}}^k} \cdots \sum_{\sigma_{N-\Delta k_{\text{max}}}^N} T(\sigma_{N-\Delta k_{\text{max}}}^N, \ldots, \sigma_{N}^+) \times R(\sigma_{N-\Delta k_{\text{max}}}^N, \ldots, \sigma_{N-1}^+(N-\Delta k_{\text{max}})\Delta t).$$  

(2.16)

The path integral interactions included in the iterative propagation are indicated in the diagram of Figure 1.

The original procedure reviewed above requires storing a multi-time reduced density matrix $R$ with initial condition

$$R(\sigma_0^+ \ldots, \sigma_{\Delta k_{\text{max}}-1}^+; 0) = \left\langle \sigma_0^+ \left| \hat{\rho}_{\text{sys}} \right| \sigma_0^- \right\rangle,$$  

(2.17)

as a complex-valued array of length $M^{2\Delta k_{\text{max}}}$, representing all possible forward-backward path segments of length $\Delta k_{\text{max}}$. The propagators $\Lambda$ and $T$ are multidimensional arrays containing $M^2 \times M^{2\Delta k_{\text{max}}}$ elements. Propagation by $N \gg \Delta k_{\text{max}}$ time steps involves $NM^{2(\Delta k_{\text{max}} + 1)}$ operations, thus the cost of the iterative procedure is negligible compared to that for direct evaluation of the path integral expression, Eq. (2.11), which involves $M^{2N}$ operations, and (unlike the latter) grows linearly with the total propagation time.
Figure 1 Diagrammatic representation of the path integral interactions included in the propagator matrices in a case where the memory length is equal to four time steps. The loops indicate terms in the exponent of the influence functional. (a) \( \Lambda \) matrix used in continued propagation. (b) T matrix used for termination.
References


Chapter 3  Filtering Scheme for Path Integral Calculations

3.1 Introduction

This work is concerned with the common situation of a system coupled to a harmonic dissipative bath, where the influence functional is available analytically. Assuming the memory interactions in the influence functional, whose strength is governed by the bath response function $\alpha(t_k - t_{k-1})$, are limited to $|k - k'| \leq \Delta k_{\text{max}}$ path integral time steps, the total number of forward-backward path segments that span the memory length is $M^{2\Delta k_{\text{max}}}$, where $M$ is the number of grid points used to represent the system [1-3]. Thus, the size of the propagator matrix becomes prohibitive as the memory length is increased. Sim and Makri have shown that the vast majority of propagator matrix elements are negligible in magnitude, and developed a Monte Carlo procedure for selecting the path segment combinations that must be retained in the propagator [4, 5]. This path filtering procedure leads to a dramatic reduction of propagator size, allowing calculations in cases of very long memory. Sim has made a significant improvement of the method through the development of an on-the-fly path selection procedure [6], which avoids the use of Monte Carlo sampling. In this scheme, new path segments are constructed at each time point by combining those of the previous step with all possible coordinate points at the new time point, retaining those with appreciable weight and re-indexing the segments. After some transient fluctuations, the number of surviving path segments typically settles to a nearly constant value.

The present chapter describes a simple and efficient variant of these schemes that can lead to substantial savings in cases where multi-site systems subject to long memory influence functional interactions are propagated for long times. To begin, all important path segments that span the memory length are identified at the beginning of the calculation using a weight selection criterion that takes into account influence functional couplings to earlier and later time points.
These paths are paired using a minimal search procedure, building a propagator matrix that is stored for use in all iterations. We also propose a simple criterion for assessing the adequacy of a particular weight threshold prior to performing the propagation. For systems characterized by long memory and slow dynamics, where tens or hundreds of thousands of iterations are required to reach the final equilibrium state, the gain in efficiency is substantial. Finally, the memory-path propagator is independent of initial conditions, thus it may be used to calculate the dynamics following different system preparations.

In section 3.2, we describe the construction of the memory-path propagator and the threshold criterion. A numerical illustration is given in section 3.3, where the method is applied to a multi-site tight-binding Hamiltonian characteristic of long-range charge transfer. Section 3.4 presents some concluding remarks.

3.2 Methodology

The path integral methodology described in the previous chapter requires the storage of matrices that scale as $M^{2\Delta k_{\text{max}}}$. For large $M$ and/or $\Delta k_{\text{max}}$, the storage demands can become very high, rendering the method impractical. As argued in previous papers [4-6], the vast majority of path segments contribute with negligible weight and thus can be omitted. Based on this observation, Sim and Makri developed a Monte Carlo procedure for filtering out path segments of low weight [4, 5], which usually leads to a dramatic size reduction of these matrices. That procedure was employed in the simulation of primary charge separation in the photosynthetic reaction center, where the medium-induced memory spans $\Delta k_{\text{max}} = 35$ path integral time steps [7, 8]. More recently, Sim proposed an on-the-fly non-Monte Carlo algorithm for eliminating low-weight path segments at each propagation step by checking the weights of stored path segments from the previous time step as these combine with the grid points of the current time [6]. The method avoids the use of Monte Carlo sampling but involves
assembly/resorting of path segments and construction of the propagator at each time step. Sim and coworkers have used the on-the-fly iterative path integral scheme to study charge transfer in DNA and in molecular wires [9-11]. Below we describe a more efficient, fully deterministic variant of these approaches for selecting important path segments and building the minimal-sized multi-time reduced density matrix $R$ and the propagator at the start of the calculation, thus avoiding repeated path segment identification and sorting. We suggest a procedure for constructing the propagator matrix without searching through the entire set of retained path segments to identify matching elements. We also discuss a simple way of predetermining whether a specific set of chosen path segments is adequate for propagation over the desired time length.

To begin, we choose a threshold $\theta$, below which path segments will be dropped. This threshold serves as a convergence parameter. The desired paths are built recursively, starting with all possible two-point segments $\sigma_1^+, \sigma_2^+$ and successively adding time points with coordinates $\sigma_3^+, \sigma_4^+$, etc. Prior to each path lengthening step, segments of weight smaller than $\theta$ are dropped. The weight $p_{\alpha}^{(n)}$ of an $n$-point path segment $\alpha$ with coordinates $\sigma_1^+, \sigma_2^+, \ldots, \sigma_n^+$ is defined as

$$p_{\alpha}^{(n)} = \prod_{k=1}^{n-1} K(\sigma_k^+, \sigma_{k+1}^+) \exp \left( -\frac{1}{\hbar} \sum_{k=1}^{n} \sum_{k=1}^{k} (\sigma_k^+ - \sigma_k^-)(\eta_{k,k}^- - \eta_{k,k}^+ \sigma_k^-) \right).$$

(3.1)

where $K$ is the propagator for the reference system Hamiltonian $H_0$. Thus the path construction proceeds as follows: Each grid point $\sigma_1^+$, is combined with all grid points to form the two-point segment $\sigma_1^+, \sigma_2^+$. Of all $M^4$ two-point segments obtained this way, those with weight $p_{\alpha}^{(2)} < \theta$ are dropped. Next, the retained segments are combined with the $M^2$ grid points $\sigma_1^+$, giving rise to three-point segments with coordinates $\sigma_1^+, \sigma_2^+, \sigma_3^+$, which are retained only if $p_{\alpha}^{(3)} \geq \theta$. After
the first few steps, the weight criterion eliminates the vast majority of new possibilities, thus the number $L$ of retained paths when $n = \Delta k_{\text{max}}$ is very small compared to $M^{2\Delta k_{\text{max}}}$.

The above procedure is fully deterministic and guarantees selection of all path segments of length $\Delta k_{\text{max}}$ whose weight is equal to or greater than $\theta$. Further, the procedure is invariant with respect to a shift of the time indices, i.e.

$$
\sigma^+_{\Delta k_{\text{max}}} + 1, \sigma^+_{\Delta k_{\text{max}}} + 2, \ldots, \sigma^+_M
$$

will produce the same segments. As a result, the collected path segments can be used for the entire propagation. When the desired propagation time is long (as in calculations presented in the next section, which involve $\sim 10^5$ iterations), avoiding the search for above-threshold path segments and construction of the relevant propagation matrix at each propagation step offers a very significant simplification and acceleration of the calculation.

Once all path segments of length $\Delta k_{\text{max}}$ which satisfy the selection criterion have been found, one must build and store the propagator matrix $\Lambda$. Two path segments $\alpha$ and $\beta$, with coordinates $\sigma^+_0, \ldots, \sigma^+_{\Delta k_{\text{max}} - 1}$ and $\sigma^+_1, \ldots, \sigma^+_M$, respectively, give rise to a nonzero propagator matrix element if these paths share a common set of coordinate values $\sigma^+_1, \ldots, \sigma^+_{\Delta k_{\text{max}} - 1}$. For this reason the vast majority of the propagator matrix elements are zero. Searching for path pairs that combine to nonzero elements is a process which in principle scales quadratically with the number $L$ of retained path segments, although faster than $L^2$ search algorithms can be implemented. In the present case, the structure of Eq. (3.1) suggests a simple and economical alternative to a conventional search: During the path construction process, each path segment of length $\Delta k_{\text{max}}$ is assigned to a bin based on its weight according to Eq. (2.14). For a given path segment $\beta$, we attach each possible value of $\sigma^+_0$ to construct all possible paths $\alpha$ and calculate the corresponding weights. Since the weight of each path $\alpha$ is known, one needs to search only...
within a particular bin to identify the path index with the given coordinates. If the bin size is sufficiently small, the necessary search is very fast.

A question of much practical significance is how to determine the threshold value to obtain accurate results while retaining as small a set of path segments as possible. Since $\theta$ is a convergence parameter, the most straightforward way of answering this question is to compare propagation results obtained with a few values of $\theta$ until convergence has been achieved. To minimize the number of costly propagations, we propose below a criterion for predetermining whether a specific threshold value is adequate.

Clearly, propagation will conserve the trace of the reduced density matrix exactly if all path segments have been included. However, when $L \ll M^{2\Delta k_{\text{max}}}$ the iterative procedure is not strictly unitary. In such cases errors tend to accumulate at an exponential rate related to the eigenvalues of the propagator matrix. Because at later stages in the propagation the reduced density matrix has generally deviated significantly from its initial value, likely having spread over all system sites, we examine deviations from unitarity by investigating the matrix that arises if the selected path segments are used to propagate all possible initial conditions. To this end we examine deviations from the identity

$$Z^{-1} \text{Tr} \left(e^{-iH\Delta k_{\text{max}} \Delta t/h} \left| \sigma_0^+ \right\rangle \langle \sigma_0^+ \right| e^{-\beta H_{\text{bath}}} \left| \sigma_0 \right\rangle \langle \sigma_0 \right| e^{iH\Delta k_{\text{max}} \Delta t/h} \right) = \left\langle \sigma_0 \left| \sigma_0^+ \right\rangle \right| = \delta_{\sigma_0, \sigma_0^+}. \quad (3.2)$$

The trace in this expression can be evaluated by summing the propagator $T$ over all path segments with coordinates $\sigma_{k_1\pm}, \ldots, \sigma_{k_{\text{max}}\pm}$. If all path segments are included in the propagator, the result of the operation described in Eq. (3.2) is the identity matrix. Thus, examination of the deviation from identity of the matrix evaluated with the paths corresponding to a particular weight threshold $\theta$ provides an accuracy criterion. The deviations of the eigenvalues (diagonal elements) of this matrix from unity provide an estimate of the maximum propagation time attainable without significant loss of accuracy.
3.3 Application: Tight-binding model for long range charge transport

Charge and exciton transport in extended systems are strongly affected by decoherence due to interaction with phonons and molecular vibrations. Such processes are often strongly coupled to lower frequency bath degrees of freedom, which induce long-time memory effects that may be very important to the process of interest. The interplay among the frequencies and electronic coupling values of the system, the time scales of the bath, as well as the value of temperature and overall strength of dissipation can lead to rich dynamics. In this section we apply this methodology to a tight binding model of charge transport in extended systems.

The model Hamiltonian consists of seven sites with coordinates $\sigma_i = i, i = 0, \ldots, 6$ and energies $\epsilon_j$, where $j = 0$ corresponds to the electron donor. All nearest-neighbor site couplings are set to $V$. Thus, the reference Hamiltonian matrix has the form

$$
\hat{H}_0 = \epsilon_0 |u_0\rangle\langle u_0| + \sum_{i=1}^{6} \epsilon_i |u_i\rangle\langle u_i| + V \sum_{i=0}^{5} (|u_i\rangle\langle u_{i+1}| + |u_{i+1}\rangle\langle u_i|).
$$

The donor energy is set to $\epsilon_0 = 1$, all other energies $(j = 1, \ldots, 6)$ are set to $\epsilon_j = 0$, and the site-site couplings are $V = -0.025$ in atomic units ($\hbar = 1$). It is assumed that only the donor is populated initially. Interactions with phonons/molecular vibrations are modeled by a harmonic bath described by an Ohmic spectral density [12],

$$
J(\omega) = \frac{2\pi\hbar\omega}{q_0^2} \xi e^{-\omega/\omega_c},
$$

where $\xi$ is the dimensionless Kondo parameter (a measure of the dissipation strength), $\omega_c$ is a cutoff frequency which determines the timescale of the bath, and $q_0 = 1$ is the site-to-site distance. The inverse temperature is $\beta = 2$. We examine two values of parameters that correspond to the same reorganization energy, $\omega_c = 4$, $\xi = 0.03$ and $\omega_c = 0.4$, $\xi = 0.3$. The second of these conditions gives rise to long memory. Using a path integral time step $\Delta t = 0.8$. 

23
calculations converged with $\Delta k_{\text{max}} = 6$ in the case of the fast ($\omega_c = 4$) bath but required $\Delta k_{\text{max}} = 40$ in the case of the slow ($\omega_c = 0.4$) bath. In the latter case the dimension of the propagator matrix prior to filtering is $7^{80} \times 49$. Propagation to the final time involved 60,000 iterations.

We begin by discussing the convergence characteristics of the method in the more challenging case where the charge transfer system is coupled to the sluggish, long memory bath characterized by $\omega_c = 0.4$, $\xi = 0.3$.

Table 1 illustrates the threshold selection criterion discussed in section 3.2 by presenting the trace of the identity matrix in Eq. (3.2). Since the Hamiltonian has seven sites, the exact value of this trace is 7. It is seen that the highest threshold value chosen, $\theta = 10^{-6}$, leads to deviations in the third decimal place, while for the values $\theta = 10^{-7}$ and $\theta = 10^{-8}$ deviations of the trace from the theoretical value are in the fourth and fifth decimal place, respectively. To examine the validity of these estimates, we show in Figure 2 the calculated population of the last site and the sum of all site populations. One observes that the accuracy estimates given by the identity matrix criterion with the thresholds mentioned above are indeed accurate roughly up to $10^7$, $10^8$ and $10^9$ time units. Further, an even smaller threshold with value $\theta = 5 \times 10^{-9}$ yields results indistinguishable (within the shown propagation interval) from those obtained with $\theta = 10^{-8}$, in line with the prediction based on Eq. (3.2).

Figure 3 shows the number of retained path segments at the smallest threshold value, $\theta = 5 \times 10^{-9}$, as a function of the number of memory steps $\Delta k_{\text{max}}$. It is seen that this number grows very slowly with $\Delta k_{\text{max}}$, so the memory time can be increased to very large values without a significant increase in computational effort. For comparison, Figure 3 also shows the exponential growth of the number of path segments in the absence of weight-based filtering, which rapidly exceeds computer storage capabilities.
Figure 4 shows the ratio of the number of propagator elements per retained path segment for the data values shown in Figure 3. It is seen that the number of stored propagator elements is much smaller than \( \frac{L}{M} = 49 \), decreasing from about 5 for the \( \Delta k_{\text{max}} = 6 \) to 1.5 for \( \Delta k_{\text{max}} = 40 \). The very sparse nature of the propagator matrix makes its storage feasible and practical, so that the computationally more intensive search for path segments and sorting does not need to be repeated at every propagation step.

In both cases considered the electronic coupling matrix element is much smaller than the donor energy gap, thus population transfer is mediated by the bath. The site populations are shown in Figure 5 and Figure 6 for the two cases of fast and slow bath, respectively. In both cases the populations decay to the long-time equilibrium values. However, the transfer is considerably faster in the case of the slower bath. In this case, the closer match of the bath frequencies to the energy gap leads to a rapid population of site 1, but reorganization of this slower bath slows down the transfer to site 2, leading to transient charge buildup on the first site that rises 40% about its long-time value. A similar but progressively less pronounced population buildup is also observed on other sites. In spite of these slower site-to-site steps, the population of the last site rises faster when the system is coupled to the slower bath. Thus it is seen that the effects of long bath memory on charge transport processes can be rather significant.

3.4 Concluding Remarks

Since the original formulation of numerically exact iterative path integral schemes for exact propagation of a system coupled to a dissipative environment, several variants have been developed and applied. The use of filtering algorithms to eliminate the majority of system path segments that span the memory length leads to a dramatic reduction in storage, enabling application to more demanding situations with long memory. The on-the-fly variant of that scheme offers a simpler, deterministic way of identifying statistically significant path segments at
each propagation step, avoiding the use of a Monte Carlo random walk. The present chapter further increases the efficiency of the procedure by constructing these path segments and the propagator matrix at the start of the calculation, eliminating the need for selection and sorting at every time point. Further increase of efficiency is achieved through path segment binning, which accelerates the search for propagator matrix elements, and through a simple identity matrix criterion for assessing the adequacy of a chosen path selection threshold prior to performing the propagation.

We have used the method to examine charge transfer in simple model of long-range electron transfer, where the charge transfer states are modeled in terms of a seven-site Hamiltonian coupled to a dissipative bath representing solvent modes and molecular vibrations. The effects of bath-induced memory are investigated with two model spectral densities that correspond to the same reorganization energy. We find that a lower frequency bath gives rise to faster charge transfer dynamics accompanied by substantial transient charge buildup on sites close to the donor.

Thorough investigations of bath-induced memory effects on long range electron transfer in biological systems, as well as charge transport in molecular wires, are in progress. In particular, charge transport implies a sustainable steady-state current, which requires a mechanism for charge recirculation. Such a model has recently been developed in our group and dynamical calculations using the scheme described in the present chapter is reported in Chapter 4. Finally, in order to treat situations where the bath is characterized by multiple timescales which give rise to very long memory, it may be necessary to incorporate the present memory-path propagator methodology with a path integral renormalization approach that has just been developed in our group [13].
3.5 Figures

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>Trace of identity matrix</th>
</tr>
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<tr>
<td>$10^{-6}$</td>
<td>6.997106</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>6.999864</td>
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<tr>
<td>$10^{-8}$</td>
<td>6.999981</td>
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<tr>
<td>$5 \times 10^{-9}$</td>
<td>6.999988</td>
</tr>
</tbody>
</table>

Table 1. Trace of the identity matrix criterion (Eq. (3.2)) in the case of the slow bath ($\omega_0 = 0.4$, $\xi = 0.3$) with $\Delta k_{\text{min}} = 40$ for various values of the threshold parameter.
Figure 2 Population of the last site and trace conservation as a function of time in the case of the slow bath (ω_0 = 0.4, ξ = 0.3) for Δk_{max} = 40 for various values of the threshold parameter. Dotted line: \( \theta = 10^{-4} \). Dashed line: \( \theta = 10^{-3} \). Solid line: \( \theta = 10^{-2} \).

Markers: \( \theta = 5 \times 10^{-3} \).
Figure 3 Number of path segments as a function of the number of memory steps. Solid circles: segments selected with threshold value $\theta = 5 \times 10^{-6}$. Hollow squares: number of segments in the absence of weight-based filtering.
Figure 4 Number of propagator matrix elements per path segment as a function of the number of retained path segments for $\Delta k_{\text{max}} = 6 - 40$ and $\theta = 5 \times 10^{-3}$. Reading the points from left to right, they correspond to $\Delta k_{\text{max}} = 6, 10, 14, 18, 22, 24, 26, 30, 34, 38, 40$, respectively.
Figure 5 Site populations in the case of a fast bath with $\omega_4 = 4$, $\xi = 0.03$. The decreasing curve shows the population of the donor, while the other curves from left to right show the rise of the populations of sites 1, ..., 6.
Figure 6 Site populations in the case of a slow bath with $\omega_0 = 0.4$, $\xi = 0.3$. The decreasing curve shows the population of the donor, while the other curves from left to right show the rise of the populations of sites 1,...,6.
References


Chapter 4  Molecular Wires

4.1  Introduction

A molecular wire [1, 2] is used to transfer electrons between a donor and acceptor electrode through a molecular entity. Electron conduction occurs through the lowest unoccupied molecular orbital (LUMO), but holes can also act as charge carriers by conducting via the highest occupied molecular orbital (HOMO) [3-5]. The interaction between the molecular orbital and the metal surface states also determines the position of the metal Fermi level relative to the molecular levels. As a consequence, the junction connecting the molecular wire and the electrodes is crucial to the electron transport process. On the other hand, the electronic structure of the molecular core usually is largely undisturbed by the adsorption onto the metallic surface. Assuming that the mixing between a molecule and an electrode is relatively weak, the Fermi level of the metals lies within the HOMO-LUMO gap of the molecular wire, following an initial charge rearrangement.

In this chapter we focus on LUMO-dominated electron conduction. We assume that the metal Fermi energy lies mid-gap between the HOMO and LUMO states and that the applied voltage is a linear ramp. The full treatment of electron transport through a metal-molecule-metal nanojunction is a challenging task, requiring the use of many-body theory and/or analogous simulation tools. A one-electron tight binding model [6-11] has been used to simplify this many-body problem. In this description, the electron conduction is depicted as an elastic scattering process, where the steady-state current can be inferred from the total transfer rate between donor and acceptor electrodes.

Our study employs a one-dimensional molecular wire of \( N \) identical sites (orbitals) with one state per site, as shown in Figure 7. The molecular sites interact with their nearest neighbors, and the edge sites are coupled to the electrodes. The two identical electrodes serve as reservoirs of
non-interacting one-electron states, which form a continuum [12]. Following standard procedures, we replace this infinite-dimensional model by an effective $N \times N$ non-hermitian Hamiltonian, where the effects of the metal states enter via complex-valued self-energy terms. To observe a constant current in this time-dependent picture we introduce a "recharging" model, where charge is added to or removed from the edge sites until the electron population in the wire reaches a steady state. Dissipative effects from the environment are included by coupling the sites of the wire to a harmonic dissipative bath. We use a numerically exact path integral methodology developed earlier in our group, which we adapt to the problem at hand, to calculate the time-dependent density matrix of this system in order to study the characteristics of charge transport as a function of wire length and wire-electrode coupling.

Section 4.2 describes the Hamiltonian for the wire-electrode system and its reduction to an effective complex-valued matrix. The recharging model is described in section 4.3 and illustrated with numerical results. In section 4.4 we discuss the coupling of the effective Hamiltonian to a harmonic bath mimicking the dissipative effects of the environment and we adapt the iterative path integral methodology, which enables a numerically exact propagation of the reduced density matrix, to the recharging model. The results of our calculations are presented and discussed in section 4.5. Finally, some concluding remarks are given in section 4.6.

4.2 The Molecular Wire Hamiltonian

The one-dimensional molecular wire of $N$ identical sites (orbitals) with one state per site is shown in Figure 7. We assume that the donor and acceptor electrodes are identical, that they are coupled only to their immediate neighbors in the wire according to the Anderson-Newns chemisorption theory, and that the wire-electrode coupling $V_{w-e}$ is the same at both junctions. The molecular wire is described by a tight-binding model according to the Hamiltonian
\[
\hat{H}_s = \sum_i^N \epsilon_D^{(i)} |\lambda_D^{(i)}\rangle \langle \lambda_D^{(i)}| + \sum_{i}^{N} E_i |s_i\rangle \langle s_i| + \sum_i^N \epsilon_A^{(i)} |\lambda_A^{(i)}\rangle \langle \lambda_A^{(i)}| + \hat{V}
\] (4.1)

\[
\hat{V} = \sum_i V_{w-e} \left( |\lambda_D^{(i)}\rangle \langle s_i| + |s_i\rangle \langle \lambda_D^{(i)}| \right) + \sum_{i=1}^{N-1} V_{w-w} \left( |s_i\rangle \langle s_{i+1}| + |s_{i+1}\rangle \langle s_i| \right)
\]

\[
+ \sum_i V_{w-w} \left( |\lambda_A^{(i)}\rangle \langle s_N| + |s_N\rangle \langle \lambda_A^{(i)}| \right),
\] (4.2)

where \(|s_i\rangle, \ell = 1, 2, \cdots, N\) are the molecular sites with physical coordinates (along the molecular wire axis) \(s_i\), and energies \(E_i\), \(|\lambda_D^{(i)}\rangle\), \(|\lambda_A^{(i)}\rangle\) and \(\epsilon_D^{(i)}\), \(\epsilon_A^{(i)}\) are the states and energies of the donor and acceptor reservoirs, respectively, and \(i\) is a continuous index. For simplicity we assume that the coupling of the two edge molecular sites to the metal states has the same value \(V_{w-e}\). Each site in the wire interacts only with its nearest neighbors. We assume that the molecular sites are identical (homogeneous wire), thus the site energies have the same value \(E_i = E_m\) in the absence of external voltage, and that the site-site couplings \(V_{w-w}\) are identical. Assuming the electrostatic potential drops linearly along the wire, the site energies are given by

\[
E_i = E_m - \frac{\ell}{N+1} e_0 \Omega
\] (4.3)

where \(\Omega\) is the voltage applied across the two electrodes and \(e_0\) is the absolute value of the electron charge.

In the elastic scattering model [7, 8] the electronic conductance via a molecular bridge is proportional to the transition probability per unit time from the donor to the acceptor electrode. Evaluation of the transition rate involves calculating the transition matrix determined by Eq. (4.1) and Eq. (4.2), whose dimension is infinite. Using Löwdin’s partitioning technique in [7], it has been shown that the infinite-dimensional matrix problem of the electrode-wire-electrode system can be reduced to an \(N \times N\) problem. The resulting reduced Hamiltonian (which includes only
the molecular wire sites) is no longer hermitian, as it describes an open system. In matrix form, the reduced Hamiltonian of the molecular wire system is [9]
\[
H = \begin{bmatrix}
E_1 + \sum_{D} & V_{w,w} & 0 & \cdots & 0 & 0 & 0 \\
V_{w,w} & E_2 & V_{w,w} & \cdots & 0 & 0 & 0 \\
0 & V_{w,w} & E_3 & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \cdots & E_1 & V_{w,w} & 0 \\
0 & 0 & 0 & \cdots & V_{w,w} & E_{N-1} & V_{w,w} \\
0 & 0 & 0 & \cdots & 0 & V_{w,w} & E_N + \Sigma_A
\end{bmatrix},
\]
(4.4)
where the presence of complex-valued self-energies $\Sigma_D$ and $\Sigma_A$ at sites 1 and $N$ arises from the interaction between the reservoirs and the wire. The imaginary part of the self-energy,
\[
\Gamma_k(E) / 2 \equiv -\text{Im}\Sigma_k = \pi V_{w,e}^2 \rho_k(E),
\]
(4.5)
(where $K = D$ or $A$, $E$ is the electron injection energy, and $\rho_k(E)$ is the density of states at energy $E$) is the spectral function, which determines the rate of losing electrons to the reservoirs. The spectral function in Anderson-Newns chemisorption theory [13, 14] is given by the expression
\[
\Gamma_k(E) / 2 = \frac{V_{w,e}^2}{2\gamma} \sqrt{4\gamma^2 - (E - E^K_f)^2}, \quad |E - E^K_f| < 2\gamma,
\]
(4.6)
where $E_f$ is the Fermi energy of the metal and $4\gamma$ represents the energy bandwidth of the two reservoirs. Using scattering theory it can be shown that the conductance for small voltage and low temperature is [7, 8, 15-22]
\[
g(E) = \frac{2e^2}{h} \Gamma_D(E_f) \Gamma_A(E_f) \left| G_{N,1}(E_f) \right|^2
\]
(4.7)
where $G_{N,1}$ is the $N,1$ component of the wire-reservoir Green’s function. The equation above is known as the Landauer formula. The real part of the self-energy satisfies the relation
\[
\Lambda_k(E) = \frac{\rho}{2\pi} \int_{-\infty}^{\infty} \frac{\Gamma_k(E')dE'}{E - E'},
\]
(4.8)
where $\mathcal{P}$ is the principal part of the integral.

In the tight-binding approximation, the molecular wire states form an energy band of width $4V_{\text{w-w}}$ centered around $E_0$. At low temperature and small voltage the conduction behavior of the wire generally falls into three categories, depending on whether the injecting energy level is inside or outside the band. When the injecting energy lies outside the wire band (the nonresonant regime) the conductance decreases exponentially with the length of the molecular wire. On the other hand, when the injection energy is in resonance with one of the eigenstates of the molecular wire (the resonant regime), the conductance exhibits a sharp spike. As the energy levels within the discrete band of a finite-length wire fluctuate with the number of molecular sites, the conductance at a fixed energy exhibits oscillatory behavior with wire length in this regime. Finally, it has been shown that within a narrow window where the electron energy is nearly resonant with the molecular states, the conductance will drop off quadratically with wire length [8].

### 4.3 The Recharging Model

As the electron propagates along the wire, reaching the last molecular site, charge is expected to leak out continuously by virtue of the imaginary term in the self-energy representing the acceptor electrode. To prevent the charge from disappearing completely after a short period, additional charge must be supplied continuously by the donor electrode. In the real system this task is performed by the battery, which recirculates the electrons ejected into the acceptor electrode. To mimic this process, we introduce the recharging model described below.

First, we augment the system Hamiltonian, adding a virtual state $|s_0\rangle$ with energy $E$ at site $\ell = 0$. This state represents the state of the donor electrode that supplies electrons to the molecular wire. Thus, the augmented $(N+1) \times (N+1)$ Hamiltonian matrix of the system has the form
Initially, a single electron is injected from this state into the molecular wire, thus the initial density operator (averaged with respect to the dissipative bath introduced in the next section) has the form

\[ \tilde{\rho}_0 = |s_0\rangle \langle s_0| \]  

(4.10)

After each time step \( \Delta t \) of electron propagation along the wire, the population at site 0 is adjusted according to the following prescription [23]:

\[ \langle s_0 | \tilde{\rho}(k\Delta t) | s_0 \rangle \to \langle s_0 | \tilde{\rho}(k\Delta t) | s_0 \rangle = 1 - \alpha_s \sum_{i=1}^{N} \langle s_i | \tilde{\rho}(k\Delta t) | s_i \rangle. \]  

(4.11)

Here \( \tilde{\rho}(t) \) is the reduced density operator of the system discussed in the next section and \( \alpha_s \) is the recharging parameter. The last term in Eq. (4.11) constitutes an adjustment to the charge population of the electron supplying level due to the image charge, whose value is determined by the instantaneous population of the electron on the molecular bridge.

The same procedure is repeated at each time step. As the total population in the wire begins to increase, the population of the injecting site starts to decrease following Eq. (4.11). As a result, the population gradient between sites 0 and 1 begins to decrease, thus the recharging process slows down. On the other hand, when the total electron population in the molecular wire begins to be depleted because electrons start to leak out of the system at the right end site, the population gradient between the injecting level and site 1 will increase; as a result, electrons are then injected into the wire to balance the loss until a steady state is reached. At long times, the total population...
of the molecular wire reaches an equilibrium value from which the current is extracted. Since the total charge population at site \( N \) is \( \langle s_N | \hat{\rho}(t) | s_N \rangle \) and the wire system is losing electrons at site \( N \) to the acceptor electrode at a rate given by \( \Gamma_{\Lambda}(E)/\hbar \), the equilibrium current can be obtained from the relation

\[
I(E) = \lim_{t \to \infty} \frac{e_0}{\hbar} \langle s_N | \hat{\rho}(t) | s_N \rangle \Gamma_{\Lambda}(E). \tag{4.12}
\]

Within the recharging model, the total current at low temperature can then be determined from the expression

\[
I_R = \lim_{t \to \infty} e_0 \int_{E_F - \epsilon}^{E_F} dE \rho_{\Omega}(E) \langle s_N | \hat{\rho}(E, \Omega, t) | s_N \rangle \Gamma_{\Lambda}(E, \Omega). \tag{4.13}
\]

With the help of Leibniz integral rule, we can expand (4.13) to linear order in \( \Omega \). The conductance \( g_R \) is extracted by taking the limit of the ratio \( I_R/\Omega \) as \( \Omega \) goes to zero. Thus we obtain,

\[
g_R = \lim_{\Omega \to 0} \frac{2 e_0^2}{\hbar} \frac{\Gamma_{\Lambda}(E_F) \langle s_N | \hat{\rho}(E_F, t) | s_N \rangle \Gamma_{\Lambda}(E_F)}{V_{w-e}^2}, \tag{4.14}
\]

where the factor of 2 takes into account electron spin degeneracy. Note that in (4.14), the injecting site’s energy is set to the Fermi level and it solely contributes to the conductance. In principle, the recharging process should be performed with \( \Delta t \to 0 \); however, for the case of zero dissipation, decreasing the time step by a factor of 1/16 changes the conductance by less than one percent from its initial value. In the calculations of section 4.5 the wire population and current converged with \( \Delta t = 2.5 \) fs. We report the conductance in units of \( 2e_0^2/\hbar \).

Calculations within this recharging scheme show the same qualitative behavior as the Landauer formula (Eq. (4.7)). Namely, in the resonance regime, the conductance exhibits an oscillatory dependence on wire length, and in the nonresonance regime, the conductance drops exponentially with length. Moreover, the conductance has a weak dependence on the recharging
parameter, $\alpha_R$ [23]. The calculations presented in section 4.5 were performed with the recharging parameter set to $\alpha_R = 0$. In this work, we will label this recharging scheme as Recharging Method I.

In Figure 8 we compare the variation with wire length of the conductance as given by scattering theory (Eq. (4.7)) and Recharging Method I. Due mainly to the introduction of the injecting level into the reduced Hamiltonian, the resonance structure is changed, leading to substantial changes in the conductance, particularly near the observed spikes where the effects of resonance are most pronounced.

By modifying the recharging scheme (in the case $\alpha_R = 0$) such that, after each time step, we reverse the evolution of the first row and column of the density matrix (all possible $\rho_{0,i}, \rho_{i,0}$) stemming from the 0,1 element of the Hamiltonian (Eq. (4.9)), we can obtain exactly the values predicted by the Landauer formula. This is because the recharging site now evolves as pure phase factor which acts as a driving force term on the molecular wire, supplying charge to the wire which then gets dissipated away to the leads. Segal et al have demonstrated that for such a set up the conductance agrees with the Landauer prediction [24]. Equivalently, we can set the 0,1 matrix element of the wire Hamiltonian (Eq. (4.9)) to zero and evolve the density matrix by applying the evolution operators of this now modified Hamiltonian. Results using this recharging scheme will be labeled from now on as Recharging Method II.

In Figure 9, we compare the conductance given by scattering theory (Eq. (4.7)) and Recharging Method II. We see that there is excellent agreement between the two approaches. However, deviations between from the Landauer formula are expected for large values of the self-energy because Landauer theory contains a self-energy term in the first and last site of the wire Hamiltonian (Eq. (4.4)) stemming from the wire interaction with left and right electrode.
The recharging Hamiltonian (Eq. (4.9)) only contains the self-energy term originating from the right electrode.

### 4.4 Dissipation

Charge propagation in the wire-electrode system is subject to dissipative forces, which arise from coupling of the electron to molecular vibrations. Such dissipative interactions provide an additional (and different) loss mechanism that tends to destroy coherent charge motion within the wire. Recent theoretical efforts on the inelastic electron transmission in molecular wires used a Holstein-type model to model such dissipative interactions [25-27]. The effects of dephasing and thermal relaxation on electron transport through molecular wires have also been studied using a system-bath Hamiltonian with bilinear coupling [2, 28].

To investigate the effects of dissipation on the dynamics of charge transport, we augment the molecular wire Hamiltonian of Eq. (4.4) to include weak bilinear coupling to a harmonic dissipative bath,

$$\hat{H} = \hat{H}_s + \hat{H}_{sb},$$  \hspace{1cm} (4.15)

where

$$\hat{H}_{sb} = \sum_j \frac{\hat{p}_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2 \left( \frac{\hat{x}_j - \frac{e_j}{m_j}\hat{s}}{\omega_j} \right)^2 \equiv \hat{H}_b + \hat{H}_{int}$$  \hspace{1cm} (4.16)

is the Hamiltonian for the harmonic bath $\hat{H}_b$ and its interaction $\hat{H}_{int}$ with the molecular wire system. In Eq. (4.16) $\hat{s}$ is the position of the electron along the molecular wire which takes discrete values $0, q_o, 2q_o, \ldots, (N - 1)q_o, Nq_o$ for an $N$ site wire, where $q_o$ is the spacing separating two wire sites. This system-bath Hamiltonian is of the exact form as described in Chapter 2. In the present study we model the spectral density (see Eq. (2.7) and Refs. [29, 30]) as an Ohmic bath (Eq. (3.4)), where $q_o$ is set to one.
In section 4.5 we report numerical results on the charge population of various sites. This can be obtained from the reduced density matrix,

\[
\rho(t) \equiv \text{Tr}_b \left( e^{-i\alpha_b t} \hat{\rho}(0) e^{i\alpha_b t} \right),
\]

(4.17)

where \( \hat{\rho}(0) = \rho(0) e^{-i\alpha_b t} / \text{Tr}_b e^{-i\alpha_b t} \) is the initial condition describing the state of the charge on the donor electrode. We apply the methodology of Chapter 2 and the filtering scheme of Chapter 3 to extract the populations. However, the presence of the recharging operator in Recharging Method I complicates its representation in the form of the path integral and thus does not allow direct application of the iterative procedure described in Chapter 2. To circumvent this difficulty, Dong and Makri have demonstrated that the reduced density matrix with recharging operations performed at each time step can be obtained from the sum of earlier-time density matrices propagated in the absence of recharging, which thus are amenable to the iterative path integral procedure described above. The manipulations that lead to this decomposition is described in Ref. [23] and are specific to a recharging parameter \( \alpha_r \) set to zero. Here we just show the main result.

The recharged reduced density matrix at time \( n\Delta t \) is given by

\[
\tilde{\rho}_{\alpha}(n\Delta t) = \sum_{m=0}^{n} \tilde{\rho}_{\alpha}(m\Delta t)
\]

(4.18)

where,

\[
\tilde{\rho}_{\alpha}(n\Delta t) = \sum_{s_{k_0}} \cdots \sum_{s_{k_{n-1}}} \rho(s_{k_0}^+, s_{k_0}^-) U(s_{k_0}^- | s_{k_0}^+) \rho(s_{k_1}^+, s_{k_1}^-) U(s_{k_1}^- | s_{k_1}^+) \cdots \rho(s_{k_n}^+, s_{k_n}^-) U(s_{k_n}^- | s_{k_n}^+)
\]

(4.19)

In (4.19) the reduced density matrix is propagated \( n \) time steps. However, each propagation step is followed by the application of operator \( \hat{\rho}_{\alpha} \).
\[ \hat{\mathcal{H}} = \hat{\mathcal{H}}_0 - |s_0\rangle\langle s_0| \hat{\mathcal{H}}_s|s_0\rangle \langle s_0|. \] (4.20)

which sets the population of the recharging site to zero. Finally, the effect of the dissipative bath for a specific path configuration \( s_{k_1}^+, s_{k_1}^-, s_{k_1}^+, \cdots, s_{k_n}^+ \) is included through the discretized influence functional factor \( F(s_{k_1}^+, s_{k_1}^-, s_{k_1}^+, \cdots, s_{k_n}^+; \Delta t) \) which was defined in Eq. (2.12).

In the case of Recharging Method II, we directly apply the path integral methodology of Chapter 2 and use the modified system Hamiltonian (Eq. (4.9) with the 0,1 element set to zero).

### 4.5 Results

In this section we present the results of numerical calculations on the molecular wire model using the methodology described in the previous section. We monitor the site populations \( P_i \) and the electron conductance \( g_R \) with emphasis on their dependence on dissipation strength and wire electrode coupling.

The Fermi energy of the electrodes is set equal to zero. The site energies of the molecular wire are set to \( E_m = 0.1 \) eV, and \( \gamma = 1.0 \) eV. The cutoff frequency of the bath is chosen to be \( h\omega_c = 0.5 \) eV = 4033 cm\(^{-1}\). The temperature for Recharging Method I is set to \( k_B T = 0.0025 \) eV = 29 K for the resonant regime and \( k_B T = 0.075 \) eV = 870 K for the nonresonant regime. For Recharging Method II, the temperature is set to \( k_B T = 0.0025 \) eV = 29 K for the resonant regime and \( k_B T = 0.025 \) eV = 290 K for the nonresonant regime. The Kondo parameter \( \xi \) is set to 0.025 and the time step, \( \Delta t \), is equal to 2.5 fs. For Recharging Method I, the recharging factor \( \alpha_r \) is set to zero.

Depending on the strength of the wire site-site coupling, the Fermi energy of the electrodes may lie within or outside the energy band of the molecular wire, resulting in resonant and nonresonant regimes. Schematic representations of the energy level diagrams in these two cases...
are given in Figure 10. For the value of site-site coupling $V_{w-w} = -0.24 \text{ eV}$ the energy band of molecular wire states extends between $\pm 0.48 \text{ eV}$ relative to its central value of $0.1 \text{ eV}$. For these parameters the Fermi level of the donor electrode lies within the energy band of the molecular wire (see Figure 10) and thus the system is in the resonant regime. With the choice $V_{w-w} = -0.04 \text{ eV}$ the energy band of molecular wire states extends only between $\pm 0.08 \text{ eV}$ relative to its central value of $0.1 \text{ eV}$, and thus the Fermi level of the donor electrode lies outside the energy band of the molecular wire and the system is in the nonresonant regime. In the sections that follow, we present sets of results in the resonant and nonresonant regime utilizing Recharging Method I and Recharging Method II.

### 4.5.1 Recharging Method I

#### 4.5.1.1 Resonant Regime

Figure 11 shows the site populations for molecular wires of $N = 4$ and 6 sites for weak and strong wire-electrode coupling. The site populations exhibit oscillatory patterns at small values of the wire-electrode coupling, progressively attaining near-constant values as the coupling parameter becomes large. However, the presence of dissipation, albeit weak, destroys any oscillatory structure. It is also seen that weak dissipation has a noticeable but not large effect on the electron population along the wire in this regime. This is a consequence of the rapid current flow through the wire in the resonant case.

The conductance is shown in Figure 12 as a function of wire-electrode coupling for wires of length $N = 3 – 6$. As expected from the site population graphs, the conductance exhibits a weak dependence on dissipation strength in this regime, which is monotonic at small coupling and eventually decreases with $V_{w-e}$. Thus for low values of the wire-electrode coupling, dissipation slightly enhances the conductance, and for high wire electrode coupling, dissipation slightly
diminishes the conductance value. The variation of the conductance with molecular wire length is shown in Figure 13. With zero dissipation, one observes that the conductance oscillates with the molecular wire length, as argued in earlier work [23], with even-$N$ wires exhibiting higher conductance than those with $N-1$ sites. As coupling to the bath is introduced these structures become less prominent and eventually are wiped out.

The rate of convergence varies depending on the number of sites and wire electrode coupling, $V_{w-e}$. In the resonant regime, incrementing memory from $\Delta k_{\text{max}} - 1$ to $\Delta k_{\text{max}}$ results in a percent difference of at most 11.8% (this was the case for 6-site wire at $V_{w-e} = 0.18 \text{ eV}$). We expect the corrections in memory to be smaller than this upper bound. The percent difference in changing the time step $\Delta t$ from 3 fs to 2.5 fs is at most 11.24% (this was for a 4-site wire at $V_{w-e} = 0.1 \text{ eV}$). Thus, a set of calculations with a time step smaller than 2.5 fs is qualitatively similar to the numbers reported in this study. For the calculations in this case, the memory cutoff $\Delta k_{\text{max}}$ varies between 4 and 5.

4.5.1.2 **Nonresonant Regime**

Figure 14 shows the site populations and the conductance for molecular wires of different lengths. In this nonresonant case charge transfer occurs slower within the molecular wire, leading to depletion of sites sufficiently far from the recharging donor electrode. As a consequence, site populations near the acceptor electrode are small, and the molecular wire displays a conductance which decreases rapidly with wire length.

As can be seen from Figure 14 and Figure 15, dissipation has a dramatic effect on conductance in the nonresonant regime. As the wire length increases to 6 sites, the conductance of the dissipation-free molecular wire system decreases exponentially to very small values. However, when these wires are in contact with a weakly dissipative medium, the conductance
increases dramatically, attaining values that are on the same order of magnitude in all systems studied, irrespective of molecular wire length.

This effect is seen more clearly in Figure 16, which shows the relative (percent) change in conductance induced by coupling to a weakly dissipative environment. Already with $N = 4$, the dissipative bath of $\xi = 0.025$ leads to a one hundred fold enhancement of conductance at moderate values of wire-electrode coupling, while with $N = 6$ the relative increase exceeds four orders of magnitude. In Figure 17, we plot the conductance as function of wire length. Note that dissipation replaces the exponential scaling with nearly a length-independent conductance.

In the non-resonant regime, increasing the memory from $\Delta k_{\text{max}} - 1$ to $\Delta k_{\text{max}}$ results in a percent difference of at most 6.33% (this was the case for a 4-site wire at $V_{\text{w-e}} = 0.1$ eV). We expect the corrections beyond the memory cutoff to be smaller than this upper bound. The percent difference in changing the time step $\Delta t$ from 3 fs to 2.5 fs is at most 11.76% (3-site wire at $V_{\text{w-e}} = 0.1$ eV). Thus, a set of calculations for a time step less than 2.5 is qualitatively similar to the numbers reported in this study. For these results, $\Delta k_{\text{max}}$ ranges from 4 to 5.

### 4.5.2 Recharging Method II

#### 4.5.2.1 Resonant Regime

Figure 18 shows the site populations for molecular wires of $N = 4$ and 6 sites for weak and strong wire-electrode coupling. In this case, the oscillatory structures are more prominent than for Recharging Method I. Like the previous method however, weak dissipation wipes out any oscillatory pattern with the final population attaining values not too far from the dissipation-free case.

The conductance is shown in Figure 19 as a function of wire-electrode coupling for wires of length $N = 3 - 8$. The conductance in this resonant regime is large. For this recharging method,
the conductance increases monotonically with wire-electrode coupling for both zero and weak dissipation. Like Recharging Method I, dissipation tends to slightly enhance the conductance. If, however, the dissipation-free conductance is large enough, dissipation causes a decrease in the conductance. In either case, however, the conductance does not stray too far from the dissipation free result. Similar behavior is observed in Recharging Method I. The variation of the conductance with molecular wire length is shown in Figure 20. Once again, with zero dissipation, one observes that the conductance oscillates with the molecular wire length. When coupling to the bath is introduced, these structures exhibit damped oscillations.

Similar to Recharging Method I, the rate of convergence varies depending on the number of sites and wire electrode coupling, $V_{w-e}$. In the resonant regime, incrementing memory from $\Delta k_{\text{max}} - 1$ to $\Delta k_{\text{max}}$ results in a percent difference of at most 4.23% (this was the case for 6-site wire at $V_{w-e} = 0.02$ eV). The percent difference in varying the time step $\Delta t$ from 3 fs to 2.5 fs is at most 2.80% (again for a 6-site wire at $V_{w-e} = 0.02$ eV). Thus, this set of results is very well converged. The memory cutoff $\Delta k_{\text{max}}$ varies between 3 and 5.

4.5.2.2 Nonresonant Regime

Similar to Recharging Method I, for a wire of fixed size, the population drops off exponentially with site number, so that the conductance attains a very small value with zero dissipation. When dissipation is present, the conductance is again greatly enhanced, as evident in figures Figure 21 and Figure 22. The relative percent changed is presented in Figure 23. With $N = 4$, the dissipative bath of $\xi = 0.025$ leads to a one hundred fold enhancement of conductance, while with $N = 6$ the relative increase exceeds three orders of magnitude. In Figure 24, we plot the conductance dependence on length. The presence of the bath counters the exponential drop off such that the conductance is almost independent of length. The same behavior is seen for Recharging Method I.
Varying the memory cutoff from $\Delta k_{\text{max}} - 1$ to $\Delta k_{\text{max}}$ results in a percent difference of at most 6.14% (this was the case for a 3-site wire at $V_{w,e} = 0.04 \text{ eV}$). The percent difference in changing the time step $\Delta t$ from 3 fs to 2.5 fs is at most 2.69% (again 3-site wire at $V_{w,e} = 0.04 \text{ eV}$). Thus, a set of calculations for a time step less than 2.5 fs is qualitatively similar to the numbers reported in this study. The memory cutoff, $\Delta k_{\text{max}}$, has been set to 6.

### 4.6 Concluding Remarks

We have presented a real time path integral study of conductance in molecular wire models. The extraction of a steady-state current from the site populations in this time-dependent picture became possible via the recharging model introduced in section 4.3, which prevents the rapid depletion of charge population from the molecular wire into the metal electrodes. Using the recharging model, along with an iterative methodology for evaluating the real-time path integral adapted to the present case, we investigated the dependence of the conductance on molecular wire length, wire-electrode coupling and dissipative interactions mimicking molecular vibrations in the resonant and non-resonant regimes.

In the absence of dissipative interactions, the results of our study are largely in line with the predictions of the elastic scattering formalism. Specifically, we observe an exponential drop-off of the conductance in the off-resonant regime, as well as an oscillatory dependence when the Fermi level of the donor electrode is in resonance with the eigenvalue band of the molecular wire. The availability of site populations in the present time-dependent study offers additional insight into the mechanism of electron conduction in these systems.

We have examined for the first time the effects of weakly dissipative (also known as inelastic) processes on electron conductance in molecular wires using a harmonic oscillator bath to mimic the effects of molecular vibrations. In the resonant regime, our calculations suggest that
coupling to a weakly dissipative environment induces only minor changes to the conductance. However, we find that dissipative processes have a dramatic effect on conductance in the off-resonant case, in particular for longer wires where the conductance is extremely small in the absence of dissipation. In this regime coupling to a dissipative environment tends to increase the conductance by an amount that grows exponentially with the length of the molecular wire. This effect essentially counteracts the exponential decrease with wire length characteristic of the non-resonant regime in dissipation-free systems, leading to a conductance that exhibits a weak dependence on molecular wire length.
4.7 Figures

Figure 7 Schematic representation of a molecular wire of length $N$. The circles indicate the LUMO of the molecular units. Courtesy of Ref [23].
Figure 8 Comparison of the length dependence of the conductance as obtained from elastic scattering theory (Eq (4.7)) and Recharging Method II with recharging factor $\alpha_0 = 0$. We use a time increment of $\Delta t = 5/8$ fs. The other system parameters are $\gamma = 1$ eV, $E_p = 0.1$ eV, $V_{we} = 0.04$ eV and $E_p = 0$. Solid line and squares: recharging model. Dashed line and circles: elastic scattering theory. (a) Resonant regime with $V_{we} = -0.24$ eV. (b) Nonresonant regime with $V_{we} = -0.04$ eV. Courtesy of Ref. [23]
Figure 9 Comparison of the length dependence of the conductance as obtained from elastic scattering theory (Eq (4.7)) and Recharging Method II. The other system parameters are $\gamma = 1\, \text{eV}$, $E_p = 0.1\, \text{eV}$, $V_{\text{w}} = 0.04\, \text{eV}$ and $E_x = 0$. Solid lines: Recharging Method II. Solid circles: elastic scattering theory. (a) Resonant regime with $V_{\text{w}} = -0.24\, \text{eV}$. (b) Nonresonant regime with $V_{\text{w}} = -0.04\, \text{eV}$.
Figure 10 Schematic representation of the molecular wire/electrode energy level diagram.

The site energies are depicted as short thick lines, while the molecular wire eigenstates are shown as long thin lines. The external voltage is small on the scale of the energy band. (a) Resonant regime. (b) Nonresonant regime.

Courtesy of Dr. Ke Dong.
Figure 11 Site populations for various molecular wires with length $N$ and wire-electrode coupling $V_{\text{w-e}}$. The system is in the resonant regime with $V_{\text{w-e}} = -0.24\text{eV}$. Solid lines: $\xi = 0$. Dashed lines: $\xi = 0.025$. Recharging Method I
Figure 12 The conductance for molecular wires of length $N$ as a function of the wire-electrode coupling $V_{w-e}$. The system is in the resonant regime with $V_{w-w} = -0.24$ eV. Solid line $\xi = 0$. Dashed lines: $\xi = 0.025$. Recharging Method I
Figure 13 The conductance as a function of the molecular wire length at different values of the wire-electrode coupling $V_{\text{w-e}}$. The system is in the resonant regime with $V_{\text{w-w}} = -0.24\text{eV}$.

Solid lines: $\xi = 0$. Dashed lines: $\xi = 0.025$. Recharging Method I.
Figure 14 Site populations for various molecular wires with length $N$ and wire-electrode coupling $V_{w-e}$. The system is in the off-resonant regime with $V_{w-e} = -0.04$ eV. Solid lines: $\xi = 0$. Dashed lines: $\xi = 0.025$. Recharging Method I
Figure 15 The conductance for molecular wires of length $N$ as a function of the wire-electrode coupling $V_{w-e}$. The system is in the off-resonant regime with $V_{w-w} = -0.04\text{eV}$. Solid lines: $\xi = 0$. Dashed lines: $\xi = 0.025$. Recharging Method I
Figure 16 The percent change in the conductance due to dissipation for a molecular-wire system of length $N$ as a function of the wire-electrode coupling strength $V_{w-e}$. The system is in the off-resonant regime with $V_{w-w} = -0.04$ eV. Solid lines: $\xi = 0.025$. Recharging Method I
Figure 17 The conductance as a function of the molecular wire length for $V_{w-e} = 0.1$ eV. The system is in the off-resonant regime with $V_{w-w} = -0.04$ eV. Solid lines: $\xi = 0$. Dashed lines: $\xi = 0.1$. Recharging Method I
Figure 18 Site populations for various molecular wires with length $N$ and wire-electrode coupling $V_{w-e}$. The system is in the resonant regime with $V_{w-e} = -0.24\,\text{eV}$. Solid lines: $\xi = 0$. Dashed lines: $\xi = 0.025$. Recharging Method II.
Figure 19 The conductance for molecular wires of length $N$ as a function of the wire-electrode coupling $V_{w-e}$. The system is in the resonant regime with $V_{w-w} = -0.24$ eV. Solid line $\xi = 0$. Dashed lines: $\xi = 0.025$. Recharging Method II
Figure 20 The conductance as a function of the molecular wire length at different values of the wire-electrode coupling $V_{w-e}$. The system is in the resonant regime with $V_{w-e} = -0.24$ eV.

Solid lines: $\xi = 0$. Dashed lines: $\xi = 0.025$. Recharging Method II
Figure 21 Site populations for various molecular wires with length $N$ and wire-electrode coupling $V_{\text{w-e}}$. The system is in the off-resonant regime with $V_{\text{w-w}} = -0.04\,\text{eV}$. Solid lines: $\xi = 0$. Dashed lines: $\xi = 0.025$. Recharging Method II
Figure 22 The conductance for molecular wires of length $N$ as a function of the wire-electrode coupling $V_{w-e}$. The system is in the off-resonant regime with $V_{w-w} = -0.04\text{eV}$. Solid lines: $\xi = 0$. Dashed lines: $\xi = 0.025$. Recharging Method II
Figure 23 The percent change in the conductance due to dissipation for a molecular-wire system of length $N$ as a function of the wire-electrode coupling strength $V_{w-e}$. The system is in the off-resonant regime with $V_{w-w} = -0.04$ eV. Solid lines: $\xi = 0.025$. Recharging Method II.
Figure 24 The conductance as a function of the molecular wire length for $V_{e} = 0.1 \text{ eV}$. The system is in the off-resonant regime with $V_{w} = -0.04 \text{ eV}$. Solid lines: $\xi = 0$. Dashed lines: $\xi = 0.1$. Recharging Method II
References


Chapter 5  Quantum-Classical Path Integral: Classical Memory and Weak Quantum Nonlocality

5.1 Introduction

As mentioned in Chapter 1, the difficulty of obtaining accurate solutions to the Schrödinger equation increases exponentially with the number of degrees of freedom. This situation necessitates the use of approximations for studying the real-time dynamics of large molecular systems or condensed phase processes. For many chemical or biological processes of interest, molecular dynamics methods, which are based on the classical equations of motion for the coordinates of the nuclei on a single Born-Oppenheimer potential energy surface, are adequate and practical for simulations with millions of atoms. On the other hand, nonadiabatic effects allowing electronic transitions are commonly encountered in chemical and biological processes. Such effects, along with zero-point energy and tunneling, require a quantum mechanical treatment.

Since a quantum mechanical description is often necessary only for a small number of degrees of freedom, mixed quantum-classical treatments are extremely appealing. However, the difference in the structure of quantum and classical theory makes it difficult to devise quantum-classical approximations that are consistent and accurate in a variety of situations. Perhaps the oldest quantum-classical approximation is the Ehrenfest model [1], which is also closely connected to time-dependent self-consistent field approximations [2, 3]. These methods integrate the trajectories for the nuclei under the influence of a force averaged with respect to the wavefunction of the quantum system. In the context of electronic transitions, the Ehrenfest model implies that the nuclear trajectory moves on the average Bohn-Oppenheimer potential, an assumption which can lead to unphysical results [4]. Pechukas has described a semiclassical
approximation in which the classical trajectory is determined along with the evolution of the quantum wavefunction between initial and final states in a self-consistent way [5]. The procedure is rigorous and accurate, but the self-consistent determination of the trajectory is very demanding, making the method impractical for large-scale simulation.

The pioneering work of Tully in the 1970s introduced the so-called surface hopping methods [6], in which trajectories can incur electronic transitions at random times specified by the magnitude of the nonadiabatic coupling strength. The surface hopping model corrects the most serious shortcomings of the Ehrenfest model, allowing for population branching [7]. The surface hopping method, in particular its “fewest switches” version [4], also known as molecular dynamics with quantum transitions (MDQT), has been applied to proton transfer processes [8], and its generalized multiconfigurational version has been used to simulate multiple proton transfer and proton-coupled electron transfer [9]. Other surface hopping schemes that utilize the Pechukas force for short time intervals or a mean field force are also available and have been applied to condensed phase processes [10-13]. Similar in spirit to surface hopping is the multiple spawning method, which calculates quantum mechanical transition amplitudes using local basis sets that surround classical trajectories [14]. A different idea for treating nonadiabatic dynamics via classical trajectories was originally proposed by Meyer and Miller [15] and further developed by Stock and Thoss [16]. This involves mapping each electronic state on a pair of action-angle variables, thus replacing discrete states by continuous degrees of freedom which are directly amenable to standard classical or semiclassical trajectory treatments on a single potential surface, circumventing the need for hops between quantum states [17]. Another approach involves solving the quantum-classical Liouville equation, which involves a first-order expansion in the ratio of masses corresponding to the quantum and classical particles [18, 19]. Bohm’s quantum trajectory formulation has also been exploited in the development of nonadiabatic dynamics approximations [20-22].
In this work we describe a rigorous, yet practical path integral approach to quantum-classical dynamics. As is well known, starting from the full path integral formulation of the density matrix and taking the $\hbar \to 0$ limit with respect to the “heavy” particles (e.g., the nuclei in the case of nonadiabatic dynamics, or just the heavier atoms in the case of proton transfer), which are referred to as the “bath” or “solvent”, restricts the path sum to classical trajectories for these particles, maintaining the full quantum path sum for the “light” particles (e.g., the electronic degrees of freedom or the hydrogen atoms). It is clear that such quantum-classical path integral (QCPI) treatments are theoretically sound and should provide a faithful description of the dynamics, while the classical trajectory treatment of the majority of degrees of freedom is appealing for application to condensed phase systems or large biomolecules. Yet, evaluation of real-time path integral expressions is an extremely difficult task, requiring computational resources that scale exponentially with propagation time. Thus, the major challenge is how to evaluate the QCPI expression without making additional severe approximations.

In this work and also in Chapter 6, we address this challenge. We point out that the quantum path summed expression is a smooth function of the initial coordinates of those degrees of freedom treated via classical mechanics, allowing efficient evaluation of the phase space integral by Monte Carlo methods [23]. Further, we argue that the classical or near-classical character of these degrees of freedom offers an advantageous starting point that captures the bulk of the effects on the quantum system from the bath, including the partial destruction of coherence; this is so because time nonlocality is a strictly quantum mechanical phenomenon and plays a minor role in the classical limit. In Chapter 6 we present efficient discretized QCPI expressions and develop a systematic methodology for including this residual quantum nonlocality (which is associated with quantum decoherence) that should converge with modest amount of computational effort in many situations of interest. The QCPI approach is quite general and can be used to propagate the density matrix or to evaluate time correlation functions at zero or finite
temperature, and is easy to combine with standard molecular dynamics software. In addition, it may be used in conjunction with purely classical or upgraded semiclassical versions of the bath dynamics.

In section 5.2 we discuss quantum-semiclassical and quantum-classical path integral expressions and examine the behavior of the integrand as a function of initial trajectory coordinates. The features of the quantum-classical path sum are analyzed in section 5.3, where we point out that bath-induced memory vanishes in the classical limit, which corresponds to the classical path approximation, and that time nonlocality plays a minor role under near-classical or weak-coupling conditions. These ideas are illustrated with numerical examples in section 5.4. Finally, a summary and outlook are given in section 5.5.

5.2 Quantum-Semiclassical and Quantum-Classical Path Integral

The degrees of freedom of the quantum mechanical system are described by the coordinate $s$, while $x$ describes collectively the coordinates of the bath particle(s) with mass $m_b$, which are to be treated via classical trajectories. The Hamiltonian has the form

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

(5.1)

where $H_0$ describes the quantum particle, $T_b$ is the kinetic energy of the classical degrees of freedom and $V$ is the interaction potential. We focus on the reduced density matrix of the quantum subsystem at the time $t$,

$$
\rho_{\text{red}}(s^+_t, t) = \int dx_t \left\langle s^+_t \left| e^{-\frac{i}{\hbar}Ht} \rho(0) e^{\frac{i}{\hbar}Ht} \right| s^-_i \rightangle

= \int dx_t \int dx_0 \int ds_0 \left\langle s^+_t \left| e^{-\frac{i}{\hbar}Ht} \right| s^+_0 \right\rangle \left\langle s^+_0 \left| \rho(0) \right| s^-_0 \right\rangle \left\langle s^-_0 \left| e^{\frac{i}{\hbar}Ht} \right| s^-_i \right\rangle.

$$

(5.2)

Using the path integral [24, 25] representation of the forward and backward propagators, the reduced density matrix becomes

$$
\rho_{\text{red}}(s^+_t, t) = \int \mathcal{D}s e^{rac{i}{\hbar}S} \frac{1}{e^{\frac{i}{\hbar}S}} F[S] \left| e^{\frac{i}{\hbar}S} \right|

$$

(5.3)
where $\mathcal{D}s^\pm$ denotes a functional integral (i.e., sum with appropriate prefactors) with respect to all forward and backward system paths $s^\pm$ with final values $s^\pm_f$, $\Phi_0$ is the action integral for the bare system, and

$$F[s^\pm] = \text{Tr}_b \left( \hat{U}_0^+ [s^+] \hat{\rho}(0) \hat{U}_0^{-1}[s^-] \right)$$

(5.4)

is the influence functional [26]-10 from the bath. In Eq. (5.4) $U_0[s^\pm]$ is the time evolution operator for the time-dependent bath Hamiltonian $H_b$ along the system path $s^\pm$. Equations (5.3) and (5.4) are exact. Applying the semiclassical approximation in the Herman-Kluk coherent state representation [27], Makri and Thompson have obtained the following forward-backward semiclassical dynamics (FBSD) approximation to the influence functional [28, 29]:

$$F_{\text{FBSD}}[s^\pm] = \int dx_0 \int dp_0 D_{\text{FBSD}}(x_0, p_0 ; [s^\pm]) e^{i \Phi_{\text{FBSD}}(x_0, p_0 ; [s^\pm]) / \hbar}$$

(5.5)

Here $\left| x_0, p_0 \right>$ are coherent states, whose wavefunctions are

$$\langle x | x_0, p_0 \rangle = \frac{(2\pi)^{\frac{3}{4}}}{\pi^{\frac{3}{4}}} e^{-\frac{1}{\sqrt{2}} p_0 (x-x_0)}$$

(5.6)

and $\Phi_{\text{FBSD}}$ is the net action along a classical trajectory originating at $x_0, p_0$, integrated first forward in time under the time-dependent bath Hamiltonian $H_b(s^+(t'))$ and subsequently backward in time under $H_b(s^-(t'))$. The weight of each trajectory is specified by the function

$$D_{\text{FBSD}}(x_0, p_0 ; [s^\pm]) = (2\pi\hbar)^{\frac{3}{4}} C(x_0, p_0) \left( s^+_0 x_0 p_0 \right) |\hat{\rho}(0)| s^-_0 x_0 p_1 \rangle.$$ 

(5.7)

Here $x_i, p_i$ are the final phase space coordinates of the forward-backward trajectory, and the derivatives of these coordinates with respect to the initial ones determine the prefactor $C(x_0, p_0)$.

The FBSD expression (5.5) is the rigorous stationary phase limit of the influence functional and produces the exact Feynman-Vernon influence functional [26] if the classical particle is described
by a quadratic Hamiltonian linearly coupled to the quantum system. Unlike semiclassical expressions for the time evolution of a wavefunction, the partial cancellation of the forward and backward actions in Eq. (5.5) tempers naturally the oscillatory character of the integrand, allowing efficient evaluation of the integral by Monte Carlo methods.

If the forward and backward trajectories do not differ significantly (e.g., for small coupling and/or short times), the final phase space coordinates \( x_f, p_f \) of the trajectory will be close to the initial values \( x_0, p_0 \) and the forward and backward actions will not differ substantially. Under these conditions one may proceed as in the derivation of the FBSD approximation for time correlation functions [30, 31] to obtain a quasiclassical approximation to Eq. (5.5), in which the forward and backward trajectories are replaced by a single trajectory that experiences the average of the forces along the forward and backward system paths,

\[
F_{\text{coh}}^\text{class} (s^\pm) \approx \int dx_0 \int dp_0 D_{\text{coh}}^\text{class} (x_0, p_0; s_0^\pm) e^{i \Phi_0^\text{class} (x_0, p_0; s_0^\pm) \pm i \hbar},
\]

where

\[
D_{\text{coh}}^\text{class} (x_0, p_0; s_0^\pm) = (2\pi\hbar)^{-1} \left( \frac{1}{s_0^+ x_0 p_0} \hat{\rho}(0) \left| \begin{array}{c} \hat{\rho}(0) \left| s_0^- x_0 p_0 \right) - 2 \gamma \left( \hat{\rho}(0) \left| \hat{x} - x_0 \right) \hat{\rho}(0) \left| \hat{x} - x_0 \right) \left| s_0^- x_0 p_0 \right) \end{array} \right) \right) \] (5.9)

and the action \( \Phi_0^\text{class} \) is the difference of the action integrals along the classical trajectory experiencing the force exerted by the quantum particle traversing its forward and backward paths. This expression provides an excellent approximation to the influence functional from a high-temperature bath. Eq. (5.9) is similar to the quasiclassical influence functional of Shi and Geva [32],

\[
F_{\text{Wigner}}^\text{class} (s^\pm) \approx \int dx_0 \int dp_0 D_{\text{Wigner}}^\text{class} (x_0, p_0; s_0^\pm) e^{i \Phi_0^\text{class} (x_0, p_0; s_0^\pm) \pm i \hbar}
\]

which employs the Wigner transform [33] of the initial density,
The relation between Equations (5.9) and (5.11) is easily established by recognizing the coherent state density in Eq. (5.9) as an expansion of the Wigner function [34, 35]. Eq. (5.10) is the influence functional equivalent of the linearized path integral (LPI) approximation [36, 37] for time correlation functions, which provides an alternative derivation of the linearized semiclassical initial value representation (LS-IVR) result obtained earlier by Wang, Sun and Miller [38]. We also note that the combination of a path integral description of the system with a linearized approximation to the influence functional is very similar in spirit to the (double) semiclassical-classical treatment of Sun and Miller [39], which can account for phase interference in the quantum system, while retaining a simpler classical description of the bath. A similar double semiclassical/FBSD approximation has also been described [40].

Alternatively, a classical approximation may be obtained by using the high-temperature Trotter approximation to the density operator in the coordinate representation and substituting the coordinate (van Vleck [41]) semiclassical representation of the forward and backward propagators in Eq. (5.4). Linearizing about the difference coordinates of the density matrix element, evaluating the resulting Gaussian integral with respect to the difference coordinate and changing integration variables to obtain an initial value representation leads to the following approximation to the influence functional:

$$D_{Wigner}^{\text{class}}(x_0, p_0; s^\pm) = (2\pi\hbar)^{-1} \int d\Delta x_0 \left< s^+_0, x_0, s^-_0; \rho(0), s^-_0, x_0 \right> e^{-\beta\Delta x_0^2/\hbar}, \quad \Delta x_0 = x_0^+ - x_0^-.$$

(5.11)

where

$$D_{\text{Boltzmann}}^{\text{class}}(x_0, p_0; s^\pm) = (2\pi\hbar)^{-1} Z_{\text{cl}}^{-1} e^{-\beta p^2_0/2m - \beta V(s^\pm_0; x_0)}.$$

(5.13)

is recognized as the classical Boltzmann factor.

Equations (5.8)-(5.9), (5.10)-(5.11) and (5.12)-(5.13) are quantum-classical expressions which may be used as warranted by the particular situation of interest. For example, the
Boltzmann-weighted density of Eq. (5.13), which provides the simplest form for sampling the phase space of the bath, is sufficiently accurate at high temperature. The use of this classical weight in the path integral expression is analogous to a single-bead treatment of the heavier atoms in equilibrium path integral calculations, while the more quantum mechanical system coordinates are quantized in terms of multiple path integral beads. The two quasiclassical expressions allow full quantization of the density, accounting for zero point energy effects that may be important for light atoms and/or at low temperatures. Of these, the coherent state expression is easier to quantize using an imaginary time path integral method with multiple beads [42]. The Wigner-weighted expression produces the exact influence functional at any temperature for a harmonic bath, but the Wigner transform is considerably harder to evaluate accurately in the case of an anharmonic many-particle Hamiltonian, although accurate and practical procedures for this task have recently been reported [43, 44]. The main difference between these quantum-classical approximations and the quantum-semiclassical FBSD expression is that the semiclassical influence functional, Eq. (5.5), involves trajectories that experience the actual force exerted by the system in its instantaneous quantum state, while the classical expressions employ the average of the forces in the two quantum states on the forward and backward paths. Thus, the quantum-semiclassical treatment should be more accurate in general, but its computational cost is somewhat higher.

Since integration of the classical equations of motion is much more efficient than full solution of the Schrödinger equation, the quantum-(semi)classical approximations to the path integral expression are very attractive for simulating the dynamics in situations where the majority of particles are well approximated by classical mechanics. Unlike widely employed quantum-classical wavefunction methods, where the force experienced by the classical trajectory is averaged with respect to the wavefunction of the quantum particle [2], the quantum-(semi)classical path integral expressions (QCPI) allow for a faithful description of the dynamics.
For example, it is known that some versions of mean-field-type (also referred to as quantum-classical time-dependent self-consistent field) methods fail to account for the dynamics of linearly coupled harmonic oscillators or wavepacket splitting and tunneling [45], and that the analogous Ehrenfest model fails to predict correct branching ratios in avoided crossing models [4]. By contrast, Eq. (5.5) and (5.10) (and also Equations (5.8) and (5.12) at high temperature) produce the exact value of the reduced density matrix if the classical particles are described by a quadratic Hamiltonian linearly coupled to the system. With these considerations in mind we now turn to the evaluation of the reduced density matrix using a quantum-(semi)classical path integral approximation.

Employing the standard discretization of the path integral [25] based on the Hamiltonian partitioning suggested by Eq. (5.1) with a time step $\Delta t = t/N$, in conjunction with the influence functional approximations (5.5)-(5.11), leads to quantum-semiclassical or quantum-classical path integral expressions of the form

$$\tilde{\rho}(s^+_N; N\Delta t) = \frac{1}{(2\pi\hbar)^{-N/2}} \int ds_0^+ \cdots ds_{N-1}^+ \int dp_0 \langle s_0^+ | e^{-i\hat{H}_{\Delta t}^{\text{bath}}} | s_{N-1}^+ \rangle \cdots \langle s_N^+ | e^{-i\hat{H}_{\Delta t}^{\text{bath}}} | s_0^+ \rangle \times \langle s_0^- | e^{i\hat{H}_{\Delta t}^{\text{bath}}} | s_1^- \rangle \cdots \langle s_{N-1}^- | e^{i\hat{H}_{\Delta t}^{\text{bath}}} | s_N^- \rangle D(x, p; T) e^{i\hat{H}_{\Delta t}^{\text{bath}}} e^{i\Phi_{T}(x, p; t_0, t_1, \cdots, t_N) \hbar}$$

(Note that in the case of the FBSD influence functional, the density function $R$ depends on the final trajectory values as well, but as discussed in Ref. [28], it can be separated into a part that depends only on initial conditions and another part that can be combined with the other integrand factors. For simplicity we do not indicate this partitioning explicitly in Eq. (5.14).) These expressions involve a sum with respect to all discretized system paths and a phase obtained from the Newtonian trajectory of the bath, which is subject to time-dependent forces specific to the particular combination of forward-backward system paths.

As discussed in Chapter 1, the computational difficulty of evaluating the path integral is that the number of discretized system paths grows exponentially with the number of time steps,
while the nonlocality of the influence functional prevents a simple step-by-step evaluation of the multidimensional integral. As a consequence, the required number of integrand evaluations quickly becomes prohibitively large, while Monte Carlo evaluation of the multidimensional integral with respect to the auxiliary path integral variables encounters extreme difficulties due to phase cancellation [46, 47]. In Chapter 2 decoherence properties of polyatomic (harmonic or nonlinear) environments was exploited to convert the multidimensional path integral into a series of low-dimensional integrals which involve relatively short path segments that span the bath-induced nonlocality, allowing an iterative propagation of the reduced density matrix [48-54]. In the case where the environment is quadratic (or may be mapped on an effective harmonic bath), iterative path integral-influence functional methods are both easy to implement and efficient. In cases of long bath-induced memory, filtering techniques (see Chapter 3 and Refs. [51, 55-57]) and a recent path integral renormalization procedure [58] can lead to substantial computational savings.

Switching the order of the integration variables and assuming for convenience of notation that the initial density factorizes, such that

$$D(x_0, p_0; s_0^\pm) = \rho_{\text{red}}(s_0^\pm; 0) P(x_0, p_0),$$

(5.15)

(This is not a crucial assumption and can be removed by moving the integration with respect to $s_0^\pm$ from Eq. (5.17) to Eq. (5.16).) Eq. (5.14) may be rewritten in the following form:

$$\rho_{\text{red}}(s_N^\pm; N\Delta t) = \int dx_0 \int dp_0 \, P(x_0, p_0) Q(x_0, p_0; s_N^\pm).$$

(5.16)

In this expression the initial density is propagated via multiplication with the "quantum influence function" $Q$, which contains all dynamical effects due to the interaction of the bath with the quantum system, which modify the phase space density of the bath. The quantum influence function is given by the expression
\[ Q(x_0, p_0; s_N^\pm) = \int ds_0^\pm \cdots \int ds_{N-1}^\pm \left< s_N^+ \left| e^{-i\hat{H}_p \Delta t} \right| s_{N-1}^+ \right> \cdots \left< s_1^+ \left| e^{-i\hat{H}_p \Delta t} \right| s_0^+ \right> \rho_{\text{red}}(s_0^+; 0) \times \left< s_0^- \left| e^{i\hat{H}_p \Delta t} \right| s_1^- \right> \cdots \left< s_{N-1}^- \left| e^{i\hat{H}_p \Delta t} \right| s_N^- \right> e^{i\Phi_k(x_0, p_0; s_0^+ \ldots s_N^-)/\hbar} \] 

(5.17)

This expression involves quantum amplitude factors for the system and phase factors for the interaction between quantum and classical particles, summed with respect to all paths of the quantum system.

5.3 Classical Memory, Quantum Nonlocality and Near-Classical Conditions

Assuming the quantum influence function can be evaluated numerically, integration with respect to the phase space coordinates of the classical particles must be performed by Metropolis Monte Carlo methods [23]. Because the phase of the FBSD or classical influence functional expressions involves the net forward-backward action, which tends to be small due to cancellation [28, 29], the integrand is not a highly oscillatory function of the phase space variables \( x_0, p_0 \). In addition, summation over the system paths smoothes this phase further, making the Monte Carlo evaluation of the integral in Eq. (5.16) very practical even with hundreds of bath particles. (We will revisit this point near the end of this section.) Thus, the main computational challenge is the evaluation of the quantum influence function, Eq. (5.17).

In the absence of interaction with the classical particle and with a factorized initial condition, Eq. (5.17) reduces to the discretized path integral for the quantum system. Because each variable \( s_k^\pm \) is coupled only to those with adjacent indices (i.e., to \( s_{k\pm1}^\pm \)) in this case, one may evaluate the path sum iteratively (after discretizing the system coordinate) by performing a series of matrix-vector multiplications,

\[ \rho_{\text{red}}(s_{k+1}^\pm; (k+1)\Delta t) = \int ds_k^\pm \left< s_{k+1}^- \left| e^{-i\hat{H}_p \Delta t/\hbar} \right| s_k^+ \right> \rho_{\text{red}}(s_k^\pm; k\Delta t) \left< s_k^- \left| e^{i\hat{H}_p \Delta t/\hbar} \right| s_{k+1}^- \right> \]  

(5.18)
The absence of nonlocal couplings from the path integral expression for the bare system, which allows the iterative decomposition of Eq. (5.18), can be traced to the underlying time-dependent Schrödinger equation, which is local in time. The same locality exists in the presence of system-bath coupling if one works with the full Schrödinger equation for the system and bath, i.e., one may still evaluate the full (quantum mechanical) path integral via an iterative procedure for the wavefunction or density matrix of the composite system described by $s$ and $x$. On the other hand, a partial integration with respect to either of these degrees of freedom, which leads to influence functional descriptions [26] (for example, Eq. (5.3)), destroys the local character of the dynamics, introducing distant couplings of the path integral variables which are commonly referred to as “memory”.

It is easy to see that a classical trajectory approximation to the bath dynamics, even if one works in the full space of system and bath coordinates, also introduces nonlocal effects. This is so because a classical trajectory depends on the coordinates of each forward-backward system path at all time points. If the quantum system is described by a grid of $M$ coordinate values, there will be a total of $(M^2)^N$ trajectories emanating from a single initial phase space point upon propagation by $N$ path integral time steps. (Note, of course, that the number of distinct force values due to the system coordinate may be somewhat smaller than $M^2$ in special cases because of symmetry, implying that a fraction of these trajectories may be identical. Still, the number of trajectories increases exponentially with the number of path integral steps.) This trajectory proliferation is the quantum-classical manifestation of time nonlocality. Below we explore the significance of this nonlocality in various regimes, in the interest of devising efficient strategies for evaluating the quantum influence function and the reduced density matrix of the quantum system.

It is useful to begin by understanding the connection between the apparent nonlocality of the classical trajectories in the quantum influence function and the memory/nonlocality in its
integrated form, the influence functional. To this end, we consider the case where the classical
particle experiences a harmonic potential and is linearly coupled to the quantum system, i.e.,
\[ V(s, x) = \frac{1}{2} m_s \omega^2 x^2 - c s x. \]  
(5.19)

Its trajectory in the classical treatments (which involve the average of the forces along the
forward and backward system paths) is given by the expression
\[ x(t) = x_0 \cos \omega t + \frac{p_0}{m_s \omega} \sin \omega t + \frac{c}{2 m_s \omega^2} \int_0^t dt' \left[ s^+(t') + s^-(t') \right] \sin \omega(t-t'), \]
(5.20)
i.e., the trajectory depends on the entire history of the system path. This is the source of memory
in the classical generalized Langevin equation. The relevant action integral is
\[ \Phi(b,c,x) = \int_0^t dt' \left[ s^+(t') - s^-(t') \right] x(t'). \]  
(5.21)
Substituting the trajectory expression in Eq. (5.21), the action becomes
\[ \Phi(b,c,x) = c x_0 \int_0^t dt' \left[ s^+(t') - s^-(t') \right] \cos \omega t' + c \frac{p_0}{m_s \omega^2} \int_0^t dt' \left[ s^+(t') - s^-(t') \right] \sin \omega t' \]
\[ + \frac{c^2}{2 m_s \omega^2} \int_0^t dt' \int_0^t dt'' \left[ s^+(t') - s^-(t') \right] \left[ s^+(t'') + s^-(t'') \right] \sin \omega(t'-t'') \]  
(5.22)
Assuming a factorized initial condition with the bath at thermal equilibrium,
\[ \hat{\rho}(0) = \hat{\rho}_{\text{red}}(0) Z_0^{-1} e^{-\beta \hat{H}_b^{0}} \]  
(5.23)
where \( \hat{\rho}_0(0) \) is the initial density operator of the quantum system, \( \hat{H}_b^{0} \) is the classical harmonic
oscillator Hamiltonian and \( Z_b \) is its partition function, the Wigner transform of the initial density
has the form
\[ W(x_0, p_0; s_0^+) = \left\langle s_0^+ \right| \hat{\rho}_0 \left| s_0^- \right\rangle (h\pi)^{-1} \tanh \left( \frac{1}{2} \beta \omega \right) e^{-\tanh \left( \frac{1}{2} \beta \omega \right) (m_0 a^2 / h + p^2 / m_0 m_0)} \]  
(5.24)
It is straightforward to perform the Gaussian integral with respect to the phase space variables.
The double time integral term in the action does not depend on the integration variables, so it
remains in the result as a multiplicative factor. The terms that depend on the initial position and momentum of the bath give

$$\exp \left[ -\frac{c^2}{4m_0 \omega \hbar} \coth \left( \frac{i}{2} \hbar \omega \beta \right) \left( \int_0^t dt' \Delta s(t') \cos \omega \tau' \right)^2 + \left( \int_0^t dt' \Delta s(t') \sin \omega \tau' \right)^2 \right]$$  (5.25)

where

$$\Delta s(t') = s^+(t') - s^-(t').$$  (5.26)

Rewriting each quadratic term as a double integral and taking advantage of the form of the integrand to modify the upper limit of the inner integration variable, Eq. (5.25) becomes

$$\exp \left[ -\frac{c^2}{2m_0 \omega \hbar} \coth \left( \frac{i}{2} \hbar \omega \beta \right) \int_0^t dt' \int_0^t dt'' \Delta s(t') \Delta s(t'') \left( \cos \omega \tau' \cos \omega \tau'' + \sin \omega \tau' \sin \omega \tau'' \right) \right]$$  (5.27)

Recognizing the last factor as the cosine of the difference argument and combining Eq. (5.27) with the coordinate-free term, one obtains

$$F_{\text{Wigner}}^{\text{class}} = \exp \left[ -\frac{1}{\hbar} \int_0^t dt' \int_0^t dt'' \left( \alpha(t' - t'') \Delta s(t'') s^+(t') - \alpha(t' - t'') s^+(t') \Delta s(t'') \right) \right]$$  (5.28)

where

$$\alpha(t' - t'') = \frac{c^2}{2m_0 \omega \hbar} \left( \coth \left( \frac{i}{2} \hbar \omega \beta \right) \cos \omega(t' - t'') - i \sin \omega(t' - t'') \right).$$  (5.29)

Eq. (5.28) is recognized as the standard Feynman-Vernon influence functional [26] from a monochromatic harmonic bath. The extent of nonlocality is determined by the range of the kernel $\alpha$, which is infinite in the case of a single harmonic oscillator because of the purely oscillating form of Eq. (5.29).

Even though both terms in Eq. (5.29) appear nonlocal in time, the memory associated with the real part of the influence functional is not present in its equivalent form, Eq. (5.25). Makri pointed out this fact in earlier work [59], noting that the nonlocality of the real part of the influence functional is of a classical origin and is removable through the introduction of auxiliary
variables (which may be chosen as the bath trajectory coordinates). An analogous behavior is observed in the classical generalized Langevin equation [60]. Since the real part dominates in the classical limit, one sees that the influence functional memory need not be dealt with explicitly under near-classical conditions. By contrast, the purely quantum mechanical imaginary part is truly nonlocal [59]. Under non-classical conditions, when the imaginary part contributes significantly, the time nonlocality may be finite only by virtue of the self-decoherence properties of the bath, which in turn are determined by its frequency composition.

The real part of the influence functional arises from the coupling-independent terms, which correspond to the homogeneous solution of Hamilton’s differential equations in the case of a harmonic oscillator. In the absence of the inhomogeneous part, the trajectories are independent of the system path and are given by

$$x_{\text{free}}(t) = x_0 \cos \omega t + \frac{p_0}{m_0 \omega} \sin \omega t.$$

(5.30)

Thus, all trajectories arising from a given initial condition are identical if \( c = 0 \), i.e., there is a single trajectory from each phase space point.

The behavior described above is not restricted to harmonic potentials. In the general case of a nonlinear bath, the unperturbed (free) bath trajectory still provides an excellent approximation to the actual trajectory under classical-like conditions. Writing

$$x(t) = x_{\text{free}}(t) + x_{\text{int}}(t),$$

(5.31)

one may separate the action into similar terms,

$$\Phi_b^{\text{class}}(x_0, p_0; [s^\pm]) = \Phi_b^{\text{free}}(x_0, p_0; [s^\pm]) + \Phi_b^{\text{int}}(x_0, p_0; [s^\pm])$$

(5.32)

where

$$\Phi_b^{\text{free}}(x_0, p_0; [s^\pm]) = -\int_0^T V\left(s^- (t'), x_{\text{free}} (t')\right) - V\left(s^- (t'), x (t')\right) dt'.$$

(5.33)
is a local (memory-free) action. All time nonlocality is in the “quantum” part $\Phi^\text{inter}$. Upon integration, this part will give rise to a quantum mechanical contribution to the influence functional. In the case of a harmonic bath linearly coupled to the quantum system, this term is independent of initial conditions, leading to a temperature-independent contribution. Of course this term will not be independent of initial conditions in the case of a nonlinear bath, thus its contribution to the influence functional is expected to be (mildly) temperature-dependent.

The system-independent (“free bath”) trajectory, which leads to a local action, should provide an excellent approximation whenever the effects of the quantum system on the classical particle (the “back reaction”) are weak. As argued above, this is the case at high temperature, which causes the phase space density of the classical particle to be very broad and thus the energy and amplitude of oscillation to be very large for the majority of trajectories. Indeed, such a system-free trajectory treatment is commonly employed to simulate the effects of the radiation field as long as the number of photons (i.e. the field’s quantum number) is large, validating the treatment of the quantum field as a classical oscillating dipole for the purpose of studying absorption or stimulated emission of light [61]. In the context of chemical dynamics this approximation is often referred to as the classical path model.

At a fixed temperature and with specific bath parameters, the degree of trajectory deviation from the free bath limit depends on the magnitude of the system-bath coupling. Thus, even at relatively low temperatures, the system-free part of the solution to the classical equation of motion still dominates if the system-bath coupling is weak. In this situation the classical path approximation (with different trajectories for each phase space point sampled from the phase space distribution) should still be excellent, implying it is still possible to evaluate the path sum by an iterative procedure that employs the $M^2 \times M^2$ propagator matrix for the bare system. As the parameters are changed to deviate from such memory-free situations, the nonlocal part of the action will become increasingly important. Nonlocal effects spanning a single path integral time
step can be included by allowing each trajectory to depend on the instantaneous force exerted by the system at a randomly chosen value of the system coordinate. This approximation, which we call the “random hop model”, retains a single trajectory for each system path, allowing iterative evaluation of the path sum with an effective $M^2 \times M^2$ propagator matrix which amounts to the same computational effort as that required to propagate the quantum system. This random hop approximation is somewhat reminiscent of surface hopping methods, although the hops occur at specified times and no momentum/energy adjustment is made to the trajectory.

Nevertheless, when the effects of nonlocality are substantial, it will be necessary to include them beyond the classical path or random hop approximations. This implies that one must include explicitly the dependence of a classical trajectory on system paths beyond a single step. It is possible to devise such an iterative methodology, where the detailed force on a trajectory by the quantum system is felt up to $m$ time steps, by iterating the matrix of the $M^{2m}$ possible trajectory segments. The procedure is analogous to the tensor propagator methodology and is described in Chapter 6. Once the convergence parameter $m$ reaches the decoherence length, the bath loses memory of the detailed dynamics that occurred more than $m$ time steps earlier, and the calculation converges to the full path sum whose direct evaluation would require the determination of $M^{2N}$ trajectories for each initial condition.

In light of the above analysis, we comment again on the dependence of the quantum influence function on the initial phase space coordinates. In the limit of a classical bath (or, equivalently, within the classical path QCPI approximation), this function is equal to the density matrix of the quantum system driven by a time-dependent external field which arises from the free bath trajectory. Thus, the trace of the quantum influence function equals unity in this approximation, and its diagonal elements are nonnegative and cannot exceed unity. As a result, Eq. (5.17) is a smooth and positive function, allowing efficient evaluation by Monte Carlo methods. The above remarks are not true in the case of a nonclassical bath. When quantum
nonlocality is significant, the quantum influence function can have values that are negative or exceed unity, although its trace is always conserved. The larger spread of the integrand can lead to slower convergence of the Monte Carlo average. In practice, we find that under common conditions the quantum influence function remains mostly positive and the Monte Carlo evaluation of the integral converges very well.

5.4 Numerical Illustrations

In this section we illustrate the nature of the dynamics in the near-classical or weak coupling limit, the effectively local character of the dominant influence functional contribution and the relatively minor role of nonlocality, which allow efficient evaluation of the QCPI expression. The observed behaviors are relevant to any (classical or semiclassical) QCPI formulation where the quantum system is treated by a full path integral while the dynamics of the bath particles is captured via classical trajectories. In this chapter we are not concerned with the relative accuracy of classical, quasiclassical or semiclassical treatments of the bath. Such comparisons will be reported in future work.

Our test model is the standard two-level system (TLS) coupled to a dissipative bath of harmonic oscillators, for which the system and bath terms of Eq. (5.1) are given by the expressions

\[ H_0 = -\hbar \Omega \sigma_x \]  

(5.34)

and

\[ H_b = \sum_j \left( \hat{p}_j^2 + \frac{1}{2} m \omega_j^2 \hat{x}_j^2 - c \sigma_z \hat{x}_j \right) \]  

(5.35)

where \( \sigma_x \) and \( \sigma_z \) are the standard 2×2 Pauli spin matrices. This Hamiltonian serves as a rich model for condensed phase tunneling [62] and is frequently employed in the description of charge transfer between two equivalent sites. In this case the two diagonal terms of the 2×2
Hamiltonian matrix correspond to the two coupled diabatic potentials, which are assumed to be quadratic functions by virtue of the linear response approximation. The dynamics of the dissipative TLS (or a multi-level system interacting with a harmonic dissipative bath) can be evaluated efficiently to arbitrary accuracy using the iterative tensor multiplication methodology (See Chapter 2 and Refs. [48-50]) which is based on a finite-memory decomposition of the influence functional with the quasidiabatic partitioning of the system-bath propagators [63]. We use the dissipative TLS model here only for convenience because it is amenable to accurate treatment for comparison, but it should be clear that the trajectory-based QCPI method is completely general and applicable to any anharmonic polyatomic bath. We choose the factorized initial condition [62]

$$\hat{\rho}(0) = |i\rangle\langle i| \frac{e^{-\beta H_{0}^{\text{free}}}}{\text{Tr} e^{-\beta H_{0}^{\text{free}}}}$$

(5.36)

where $H_{b}^{\text{free}}$ is the Hamiltonian of the bath in the absence of coupling to the system. We use the common Ohmic form to model the spectral density of the bath (Eq. (3.4)) with $\omega_{0}$ set to two.

The continuous bath is discretized into a sum of 60 oscillators whose frequencies and coupling coefficients are evaluated using a logarithmic discretization of the spectral density [64] with a maximum frequency equal to $\omega_{\text{max}} = 4\omega_{0}$. This discretization yields converged results for the time lengths of interest. The discrete bath QCPI results are compared to numerically exact results obtained using the tensor propagator influence functional methodology. The QCPI calculations employed a Monte Carlo sampling of 60,000 phase space points (i.e. an average of 500 sampling points per integration variable). This averaging led to small statistical uncertainty in the propagated reduced density matrix, with a standard deviation comparable to the size of the markers in the figures. We report the expectation value of the system position as a function of time obtained with the QCPI expression within the classical path approximation, the simple
random hop model and the full QCPI result that includes the nonlocal quantum mechanical contributions from the bath, summed via the iterative scheme described in detail in Chapter 6.

Figure 25 shows the population of site 1 in an overdamped regime corresponding to $\omega_\gamma = 2.5 \Omega$, $h\Omega \beta = 0.2$, and Kondo parameter $\xi = 1.2$. These parameters correspond to strong dissipation and a high temperature with respect to the TLS tunneling splitting, and the TLS populations exhibit exponential relaxation. Because of the large value of the Kondo parameter the calculation required a small path integral time step given by $\Omega \Delta t = 0.125$. The calculation was performed using the classical Boltzmann factor to sample initial conditions for the classical trajectories. We note that the bath degrees of freedom near the peak of the spectral density are at a moderately high temperature ($h\omega_\beta = \hbar$), but the highest frequency modes are at a rather low temperature ($h\omega_{\Delta max} \beta = 2$). The QCPI calculation with either the classical path approximation or the random hop model yields reasonable results. Even though the dynamics of the TLS driven by the unperturbed bath trajectory is purely oscillatory, the phase space averaging is able to account correctly for the quenching of these oscillations and capture the observed incoherent decay. Small deviations from the exact result arise because of the high frequency bath oscillators, which are in a relatively low temperature regime.

Figure 26 shows results in a weak-to-moderate dissipation, low-temperature regime characterized by $\omega_\gamma = 5 \Omega$, $h\Omega \beta = 5$, $\xi = 0.3$. The TLS now displays quenched oscillations. The bath is at a very low temperature in this case and the nonlocal contributions (which correspond to the imaginary term of the influence functional) are expected to be comparable to those from the local terms. We note that the quantum mechanical character of the bath is very pronounced under the chosen conditions, such that a classical treatment of its dynamics may not be well justified. The QCPI results with the classical path approximation, while qualitatively correct, exaggerate the oscillatory character of the dynamics. Yet, because of system-bath coupling is not very strong, the corrections to the classical path QCPI result are of modest
magnitude. Also shown in the figure are QCPI results with the random hop model, as well as converged QCPI results that include the full quantum nonlocality, obtained via the iterative QCPI methodology presented in Chapter 6. It is seen that inclusion of these nonlocal interactions is able to correct the classical path approximation in a quantitative manner, and the converged QCPI results are in excellent agreement with those of the exact path integral calculation.

Figure 27 shows the quantum influence function corresponding to the population of state 1 at the phase space coordinates sampled during the Monte Carlo random walk. It is seen that the quantum influence function is always between zero and unity within the classical path QCPI approximation. The random hop QCPI calculation leads to values that spread somewhat outside this interval. The full inclusion of quantum nonlocality gives rise to a larger spread of the quantum influence function, which includes negative values. Still, this spread is not sufficiently large to present a significant obstacle to the convergence of the Monte Carlo estimate of the integral.

5.5 Concluding Remarks

Quantum-classical treatments may offer the only pragmatic approach for simulating the dynamics of complex condensed phase or biological systems with hundreds or thousands of atoms. The main theoretical challenge in this endeavor is to devise theoretical treatments that are rigorous, consistent and practical. The difficulty in this regard lies in the nature of quantum mechanics, which is nonlocal and invokes delocalized wavefunctions, while classical theory is based on the local characteristics of trajectories. In this regard, Feynman’s path integral formulation of quantum mechanics provides the perfect common ground for the development of theoretically sound quantum-classical treatments that do not invoke any approximations beyond the use of Newton’s laws for the classical particles. However, evaluation of the path integral generally seems to present unsurmountable difficulties.
In this work we have presented an analysis of the quantum-classical path integral, which suggests that the very nature of the classical assumption should make such calculations feasible. In the limit of a purely classical environment, a QCPI expression reduces to the ensemble average of a driven quantum system, which can be evaluated straightforwardly and efficiently. Quantum effects in the solvent dynamics manifest themselves as nonlocal contributions to the action, which lead to a proliferation of trajectories and seem to obviate an iterative evaluation of the path sum. However, because these quantum effects are by assumption relatively minor, simple treatments such as a random hop model are able to capture some of these corrections. In the following chapter, we describe an iterative decomposition of the path sum which allows full evaluation of the path integral with modest amounts of effort. Further, based on the excellent starting point offered by the form of the fully classical limit (i.e., the classical path approximation to the QCPI result), we suspect that simple and powerful tools for such calculations will become available. Work along these lines is in progress in our group.
Figure 25 Average position of the TLS for $\omega_0 = 2.5 \Omega$, $\hbar \Omega \beta = 0.2$, $\xi = 1.2$. Green line: classical path QCPI approximation. Orange line: random hop QCPI approximation. Red markers: converged iterative QCPI calculation with quantum nonlocality spanning 5 path integral time steps. Black line: exact results obtained via the iterative path integral methodology based on the analytical Feynman-Vernon influence functional. The results of the classical path approximation and the random hop model are almost indistinguishable in this case.
Figure 26 Average position of the TLS for $\omega = 5\Omega$, $h\Omega \beta = 5$, $\xi = 0.3$. Green line: classical path approximation. Orange line: random hop model. Red markers: converged iterative QCPI calculation with quantum nonlocality equal to 6 path integral time steps. Black line: exact results obtained via the iterative path integral methodology based on the analytical Feynman-Vernon influence functional.
Figure 27 The quantum influence function at the first 10,000 steps of the Monte Carlo walk for the parameters given in Figure 26. Red points: classical path QCPI approximation. Green points: random hop QCPI approximation. Blue points: QCPI path sum with full quantum nonlocality.
References


Chapter 6 Quantum-Classical Path Integral: Numerical Methodology

6.1 Introduction

Classical mechanics often provides an adequate and efficient tool for simulating the dynamics of complex systems with thousands or atoms. The major shortcoming of classical treatments is the neglect of quantum mechanical effects, which can be significant for light atoms such as hydrogen at low temperatures, and absolutely crucial to the description of electron transfer processes and photochemical reactions that evolve on coupled Born-Oppenheimer potential surfaces. The desire to include important quantum mechanical effects in the description of select degrees of freedom, while maintaining a computationally efficient classical treatment of the majority of atoms, has motivated the development of quantum-classical approximations (see, for example, references 1-21 of Chapter 5).

In Chapter 5 we explored the feasibility of rigorous quantum-classical path integral (QCPI) calculations. In general, evaluation of the real-time path integral [1] presents an extremely difficult task because it requires evaluation of a multidimensional integral with a highly oscillatory integrand, a situation that cannot be handled successfully by Monte Carlo methods [2]. In Chapter 5 we analyzed the influence of a nearly classical environment on a quantum system. This analysis led to much optimism for the development of efficient QCPI algorithms. The main idea derives from the observation [3] that the effects on the quantum system by a purely classical bath amount to an action that is local in time, allowing efficient iterative evaluation of the path integral. Deviations of the environment from the strict classical limit introduce nonlocal interactions that seem to require a full evaluation of the path sum. However, the relatively minor role of these nonlocal quantum effects invites a variety of efficient
treatments, which may range from simple approximate schemes to elaborate numerically exact algorithms. The present chapter aims at laying the groundwork for the development of such methods.

We begin by describing in section 6.2 a computationally optimal formulation of QCPI. We derive expressions that allow the use of different time steps for the quantum and classical degrees of freedom and which maximize the path integral time step by avoiding to the extent possible the Trotter splitting of terms that involve the quantum system. Further, we adopt energy truncated propagators [4, 5] in discrete variable representations of the path integral [6], which lead to path-dependent weights that effectively eliminate the majority of paths. Classical trajectories incur transitions to other quantum states at regular time intervals, but these transitions are costly, thus their number is effectively limited. In particular, our treatment leads to trajectory-dependent propagators, such that the cost of a quantum transition depends on the required amount of solvent reorganization. As described in section 6.3, these features minimize the number of paths that must be included in the QCPI expression.

Still, many processes require long-time simulation, which requires the evaluation of very large numbers of terms. Taking advantage of the decoherence properties of condensed phase environments as in the case of a system coupled to a dissipative bath [7-13], we develop in section 6.4 an iterative methodology for decomposing the path sum into a series of operations that involve paths segments of length determined by the quantum nonlocality. By varying the span of these paths until convergence is reached, one obtains the full QCPI result with effort that scales linearly with the total propagation time. In section 6.5 we illustrate the methodology with numerical examples on symmetric and biased two-level systems interacting with dissipative baths, for which accurate results are available. We conclude in section 6.6 with a summary and outlook.
6.2 Discretized Quantum-Classical Path Integral

We use the notation of Chapter 5, where the quantum mechanical degrees of freedom are described collectively by the coordinate $s$ and momentum $p_s$, and $x$ describes the coordinates of the bath or solvent particle(s) with mass $m_b$, which are to be treated as classical. In the spirit of the Born-Oppenheimer approximation, we begin by separating out the kinetic energy $T_b$ of the classical degree(s) of freedom, writing the total Hamiltonian as

$$\hat{H} = \hat{H}_{qu}(\hat{s}, \hat{p}_s, \hat{x}) + T_b(\hat{p})$$

(6.1)

where

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

(6.2)

Here $H_{qu}$ is the Hamiltonian describing the quantum subsystem (whose internal dynamics is given by $H_0$) and its potential interaction $V$ with the classical particle(s). Our goal is to calculate the reduced density matrix of the quantum subsystem at the time $t = N\Delta t$,

$$\rho_{red}(s_N^+, N\Delta t) = \int dx_N^+ \rho(s_N^+, x_N^+, N\Delta t) \delta(x_N^+ - x_N^-)$$

(6.3)

where

$$\rho(s_N^+, x_N^+; N\Delta t) = \left\langle s_N^+ x_N^+ | e^{-i\hat{H} N\Delta t/\hbar} \hat{p}(0) e^{i\hat{H} N\Delta t/\hbar} | s_N^- x_N^- \right\rangle$$

(6.4)

is the full density matrix, the trace in Eq. (6.3) is with respect to the bath and $\Delta t$ is the time step to be used in the path integral discretization of the forward and reverse evolution operators. Using the identity $e^{z \hat{H} N\Delta t/\hbar} = (e^{z \hat{H} \Delta t/\hbar})^N$ and inserting complete sets of system coordinate states between each pair of exponentials, one obtains the following discretized path integral [1] form of the density matrix,
\[
\rho(s_N^+, x_N^+; N\Delta t) = \int ds_0^+ \int ds_1^+ \cdots \int ds_{N-1}^+ \int dx_0^+ \int dx_1^+ \cdots \int dx_{N-1}^+ \\
\times \left\langle s_N^+, x_N^+ \right| e^{-i\hat{H}_{\Delta t}/\hbar} \left| s_{N-1}^+, x_{N-1}^+ \right\rangle \cdots \left\langle s_1^+, x_1^+ \right| e^{-i\hat{H}_{\Delta t}/\hbar} \left| s_0^+, x_0^+ \right\rangle \left\langle s_0^+, x_0^+ \right| \hat{\rho}(0) \left| s_0^-, x_0^- \right\rangle \\
\times \left\langle s_0^-, x_0^- \right| e^{i\hat{H}_{\Delta t}/\hbar} \left| s_1^-, x_1^- \right\rangle \cdots \left\langle s_{N-1}^-, x_{N-1}^- \right| e^{i\hat{H}_{\Delta t}/\hbar} \left| s_N^-, x_N^- \right\rangle 
\]

(6.5)

which is equivalent to the following iterative hierarchy:

\[
\rho \left( s_{k+1}^+, x_{k+1}^+; (k+1)\Delta t \right) = \int ds_k^+ \int dx_k^+ \left\langle s_{k+1}^+, x_{k+1}^+ \right| e^{-i\hat{H}_{\Delta t}/\hbar} \left| s_k^+, x_k^+ \right\rangle \\
\times \rho \left( s_k^+, x_k^+; k\Delta t \right) \left\langle s_k^-, x_k^- \right| e^{i\hat{H}_{\Delta t}/\hbar} \left| s_{k+1}^-, x_{k+1}^- \right\rangle 
\]

(6.6)

Note that no approximations have been introduced up to this point, so Equations (6.5) and (6.6) are exact for any value of the time step \( \Delta t \).

One would like to evaluate the path integral expression using a classical trajectory approximation to reduce the multidimensional integral for the classical particles to an integral with respect to initial conditions. There are several ways to proceed in order to introduce classical mechanical approximations to the bath degrees of freedom. The most obvious starting point is the semiclassical form of the coordinate propagators for the bath (whose Hamiltonian is parametrically dependent on the system path, thus effectively time-dependent). Since the starting points of these trajectories are constrained only by the initial density matrix, the forward and backward trajectories in such a double semiclassical [14] expression are allowed to differ substantially, even if the corresponding system-induced forces are the same. Thus, a double semiclassical treatment allows the inclusion of quantum interference for the bath particles, which is impractical and unwarranted given the assumed near-classical nature of these particles. A more practical treatment arises by implementing a forward-backward semiclassical dynamics [15, 16] (FBSD) approximation, which imposes trajectory continuity at the endpoint. In this treatment, the forward and backward trajectories of the classical particles are identical if the corresponding system paths are the same, but are otherwise distinct and in fact may differ substantially. An even simpler treatment arises if one constrains the phase space coordinates at the starting point of
the trajectories. This linearized semiclassical initial value representation [17] (LS-IVR) or linearized path integral [18, 19] (LPI) treatment (also known as the Wigner model [20]) gives rise to forward and backward trajectories that are always identical and which are propagated subject to the average of the forces exerted by the system along its forward and backward paths. Thus, the LS-IVR/LPI and FBSD treatments, which are very similar when applied to all degrees of freedom, [21] are quite different when implemented in the path integral context to approximate the influence functional from a bath coupled to the quantum system. While the FBSD treatment should offer a better description of the system-bath interaction in such cases, it is likely that the LPI approximation is also quite adequate in many situations. In this chapter we are not concerned with the relative accuracy of these approximate treatments. Our goal is to present the general framework for devising a rigorous and practical quantum-classical methodology that employs a full path integral description of the quantum system and a classical trajectory description of the bath. For simplicity we focus mostly on the LPI approach, but it should be clear that the approach described in sections 6.3 and 6.4 is applicable in conjunction with a trajectory treatment of the bath at any level. Below we derive discretized QCPI expressions, taking particular care to utilize separate time steps for the quantum and classical paths and to obtain an expression where multiple quantum transitions are costly, thus highly improbable. These features of our formulation can easily be applied to the quantum-semiclassical formulation as well, and are essential for computational efficiency.

It is useful to define the Wigner transform [20] of the initial density matrix with respect to the classical coordinates,

$$W(s_0^+, s_0^-, p_0) = (2\pi\hbar)^{-1} \int d\Delta x_0 \rho_0(s_0^+, s_0^-) e^{-\pi\Delta x_0^2/\hbar},$$  

(6.7)

where

$$\bar{x}_k = \frac{1}{2}(x_k^+ + x_k^-), \quad \Delta x_k = x_k^+ - x_k^-.$$  

(6.8)
are sum and difference coordinates for the classical particle. From Eq. (6.7) one obtains the inverse relation
\[
\rho_n(s_n^+, x_n^+) = \int \mathcal{D}p e^{i\frac{\pi n}{\hbar} A_0}.
\]

To arrive at a classical trajectory approximation for the bath, it is necessary to separate the bath kinetic energy from the rest of the Hamiltonian in the time evolution operators. This procedure is valid for a small time step, which we denote as \( \delta t \). Factoring the time evolution operator according to the Hamiltonian partitioning of Eq. (6.1), the propagator becomes
\[
\begin{split}
\langle s_{k+1} x_k \rangle e^{-i\hat{H}_x \delta t / \hbar} \left| s_k x_k \right> = \langle s_{k+1} x_k \rangle e^{-i\hat{H}_x \delta t / 2\hbar} e^{-i\hat{H}_x \delta t / 2\hbar} e^{-i\hat{H}_x \delta t / 2\hbar} \langle s_k x_k \rangle e^{-i\hat{H}_x \delta t / 2\hbar} e^{-i\hat{H}_x \delta t / 2\hbar} e^{-i\hat{H}_x \delta t / 2\hbar} \\
= \langle s_{k+1} \rangle e^{-i\hat{H}_x (s_{k+1}) \delta t / 2\hbar} e^{-i\hat{H}_x (s_{k+1}) \delta t / 2\hbar} e^{-i\hat{H}_x (s_{k+1}) \delta t / 2\hbar} \langle s_k \rangle \langle x_{k+1} \rangle e^{-i\hat{H}_x \delta t / 2\hbar} \langle x_k \rangle.
\end{split}
\]

Here \( \hat{H}_x(x) \) is the Hamiltonian for the quantum system evaluated at the coordinate \( x \) of the classical particle. To proceed, we switch to sum/difference coordinates. In these coordinates the product of kinetic energy propagators is given by the expression
\[
\begin{split}
\langle x_{k+1}^+ \rangle e^{-i\hat{H}_x \delta t / \hbar} \left| x_k^+ \right> \langle x_k^+ \rangle e^{i\hat{H}_x \delta t / \hbar} \left| x_{k+1}^+ \right> = \frac{m_k}{2\pi \hbar \delta t} e^{im_k(x_{k+1}^+ - x_k^+)/(\Delta x_k \delta t / \hbar)}.
\end{split}
\]

Next, we note that the density matrix of the near-classical bath should be peaked about \( x_k^+ = x_k^- \). Based on this, we linearize the Hamiltonian operator for the quantum system about the average position of the classical particle,
\[
\hat{H}_{qu}(x_k^+) = \hat{H}_{qu}(x_k^-) + \hat{V}'(x_k^-) (x_k^+ - x_k^-) = \hat{H}_{qu}(x_k^-) + \frac{1}{2} \hat{V}'(x_k^-) \Delta x_k
\]

where
\[
\hat{V}'(x) \equiv \frac{\partial}{\partial x} \hat{H}_{qu}(x).
\]

Since \( \delta t \) (and also \( \Delta x_k \)) has a small magnitude, we factor the half-step evolution operators in Eq. (6.10):
\[
\left\langle \hat{s}^\dagger_{k+1} \right| e^{-i\hat{H}_\mu(s_i^0,\tau_0,\Delta_\mu,\delta\tau/2b)} e^{-i\hat{\Pi}_\mu(s_i^0,\tau_0,\Delta_\mu,\delta\tau/2b)} \left| \hat{s}^\dagger_i \right\rangle \\
= e^{-iV(s_i^0,\tau_0,\Delta_\mu,\delta\tau/2b)} \left\langle \hat{s}^\dagger_{k+1} \right| e^{i\hat{H}_\mu(\tau_0,\Delta_\mu,\delta\tau/2b)} e^{i\hat{\Pi}_\mu(\tau_0,\Delta_\mu,\delta\tau/2b)} \left| \hat{s}^\dagger_i \right\rangle e^{-iV(s_i^0,\tau_0,\Delta_\mu,\delta\tau/2b)}. \tag{6.14}
\]

Substituting Equations (6.9), (6.10), (6.11) and (6.14) in Eq. (6.6), the first step in the path integral expression becomes
\[
\left\langle s_i^0, x_i^0 \right| \hat{\rho}(\delta t) \left| s_i^0, x_i^0 \right\rangle = \frac{m_0}{2\pi \hbar} \int ds_0^+ \int d\pi_0 \int d\Delta_\mu \int d\delta t \ W(s_0^+, \pi_0, \delta t) e^{i\pi \Delta_\mu/\hbar} \\
\times \left\langle s_0^+ \right| e^{-i\hat{H}_\mu(\pi_0, \delta\tau/2b)} e^{-i\hat{\Pi}_\mu(\pi_0, \delta\tau/2b)} \left| s_0^+ \right\rangle e^{i\hat{\Pi}_\mu(\pi_0, \delta\tau/2b)} e^{i\hat{H}_\mu(\pi_0, \delta\tau/2b)} \left| s_i^- \right\rangle \tag{6.15}
\]

where
\[
\overline{V'}(s_i^0, \tau_i) = \frac{1}{2} \left[ V'(s_i^0, \tau_i) + V'(s_i^0, \tau_i) \right]. \tag{6.16}
\]

is the (negative of the) average force exerted on the classical particle by the quantum system. Integrating with respect to the difference variable we arrive at the result
\[
\left\langle s_i^0, x_i^0 \right| \hat{\rho}(\delta t) \left| s_i^0, x_i^0 \right\rangle = \int ds_0^+ \int dx_0 \int d\pi_0 \ W(s_0^+, \pi_0, \delta t) e^{i\pi (\tau_i - \tau_0)} e^{i\pi \Delta_\mu/\hbar} \\
\times \left\langle s_0^+ \right| e^{-i\hat{H}_\mu(\pi_0, \delta\tau/2b)} e^{-i\hat{\Pi}_\mu(\pi_0, \delta\tau/2b)} \left| s_0^+ \right\rangle e^{i\hat{\Pi}_\mu(\pi_0, \delta\tau/2b)} e^{i\hat{H}_\mu(\pi_0, \delta\tau/2b)} \left| s_i^- \right\rangle \tag{6.17}
\]

The delta function in this expression vanishes unless
\[
\tau_i = \tau_0 + m_0^{-1} \pi_0 \delta t - \frac{1}{2} m_0^{-1} \overline{V'}(s_0^+, \tau_0) \delta t^2 \tag{6.18}
\]
i.e., the average value \( \tau_i \) of the endpoint coordinates of the classical particle must be equal to the value predicted by the initializing step in the classical velocity Verlet algorithm for the initial condition \( \tau_0, \pi_0 \) and subject to a constant force given by Eq. (6.16).

Next, consider the second time step in the propagation of the density matrix. Multiplying Eq. (6.17) by forward and backward propagators and repeating the previous steps, we find
According to the delta function in this expression, the average coordinate of the classical particle is given by

$$\bar{x}_2 = 2\bar{x}_1 - \bar{x}_0 - m_b \nabla'(s_1^+ + \bar{x}_0) \delta t^2.$$  

(6.20)

Since $\nabla'/m_b$ is the acceleration at the time $\delta t$, Eq. (6.20) is the Störmer-Verlet formula for the classical coordinate $\bar{x}_2$ at the time $2\delta t$.

Repeating the last step, one obtains the following expression for the density matrix at the time $n\delta t$:

$$\begin{align*}
\langle s_n^+ x_n^+ | \hat{\rho}(n\delta t) | s_n^- x_n^- \rangle &= \int \! dx_0 \int \! dp_0 \int \! ds_n^+ \int \! ds_n^- \cdots \int \! ds_{n+1}^- \; W(s_0, \bar{x}_0, p_0) e^{i m_b (\bar{x}_n - \bar{x}_0) \Delta t / \delta t} \\
&\times \langle s_n^+ | e^{i \hat{H}_s(\bar{x}_n) \delta t / 2} e^{-i \hat{H}_s(\bar{x}_{n+1}) \delta t / 2} s_n^- \rangle \cdots \langle s_1^+ | e^{-i \hat{H}_s(\bar{x}_1) \delta t / 2} e^{i \hat{H}_s(\bar{x}_0) \delta t / 2} s_1^- \rangle \\
&\times e^{-i \nabla'(s_1^+ + \bar{x}_0) \delta t} \delta (\bar{x}_n - 2\bar{x}_{n-1} + \bar{x}_{n-2} + m_b \nabla'(s_1^+ + \bar{x}_0) \delta t^2) \\
&= \rho_{\text{red}}(s_n^+; n\Delta t),
\end{align*}$$

(6.21)

which (dropping the bars to simplify the notation) leads to the reduced density matrix

$$\begin{align*}
\rho_{\text{red}}(s_n^+; n\Delta t) &= \int \! dx_0 \int \! dp_0 \int \! ds_n^+ \int \! ds_n^- \cdots \int \! ds_{n+1}^- \; W(s_0, x_0, p_0) \\
&\times \langle s_n^+ | e^{i \hat{H}_s(x_n) \delta t / 2} e^{-i \hat{H}_s(x_{n+1}) \delta t / 2} s_n^- \rangle \cdots \langle s_1^+ | e^{-i \hat{H}_s(x_1) \delta t / 2} e^{i \hat{H}_s(x_0) \delta t / 2} s_1^- \rangle \\
&\times e^{-i \nabla'(x_1^+ + x_0) \delta t} \delta (x_n - 2x_{n-1} + x_{n-2} + m_b \nabla'(x_1^+ + x_0) \delta t^2) \\
&= \rho_{\text{red}}(s_n^+; n\Delta t).
\end{align*}$$

(6.22)

where $x_i$ is the coordinate of a classical trajectory propagated from $x_0, p_0$ subject to the force given by Eq. (6.16).

The propagators in Eq. (6.22) may be further manipulated to produce the LPI result. By factoring the propagator according to the system and interaction components of Eq. (6.2),
\[
\langle s^+_k | e^{i\hat{H}_0(x_k)\Delta t/2\hbar} | s^+_k \rangle = e^{iV(s^+_0, x_0)\Delta t/2\hbar} \langle s^+_k | e^{i\hat{H}(s^+_k, x_k)\Delta t/\hbar} | s^+_k \rangle e^{iV(s^+_k, x_k)\Delta t/2\hbar} \tag{6.23}
\]

Eq. (6.22) becomes
\[
\rho_{\text{red}}(s^+_n; n\Delta t) = \int dx_0 \int dp_0 \int ds^+_0 \int ds^+_1 \ldots \int ds^+_n W(s^+_0, x_0, p_0) \\
\times \langle s^+_n | e^{-i\hat{H}_0\Delta t/\hbar} | s^+_n \rangle \ldots \langle s^+_n | e^{-i\hat{H}_0\Delta t/\hbar} | s^+_n \rangle \langle s^+_0 | e^{i\hat{H}(s^+_0, x_0)\Delta t/\hbar} | s^+_0 \rangle \ldots \langle s^+_0 | e^{i\hat{H}(s^+_0, x_0)\Delta t/\hbar} | s^+_0 \rangle \\
\times e^{\sum_{m=0}^{n-1} V(s^+_m, x_m) + \sum_{m=0}^{n} V(s^+_m, x_m) - \sum_{m=0}^{n} V(s^+_m, x_m) - \sum_{m=0}^{n} V(s^+_m, x_m)} \\
\tag{6.24}
\]

The last factor is recognized as the trapezoid rule-discretized form of the action integral in the LPI expression.

Equations (6.22) or (6.24) may be used as they stand. However, they are rather inefficient, because they require a number of time path integral time slices equal to the number of elementary trajectory time steps. In many situations, one expects the path integral time step to be significantly larger than that required in the Verlet integrator. This is so because the system propagators (and in the case of Eq. (6.22) the propagators for the system and the system-bath coupling) are to be evaluated exactly [4]. We thus wish to obtain a QCPI expression where the classical and quantum degrees of freedom are subject to different time steps. To this end, we revisit Eq. (6.14), noting again that the near-classical nature of the bath implies that \( \Delta x \) are small. This permits us to move the force operator past the second exponential in order to evaluate it at the ket coordinate. This procedure may be repeated, replacing \( V(s^+_0, x_0) \) by \( V(s^+_k, x_k) \) in the first \( n \) propagators and by \( V(s^+_k, x_k) \) in the next \( n \) such factors. The resulting density matrix is still given by the same expression, but the force that governs the motion of the classical particles is now given by \( \overline{V}(s^+_k, x_k) \) for \( k = 0, \ldots, n \) and by \( \overline{V}(s^+_k, x_k) \) for \( k = n+1, \ldots, 2n \). Since the classical trajectory no longer depends on the coordinates \( s^+_0 \ldots s^+_n \), we may remove the resolution of the identity to collapse \( 2n \) path integral time steps into one, i.e.,
\[
\langle s_{2n-2}^b s_{2n-2}^a \mid \hat{\rho}(2n\delta t) \mid s_{2n-2}^b s_{2n-2}^a \rangle = \int dx_0 \int dp_0 W(s_0^b, x_0, p_0) e^{i p_0 \cdot (s_0^b - s_{2n-2}^a) / \delta t} \times \langle s_{2n-2}^b \mid e^{-i \hat{H}_e(x_0) \delta t / \delta \hat{p}_0} \cdots \hat{c}(x_0) \delta t / \delta \hat{p}_0} \cdots e^{-i \hat{H}_e(x_0) / \delta \hat{p}_0} \mid s_{2n-2}^a \rangle \times e^{i \hat{c}(x_0) \delta t / \delta \hat{p}_0} \cdots \hat{c}(x_0) \delta t / \delta \hat{p}_0} \cdots e^{i \hat{H}_e(x_0) / \delta \hat{p}_0} \mid s_{2n-2}^a \rangle \]

(6.25)

Choosing \( \Delta t = 2n\delta t \) and relabeling the path integral variables, we arrive at the following expression for the reduced density matrix,

\[
\rho_{\text{red}}(s_{2n}^b ; N\Delta t) = \int dx_0 \int dp_0 \int ds_0^b \int ds_{N-1}^b W(s_0^b, x_0, p_0) \times \langle s_{2n}^b \mid e^{-i \hat{H}_e(s_0^b, \chi(t)) \delta t / \delta \hat{p}_0} \cdots \hat{c}(s_0^b, \chi(t)) \delta t / \delta \hat{p}_0} \cdots e^{-i \hat{H}_e(s_0^b, \chi(t)) / \delta \hat{p}_0} \mid s_{N-1}^b \rangle \times \langle s_{N-1}^b \mid e^{i \hat{c}(s_0^b, \chi(t)) \delta t / \delta \hat{p}_0} \cdots \hat{c}(s_0^b, \chi(t)) \delta t / \delta \hat{p}_0} \cdots e^{i \hat{H}_e(s_0^b, \chi(t)) / \delta \hat{p}_0} \mid s_{N-1}^b \rangle \times e^{i \hat{c}(s_0^b, \chi(t)) \delta t / \delta \hat{p}_0} \cdots \hat{c}(s_0^b, \chi(t)) \delta t / \delta \hat{p}_0} \cdots e^{i \hat{H}_e(s_0^b, \chi(t)) / \delta \hat{p}_0} \mid s_{N-1}^b \rangle \]

where the classical trajectory is integrated subject to a force given by \( \vec{V}'(s_0^b, x(t')) \) for \( 0 \leq t' < \frac{1}{2} \Delta t \), \( \vec{V}'(s_0^b, x(t')) \) for \( \frac{1}{2} \Delta t \leq t' < \frac{3}{2} \Delta t \), etc. Factoring the exponential operators into system and interaction potential components and taking the limit \( \delta t \to 0 \), Eq. (6.26) reverts to the phase form,

\[
\rho_{\text{red}}(s_{2n}^b ; N\Delta t) = \int dx_0 \int dp_0 \int ds_0^b \int ds_{N-1}^b W(s_0^b, x_0, p_0) \times \langle s_{2n}^b \mid e^{-i \hat{H}_e(s_0^b, \chi(t)) / \delta \hat{p}_0} \cdots \hat{c}(s_0^b, \chi(t)) / \delta \hat{p}_0} \cdots e^{-i \hat{H}_e(s_0^b, \chi(t)) / \delta \hat{p}_0} \mid s_{N-1}^b \rangle \times \langle s_{N-1}^b \mid e^{i \hat{c}(s_0^b, \chi(t)) / \delta \hat{p}_0} \cdots \hat{c}(s_0^b, \chi(t)) / \delta \hat{p}_0} \cdots e^{i \hat{H}_e(s_0^b, \chi(t)) / \delta \hat{p}_0} \mid s_{N-1}^b \rangle \times e^{i \hat{c}(s_0^b, \chi(t)) / \delta \hat{p}_0} \cdots \hat{c}(s_0^b, \chi(t)) / \delta \hat{p}_0} \cdots e^{i \hat{H}_e(s_0^b, \chi(t)) / \delta \hat{p}_0} \mid s_{N-1}^b \rangle \]

where \( t = N\Delta t \) and the force dependence is given above. Often Eq. (6.27) will be adequate, but Eq. (6.26) can lead to higher efficiency for two reasons: First, the magnitude of the path integral time step \( \Delta t \) is constrained in Eq. (6.26) by the commutator between \( V' \Delta t \) and \( H_o \), and thus can be substantially larger than the time step allowed by Eq. (6.27), where the entire potential \( V \) was
split from $H_0$. Second, the dependence of the time evolution operators on trajectories in Eq. (6.26) effectively eliminates contributions from the majority of system paths whose weight is negligible because they correspond to large solvent reorganization energy. This point is discussed in more detail in section 6.3. Note that the trajectory dependence on the system path is symmetric in both expressions, i.e., a trajectory experiences the force from each system endpoint over half of the time step.

6.3 Hopping penalty and solvent reorganization

For a given time step, the number of paths in a discretized path integral calculation can be effectively reduced if certain paths can be neglected because of their vanishing probability. For a general Hamiltonian in continuous coordinates, the first step in this direction is to use energy filtering procedures (e.g., discrete variable representations [6] constructed in terms of truncated eigenstate expansions [4, 5]) rather than phase forms (e.g., Trotter-type [22] expressions) to construct system propagators with coordinate-dependent weights. In general, such energy-filtered propagators decay to zero as the distance of the two endpoints increases [23]. Thus, the system propagator product in the integrand of Eq. (6.27) has a small magnitude if the path $s_0, \ldots, s_N$ is very jagged. In the language of electronic transitions, the weight of a configuration that changes electronic state many times is very small. According to Eq. (6.27), this weight reflects simply the “penalty” associated with quantum transitions and is independent of the spatial location of a trajectory at these transition instants.

Eq. (6.26) on the other hand uses propagators whose weights depend on the position of the classical particle. This dependence is beneficial in two ways: First, the coupling between quantum states (e.g. diabatic surfaces) decays rapidly away from (avoided) crossing configurations. Eq. (6.26) insures that no quantum transitions will be allowed in regions of negligible coupling, thus eliminating large numbers of unnecessary paths. Second, Eq. (6.26)
discourages transitions accompanied by costly solvent reorganization. These features allow elimination of the vast majority of system paths, thus resulting in a dramatic decrease of computational cost. The phase form of the LPI expression, Eq. (6.27), cannot take advantage of such dynamic path elimination.

Systematic procedures for filtering through the vast space of paths have been described in detail in the context of path integral calculations augmented by the Feynman-Vernon influence functional (see Chapter 3 and Refs. [11, 24-26]). It is straightforward to adapt these schemes to the present situation. Consider, for example, a trajectory that starts at the coordinate $x(0)$ in quantum state 1. At the end of the first path integral time step, the trajectory position has the value $x(\Delta t)$. Suppose the given path attempts to switch the electronic state to 2. If the potential energy at $x(\Delta t)$ is very high in this state, the propagator element will have a relatively small but still acceptable weight, so one continues by propagating the trajectory for a second time step to the value $x(2\Delta t)$, which happens to be a point of low energy for state 2 but a high energy value for state 1. If the system path attempts to move the trajectory back to state 1, the product of propagator weights may drop below the acceptable weight threshold. When this happens the path is dropped and the next candidate from the set of paths is considered. When the coupling between system and solvent is strong, the vast majority of attempted path configurations are rejected within a few time steps, such that the number of retained paths eventually grows slowly (rather than exponentially) with the number of path integral slices.

Further, the form of Eq. (6.26) is amenable to iterative Monte Carlo [27-30] (IMC) algorithms. If the quantum system consists of several degrees of freedom, the use of the complete space of DVR coordinates as possible coordinates of the quantum paths should be wasteful. In its simplest form, IMC can be employed simply to preselect statistically important system coordinates from which quantum paths can be constructed as described above. A full
implementation of IMC will incorporate importance sampling in system path space into the QCPI approach, extending its feasibility to systems with several quantum particles.

### 6.4 Iterative Evaluation of the Quantum-Classical Path Integral

We now discuss various procedures for the numerical evaluation of QCPI expressions. The ideas presented in this section can be adapted to any of several path integral formulations involving classical trajectories. We assume that the phase space density of the classical particles is available.

The QCPI expression (Eq. (6.26) or (6.27) in the case of the LPI approximation with a Wigner weight or its fully classical bath variant, or a coherent state quasiclassical or FBSD approximation) has the form

\[
\rho_{\text{rel}}(s^+_N, N\Delta t) = \int dx_0 \int dp_0 P(x_0, p_0) Q(s^+_N, x_0, p_0; N\Delta t)
\]

(6.28)

where \( Q(s^+_N, x_0, p_0; N\Delta t) \) is the quantum influence function, i.e. the sum with respect to system paths, which also depends on the classical dynamics of the bath from the given initial condition \( x_0, p_0 \). For notational convenience we assume a factorizable initial condition, such that

\[
W(s^+_0, x_0, p_0) = \rho_{\text{rel}}(s^+_0) P(x_0, p_0).
\]

(6.29)

For concreteness, we describe the iterative QCPI methodology for the phase version of the LPI expression, Eq. (6.27). The procedure that follows is straightforwardly adapted to the solvent-dependent propagator expression, Eq. (6.26), and to any other QCPI formulation.

As explained in detail in Chapter 5 and seen from Eq. (6.26) or (6.27), every initial condition gives rise to a trajectory along each system path \( s^+_0, \ldots, s^+_{N-1} \), i.e., \( M^{2N} \) trajectories if the system is represented in terms of \( M \) states/sites. If \( M \) is small, as in the case of electron transfer dynamics involving two or three states, and the quantity of interest requires propagation for a relatively small number of time steps \( (N - 10) \), the direct summation with path filtering probably
is the most efficient way to proceed. If, however, the information sought requires long time propagation, one needs to resort to an iterative approach. Below we describe the adaptation of the iterative tensor propagator formulation of the path integral to the calculation of the quantum influence function within the QCPI framework.

In the limit of a truly classical bath, each trajectory is practically unperturbed by the interaction with the quantum subsystem. In this limit the classical path approximation is excellent. Because in this limit the classical trajectory is independent of the system path, there is a single trajectory from each initial condition and the classical phase in Eq. (6.27) is a function of \( x_0, p_0 \). It is then straightforward to evaluate the path sum via the following iterative procedure:

\[
Q\left(s^\pm_{k+1}, x_0, p_0; (k+1)\Delta t\right) = \int ds_k^\pm \left| s^+_{k+1} \right| e^{-i\hat{H}_0 \Delta t / \hbar} \left| s^+_{k} \right| Q\left(s^\pm_{k}, x_0, p_0; k\Delta t\right) \left| s^-_{k} \right| e^{i\hat{H}_0 \Delta t / \hbar} \left| s^-_{k+1} \right|
\]

\[
\times e^{\frac{i}{\hbar} \int_{t_k}^{t_{k+1}} \left[-V\left(s^+_{k}, t\right) - V\left(s^-_{k}, t\right)\right] dt - \frac{i}{2\hbar} \int_{t_k}^{t_{k+1}} \left[-\left[\delta_{s^+_{k}, t}\right] - \left[\delta_{s^-_{k}, t}\right]\right] dt}.
\]

(6.30)

For each trajectory, Eq. (6.30) requires the same effort as the bare quantum system, i.e., the storage of \( M^2 \) values for each trajectory. Since the solvent is assumed to behave classically at the given temperature, one may replace the Wigner function by its classical limit, i.e. the classical Boltzmann factor.

If the solvent deviates from fully classical behavior, one must take into account the “back reaction”, i.e. the influence of the quantum system on the solvent trajectory. The dependence of the bath trajectory on the system path leads to the proliferation of trajectories, whose number (from each initial condition) generally equals the number of system paths. (Of course certain symmetry considerations may reduce somewhat the number of distinct trajectories.) This trajectory proliferation, which appears to obviate the iterative decomposition of the path integral, is the quantum-classical manifestation of solvent-induced memory, a concept familiar in system-bath dynamics [31]. Our goal is to develop an iterative procedure for propagating the quantum influence function, exploiting the decoherence properties of the solvent.
The coordinates of a solvent trajectory depend on the entire history of the force exerted by the quantum particle. The time-integrated potential along such a trajectory augments the quantum mechanical amplitude along the particular system path. Our analysis of the influence functional in Chapter 5 showed that in the case of a dissipative bath, the sum of these phase factors with respect to all trajectories makes a contribution that involves only the path’s recent history. This means that the details of the system force in the distant past, while altering the coordinates of an individual bath trajectory and thus changing the value of the quantum influence function, will vanish in the ensemble average and thus will not affect the value of the system’s reduced density matrix. As a result, we may ignore the dependence of a trajectory on each system path, except for a segment of the path (of length equal to the memory or decoherence time) immediately preceding the time of interest.

Suppose the memory (or decoherence) time is $\tau_{\text{mem}} = m\Delta t$. Starting with a pair of solvent phase space coordinates $x_0, p_0$, which are selected via a Monte Carlo procedure with the sampling function $P$, we generate all trajectories that result from the system force along the $M^{2(m+1)}$ path segments $s^x_0, s^x_1, \ldots, s^x_m$. (Note that we also need to specify the coordinates of $s^x_m$ to fully specify a trajectory that reaches the time $m\Delta t$ because the force acting on a trajectory is obtained from the system values at both interval endpoints.) We define the rank-$2m$ path tensor

$$R_{m+1}(s^x_0, s^x_1, \ldots, s^x_m; x_0, p_0) = \left\langle s^x_0 \left| e^{-iH_s\Delta t/\hbar} \right| s^x_1 \right\rangle \left\langle s^x_1 \left| e^{-iH_s\Delta t/\hbar} \right| s^x_2 \right\rangle \cdots \left\langle s^x_{m-2} \left| e^{-iH_s\Delta t/\hbar} \right| s^x_{m-1} \right\rangle \left\langle s^x_{m-1} \left| e^{-iH_s\Delta t/\hbar} \right| s^x_m \right\rangle$$

$$\times e^{-i\int_{x_0(0)}^{x_0(t)} V(x_0, s_t) ds_t + \sum_{i=1}^{2m} \int_{s_{i-1}(0)}^{s_{i-1}(t)} V(x_0, s_t) ds_t - \frac{\hbar}{2m} \int_{x_0(t)}^{x_0(t)} (s_m')^2}$$

$$\times e^{\frac{\hbar}{2m} \int_{x_0(0)}^{x_0(t)} V(x_0, s_t) ds_t + \sum_{i=1}^{2m} \int_{s_{i-1}(0)}^{s_{i-1}(t)} V(x_0, s_t) ds_t + \frac{\hbar}{2m} \int_{x_0(t)}^{x_0(t)} (s_m')^2}$$

(6.31)

(Note that by relabing each realization of system path coordinates as a path $\ell$, this tensor can be stored as a vector.) We construct the propagator tensor of rank $2(m+1)$.
\[ T_m \left( s_0^+, s_1^+, \ldots, s_m^+; x_0, p_0 \right) = \left\langle s_m^+ e^{-iH_{\Delta t}/\hbar} s_{m-1}^+ \right\rangle \left\langle s_{m-1}^+ e^{-iH_{\Delta t}/\hbar} s_m^+ \right\rangle \times e^{i \int_{-\Delta t/2}^{\Delta t/2} v(s_{m+1}, t^{'}) dt^{'}} \left\langle s_m^+ e^{-iH_{\Delta t}/\hbar} s_{m+1}^+ \right\rangle \]

\[ = e^{i \int_{-\Delta t/2}^{\Delta t/2} v(s_{m+1}, t^{'}) dt^{'}} \left\langle s_m^+ e^{-iH_{\Delta t}/\hbar} s_{m+1}^+ \right\rangle \]

(6.32)

This propagator is used to propagate forward by one time step according to the matrix-vector multiplication

\[ R_m \left( s_0^+, s_1^+, \ldots, s_m^+; x_0, p_0 \right) = \int ds_T \times T_m \left( s_0^+, s_1^+, \ldots, s_m^+, x_0, p_0 \right) R_{m+1} \left( s_0^+, s_1^+, \ldots, s_m^+; x_0, p_0 \right). \]  

(6.33)

(We continue to use integral notation for the system coordinate for convenience. Since the system is represented in terms of discrete coordinates which represent electronic states or DVRs, each such integral is a sum with respect to \( M^2 \) forward/backward values, which can be thought of as a quadrature approximation to the integral.) To continue, the trajectories need to be propagated by an additional time step with the forces corresponding to the coordinates \( s_1^+, \ldots, s_{m+1}^+ \). This step would increase the number of trajectories by a factor of \( M^2 \). However, the assumption of a memory time equal to \( m\Delta t \) implies that the force at \( s_0^+ \) will not affect the value of the reduced density matrix at the time \( (m+1)\Delta t \). We thus choose at random one of the \( M^2 \) force values at \( s_0^+ \) and retain the \( M^{2m} \) corresponding trajectories. Propagation of these by one time step to the time \( (m+1)\Delta t \) with the system forces at \( s_1^+, \ldots, s_m^+ \) (and the chosen \( s_0^+ \)) gives rise to \( M^{2(m+1)} \) trajectories. Constructing the propagator tensor

\[ T_{m+1} \left( s_1^+, \ldots, s_{m+1}^+; x_0, p_0 \right) = \left\langle s_{m+1}^+ e^{-iH_{\Delta t}/\hbar} s_m^+ \right\rangle \left\langle s_m^+ e^{-iH_{\Delta t}/\hbar} s_{m+1}^+ \right\rangle \times e^{i \int_{-\Delta t/2}^{\Delta t/2} v(s_{m+1}, t^{'}) dt^{'}} \left\langle s_m^+ e^{-iH_{\Delta t}/\hbar} s_{m+1}^+ \right\rangle \]

leads to the following propagated result,

\[ R_{m+1} \left( s_0^+, s_1^+, \ldots, s_{m+1}^+; x_0, p_0 \right) = \int ds_T \times T_{m+1} \left( s_0^+, s_1^+, \ldots, s_{m+1}^+, x_0, p_0 \right) R_m \left( s_0^+, s_1^+, \ldots, s_m^+; x_0, p_0 \right). \]  

(6.34)

(6.35)
Repeating the operations of the last step one can propagate the array of paths forward by any number of time steps. Note that the number of trajectories remains equal to \( M^{2(m+1)} \). At each step in the propagation the quantum influence function is extracted from the sum

\[
Q(s^+_N, x_0, p_0; N \Delta t) = \int ds_{N+1-m}^+ \cdots \int ds_{N+1}^+ R_N(s_{N+1-m}^+, \ldots, s_N^+; x_0, p_0),
\]

which is stored. Once the desired propagation time is reached, the iteration is repeated from a new \( x_0, p_0 \) pair. The Monte Carlo average of the quantum influence functions gives the reduced density matrix,

\[
\rho_{\text{tot}}(s_N^+; N \Delta t) = \int dx_0 \int dp_0 Q(s_N^+, x_0, p_0; N \Delta t), \quad N = m, m+1, \ldots
\]

In practice, the memory length \( m \) is determined by convergence.

The simplest version of the iterative QCPI scheme corresponds to \( m=1 \). This case involves the calculation and storage of \( M^4 \) trajectories from the forces corresponding to the forward-backward coordinates of each pair of adjacent time points. In this case the tensors \( R_k \) have rank 2 and the propagator tensors \( T_k \) have rank 4. In this case the storage and operations of the iterative propagation is the same as in the propagation of the bare system or the system under the driving of the free solvent trajectory (the classical path QCPI approximation). In this case the only additional cost compared to the classical path model is the computation of \( M^4 \) classical trajectories. For \( m>1 \) the iterative QCPI method utilizes tensors of higher rank.

An even less expensive variant of the \( m=1 \) procedure is the random hop QCPI model discussed in Chapter 5. This proceeds by propagating a single trajectory, chosen randomly out of the \( M^4 \) possible trajectories that arise from two system coordinates at two adjacent time points. This procedure provides a crude correction to the classical path approximation by allowing the solvent trajectory to depend on the system path. Finally, if the solvent trajectory is assumed
independent of the system coordinates, the method reduces to the classical path QCPI approximation, Eq. (6.30).

If the solvent-induced memory spans many path integral time steps, the computational cost of the iterative QCPI methodology becomes rather high. It is possible to reduce dramatically the storage and required number of operations by taking advantage of path weights. As already discussed in section III, a finite basis representation of the system Hamiltonian leads to propagators that decay to zero with increasing endpoint distance. This causes the weight of a path to be strongly dependent on the number of its kinks and the spatial regions it explores. These ideas have been described in detail in the context of the iterative path integral methodology developed by our group to propagate a system in the presence of the analytically available influence functional (see Chapter 3 and Refs [11, 24-26]), and have also been exploited through the development of IMC methods [27-30]. In the present case there are two possibilities, corresponding to the formulations of Eq. (6.26) and (6.27). The simpler “phase” QCPI procedure can benefit from trajectory-independent filtering, whereby a set of statistically significant path segments is constructed at the start of the calculation and stored for subsequent use. (akin to the procedure of Chapter 3 or Ref [25]). The selection criterion in this case is simply the weight of a system propagator matrix element. A more sophisticated procedure [26] will be required if one implements trajectory-dependent criteria as dictated by Eq. (6.26). Such a procedure should eliminate a much larger number of system paths, reducing the storage requirements of the scheme and the number of trajectories to be integrated. However, the required filtering would need to be repeated for each trajectory initial condition. The calculations reported in section 6.5 have been performed either by treating all path segments explicitly or by implementing simple trajectory-independent path filtering [25].

Last, we suspect that the iterative QCPI methodology can be made much more powerful by exploiting renormalization group ideas which allow the path integral time step to be increased
when handling distant correlations between time points [32]. This prospect is particularly appealing in the case of the QCPI, because the classical part of the solvent effect on the system is entirely local in time, while the nonlocal quantum contributions tend to be small if the solvent is indeed nearly classical. These ideas will be pursued in future work to further increase the efficiency of the iterative QCPI scheme.

6.5 Numerical Examples

We illustrate the iterative QCPI methodology with calculations on symmetric and asymmetric dissipative two-level systems (TLS). The quantum system is described by the Hamiltonian

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

(6.38)

where \( \sigma_x \) and \( \sigma_z \) are the standard \( 2 \times 2 \) Pauli spin matrices. If the absence of an energy bias ( \( \varepsilon = 0 \) ) the bare TLS is characterized by the tunneling splitting \( 2\hbar \Omega \). The TLS is coupled to a harmonic bath described by the Hamiltonian

\[
H_b = \sum_j \left( \frac{\hat{p}_j^2}{2m} + \frac{1}{2} m\omega_j^2 \hat{x}_j^2 - c_j \sigma_z \hat{x}_j \right)
\]  

(6.39)

We assume that the system is initially in state 1 and that the bath is at thermal equilibrium at the temperature \( k_B T = \beta^{-1} \). As in the previous chapter, we use the common Ohmic form to model the spectral density of the bath (Eq. (3.4)) with \( q_0 \) set to two. We discretized the bath into a sum of 60 oscillators whose frequencies and coupling coefficients are evaluated using a logarithmic discretization of the spectral density with a maximum frequency given by \( \omega_{\text{max}} = 4\omega_0 \).

The QCPI calculations employed a Monte Carlo sampling of 60,000 phase space points. We report the population of state 1 as a function of time within the classical path QCPI approximation, the simple random hop QCPI model and the iterative evaluation of the QCPI
expression which includes the nonlocal quantum mechanical contributions from the bath. To provide a challenge to the method, we choose parameters that correspond to a highly quantum mechanical bath and/or strong system-bath coupling, for which the classical path model does not provide a good approximation. The discrete bath QCPI results are compared to numerically exact results obtained using the iterative path integral methodology with the analytical Feynman-Vernon influence functional. For clarity, we do not show statistical error bars in the figures. The standard deviation of the QCPI results generally did not exceed the size of the markers used in the figures. The figures report the population of state 1, whose initial value is unity.

Figure 28 reports results for a symmetric TLS \((\epsilon = 0)\) coupled to a bath with \(\omega_c = 2.5\Omega\) at a temperature \(h\Omega\beta = 2.5\). The Kondo parameter is \(\xi = 0.6\). These conditions correspond to a moderately quantum mechanical bath coupled with significant strength to the TLS. As a result, the classical path approximation leads to rather poor results, exaggerating the TLS coherence. The path integral calculation was performed with the time step \(\Delta t = 0.25\Omega^{-1}\). As is seen in Fig. 1, the random hop QCPI model captures some of the residual decoherence arising from the quantum mechanical bath, yielding results very similar to those obtained with the \(m=1\) version of the iterative procedure. With increasing memory length, the iterative QCPI method gradually includes these decoherence effects and converges with \(m=6\), yielding results indistinguishable from those obtained from the exact calculation with the analytical Feynman-Vernon influence functional. No path filtering was necessary in this case.

Next, we present results for an asymmetric TLS with \(\epsilon = \hbar\Omega\). The first such calculation employs a weakly dissipative bath with parameters \(\omega_c = 7.5\Omega\), \(\xi = 0.1\) at a low temperature corresponding to \(h\Omega\beta = 5\). The path integral time step is \(\Delta t = 0.25\Omega^{-1}\). Since \(\hbar\omega_c\beta = 37.5\), the majority of bath degrees of freedom are practically at zero temperature and thus quantum mechanical effects should be very pronounced. Indeed, Figure 29 shows that the classical path
approximation leads to a poor description of the dynamics, predicting incorrect populations at long times. The random hop model captures some of the quantum nonlocality, and the $m=1$ version of the iterative QCPI methodology, which requires matrices of the same dimension as the bare TLS (but 16 times more trajectories than the random hop model) produces results that are halfway between those of the classical path approximation and the exact quantum mechanical results. The converged $m=5$ QCPI results are indistinguishable from those of the exact calculation.

Figure 30 shows results for the asymmetric TLS strongly coupled ($\xi=1.2$) to a slower bath ($\omega=2.5\Omega$) at an intermediate temperature ($\hbar\Omega\beta=1$). The quantum nonlocality is rather large and is crucial to the dynamics. The neglect of this strictly quantum mechanical effect in the classical path and random hop approximation leads to incorrect populations that approach $\frac{1}{2}$ at long times, failing to produce the correct equilibrium behavior. The inclusion of quantum nonlocality via the iterative QCPI scheme gradually corrects the evolution of the density matrix. The QCPI calculation converged with $m=10$ using a path integral time step $\Delta t=0.125$. Because of the somewhat long memory length, the QCPI calculation was performed with trajectory-independent path filtering. This procedure retained about $1.25\times10^7$ system path segments out of a total of $2^{30}=1.05\times10^6$ possible such segments. As discussed in other work, we expect the fraction of surviving paths to be much lower in longer memory calculations.

## 6.6 Concluding Remarks

In this chapter we have presented a QCPI formulation suitable for numerical calculations. The derived QCPI expression uses a small time step $\delta t$ for the dynamics of the classical particles, which is given by the velocity Verlet integrator, and a much larger step $\Delta t$ in the path integral slicing. The trajectories experience a force from the quantum system that acts in a symmetric fashion, being given by the value of the nearest time point within each time interval.
By using finite matrix representations of the system Hamiltonian, the quantum amplitude factor in the QCPI expression has a magnitude that is strongly dependent on the smoothness of the quantum path. This “hopping penalty” is both intuitively appealing and practically significant, virtually eliminating contributions from the vast majority of system paths which are very kinky. In addition to the standard phase version, where the interaction enters through a complex exponential involving the time-integrated system-bath potential, we obtained an expression in which the system propagators depend on the instantaneous values of the trajectory. This dependence implies that the probability of a given system path depends on the amount of solvent reorganization accompanying the required state changes. These features virtually eliminate the vast majority of system paths, which have negligible weight.

Under near-classical conditions, the main effect of the bath on the quantum system is captured by the free bath trajectory, which acts as a driving term for the system. This memory-free contribution is a classical decoherence mechanism for the system. We find that the classical path QCPI approximation, which becomes exact in the limit of a truly classical bath, yields semi-quantitative results when the bath is at relatively high temperatures and/or the system-bath coupling is weak. A very simple random hop QCPI approximation, in which trajectories experience the force from a randomly chosen state at each path integral time step, introduces some of the “back reaction” into the classical dynamics of the bath, improving the classical path QCPI approximation. Both of these approximate schemes are very inexpensive; the classical path approximation requires the calculation of a single trajectory from each initial condition, while the random hop model employs a separate (length $\Delta t$) classical trajectory for each system propagator element in the iteration.

Further improvements are possible via an iterative procedure for evaluating the QCPI expression, which accounts for the effects of memory (including quantum nonlocality) over $m$ path integral time steps via a propagator tensor whose rank increases with $m$. At the $m=1$ level
the propagator size is no larger than that required to propagate the bare quantum system, although it does require the calculation of more trajectories compared to the classical path or random hop approximations. As the memory length included in the calculation increases, the dimensions of the full propagator increase exponentially, but the propagator size can be decreased dramatically by filtering out statistically insignificant system paths. The iterative QCPI scheme converges to the full QCPI result. The QCPI methodology can be used in conjunction with a classical treatment of the solvent at any level, implying that semiclassical treatments are also possible and should in general offer higher accuracy.

Based on the physically appealing structure of the QCPI formulation and the encouraging numerical results presented in this work, we are optimistic about the feasibility of QCPI calculations of electron or proton transfer (and nonadiabatic processes in general) in solution and in biological molecules. The crucial question in this regard is whether the classical path QCPI result provides a reasonably accurate result that can be corrected with modest effort. Equilibrium quantum-classical path integral calculations suggest that a fully classical single-bead treatment of atoms with the mass of carbon or oxygen leads to quantitative results, and we hope that this behavior will also be observed in the time domain. Calculations on chemical systems will be required to answer these questions definitively. Work along these lines is in progress in our group.
6.7 Figures

Figure 28 Population of state 1 for a symmetric TLS for $\omega = 2.5\Omega$, $\hbar \beta = 2.5$, $\xi = 0.6$.

Figure 29 Population of state 1 for an asymmetric TLS with $\epsilon = \hbar \Omega$ coupled to a bath with $\omega_c = 7.5 \Omega$ and $\xi = 0.1$ at the temperature $\hbar \Omega \beta = 5$. Green line: classical path approximation. Orange line: random hop model. Blue line: iterative QCPI calculation with $m = 1$. Red markers: converged iterative QCPI calculation with $m = 5$. Black line: exact results obtained via the iterative path integral methodology based on the analytical Feynman-Vernon influence functional.
Figure 30 Population of state 1 for an asymmetric TLS with $\epsilon = \hbar \Omega$ coupled to a bath with $\omega_c = 2.5\Omega$ and $\xi = 1.2$ at the temperature $\hbar \Omega \beta = 1$. Green line: classical path approximation. Orange line: random hop model. Blue line: iterative QCPI calculation with $m = 1$. Purple dashed line: iterative QCPI calculation with $m = 4$. Red markers: converged iterative QCPI calculation with $m = 10$ using $1.25 \times 10^3$ system path segments in the propagation. Black line: exact results obtained via the iterative path integral methodology based on the analytical Feynman-Vernon influence functional.
References


Chapter 7 Conclusion

Feynman’s path integral approach provides a clear picture of the dynamics of quantum systems and approaches classical mechanics in the limit of $\hbar \to 0$. We use this formulation to study the transfer of charge across a molecular bridge coupled to a phonon bath by adding path segments spanning the nonlocal memory length induced by the system-bath interaction. The total set of such paths grows exponentially with the memory span, but by only including paths of significant weight, we counter this exponential growth and still obtain accurate results. From this study, we learn that the bath has a moderate effect on the conductance of a molecular wire if the incoming electron energy falls within the wire’s energy band. On the other hand, if the incoming energy is outside the wire’s energy band, the conductance is greatly enhanced by the bath interaction resulting in a conductance independent of molecular wire length.

We go on and use path integrals in the study of a quantum system coupled to an environment composed of heavier, classical like particles. In the strictly classical limit, defined as high temperature and/or weak system-bath coupling, the classical system evolves classically independent of any system-bath coupling. The classical trajectories are fed back to the quantum system as a time-dependent field term in its Hamiltonian. In the extreme limit of strong system-bath coupling and low temperature, the classical degrees of freedom evolve classically according to a driving force term given by the particular system forward/backward path. In turn, the classical response is felt by the quantum system because its Hamiltonian depends parametrically on the varying classical coordinate. This behavior is the manifestation of nonlocal memory effects in the dynamics of the quantum system. For problems of interest, we expect the classical limit to be a good starting point. Corrections away from this limit are taken into account by including classical paths that span a finite memory length. We increment this length until results converge. For our calculations, we average over all initial coordinate and momenta of the classical system.
We show that the integrand of this sum is a smooth function of the coordinate and momentum and thus amenable to Monte Carlo techniques. Using this quantum-classical technique we obtain excellent agreement with well-known calculations.