To my grandfather,

William F. Leathers
ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. David Micha, for his guidance and great patience. I would also like to thank both the Department of Chemistry and the Quantum Theory Project for providing a wonderful environment for study for the past years.

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DISSIPATIVE QUANTUM MOLECULAR DYNAMICS IN GASES AND CONDENSED MEDIA: A DENSITY MATRIX TREATMENT

By

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Chair: David A. Micha
Major: Chemistry

We present a study of dissipative quantum molecular dynamics, covering several different methods of treating the dissipation. We use a reduced density matrix framework, which leads to coupled integro-differential equations in time. We then develop a numerical algorithm for solving these equations. This algorithm is tested by comparing the results to a solved model.

The method is then applied to the vibrational relaxation of adsorbates on metal surfaces. We also use this model to test approximations which transform the integro-differential equations into simpler integral equations. Our results compare well to experiment, and demonstrate the need for a full treatment without approximations. This model is then expanded to allow for electronic relaxation, as well as excitation by a light pulse. The electronic relaxation occurs on a different time scale, and is treated differently than the vibrational relaxation. Our method is shown to be general enough to handle both cases.

Our next model is light-induced electron transfer in a metal cluster on a semiconductor surface. We consider both direct electronic excitation causing electron transfer, as well as indirect transfer, where there is excitation to an intermediate state which is coupled to the electron transferred state. Our results indicate vibrational relaxation plays a small role in the direct transfer dynamics, but is still important in the indirect case.
Finally, we present a mixed quantum-classical study of the effect of initial conditions, with the goal of moving towards a method capable of treating dissipation in both quantum and mixed quantum-classical systems.
CHAPTER 1
INTRODUCTION

The main aim of this work is a study of dissipative relaxation. We are interested in the dynamics of molecular systems which are embedded in a larger whole. Focusing computational effort on the region of interest, while treating the rest of the system in a less rigorous way allows us to extract the properties of interest without facing the challenge of calculating dynamics for the entire system. This separation is achieved using a reduced density matrix formulation.\textsuperscript{1,2}

A molecule on a surface naturally lends itself to this kind of partitioning. We are interested in the dynamics of the molecule and perhaps some of the nearby surface atoms. The rest of the surface could be treated in an average way. The photodesorption of molecules from surfaces has been the subject of much experimental\textsuperscript{3–6} and theoretical study,\textsuperscript{7–20} as has the vibrational relaxation of molecules on surfaces.\textsuperscript{21–24} In this work, we expand on a model of photodesorption of CO/Cu(001), adding vibrational relaxation.

Another application of molecules on a surface is metal clusters on a semiconductor surface. When the surface is exposed to a light pulse, electronic excitation occurs which may lead to charge rearrangement and a surface photovoltage.\textsuperscript{25,26} This process is relevant to the creation of solar energy cells. In this work we study different mechanisms for this charge rearrangement.

1.1 The Reduced Density Matrix

The evolution of the reduced density matrix is governed by the Liouville-von Neumann equation of motion.\textsuperscript{27,28} When we consider energy dissipation between regions, this becomes a coupled integro-differential equation. This equation can be used directly, or treated with various approximations which may reduce it to simpler differential or integral equations. These approximations often involve the assumption of short correlation times, which is not always valid when dealing with vibrational relaxation. In this work,
Energy dissipation can occur on different time scales in the same system. Electronic relaxation is a fast process, while vibrational relaxation is often much slower. These differences lead to different treatments of the dissipation, which must both be handled by our method. It may be the case that the electronic dissipation can be treated with a simplifying approximation, while the vibrational dissipation still requires the full integro-differential equation to be solved. We call the full integro-differential treatment the delayed dissipation case, because the current state of the system depends on previous states of the system.

We are concerned with the dynamics of a part of the system, which we call the primary region, coupled to the rest of the system, which we call the secondary region. If the secondary region is large enough to be considered unchanging throughout the simulation, we will refer to it as the reservoir. Separating the whole system this way allows us to focus computational effort on the primary region. The choice of the primary region can be verified by choosing a primary region of increasing size. Figure 1-1 shows delayed dissipation from the primary region to the secondary region. There are interactions between the primary and secondary regions during times $t$ and $t'$. The physical systems considered here are molecules and clusters adsorbed on surfaces, and we study the vibrational relaxation of the frustrated translation (T-mode). Initially, we consider only two vibrational states bound in a single excited state. This simple case allows us to compare results from using the delayed dissipation treatment to those obtained by using simplifying approximations.

We then proceed to add more vibrational states, which increases the number of couplings. We also allow for additional electronic states; this leads to electronic dissipation as well as vibrational dissipation. Our numerical method is shown to be capable of handling both types simultaneously. In the case of very strong coupling, the vibrational
states may not settle into an equilibrium state during a computationally reasonable time frame. In this case, we modify our method to account for these long lasting effects.

1.2 Alternative Methods

There have been several approaches put forth for propagating the Liouville-von Neumann equation with a memory kernel. One of these methods relies on a specific parameterization of the spectral density of the reservoir. This leads to coupled differential equations for the density matrix and special ‘auxiliary’ density matrices. Another approach expands the equation in terms of Laguerre polynomials. In addition, there are also methods based on path-integral frameworks. These methods can lead to exact solutions under certain conditions.

1.3 Our Method

We choose to solve the full integro-differential equation, without the need for any approximations or expansions. The Runge-Kutta method for differential equations can be expanded for use in integro-differential equations. We have chosen this method because of its simplicity - the only operations required are addition and multiplication, so it should be readily applicable to matrix equations. This method is used to solve the Liouville-von Neumann equation, but is robust enough to solve general matrix-valued integro-differential equations. This method also has the benefit of being self-starting: the only required knowledge of the system is the initial state, along with the equations which govern the time evolution.

1.4 Two State Vibrational Relaxation

The first application involves the vibrational relaxation of molecules adsorbed on surfaces. Specifically, CO/Cu(001), CO/Pt(111), and Na/Cu(001), with model parameters from electronic structure calculations. We restrict the system to a single electronic state and consider only relaxation from the first excited vibrational state down to the ground state. This simple model allows us to test our numerical method. We compare the results from solving the full integro-differential equation to those obtained from
approximations which lead to simpler expressions. The validity of these approximations depends on the temperature of the system, as well as the strength of the coupling between the molecule and the surface. We vary the temperature and coupling strength to test the effect on the results.

1.5 Vibrational and Electronic Relaxation

Focusing only on CO/Cu(001), we expand our model to include additional vibrational states, as well as an excited electronic state. Our electronic states come from previous studies of photodesorption. The system begins in the ground state, then a light pulse is added to induce electronic and vibrational excitation. In addition to the slow vibrational relaxation, there is also a fast electronic relaxation, which we treat as a Lindblad dissipation. There is a very strong vibrational coupling between the molecules and the surface.

1.6 Direct and Indirect Electron Transfer

We consider Ag₃Si(111):H, a cluster of three silver atoms on a silicon surface, to study two mechanisms of electron transfer. In the first case, there is direct excitation by a light pulse from the initial state to the electron-transferred state. This case is very similar to the previous study of CO/Cu(001), in that there is again competing fast and slow dissipation. Here, however, the vibrational coupling of the adsorbate to the surface is much weaker, leading to different dynamics.

To study indirect electron transfer, we add an additional electronic state. This state is an intermediate - the pulse excites to this state, which can then relax either back to the ground state or to the electron transferred state.

1.7 Outline of Dissertation

Chapter 2 explores the theoretical background behind this work, and gives the equations to be solved. The Liouville-von Neumann equation for the reduced density matrix is presented. We then present several approximations for dealing with dissipation.
In chapter 3 we use a mixed quantum-classical approach to study the photodissociation of NaI. We focus here on the effects of initial conditions.

The numerical method for solving these equations is derived in chapter 4. A Runge-Kutta scheme for integrating matrix equations is proposed. We test this numerical method with a previously solved model system. We then discuss the scaling of the method, along with some limitations.

Chapter 5 uses the method to study the vibrational dissipation of molecules on metal surfaces. Here we have only one electronic state, with two vibrational states. We compare our delayed dissipation treatment with the instantaneous dissipation and markovian limits.

Chapter 6 focuses on the CO/Cu(001) system, now adding more vibrational states, along with an excited electronic state. We now have electronic dissipation, as well as vibrational. We present a method for dealing with slow vibrational relaxations, which may not decay.

In chapter 7 we study the system Ag_3Si(111):H, a system with fast vibrational relaxation. In this case, we do not have the long-lived, slow decay as in the previous chapter. We study two possible mechanisms of electron transfer. In the first case, there is direct excitation from the initial state to the final. In the second case, we allow for excitation to an intermediate state.

Chapter 8 presents the conclusions of this work, along with some suggestions for future study.

Appendix A gives an overview of the computer program we have developed, along with descriptions of the input files needed and output files generated.
Figure 1-1. Delayed dissipation between the primary region (P) and the secondary region (S). There is an excitation from the ground state (g) in the P region, then there are interactions between the excited states (e) and the secondary region during times $t$ and $t'$. 
CHAPTER 2
DENSITY MATRIX EQUATION WITH DELAYED DISSIPATION

2.1 Introduction

We are primarily concerned in this work with molecular systems coupled to metal surfaces or other large systems. It is not practical to calculate the complete dynamics of the molecular system of interest along with the entirety of its surroundings. Instead, we partition the total system into a primary region of interest (called the P-region) and a reservoir. This allows us to focus computational effort on the primary region, while including the effects of the reservoir in an average way. It may be the case that a small portion of the reservoir also deserves special attention - in this case we can further partition into a primary region, a secondary region (called the S-region), and the reservoir.

It may also be the case that we can perform an additional partitioning of the system - this time into portions which must be treated quantum mechanically, as well as portions which can be treated with classical mechanics. This situation calls for a mixed quantum-classical treatment.

In this chapter we outline the numerical framework for these partitionings. We use a reduced density matrix approach, with several different methods for dealing with energy dissipation from the primary region to the reservoir. These methods include delayed dissipation, instantaneous dissipation, and markovian dissipation. When there are classical variables in the system, we use a partial Wigner transform.

2.2 Liouville Equation for Reduced Density Matrix

When dealing with a system which may be in a mixture of states, it is useful to employ a density matrix formulation. If the system is in a mixture of states \(|\Phi_n\rangle\), with the probability of being in state \(n\) as \(P_n\), we can define the density operator as

\[
\hat{\Gamma} = \sum_n P_n |\Phi_n\rangle\langle \Phi_n|,
\]  

(2–1)
with $\sum_n P_n = 1$. These states evolve over time according to the Schrödinger equation,

$$\frac{\partial}{\partial t}\left|\Phi_n\right\rangle = -\frac{i}{\hbar}\hat{H}\left|\Phi_n\right\rangle,$$

(2–2)

where $\hat{H}$ is the Hamiltonian for the entire system. The equation of motion for the density operator is then

$$\frac{\partial \hat{\Gamma}}{\partial t} = -\frac{i}{\hbar}\left[\hat{H},\hat{\Gamma}\right].$$

(2–3)

The brackets denote a commutator, $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. The expectation value for any operator $\hat{O}$ can be determined by taking the trace with the density operator,

$$\langle \hat{O} \rangle = tr\left(\hat{\Gamma}\hat{O}\right).$$

(2–4)

It is generally not feasible to calculate the entire density operator of the system. In what follows, we consider the system as a primary region coupled to a reservoir. The primary region contains the part of the system which is of the most interest. The Hamiltonian for the whole system is broken up into a primary part, a reservoir part, and the coupling between them, as

$$\hat{H} = \hat{H}_P + \hat{H}_R + \hat{H}_{PR}.$$  

(2–5)

We can take the trace over the reservoir variables to give the reduced density operator, $\hat{\rho} = tr_R\hat{\Gamma}$. This reduced density operator describes only the primary region. The equation of motion for the reduced density operator is

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_P,\hat{\rho}\right] - \frac{i}{\hbar}tr_R\left[\hat{H}_{PR},\hat{\Gamma}\right],$$

(2–6)

which is not yet a usable equation for $\hat{\rho}$, as it still contains the complete $\hat{\Gamma}$. If there is no coupling $\hat{H}_{PR}$, then this equation is similar to Equation 2–3, with a formal solution

$$\hat{\rho}(t) = \hat{U}_P(t,t_0)\hat{\rho}(t_0)\hat{U}_P^\dagger(t,t_0)$$

(2–7)
with the time evolution operator

\[ \hat{U}_P(t, t_0) = e^{-\frac{i}{\hbar} \hat{H}_P(t-t_0)}. \] (2-8)

However, it is the last term in Equation 2–6 that governs energy dissipation from the primary region to the reservoir. It can be treated through various approximations.

### 2.3 A Master Equation

#### 2.3.1 The Interaction Picture

It will be convenient in our derivation to switch to the interaction picture. We assume that the total hamiltonian is broken up as \( \hat{H} = \hat{H}_0 + \hat{V} \), where \( \hat{V} \) is a small perturbation and \( \hat{H}_0 \) is the hamiltonian for a simpler, possibly solvable system. A state vector in the interaction picture comes from

\[ |\Phi_n(t)\rangle = \hat{U}_0(t, t_0) |\Phi_n^{(I)}\rangle. \] (2-9)

The time evolution operator here is based on the Hamiltonian with no perturbation,

\[ \hat{U}_0(t, t_0) = e^{-\frac{i}{\hbar} \hat{H}_0(t-t_0)}. \] (2-10)

The equation of motion has a similar form as the Schrödinger equation,

\[ \frac{\partial}{\partial t} |\Phi_n^{(I)}(t)\rangle = -\frac{i}{\hbar} \hat{V}^{(I)} |\Phi_n^{(I)}(t)\rangle, \] (2-11)

where \( \hat{V}^{(I)} \) is the perturbation in the interaction picture. An operator \( \hat{O} \) in the interaction picture is

\[ \hat{O}^{(I)}(t) = \hat{U}_0^\dagger(t, t_0) \hat{O} \hat{U}_0(t, t_0). \] (2-12)

Turning now to our hamiltonian in Equation 2–5, we set \( \hat{V} = \hat{H}_{PR} \) and \( \hat{H}_0 = \hat{H}_P + \hat{H}_R \), so that

\[ \hat{U}_0(t, t_0) = e^{-\frac{i}{\hbar} (\hat{H}_P + \hat{H}_R)(t-t_0)}. \] (2-13)
We then have an equation of motion similar to Equation 2–3,

$$\frac{\partial \hat{\Gamma}^{(I)}(t)}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}^{(I)}_{PR}(t), \hat{\Gamma}^{(I)}(t) \right].$$

(2–14)

Taking the trace over reservoir variables leads to an expression for the reduced density matrix in the interaction picture,

$$\frac{\partial \hat{\rho}^{(I)}(t)}{\partial t} = -\frac{i}{\hbar} tr_R \left( \left[ \hat{H}^{(I)}_{PR}(t), \hat{\Gamma}^{(I)}(t) \right] \right).$$

(2–15)

2.3.2 Projection Operator Formalism

Our goal is to develop an equation for the reduced density operator which only depends on variables in the primary region. It is then useful to define projection operators which take an operator in the full system subspace and separates it into operators in the primary region variables and operators in the reservoir variables. We define the operator $\hat{P}$ as

$$\hat{P} \hat{O} = R tr_R(\hat{O}),$$

(2–16)

where $\hat{O}$ is an arbitrary operator in both primary and reservoir variables and $\hat{R}$ is a reservoir operator, with $tr_R(R) = 1$. In what follows, we will assume that the reservoir is large enough that it stays in thermal equilibrium, which means setting $\hat{R} = \hat{R}_{eq}$. We also define the operator $\hat{Q}$ as

$$\hat{Q} = 1 - \hat{P},$$

(2–17)

so that

$$\hat{O} = \hat{P} \hat{O} + \hat{Q} \hat{O}.$$  

(2–18)

It is also worth noting that $\hat{P}^2 = \hat{P}$, $\hat{Q}^2 = \hat{Q}$, and $\hat{P} \hat{Q} = \hat{Q} \hat{P} = 0$. Returning to the density operator in the interaction picture, we have

$$\hat{\Gamma}^{(I)}(t) = \hat{P} \hat{\Gamma}^{(I)}(t) + \hat{Q} \hat{\Gamma}^{(I)}(t)$$  

$$= \hat{R}_{eq} \hat{\rho}^{(I)}(t) + \hat{Q} \hat{\Gamma}^{(I)}(t).$$

(2–19)
We can then insert this expression for $\hat{\Gamma}(I)(t)$ into Equation 2–15, giving

$$\frac{\partial \hat{\rho}(I)(t)}{\partial t} = -\frac{i}{\hbar} tr_R \left( \left[ \hat{H}_{PR}(I)(t), \hat{R}_{eq} \hat{\rho}(I)(t) + \hat{Q} \hat{\Gamma}(I)(t) \right] \right). \quad (2–20)$$

Doing the same for Equation 2–14 gives

$$\frac{\partial \hat{\Gamma}(I)(t)}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}_{PR}(I)(t), \hat{R}_{eq} \hat{\rho}(I)(t) + \hat{Q} \hat{\Gamma}(I)(t) \right]. \quad (2–21)$$

Applying $\hat{Q}$ to each side gives

$$\frac{\partial \hat{Q} \hat{\Gamma}(I)(t)}{\partial t} = -\frac{i}{\hbar} \hat{Q} \left[ \hat{H}_{PR}(I)(t), \hat{R}_{eq} \hat{\rho}(I)(t) + \hat{Q} \hat{\Gamma}(I)(t) \right], \quad (2–22)$$

which is an equation of motion for $\hat{Q} \hat{\Gamma}(I)(t)$. Along with Equation 2–20, these are a coupled set of equations for the primary region, $\hat{\rho}(I)(t)$, and the rest of the density operator, $\hat{Q} \hat{\Gamma}(I)(t)$.

The second-order solution for the equation for the reduced density operator is obtained by using the first-order solution for $\hat{Q} \hat{\Gamma}(I)(t)$. The first-order solution of Equation 2–22 comes from neglecting the $\hat{Q} \hat{\Gamma}(I)(t)$ term on the right side. This gives

$$\hat{Q} \hat{\Gamma}(I)(t) = \hat{Q} \hat{\Gamma}(I)(t_0) - \frac{i}{\hbar} \int_{t_0}^{t} dt' \hat{Q} \left[ \hat{H}_{PR}(I)(t'), \hat{R}_{eq} \hat{\rho}(I)(t') \right]. \quad (2–23)$$

Using this expression in Equation 2–20 gives

$$\frac{\partial \hat{\rho}(I)(t)}{\partial t} = -\frac{i}{\hbar} tr_R \left( \left[ \hat{H}_{PR}(I)(t), \hat{R}_{eq} \hat{\rho}(I)(t) \right] \right)$$

$$- \frac{i}{\hbar^2} \int_{t_0}^{t} dt' tr_R \left( \left[ \hat{H}_{PR}(I)(t'), \hat{Q} \left[ \hat{H}_{PR}(I)(t'), \hat{R}_{eq} \hat{\rho}(I)(t') \right] \right] \right), \quad (2–24)$$

which is an integro-differential equation for the reduced density matrix, to second order with respect to $\hat{H}_{PR}$. It is possible to formulate higher-order equations; reinserting Equation 2–23 into Equation 2–22 would give a second-order result for $\hat{Q} \hat{\Gamma}(I)(t)$, which could then be used to get a third-order equation for the reduced density matrix. This method can be iterated to give any order desired. In this work we will use the second-order expression.
2.3.3 A Master Equation

If we have a primary region-reservoir coupling which can be factored as
\[ \hat{H}_{PR} = \sum_j \hat{A}_j(P)\hat{B}_j(R), \tag{2–25} \]
where \( \hat{A}_j \) depends only on the primary region and \( \hat{B}_j \) depends only on the reservoir, we can define the reservoir correlation function as
\[ C_{jk}(t) = \langle \hat{B}_j(t)\hat{B}_k(0) \rangle_R - \langle \hat{B}_j \rangle_R \langle \hat{B}_k \rangle_R, \tag{2–26} \]
where \( \langle \hat{B}_j \rangle_R = \text{tr}_R(\hat{R}_{eq}\hat{B}_j) \). Equation 2–24 then reduces to
\[ \frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar}[\hat{H}_P + \sum_j \langle \hat{B}_j \rangle\hat{A}_j, \hat{\rho}] - \frac{1}{\hbar^2} \sum_{j,k} \int_0^t dt' C_{jk}(t-t') \left[ \hat{A}_j, \hat{U}_P(t-t')\hat{A}_k\hat{\rho}(t')\hat{U}_P^\dagger(t-t') \right] - C_{jk}^*(t-t') \left[ \hat{A}_j, \hat{U}_P(t-t')\hat{\rho}(t')\hat{A}_k\hat{U}_P^\dagger \right]. \tag{2–27} \]

This can be expressed as an integro-differential equation with a memory kernel, leading to the general form
\[ \frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar}[\hat{H}', \hat{\rho}(t)] + \int_0^t \mathcal{K}(t,t')\hat{\rho}(t')dt', \tag{2–28} \]
where \( \mathcal{K} \) is a memory kernel superoperator, and \( \hat{H}' = \hat{H}_P + \sum_j \langle \hat{B}_j \rangle\hat{A}_j. \)

In the examples to follow, we solve this equation in the energy representation. We have basis states \( \{ \phi_a \} \) so that \( H_P|\phi_a\rangle = E_a|\phi_a\rangle \), which allows us to define the elements of the reduced density matrix as
\[ \rho_{ab} = \langle \phi_a | \hat{\rho} | \phi_b \rangle. \tag{2–29} \]
The master equation in the energy representation becomes

\[
\frac{d}{dt} \rho_{ab} = -i\omega_{ab}\rho_{ab} + i\frac{\hbar}{2} \sum_c \sum_j (\hat{B}_j)(A^{(j)}_{cb} \rho_{ac} - A^{(j)}_{ac} \rho_{cb}) \\
- \sum_{cd} \int_0^t dt' [M_{cd,db}(-t' - t')e^{i\omega_{da}(t-t')} \rho_{ac}(t') + M_{ac,cd}(t - t')e^{i\omega_{bc}(t-t')} \rho_{db}(t') \\
- M_{db,ac}(-t-t')e^{i\omega_{bc}(t-t')} \rho_{cd}(t') - M_{db,ac}(t - t')e^{i\omega_{da}(t-t')} \rho_{cd}(t')],
\]

with \(\hbar\omega_{ab} = (E_a - E_b)\), and

\[
M_{ab,cd}(t) = \frac{1}{\hbar^2} \sum_{j,k} C_{jk}(t) A^{(j)}_{ab} A^{(k)}_{cd},
\]

\[
A^{(j)}_{ab} = \langle \phi_a | A_j | \phi_b \rangle.
\]

### 2.3.4 Fast Dissipation Limits

The integral term in Equation 2–28 involves previous states of the system, from the current time \(t\) back to the beginning \((t = 0)\), and we call it the delayed dissipation case.

In this section, we consider two approximations which can reduce the integro-differential equation to simpler equations, greatly reducing computation time. The first approximation is what we call the instantaneous dissipation limit. The assumption is that the dissipation occurs much faster than changes in the density matrix. When this is the case, we can make the approximation \(\rho(t') = \rho(t)\); we can then move \(\rho\) outside the integral. Applying this to Equation 2–28 gives

\[
\frac{d\hat{\rho}(t)}{dt} = -\frac{i}{\hbar} \left[ \hat{H}', \hat{\rho}(t) \right] + \hat{\rho}(t) \int_0^t K(t, t') dt',
\]

which is a differential equation. This approximation will be valid when \(K(t, t')\) is large around \(t = t'\), but negligible otherwise. The dissipative part of the master equation will have terms like

\[
- \sum_{cd} \rho_{ac}(t) \int_0^t dt' M_{cd,db}(-t' - t')e^{i\omega_{da}(t-t')}.
\]

If we make the further assumption that the dissipation is so fast that the correlation function can be described by a delta function, \(C_{mn}(t) = \delta(t)C_{mn}\), the dissipative part of
the master equation becomes
\[
\left( \frac{d\rho_{ab}}{dt} \right)_{\text{diss}} = -\sum_{cd} \sum_{mn} C_{mn} \left( A_{cd}^{(m)} A_{db}^{(n)} \rho_{ac}(t) + A_{ac}^{(m)} A_{cd}^{(n)} \rho_{db}(t) - 2 A_{db}^{(m)} A_{ac}^{(n)} \rho_{cd}(t) \right),
\]
(2–35)
which can be recognized in terms of matrices (in boldface)as
\[
\left( \frac{d\rho_{ab}}{dt} \right)_{\text{diss}} = \sum_{mn} C_{mn} \left( \rho A_{\text{n}}^{(m)} A_{\text{n}}^{(n)} \right)_{ab} + \left( A_{\text{n}}^{(m)} A_{\text{n}}^{(n)} \rho \right)_{ab} - 2 \left( A_{\text{n}}^{(n)} A_{\text{n}}^{(m)} \rho \right)_{ab} \tag{2–36}
\]
\[
= C_{mn} \left( [A_{\text{n}}^{(m)} A_{\text{n}}^{(n)}, \rho]_{+} - 2 A_{\text{n}}^{(n)} A_{\text{n}}^{(m)} \rho \right)_{ab}, \tag{2–37}
\]
where \([\cdot, \cdot]_{+}\) indicates an anticommutator. We call this form Lindblad dissipation.\(^{41,42}\)

If the upper limit of the integral in the instantaneous case can be extended, we have what we call the markovian limit. In this case, the integral term becomes a constant, and it may be possible to solve the equations exactly.

2.3.5 Diadic Formulation

It may be convenient to work in the diadic formulation, where the square matrix \(\rho\) is transformed to a column matrix, \(\rho_D\). If \(\rho\) is dimension \(n \times n\), then \(\rho_D\) will have dimension \(n^2 \times 1\). It is then possible to transform Equation 2–28 into a linear form,
\[
\frac{\partial \hat{\rho}_D(t)}{\partial t} = -\frac{i}{\hbar} H'_D \hat{\rho} + \int_0^t K_D(t, t') \hat{\rho}(t') dt'. \tag{2–38}
\]
The matrices \(H'_D\) and \(K_D\) will have dimension \(n^2 \times n^2\); the form of these matrices will depend on the method of transforming \(\rho\) to \(\rho_D\).

2.4 Quantum-Classical Treatment

2.4.1 The Wigner Transform

We use a partial Wigner transform to treat mixed quantum-classical mechanics. To begin our derivation of this method, we first discuss the full Wigner transform. The Wigner transform is used to create a phase space representation of the density operator, through a Fourier transform of an operator in coordinate space,\(^{43–46}\)
\[
\Gamma_W(P, R) = \left( \frac{1}{\hbar \pi} \right)^n \int d^n y \langle Q - y | \hat{\Gamma} | Q + y \rangle e^{2i py/\hbar}, \tag{2–39}
\]
where $P$ and $R$ are momentum and position variables respectively, and $n$ is the number of degrees of freedom. It should be noted that the $1/\hbar\pi$ factor is specific to the density operator; it is chosen to allow for a symmetry with the classical Liouville equation, as well as the Liouville-von Neumann equation. For a generic operator $\hat{O}$, the Wigner transform is

$$\hat{O}_W(P, R) = \int dy \langle Q - y | \hat{O} | Q + y \rangle e^{2ipy/\hbar}. \quad (2-40)$$

Analogous to Equation 2–4, the expectation value of an operator in the Wigner representation is

$$\langle \hat{O} \rangle = \int \Gamma_W(P, R) \hat{O}_W(P, R) dpdq. \quad (2-41)$$

The transform of the product of two operators is

$$\hat{A} \hat{B} = \hat{A}_W e^{\hbar\vec{\Lambda}/2i} \hat{B}_W, \quad (2-42)$$

where $\vec{\Lambda}$ is a bidirectional operator defined as

$$\vec{\Lambda} = \frac{\partial}{\partial P} \frac{\partial}{\partial R} - \frac{\partial}{\partial R} \frac{\partial}{\partial P}, \quad (2-43)$$

so that

$$\hat{A} \vec{\Lambda} \hat{B} = \frac{\partial \hat{A}}{\partial P} \frac{\partial \hat{B}}{\partial R} - \frac{\partial \hat{A}}{\partial R} \frac{\partial \hat{B}}{\partial P}. \quad (2-44)$$

This is often abbreviated using the Poisson bracket,

$$\{ \hat{A}, \hat{B} \} = -\hat{A} \vec{\Lambda} \hat{B}. \quad (2-45)$$

We use this definition for the product to give the transform of the commutator of two operators

$$[\hat{A}, \hat{B}] = A_W e^{h\vec{\Lambda}/2i} B_W - B_W e^{h\vec{\Lambda}/2i} A_W. \quad (2-46)$$

The transformed density operator is not itself a probability distribution, but it does have many useful properties. The distribution in one variable comes from integrating out
the other, as

\[ |\psi(R)|^2 = \int \Gamma_W(P, R) dP, \quad (2{\text{-}}47) \]

\[ |\psi(P)|^2 = \int \Gamma_W(P, R) dR. \quad (2{\text{-}}48) \]

For any function of \( R \) or \( P \), we can obtain the expectation value of the function the same way as for operators

\[ \langle \hat{A}(R) \rangle = \int \Gamma_W(P, R) \hat{A}(R) dR dP, \quad (2{\text{-}}49) \]

\[ \langle \hat{B}(P) \rangle = \int \Gamma_W(P, R) \hat{B}(P) dR dP. \quad (2{\text{-}}50) \]

### 2.4.2 Partial Wigner Transform

We begin by separating the system into a set of quantum variables, \( q = (q_1, \ldots, q_n) \), and quasi-classical variables, \( Q = (Q_1, \ldots, Q_n) \). These quasiclassical variables exhibit classical motions in terms of trajectories.\(^{47}\) The density operator is then expanded in the basis of \( Q \) as

\[ \hat{\Gamma}(t) = \int dQ \int dQ' |Q\rangle \hat{\Gamma}(Q, Q', t) \langle Q'|. \quad (2{\text{-}}51) \]

We now define new coordinates, \( R = (Q + Q')/2 \) and \( S = Q - Q' \), which allows us to define the partial Wigner transform,

\[ \hat{\Gamma}_W(P, R, t) = \left( \frac{1}{\hbar \pi} \right)^n \int d^n S \langle R - S/2|\hat{\Gamma}|R + S/2\rangle e^{2iPS/\hbar}. \quad (2{\text{-}}52) \]

This is a partial transform, as \( \Gamma_W(P, R, t) \) is still an operator in the quantal variables, \( q \). For the equation of motion, we take the partial Wigner transform of Equation 2–3 to give\(^{48–50}\)

\[ \frac{\partial \hat{\Gamma}_W}{\partial t} = -\frac{i}{\hbar} \hat{H}_W \hbar \frac{\partial}{\partial R} + \frac{i}{\hbar} \hat{\Gamma}_W e^{\hbar \hat{X}/2i} \hat{H}_W. \quad (2{\text{-}}53) \]

To first order in \( \hbar \frac{\partial}{\partial R} \) this expression can be approximated as\(^{47,55}\)

\[ \frac{\partial \hat{\Gamma}_W}{\partial t} = -\frac{i}{\hbar} \{ \hat{H}_W, \hat{\Gamma}_W \} + \frac{1}{2} \left( \{ \hat{H}_W, \hat{\Gamma}_W \} - \{ \hat{\Gamma}_W, \hat{H}_W \} \right). \quad (2{\text{-}}54) \]
This approximation will be valid when the quantum variables have much smaller masses than those of the quasi-classical.$^{52-54}$

The Hamiltonian for the entire system is broken up, as

\[ \hat{H} = \hat{H}_{cl}(Q) + \hat{H}_{qu}(q) + \hat{H}_{qu-cl}(Q, q), \]  

(2–55)

where \(\hat{H}_{cl}(Q)\) is the Hamiltonian for the classical part, \(\hat{H}_{qu}(q)\) is the Hamiltonian for the quantum part, and \(\hat{H}_{qu-cl}(Q, q)\) is the coupling between them. The classical Hamiltonian consists of kinetic and potential terms,

\[ \hat{H}_{cl} = \frac{P^2}{2M} + V(Q) \hat{I}, \]

(2–56)

where \(P\) is the classical momentum operator and \(V(Q)\) is the potential. Taking the partial Wigner transform over the classical variables gives

\[ \hat{H}_{W} = \frac{P^2}{2M} + V(R) + \hat{H}_{qu}(q) + \hat{H}_{qu-cl}(R, q) \]

(2–57)

We now define

\[ \hat{H}_{qu}' = \hat{H}_{qu}(q) + \hat{H}_{qu-cl}(R, q), \]

(2–58)

\[ V' = V(R) + \hat{H}_{qu-cl}(R, q), \]

(2–59)

which leads to the equation of motion

\[ \frac{\partial \hat{\Gamma}_W}{\partial t} = -\frac{i}{\hbar} [\hat{H}_{qu}', \hat{\Gamma}_W] - \frac{P}{M} \cdot \frac{\partial \hat{\Gamma}_W}{\partial R} + \frac{1}{2} \left( \frac{\partial V'}{\partial R} \cdot \frac{\partial \hat{\Gamma}_W}{\partial P} + \frac{\partial V'}{\partial P} \cdot \frac{\partial \hat{\Gamma}_W}{\partial R} \right). \]

(2–60)

This expression can be simplified$^{47,55}$ by introducing the Hellmann-Feynman force \((F_{HF})\),

\[ F_{HF} = -\frac{tr[\hat{\Gamma}_W \partial V'/\partial R]}{tr[\hat{\Gamma}_W]} \]

(2–61)

where the trace is over the quantum variables. This leads to

\[ \frac{\partial \hat{\Gamma}_W}{\partial t} = -\frac{i}{\hbar} [\hat{H}_{qu}', \hat{\Gamma}_W] - \frac{P}{M} \cdot \frac{\partial \hat{\Gamma}_W}{\partial R} - F_{HF} \cdot \frac{\partial \hat{\Gamma}_W}{\partial P}. \]

(2–62)
This equation has been solved previously using a relax and drive algorithm.\textsuperscript{47,55}

2.4.3 Quantum-Classical Treatment with Dissipation

If there are no classical terms, Equation 2–62 reduces to Equation 2–3. If we again partition the quantum section into a primary region and a reservoir, the first term on the right hand side of Equation 2–62 will be replaced with an expression like the right side of Equation 2–27, with $\hat{\rho}$ replaced by $\hat{\rho}_W$. If there were a coupling between the quantum and classical sections which leads to dissipation, more complicated expressions would ensue.
CHAPTER 3
QUANTUM-CLASSICAL TREATMENT

3.1 Introduction

Full quantum treatments can be challenging and computationally time consuming for even moderately sized systems. It is often possible to separate a system into a part which can be treated with classical mechanics, along with a part that must be treated quantum mechanically.

In this chapter, we explore a mixed quantum-classical method, and apply it to the dissociation of a diatomic molecule. This system has been studied previously, and here we focus on the effects of choosing different initial conditions.

In previous work\textsuperscript{47,55}, the initial phase space is a uniform square grid. We call this case grid initial conditions. We consider an initial phase space consisting of a classical harmonic orbit. We call this case orbit initial conditions. The orbit phase space consists of points along an ellipse.

3.2 Dissociation of NaI

We consider here the dissociation of NaI, a process which has been previously studied using the quantum-classical treatment\textsuperscript{47,55}, as well as quantum mechanically using wavepackets.\textsuperscript{56} It has also been studied experimentally.\textsuperscript{57} Here we focus on the effect of initial conditions.

We consider two electronic states, the neutral state and the ionic. Expanding Equation 2–62 in this 2 × 2 basis, and discretizing \( P \) and \( R \) gives the matrix equation

\[
\frac{\partial \Gamma_W(P, R)}{\partial t} = -\frac{i}{\hbar} [\mathbf{H}_{qu}, \Gamma_W(P, R)] - \frac{P}{M} \frac{\partial \Gamma_W(P, R)}{\partial R} - F_{HF} \cdot \frac{\partial \Gamma_W(P, R)}{\partial P}. \tag{3–1}
\]

The phase space, made up of the set of discretized \( \{P_i, R_i\} \), also evolves in time, following classical trajectories according to

\[
\frac{dR_i}{dt} = \frac{P_i}{M}, \tag{3–2}
\]

\[
\frac{dP_i}{dt} = -F_{HF}(P_i, R_i). \tag{3–3}
\]
These expressions, along with Equation 3–1 are a coupled set of differential equations which must be solved together for each point in phase space.

The matrix elements of the Hamiltonian are

\begin{align*}
H_{11}(R) & = A_1 \exp[-\beta_1(R - R_0)], \\
H_{22}(R) & = [A_2 + (B_2/R)^8] \exp(-R/\rho) - 1/R - \lambda^+ + \lambda^-/2R^4 \\
& - C_2/R^6 - 2\lambda^+\lambda^-/R^7 + \Delta E_0, \\
H_{12}(R) & = A_{12} \exp[-\beta_{12}(R - R_x)^2].
\end{align*}

State 1 is the neutral state, and State 2 is the ionic. We assume that the system is initially in the lowest vibrational level in the ionic state, and undergoes an instant excitation to the neutral state. There is no population remaining in the ionic state, and no coherence, so that \( \Gamma_{22} = \Gamma_{12} = \Gamma_{21} = 0 \). Note that we have omitted the \( W \) subscript here for clarity. We calculate the initial value of \( \Gamma_{11} \) from

\[ \Gamma_{11}(P, R) = \frac{1}{\pi} \left[ -\left( \frac{R - R_0}{\sigma} \right)^2 - \sigma^2(P - P_0)^2 \right], \tag{3–7} \]

where \( R_0 \) is the minimum of the ionic curve and \( P_0 \) is the initial \( P \), taken to be zero. Values for other parameters used are shown in Table 3-1. A plot of the potentials is shown in Figure 3-1.

The ionic population comes from \( \Gamma_{22} \),

\[ P_I = \int dRdP \Gamma_{22}(R, P). \tag{3–8} \]

The crossing point of the curves, \( R_x \) divides the neutral population into neutral bound \( (P_{N-B}) \) for \( R < R_x \), and neutral free \( (P_{N-F}) \), the dissociated case, for \( R > R_x \), as

\begin{align*}
P_{N-B} & = \int_0^{R_x} dRdP \Gamma_{11}(R, P), \\
P_{N-F} & = \int_{R_x}^{\infty} dRdP \Gamma_{11}(R, P).
\end{align*}

\[ 33 \]
3.3 Effect of Initial Conditions

In the previous work, the initial phase space was a uniform grid, shown in Figure 3-5. Here, we choose an orbit for the initial phase space, shown in Figure 3-6. These points evolve in time according to Equations 3–2 and 3–3.

The results for the populations are shown in Figure 3-2. The populations of the neutral bound and ionic states are qualitatively similar, with the orbit method showing sharper oscillations. The population of the neutral free (dissociated) state are very similar. If we were only concerned with the yield of the photoinduced dissociation, it would not matter which initial conditions we chose.

Figures 3-3 and 3-4 show the real and imaginary parts of the quantum coherence for both the orbit and grid initial conditions. The grid method shows a larger coherence at early times, but the two methods do not give very different results. Figures 3-7 and 3-8 show the final conformation of the phase space for the grid and orbit initial conditions. The swirling nature of the phase space is similar to the phase space of classical particles in a harmonic well, like the ionic potential. The free motion, which is evident in the phase space of the grid initial conditions, does not appear here. In Figures 3-9 and 3-10 we show the average P and R, as well as their dispersions for orbit and grid initial conditions, along with full quantum results.
Table 3-1. Parameters for the NaI model.

<table>
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<th>Parameter</th>
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</tr>
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</table>

Figure 3-1. Potential curves for the NaI model
Figure 3-2. Populations for the orbit and grid initial conditions
Figure 3-3. Real part of the coherence for the orbit and grid initial conditions

Figure 3-4. Imaginary part of the coherence for the orbit and grid initial conditions
Figure 3-5. Initial form of the phase space for the grid initial conditions

Figure 3-6. Initial form of the phase space for the orbit initial conditions
Figure 3-7. Final form of the phase space for the grid initial conditions
Figure 3-8. Final form of the phase space for the orbit initial conditions
Figure 3-9. Average $P$ and $\sigma_P$ for orbit and grid initial conditions, along with full quantum results.
Figure 3-10. Average R and \( \sigma_R \) for orbit and grid initial conditions, along with full quantum results.
CHAPTER 4
NUMERICAL METHOD

4.1 A Runge-Kutta Method for Integro-Differential Equations

We begin with a general differential equation

\[ y'(t) = f(t, y(t)). \]  \hfill (4–1)

or, equivalently, the integrated form

\[ y(t) = y(t_0) + \int_{t_0}^{t} f(t', y(t'))dt'. \]  \hfill (4–2)

A Runge Kutta method for this equation from \( t_n \) to \( t_{n+1} \) has the following form \(^{58}\)

\[ k_1 = f(t_n, y(t_n)), \]

\[ k_2 = f(t_n + c_2 h, y(t_n) + h a_{21} k_1), \]

\[ k_3 = f(t_n + c_3 h, y(t_n) + h(a_{31} k_1 + a_{32} k_2)), \]

\[ \vdots \]

\[ k_m = f(t_n + c_m h, y(t_n) + h(a_{m1} k_1 + \ldots + h a_{m,m-1} k_{m-1})), \]

\[ y(t_{n+1}) = y(t_n) + h(b_1 k_1 + b_2 k_2 + \ldots + b_m k_m), \]  \hfill (4–4)

where \( m \) (an integer) is the number of stages of the method required to achieve a desired accuracy, and the \( a_{ij}, b_i, \) and \( c_i \) are real coefficients. For an example set of coefficients, see Table 4-4. The \( c_i \) satisfy the relation

\[ c_i = \sum_{j=1}^{m} a_{ij}. \]  \hfill (4–5)

We can express the \( k_i \) in a more compact form,

\[ k_i = f \left[ t_n + c_i h, y(t_n) + h \sum_{j=1}^{m} a_{ij} k_j \right], \]  \hfill (4–6)
with the constraint
\[ a_{ij} = 0, j \geq i, \] (4-7)
so that \( c_1 = 0 \). We can also write the expression for \( y(t_{n+1}) \) as
\[ y(t_{n+1}) = y(t_n) + h \sum_{i=1}^{m} b_i k_i + \mathcal{O}(h^{p+1}), \] (4-8)
where \( p \) is the order of the method. The conditions for a Runge-Kutta method to be of order \( p \) will be discussed later. We can consider the second argument of \( k_i \) as an approximation to \( y(t_n + c_i h) \),\(^{59}\) which we will call \( Y^n_i \)
\[ Y^n_i = y(t_n) + h \sum_{j=1}^{m} a_{ij} k_j, \] (4-9)
which means
\[ k_i = f(t_n + c_i h, Y^n_i), \] (4-10)
and the final expression for \( Y^n_i \) is
\[ Y^n_i = y(t_n) + h \sum_{j=1}^{m} a_{ij} f(t_n + c_j h, Y^n_j). \] (4-11)
This leads us to
\[ y(t_{n+1}) = y(t_n) + h \sum_{i=1}^{m} b_i f(t_n + c_i h, Y^n_i) + \mathcal{O}(h^{p+1}). \] (4-12)

4.1.1 Volterra Integral Equations

Before we apply Runge-Kutta techniques to our integro-differential problem, we first consider the integral case. A Volterra integral equation of the second kind has the form
\[ y(t) = g(t) + \int_{t_0}^{t} K(t, t', y(t'))dt'. \] (4-13)
Here we will restrict the discussion to the linear case
\[ y(t) = g(t) + \int_{t_0}^{t} K(t, t')y(t')dt'. \] (4-14)
If we wish to propagate this equation from $t_n$ to $t_{n+1}$, it is broken into two parts,

\begin{equation}
y(t_{n+1}) = q_n(t_{n+1}) + r_n(t_{n+1}),
\end{equation}

\begin{equation}
q_n(t) = g(t) + \int_{t_0}^{t_n} K(t, t') y(t') dt', \tag{4–16}
\end{equation}

\begin{equation}
r_n(t) = \int_{t_n}^{t} K(t, t') y(t') dt' \tag{4–17}
\end{equation}

\begin{equation}
= \int_{t_n}^{t} K(t, t') [r_n(t') + q_n(t')] dt'. \tag{4–18}
\end{equation}

Note that $q_n$, called the lag term, only depends on known values of $y(t)$ (those up to $y(t_n)$), while $r_n$, called the increment function, satisfies an integral equation, or an equivalent differential equation.

If we apply the foregoing Runge-Kutta method to the expression for $r$, we obtain

\begin{equation}
r_n(t_{n+1}) = r_n(t_n) + h \sum_{i=1}^{m} b_i K(t_{n+1}, t_n + c_i h) [R^n_i + q_n(t_n + c_i h)], \tag{4–19}
\end{equation}

\begin{equation}
R^n_i = r_n(t_n) + h \sum_{j=1}^{m} a_{ij} K(t_n + c_i h, t_n + c_j h) [R^n_j + q_n(t_n + c_j h)]. \tag{4–20}
\end{equation}

The first term, $r_n(t_n)$, is zero. If we now choose the $Y^n_i$ according to

\begin{equation}
Y^n_i = R^n_i + q_n(t_n + c_i h), \tag{4–21}
\end{equation}

we have

\begin{equation}
r_n(t_{n+1}) = h \sum_{i=1}^{m} b_i K(t_{n+1}, t_n + c_i h) Y^n_i, \tag{4–22}
\end{equation}

\begin{equation}
Y^n_i = q_n(t_n + c_i h) + h \sum_{j=1}^{m} a_{ij} K(t_n + c_i h, t_n + c_j h) Y^n_j. \tag{4–23}
\end{equation}

We can rewrite $q$ as

\begin{equation}
q_n(t) = g(t) + \sum_{i=0}^{n-1} \int_{t_i}^{t_{i+1}} K(t, t') y(t') dt'. \tag{4–24}
\end{equation}

If we apply the Runge-Kutta method for integral equations, we obtain

\begin{equation}
q_n(t) = g(t) + h \sum_{i=0}^{n-1} \sum_{j=1}^{m} b_j K(t, t_i + c_j h) Y^n_j. \tag{4–25}
\end{equation}
We can now calculate $y(t_{n+1})$, according to

$$y(t_{n+1}) = q_n(t_{n+1}) + r_n(t_{n+1}). \quad (4–26)$$

### 4.1.2 Volterra Integro-Differential Equations

We now focus on the problem of the integro-differential equation

$$\frac{d\rho(t)}{dt} = \mathcal{H}(t)\rho(t) + \int_{t_0}^{t} \mathcal{K}(t, t')\rho(t') dt', \quad (4–27)$$

which is a first order Volterra integro-differential equation. To begin, we define

$$z(t) = \int_{t_0}^{t} \mathcal{K}(t, t')\rho(t') dt', \quad (4–28)$$

this gives

$$\frac{d\rho(t)}{dt} = \mathcal{H}(t)\rho(t) + z(t). \quad (4–29)$$

The integrated form is then

$$\rho(t) = \rho(t_0) + \int_{t_0}^{t} (\mathcal{H}(t')\rho(t') + z(t')) dt'. \quad (4–30)$$

If we also define

$$\mathbf{y}(t) = \begin{pmatrix} \rho(t) \\ z(t) \end{pmatrix}, \quad (4–31)$$

$$\mathbf{M}(t, t') = \begin{pmatrix} \mathcal{H}(t) & 1 \\ \mathcal{K}(t, t') & 0 \end{pmatrix}, \quad (4–32)$$

we will have an equation similar to Equation 4–30,

$$\mathbf{y}(t) = \mathbf{y}(t_0) + \int_{t_0}^{t} \mathbf{M}(t, \tau)\mathbf{y}(\tau)d\tau. \quad (4–33)$$

This equation is the same form as the Volterra integral equation considered earlier, with the exception that we are now dealing with matrices.
The matrix $y(t)$ contains both $\rho(t)$ and $z(t)$, which have integral equations that must be solved simultaneously. If we apply the method given above, we obtain

$$Y_i^n = q_n(t_n + c_i h) + h \sum_{j=1}^{m} a_{ij} \mathcal{M}(t_n + c_i h, t_n + c_j h) Y_j^n, \quad (4-34)$$

$$r_n(t) = h \sum_{i=1}^{m} b_i \mathcal{M}(t, t_n + c_i h) Y_i^n, \quad (4-35)$$

$$q_n(t) = y(t_0) + h \sum_{l=0}^{n-1} \sum_{j=1}^{m} b_j \mathcal{M}(t, t_l + c_j h) Y_j^l, \quad (4-36)$$

$$y(t_{n+1}) = r_n(t_{n+1}) + q_n(t_{n+1}). \quad (4-37)$$

If we make the definitions

$$Y_i^n = \begin{pmatrix} P_i^n \\ Z_i^n \end{pmatrix}, \quad (4-38)$$

$$r_n(t) = \begin{pmatrix} r_n^{(\rho)}(t) \\ r_n^{(z)}(t) \end{pmatrix}, \quad (4-39)$$

$$q_n(t) = \begin{pmatrix} q_n^{(\rho)}(t) \\ q_n^{(z)}(t) \end{pmatrix}, \quad (4-40)$$

we have

$$r_n^{(\rho)}(t) = \sum_{i=1}^{m} b_i [\mathcal{H}(t_n + c_i h) P_i^n + Z_i^n], \quad (4-41)$$

$$r_n^{(z)}(t) = \sum_{i=1}^{m} b_i \mathcal{K}(t, t_n + c_i h) P_i^n, \quad (4-42)$$

$$q_n^{(\rho)}(t) = \rho(t_0) + h \sum_{l=0}^{n-1} \sum_{j=1}^{m} b_j [\mathcal{H}(t_n + c_j h) P_j^l + Z_j^l], \quad (4-43)$$

$$q_n^{(z)}(t) = z(t_0) + h \sum_{l=0}^{n-1} \sum_{j=1}^{m} b_j \mathcal{K}(t, t_n + c_j h) P_j^l, \quad (4-44)$$
and

\[ P_i^n = q_n^{(p)}(t_n + c_i h) + h \sum_{j=1}^m a_{ij} [\mathcal{H}(t_n + c_j h) P_j^n + Z_j^n], \quad (4-45) \]

\[ Z_i^n = q_n^{(z)}(t_n + c_i h) + h \sum_{j=1}^m a_{ij} K(t_n + c_i h, t_n + c_j h) P_j^n, \quad (4-46) \]

\[ \rho(t_{n+1}) = q_n^{(p)}(t_{n+1}) + r_n^{(p)}(t_{n+1}), \quad (4-47) \]

\[ z(t_{n+1}) = q_n^{(z)}(t_{n+1}) + r_n^{(z)}(t_{n+1}). \quad (4-48) \]

Note that there is no dependence on \( t \) in the expressions for \( r_n^{(p)}(t) \) and \( q_n^{(p)}(t) \), so we may write

\[ r_n^{(p)} = \sum_{i=1}^m b_i [\mathcal{H}(t_n + c_i h) P_i^n + Z_i^n], \quad (4-49) \]

\[ q_n^{(p)} = \rho(t_0) + h \sum_{l=0}^{n-1} \sum_{j=1}^m b_j [\mathcal{H}(t_n + c_j h) P_j^l + Z_j^l], \quad (4-50) \]

\[ \rho(t_{n+1}) = q_n^{(p)} + r_n^{(p)}. \quad (4-51) \]

If we set \( q_n^{(p)} = \rho_n \), we have

\[ \rho_{n+1} = \rho_n + h \sum_{i=1}^m b_i [\mathcal{H}(t_n + c_i h) P_i^n + Z_i^n], \quad (4-52) \]

and

\[ P_i^n = \rho_n + h \sum_{j=1}^m a_{ij} [\mathcal{H}(t_n + c_j h) P_j^n + Z_j^n], \quad (4-53) \]

\[ Z_i^n = q_n^{(z)}(t_n + c_i h) + h \sum_{j=1}^m a_{ij} K(t_n + c_i h, t_n + c_j h) P_j^n. \quad (4-54) \]

As above, we calculate \( q_n^{(z)} \) according to \( (z(t_0) = 0) \)

\[ q_n^{(z)}(t) = h \sum_{l=0}^{n-1} \sum_{j=1}^m b_j K(t, t_l + c_j h) P_j^l. \quad (4-55) \]
4.1.3 Order Conditions

Here we will derive some of the formulas which determine the constraints on the $a_{ij}, b_j, \text{ and } c_j$ for a given order $p$. We begin again with the simple differential equation

$$y'(t) = f(t, y(t)). \quad (4-56)$$

If our method agrees with the Taylor series of the true solution up to the terms including $h^p$, then our method is of order $p$. The Taylor expansion of this expression, up to second order, at $t = t_0 + h$, is

$$y(t_0 + h) = y(t_0) + hy'(t_0) + \frac{h^2 y''(t_0)}{2} + \mathcal{O}(h^3). \quad (4-57)$$

We now consider the Taylor series of the approximate solution at $t_1 = h$,

$$y_1(h) = y_1(t_0) + hy'_1(t_0) + \frac{h^2 y''_1(t_0)}{2} + \mathcal{O}(h^3). \quad (4-58)$$

The derivatives of the true solution at $t_0$ are

$$y'(t)|_{t=t_0} = f(t_0, y(t_0)), \quad (4-59)$$
$$y''(t)|_{t=t_0} = \frac{df(t_0, y(t_0))}{dt} + f(t_0, y(t_0)) \frac{df(t_0, y(t_0))}{dy}; \quad (4-60)$$

and for the approximate solution

$$\frac{dy_1}{dh} = \sum_{i=1}^m b_i Y_i^0 + h \sum_{i=1}^m b_i \frac{dY_i^0}{dh}, \quad (4-61)$$
$$\frac{d^2 y_1}{dh^2} = 2 \sum_{i=1}^m b_i \frac{dY_i^0}{dh} + h \sum_{i=1}^m b_i \frac{d^2 Y_i^0}{dh^2}. \quad (4-62)$$

We now set $h = 0$ and note that

$$Y_i^0|_{h=0} = f(t_0, y_0), \quad (4-63)$$
$$\frac{dY_i^0}{dh}|_{h=0} = c_i \frac{df(t_0, y_0)}{dh} + c_i f(t_0, y_0) \frac{df(t_0, y_0)}{dy}, \quad (4-64)$$
which leads to

\begin{align}
y_1(t_0)|_{h=0} &= y_0, \\
\frac{dy_1}{dh}|_{h=0} &= \sum_{i=1}^{m} b_i f(t_0, y_0), \\
\frac{d^2 y_1}{dh^2}|_{h=0} &= 2 \sum_{i=1}^{m} b_i c_i \left[ \frac{df(t_0, y_0)}{dh} + f(t_0, y_0) \frac{df(t_0, y_0)}{dy} \right].
\end{align}

(4–65) (4–66) (4–67)

Note that \( y_0 = y(t_0) \). For the two Taylor series to agree to first order in \( h \) (\( p = 1 \)), the first derivatives must agree, and we have

\[ \sum_{j=1}^{m} b_j = 1. \]  

(4–68)

For second order in \( h \) (\( p = 2 \)), we must equate the second derivatives, and obtain

\[ \sum_{j=1}^{m} b_j c_j = \frac{1}{2}. \]  

(4–69)

This method can be repeated for higher derivatives. Up to order \( p = 4 \), we have

\[ p = 3, \]

\[ \sum_{j=1}^{m} b_j c_j^2 = \frac{1}{3}, \]  

(4–70)

\[ \sum_{j=1}^{m} \sum_{k=1}^{m} b_j a_{jk} c_k = \frac{1}{6}. \]  

(4–71)
and

\[
p = 4, \quad \sum_{j=1}^{m} b_j c_j^3 = \frac{1}{6}, \tag{4-72}
\]

\[
\sum_{j=1}^{m} \sum_{k=1}^{m} b_j a_{jk} c_j c_k = \frac{1}{8}, \tag{4-73}
\]

\[
\sum_{j=1}^{m} \sum_{k=1}^{m} b_j a_{jk} c_j^2 = \frac{1}{12}, \tag{4-74}
\]

\[
\sum_{j=1}^{m} \sum_{k=1}^{m} \sum_{l=1}^{m} b_j a_{jk} a_{kl} c_l = \frac{1}{24}. \tag{4-75}
\]

In Table 4-1 we see the total number of equalities to be satisfied, \( N_p \), for a given order \( p \).

For a given \( m \), there are \( (m^2 + m)/2 \) coefficients. At \( m = 5 \) it is not possible to attain a method of order \( p = m = 5 \); there are 17 order conditions, but only 15 coefficients. In Tables 4-2 and 4-3 we see the attainable order of a Runge-Kutta method for a given \( m \), and the minimum \( m \) need to obtain order \( p \).

In Table 4-4 we see an example set of coefficients for a Runge-Kutta method with \( m = p = 4 \).

### 4.2 Implicit Formulation

The previous method is an explicit formulation. However, for some cases it may be necessary to use an implicit method.

If we adopt the diadic form, we can cast the integro-differential equation as

\[
y'(t) = V(t)y(t) + \int_{0}^{t} M(t, t')y(t')dt', \tag{4-76}
\]
where the dimensions of \( y \) are \( n^2 \times 1 \), \( V \) and \( M \) are both \( n^2 \times n^2 \). For a two-step method, we can now define

\[
A_j = \hbar n a_{j1} V(t_{n,j}) + h_n^2 a_{j1} M(t_{n,j}, t_n + d_{j1} \hbar n) \lambda_1 (d_{j1}) \\
+ h_n^2 a_{j2} M(t_{n,j}, t_n + d_{j2} \hbar n) \lambda_1 (d_{j2}) ,
\]

\[
B_j = \hbar n a_{j2} V(t_{n,j}) + h_n^2 a_{j1} M(t_{n,j}, t_n + d_{j1} \hbar n) \lambda_2 (d_{j1}) \\
+ h_n^2 a_{j2} M(t_{n,j}, t_n + d_{j2} \hbar n) \lambda_2 (d_{j2}) ,
\]

\[
C_j = \Phi_{n,j} + y_n [V(t_{n,j}) + h_n \bar{a}_{j1} M(t_{n,j}, t_n + d_{j1} \hbar n) \\
+ h_n \bar{a}_{j2} M(t_{n,j}, t_n + d_{j2} \hbar n) ],
\]

which leads to

\[
Y_{n,1} = A_1 Y_{n,1} + B_1 Y_{n,2} + C_1 ,
\]

\[
Y_{n,2} = A_2 Y_{n,1} + B_2 Y_{n,2} + C_2 ,
\]

where the dimensions of \( C \) are \( n^2 \times 1 \), \( A \) and \( B \) are both \( n^2 \times n^2 \).

### 4.3 Test System

To test our numerical procedure, we turn to a solved system, which is a two-state system coupled to a bath of harmonic oscillators. The hamiltonian is

\[
\mathbf{H}(t) = -\frac{1}{2} [\Delta(t) \mathbf{\sigma}_x + \epsilon(t) \mathbf{\sigma}_z + \zeta(t) \mathbf{\sigma}_z],
\]

where \( \Delta \) is an energy transfer matrix element, \( \epsilon(t) \) is the biasing energy which may include a driving field, and \( \zeta(t) \) is a stochastic factor which contains system-bath coupling. The \( \mathbf{\sigma}_{x,z} \) are Pauli matrices. The expectation values of these matrices, \( \langle \mathbf{\sigma}_i \rangle_t \), are defined as

\[
\langle \mathbf{\sigma}_i \rangle_t = Tr [\mathbf{\rho}(t) \mathbf{\sigma}_i].
\]

These expectation values give the population difference,

\[
\langle \mathbf{\sigma}_z \rangle_t = \rho_{11} - \rho_{22}.
\]
the real part of the coherence
\[
\frac{1}{2} \langle \sigma_x \rangle_t = \frac{1}{2} (\rho_{12} + \rho_{21}), \tag{4-84}
\]
and the imaginary part
\[
\frac{1}{2} \langle \sigma_y \rangle_t = \frac{i}{2} (\rho_{12} - \rho_{21}). \tag{4-85}
\]

Using these expectation values, and the fact that \( \rho_{11} + \rho_{22} = 1 \), we can express the density matrix as
\[
\rho(t) = \frac{1}{2} \begin{pmatrix}
1 + \langle \sigma_z \rangle_t & \langle \sigma_x \rangle_t - i \langle \sigma_y \rangle_t \\
\langle \sigma_x \rangle_t + i \langle \sigma_y \rangle_t & 1 - \langle \sigma_z \rangle_t
\end{pmatrix}. \tag{4-86}
\]

To account for the system bath coupling, we start with a bath at a constant temperature \( T \), so that
\[
\langle \zeta(t) \rangle_T = 0, \tag{4-87}
\]
and
\[
\langle \zeta(t) \zeta(0) \rangle_T = \frac{1}{\pi} \int_0^\infty J(\omega) \frac{\cosh(\frac{\omega}{2T} - i\omega t)}{\sinh(\frac{\omega}{2T})} d\omega, \tag{4-88}
\]
where \( J(\omega) \) is the spectral density of the bath, in this case taken to have an ohmic density, as
\[
J(\omega) = 2\pi \alpha \omega e^{-\omega/\omega_c}. \tag{4-89}
\]
Here \( \alpha \) is a dimensionless coupling parameter, and \( \omega_c \) is the cutoff frequency.

The time evolution of the expectation value of the Pauli matrices is governed by a set of coupled equations,\(^{60,61}\)
\[
\frac{d}{dt} \langle \sigma_z \rangle_t = \int_0^t dt' [K_a(t, t') - K_s(t, t') \langle \sigma_z \rangle_{t'}], \tag{4-90}
\]
\[
\langle \sigma_x \rangle_t = \int_0^t dt' [Y_s(t, t') + Y_a(t, t') \langle \sigma_z \rangle_{t'}], \tag{4-91}
\]
\[
\langle \sigma_y \rangle_t = -\frac{1}{\Delta(t)} \frac{d}{dt} \langle \sigma_z \rangle_t, \tag{4-92}
\]

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where $K_{s(a)}$ and $Y_{s(a)}$ are symmetric (antisymmetric) memory kernels. These kernels are

$$K_s(t, t') = \Delta(t)\Delta(t')e^{-Q'(t-t')}\cos[Q''(t - t')]\cos[\Theta(t, t')],$$  \hspace{1cm} (4–93)

$$Y_s(t, t') = \Delta(t')e^{-Q'(t-t')}\sin[Q''(t - t')]\cos[\Theta(t, t')],$$  \hspace{1cm} (4–94)

with

$$Q'(\tau) = 2\alpha \ln[\omega_c/\pi T \sinh(\pi T \tau)],$$ \hspace{1cm} (4–95)

$$Q''(\tau) = \pi \alpha \text{sgn}(\tau),$$ \hspace{1cm} (4–96)

$$\Theta(t, t') = \int_{t'}^{t} \epsilon(\tau)d\tau,$$ \hspace{1cm} (4–97)

where $T$ is the temperature of the reservoir. The antisymmetric kernels, $K_a$ and $Y_a$, are similar to the symmetric ones, except with every sine replaced by a cosine, and cosines replaced by sines. It should be noted that these kernels use the noninteracting-blip approximation (NIBA). \hspace{1cm} (4–98)

In the case of high temperatures, the approximation

$$Q'(\tau) = 2\alpha \ln(\omega_c/\pi T) + 2\alpha \pi T|\tau|$$

can be used. In this approximation, the equations can be solved exactly.

The equations for $\langle \sigma_x \rangle_t$ and $\langle \sigma_z \rangle_t$ are the ones chosen to test the computational method. Note that while the expression for $\langle \sigma_z \rangle_t$ is an integro-differential equation, $\langle \sigma_x \rangle_t$ is governed by an integral equation. Our method should work in either case.

We calculate $\langle \sigma_x \rangle_t$ and $\langle \sigma_z \rangle_t$ for two models; in Model 1 $\alpha = 0.1, T = 0.5\Delta, \epsilon = -0.5\Delta, \omega_c = 30\Delta$, and in Model 2 $\alpha = 0.05, T = 0.05\Delta, \epsilon = 0, \omega_c = 30\Delta$. For convenience, we have set $\Delta = 1$. Model 1 is a high temperature case for which the markovian limit may be applicable. Model 2 is a lower temperature, unbiased case. The initial state is one in which the population is in the state 1, with no coherence, so that $\langle \sigma_z \rangle_0 = 1$, and $\langle \sigma_x \rangle_0 = \langle \sigma_y \rangle_0 = 0$.

In Figures 4-1 and 4-2 we compare results using the Runge-Kutta method with those found in a previous study\hspace{1cm} for Model 1. Results for Model 2 are presented in Figures 4-3

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and 4-4. There is very good agreement in all cases. As a further test, we calculate $\langle \sigma_z \rangle_t$ in the high temperature limit, where exact results are available, presented in Figures 4-5 and 4-5. At short times the results agree very well, but there are some small deviations at long times. These deviations are small enough to consider our method to be a reliable one.

Finally, we calculate $\langle \sigma_z \rangle_t$ for Model 1 in two approximations - the instantaneous dissipation limit, and the Markovian limit. In the instantaneous dissipation limit, we assume the kernels are rapidly changing relative to $\langle \sigma_z \rangle$. We then assume $\langle \sigma_z \rangle_t' = \langle \sigma_z \rangle_t$ so that

$$\frac{d}{dt} \langle \sigma_z \rangle_t^{ID} = \int_0^t dt' K_n(t, t') - \langle \sigma_z \rangle_t^{ID} \int_0^t dt' K_s(t, t'). \quad (4-99)$$

In the Markovian limit, we assume the integral in 4-99 can be extended to infinity, giving

$$\frac{d}{dt} \langle \sigma_z \rangle_t^{ID} = \int_0^\infty dt' K_n(t, t') - \langle \sigma_z \rangle_t^{ID} \int_0^\infty dt' K_s(t, t'). \quad (4-100)$$

The results are shown in Figure 4-7. All three methods give the same value at long (equilibrium) times, however neither method fully describes the short time dynamics. The Markovian limit yields an exponential decay, while in the instantaneous case there are oscillations that are damped compared to the delayed dissipation case.

### 4.4 Scaling and Limitations

The majority of the computer processing time in this method is devoted to calculating the $q_n^{(z)}$ term, which grows more expensive as more steps are taken. The methods scales in processing time as (number of steps)$^2$. As we are dealing with matrices, it also scales as (number of states)$^2$. However, $q_n^{(z)}$ requires quantities that have already been calculated - values from previous steps. It is easy to divide $q_n^{(z)}$ into chunks which do not depend on each other, so this process can be split among several processors. The program has been designed with this feature, and scales linearly with the number of processors allotted; e.g. it will run twice as fast if twice as many processors are allotted. We have used both the OpenMP standard,\(^{63}\) as well as the MPI standard.\(^{64}\) It should be noted that either one
standard or the other is used, not both. The program must be compiled with different options for each standard.

The memory required for the program to run may also become an issue as larger and longer runs are considered. As written, the numerical method requires the storage of all of the previous values of the density matrix, along with the intermediate values within each time step ($m$ of them at each step).

4.5 The Memory Time

By default, the memory term involves all previous states, back to the beginning of the simulation. As more steps are taken, the process becomes more expensive. It may, however, be possible to reduce the running time with the concept of a memory time ($t_{\text{mem}}$). In this case, correlations longer then $t_{\text{mem}}$ are neglected. This means setting

$$z(t) = \int_{t_{\text{mem}}}^{t} K(t, t') \rho(t') dt'$$

for $t > t_{\text{mem}}$. For a fixed step size, $t_{\text{step}}$, the method scales as $(t_{\text{mem}}/t_{\text{step}})^2$, but will scale linearly with $t$ once $t > t_{\text{mem}}$.

The option of using a memory time will depend on the system being studied. The memory time depends on the kernel, $K(t, t')$; it will be the cutoff time after which the kernel is negligible,

$$K(t, t') \approx 0,$$

$$t - t' > t_{\text{mem}}.$$  (4–102)

In the case of Equation 2–30, the memory time will depend on the correlation function, $C(t)$. If the correlation function is small enough to be neglected after $t_{\text{mem}}$, then the entire kernel will be small enough to be neglected, since each term is multiplied by $C(t)$. The
The dissipative part of the master equation is then

\[
\left( \frac{d}{dt} \rho_{ab} \right)_{\text{diss}} = - \sum_{cd} \int_{t_{\text{mem}}}^{t} dt' [M_{cd,ab} (- (t - t')) e^{i \omega_{da} (t - t')} \rho_{ac}(t') + M_{ac,cd} (t - t') e^{i \omega_{bc} (t - t')} \rho_{db}(t') \\
- M_{db,ac} (- (t - t')) e^{i \omega_{bc} (t - t')} \rho_{cd}(t') - M_{db,ac} (t - t') e^{i \omega_{da} (t - t')} \rho_{cd}(t')].
\]

Note that the minimum value of \( t' \) is \( t - t_{\text{mem}} \), which means that we can discard any previous values of \( \rho(t') \) where \( t' < t - t_{\text{mem}} \), potentially reducing computational memory overhead.

The idea of a memory time also leads to a different way of treating the initial state of a system. Often the initial state of a system is assumed to be in thermal equilibrium at a specified temperature. It is then natural to assume that the system will remain in that state in the absence of any external driving force. However, the memory kernel at early times in general will not vanish, leading to changes in the populations. Beginning the simulation has the effect of switching on the correlations between the primary region and the medium. One approach to dealing with this is to run the simulation without any external driving forces until the system returns to equilibrium and then apply any nonequilibrium influences, such as a light pulse.

Using the memory time allows for a different approach. We consider the system to be in thermal equilibrium, and to have been in that equilibrium for the duration of \( t_{\text{mem}} \). This means setting

\[
\rho(- t_{\text{mem}} < t < 0) = \rho(0) = \rho_{eq},
\]

where \( \rho_{eq} \) is the equilibrium density matrix. Doing so allows us to account for correlations occurring before the beginning of the simulation, without actually calculating any dynamics for those previous times. Returning to Equation 2–28, at \( t = 0 \) we will have

\[
\frac{\partial \hat{\rho}(0)}{\partial t} = - \frac{i}{\hbar} \left[ \hat{H}', \hat{\rho}(0) \right] + \int_{-t_{\text{mem}}}^{0} \mathcal{K}(t, t') \hat{\rho}(t') dt',
\]

\[\text{(4–105)}\]
and at the first step in the simulation, $t_1$,

$$\frac{\partial \hat{\rho}(t_1)}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}', \hat{\rho}(t_1) \right] + \int_{t_1-t_{mem}}^{t_1} \mathcal{K}(t, t') \hat{\rho}(t') dt'. \quad (4–106)$$

Negative values of $\rho$ are handled according to Equation 4–104. If we choose our memory time properly, there should be no initial dynamics - the system will be in a true equilibrium.

### 4.6 Conclusion

In this chapter we have developed a method for solving integro-differential equations based on the Runge-Kutta algorithm. The order of the method depends on the number of steps in each iteration, along with a set of constants chosen. The order requirements, along with the conditions that the constants must fulfill, have been discussed.

We then tested this method on a solved example found in the literature, using a fourth-order four step explicit method. Our method gives excellent agreement, for both integral and integro-differential equations. This method can be used with matrices, so it is applicable to the second-order equation of motion for the reduced density matrix.

Table 4-1. Number of equalities to be satisfied for a given order of the Runge-Kutta method

<table>
<thead>
<tr>
<th>$p$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_p$</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>17</td>
<td>37</td>
<td>85</td>
<td>200</td>
<td>486</td>
<td>1205</td>
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</table>

Table 4-2. Highest attainable order of an explicit Runge-Kutta method for a given $m$

<table>
<thead>
<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 4-3. Minimum $m$ needed to attain a given order $p$

<table>
<thead>
<tr>
<th>$p$</th>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
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</thead>
<tbody>
<tr>
<td>$m$</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>6</td>
<td>7</td>
<td>9</td>
<td>11</td>
<td>12</td>
</tr>
</tbody>
</table>

59
Figure 4-1. $\langle \sigma_z \rangle_t$, Model 1: our results (solid curve) and selected points from Grifoni et al. (points)

Figure 4-2. $\langle \sigma_x \rangle_t$, Model 1: our results (solid curve) and selected points from Grifoni et al. (points)
Figure 4-3. \( \langle \sigma_z \rangle_t \), Model 2: our results (solid curve) and selected points from Grifoni et al. (points)

Figure 4-4. \( \langle \sigma_x \rangle_t \), Model 2: our results (solid curve) and selected points from Grifoni et al. (points)
Figure 4-5. $\langle \sigma_z \rangle_t$, Model 1: the high temperature limit. Exact results (solid curve) and calculated results (dashed curve)

Figure 4-6. $\langle \sigma_z \rangle_t$, Model 2: the high temperature limit. Exact results (solid curve) and calculated results (dashed curve)
Table 4-4. Example coefficients

<table>
<thead>
<tr>
<th>c</th>
<th>$A = {a_{ij}}$</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>0 0 0 0 0</td>
</tr>
<tr>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$ 0 0 0</td>
</tr>
<tr>
<td>$\frac{1}{2}$</td>
<td>0 $\frac{1}{2}$ 0 0</td>
</tr>
<tr>
<td>1</td>
<td>0 0 1 0</td>
</tr>
<tr>
<td>$b^T$</td>
<td>$\frac{1}{6}$ $\frac{1}{3}$ $\frac{1}{3}$ $\frac{1}{6}$</td>
</tr>
</tbody>
</table>

Figure 4-7. $\langle \sigma_z \rangle_t$, Model 1: delayed dissipation (solid curve), instantaneous dissipation (dashed curve), and the Markoff limit (dotted curve)
CHAPTER 5
VIBRATIONAL RELAXATION OF ADSORBATES ON METAL SURFACES

5.1 Introduction

We now have a general numerical method for integro-differential equations, which can be used to study dissipative dynamics of molecular systems. In this chapter, we consider the vibrational relaxation of adsorbates on metal surfaces - specifically CO/Cu(001), CO/Pt(111), and Na/Cu(001). Previous work on these systems\textsuperscript{8,15,18} considered only electronic dissipation. Here we focus on vibrational dissipation.

We consider the frustrated translation of the adsorbate, and examine the effects of different coupling strengths and temperatures. We also demonstrate the instantaneous and markovian limits. We consider only the ground and first excited vibrational state, which leads to relatively simple expressions for the populations and coherences. In later chapters, we will study the complex dynamics which arises from adding more states.

5.2 Model Details

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5.2 Model Details

Here we are concerned with the frustrated translation (T-mode) of an adsorbate on a metal surface. The T-modes are low energy vibrations, and are populated at the temperatures studied. The specific systems studied are CO/Cu(001), CO/Pt(111), and Na/Cu(001) which have been the subject of much experimental and theoretical work.\textsuperscript{29,37,65–68} We consider the frustrated T-mode (the P or primary region) as a harmonic oscillator coupled to a bath of harmonic oscillators\textsuperscript{69} (the R or reservoir) with the Hamiltonian

\[ \hat{H} = \hat{H}_P + \hat{H}_R + \hat{H}_{PR}, \]  
\[ \hat{H}_P = \hbar \omega_0 \hat{a}^\dagger \hat{a}, \]  
\[ \hat{H}_R = \sum_j \hbar \omega_j \hat{b}_j^\dagger \hat{b}_j, \]  
\[ \hat{H}_{PR} = \hbar \sum_j \kappa_j (\hat{a}^\dagger \hat{b}_j^\dagger + \hat{a}^\dagger \hat{b}_j + \hat{a} \hat{b}_j^\dagger + \hat{a} \hat{b}_j), \]
where $\omega_0$ is the vibrational frequency of primary region, and $\hat{a}$ and $\hat{a}^\dagger$ are the creation and annihilation operators for the primary region. The $\hat{b}_j$ and $\hat{b}_j^\dagger$ are creation and annihilation operators for mode $j$ of the reservoir $R$, with frequency $\omega_j$, and coupling strength $\kappa_j$.

We can now define

$$\hat{q} = \frac{1}{\sqrt{2}}(\hat{a}^\dagger + \hat{a}),$$

(5–5)

$$\hat{B} = \hbar \sqrt{2} \sum_j \kappa_j (\hat{b}_j^\dagger + \hat{b}_j) = 2 \hbar \sum_j \kappa_j \hat{Q}_j,$$

(5–6)

so that

$$\hat{H}_{PR} = \hat{q} \hat{B}.$$  

(5–7)

Note that $\hat{q}$ is dimensionless, while $\hat{B}$ has the dimensions of energy. This gives a coupling which is separated into two parts, one which depends only on the primary region ($\hat{q}$), while the other depends only on the reservoir ($\hat{B}$). With this type of coupling, we can use a master equation similar to Equation 2–30

$$\frac{\partial}{\partial t} \rho_{ab} = -i\omega_{ab} \rho_{ab} + \frac{i}{\hbar} \sum_{c} \langle \hat{B} \rangle (q_{cb} \rho_{ac} - q_{ac} \rho_{cb})$$

$$- \sum_{cd} \int_0^t dt' [M_{cd,db}(-(t-t'))e^{i\omega_{da}(t-t')} \rho_{ac}(t') + M_{ac,cd}(t-t')e^{i\omega_{bc}(t-t')} \rho_{db}(t')]$$

$$- M_{db,ac}(-(t-t'))e^{i\omega_{bc}(t-t')} \rho_{cd}(t') - M_{db,ac}(t-t')e^{i\omega_{da}(t-t')} \rho_{cd}(t')]$$

(5–8)

where $\omega_{ab} = (E_a - E_b)/\hbar$, $H_P \phi_a = E_a \phi_a$, and

$$q_{ab} = \langle \phi_a | \hat{q} | \phi_b \rangle,$$

(5–9)

$$M_{ab,cd}(\tau) = \frac{1}{\hbar^2} C(\tau) q_{ab} q_{cd}.$$  

(5–10)

Note that we have expanded $\rho$ in the basis $\{\phi_a\}$, the eigenstates of $\hat{H}_P$, with energies $E_a = \hbar \omega_0 (a + 1/2)$. In this system, $\langle \hat{B} \rangle = 0$.

Equation 5–8 can be simplified using the relations

$$q_{ab} = q_{ba} = \frac{1}{\sqrt{2}} (\delta_{a,b+1} \sqrt{b+1} + \delta_{a,b-1} \sqrt{b}),$$

(5–11)
and

\[ q_{aa} = 0. \]  \quad (5-12)

If we consider only the ground (0) and first excited state (1), we have, after some rearrangement, and setting \( \hbar = 1 \),

\[
\frac{d}{dt} \rho_{00} = -\frac{1}{2} \int_0^t [4 \cos(\omega_0(t - t')) \text{Re}\{C(t - t')\} \rho_{00}(t')] dt',
\]

\[
\frac{d}{dt} \rho_{11} = -\frac{1}{2} \int_0^t [4 \cos(\omega_0(t - t')) \text{Re}\{C(t - t')\} \rho_{11}(t')] dt',
\]

\[
\frac{d}{dt} \rho_{01} = i\omega_0 \rho_{01} - i \int_0^t 2 \text{Re}\{C(t - t')\} \text{Im}\{\rho_{01}(t')\} dt',
\]

\[
\frac{d}{dt} \rho_{10} = -i\omega_0 \rho_{10} - i \int_0^t 2 \text{Re}\{C(t - t')\} \text{Im}\{\rho_{10}(t')\} dt'.
\]

For a two-state case, with this choice of \( q_{ab} \), there is no coupling between the states. This is because we are dealing with only a \( 2 \times 2 \) matrix, and we can simplify the equations using the relations \( \rho_{00} + \rho_{11} = 1 \) and \( \rho_{01} = \rho_{10}^* \), where the * superscript indicates the complex conjugate. However, as we will see in later chapters, for three or more states, couplings do appear.

If we assume the instantaneous dissipation limit, we can take \( \rho \) outside of the integral, and for the ground state population we have

\[
\frac{d}{dt} \rho_{00}^{(ID)} = -\frac{1}{2} \rho_{00}^{(ID)} \int_0^t 4 \cos(\omega_0(t - t')) \text{Re}\{C(t - t')\} dt'
\]

\[
- \int_0^t \left( C(-(t - t')) e^{-i\omega_0(t-t')} + C(t-t') e^{i\omega_0(t-t')} \right) dt',
\]

which is an integral equation. Extending the integral to infinity gives the markoff limit,

\[
\frac{d}{dt} \rho_{00}^{(ID)} = -\frac{1}{2} \rho_{00}^{(ID)} \int_0^\infty 4 \cos(\omega_0(t - t')) \text{Re}\{C(t - t')\} dt'
\]

\[
- \int_0^\infty \left( C(-(t - t')) e^{-i\omega_0(t-t')} + C(t-t') e^{i\omega_0(t-t')} \right) dt'.
\]
5.3 The Correlation Function

We yet need the time correlation function $C(t)$, which can be obtained from the spectral function $J(\omega)$ from

$$C(t) = \int_0^\infty \left[ \cos(\omega t) \coth \left( \frac{\hbar \omega}{2k_B T} \right) - i \sin(\omega t) \right] \omega^2 J(\omega) d\omega. \quad (5–19)$$

The spectral function can be derived from the spectral density, $g(\omega)$, and the coupling strength, $\kappa(\omega)$, through $\omega^2 J(\omega) = 2g(\omega)|\kappa(\omega)|^2$. We use a Debye model, so that

$$g(\omega) = 18\pi N \omega^2 / \omega_D^3, \quad (5–20)$$

where $\omega_D$ is the Debye phonon cutoff frequency, so $g(\omega) = 0$ for $\omega > \omega_D$, and $N$ is the number of lattice atoms. For the couplings, we follow and use

$$|\kappa(\omega)|^2 = [p + q(\omega - \omega_0)]/N, \quad (5–21)$$

which gives

$$J(\omega) = 36\pi[p + q(\omega - \omega_0)]/\omega_D^3, \quad (5–22)$$

where $p$ and $q$ are parameters which depend on the system. The values of these and other parameters used in the calculations are given in Table 5-1.

The imaginary part of the correlation function, which is temperature independent, can be integrated exactly. For $t = 0$, the real part can be integrated exactly as well. For $t \neq 0$, however, this is not the case. For large enough temperatures, we can use the approximation

$$\coth \left( \frac{\hbar \omega}{2k_B T} \right) \approx \frac{2k_B T}{\hbar \omega} + \frac{\hbar \omega}{6k_B T}. \quad (5–23)$$

This leads to an expression that can be integrated exactly. This approximation has been tested, and shown to give excellent agreement down to temperatures as low as 100K.

The correlation functions that arise from these parameters are shown in Figure 5-1 for temperatures of 150K, 300K, and 450K.
Increasing the temperature increases the magnitude of the real part of the correlation function, but has no effect on the frequency of the oscillations. This frequency is about $9.6 \times 10^{-4}$ au$^{-1}$, which is close to the Debye frequency. The correlation function is largest at short times, showing a $1/t$ type decay at long times.

5.4 Results

For each system, we have the initial conditions of the population entirely in the excited state with no coherence, so that $\rho_{11} = 1$, $\rho_{00} = 0$, and $\rho_{01} = \rho_{10} = 0$. We then follow the relaxation towards thermal equilibrium, for temperatures of 150K and 300K. The results are shown in Figures 5-2, 5-3, and 5-4. In each case, we see large initial oscillations, which relax towards equilibrium within 30,000 to 50,000 au. Increasing the temperature seems to damp the oscillations, with relaxation to equilibrium coming sooner. This increase is in qualitative agreement with experiment.\textsuperscript{67}

We have also repeated the runs for CO/Cu(001) with different coupling strengths, to test the effect on the relaxation. In Figure 5-5 we see the effect of reducing the coupling to 80% of normal, while in Figure 5-6 the coupling has increased to 120%. The coupling is linear in $p$ and $q$, so multiplying each by 0.8 has the effect of decreasing it to 80% of normal. To increase to 120%, we multiply by 1.2. Decreasing the coupling means weaker interactions with the reservoir, leading to more oscillations and an increase in relaxation time. Increasing the coupling has the reverse effect. In each case, the final equilibrium values are the same.

We have also tested the applicability of the instantaneous and markovian limits. Results for CO/Cu(001) at 150K are shown in Figure 5-7. The instantaneous dissipation limit shows very strong oscillations, even surpassing 1 (full population). This shows that instantaneous dissipation does not work in this case. That is to be expected, as the correlation function does not decay rapidly enough. The markovian limit shows a very fast exponential rise to the equilibrium value. The markovian limit thus gives correct values at
long times, but cannot capture the short time dynamics like the full delayed dissipation treatment can.

Finally, we present results for the quantum coherences for CO/Cu(001) in Figures 5-8 and 5-9. The coherences are not coupled to the populations, so if they are zero initially, then they will remain zero. For these runs, the initial conditions are $\rho_{01} = 0.1 + 0.1i$. Both the real and imaginary parts of the coherence decay over longer periods of time than the populations, showing oscillations on the order of $\omega_0$, gradually going to zero. At short times, the imaginary part has a similar pattern to the populations.

Our initial conditions are that the population begins entirely in the excited state, with no coherence. This would be achieved by a very rapid transition from the ground state to the excited state. In fact, experimental studies have shown that there is a very fast excitation, followed by a slow relaxation.\textsuperscript{22} The relaxation time from experiment for CO/Cu(001) at 150K is a few picoseconds.\textsuperscript{22,67} Our calculations show relaxation in about one picosecond (1 ps = 41,300 au), which is a good qualitative agreement. In addition, experiments have shown a decrease in the relaxation time at higher temperatures, which is the trend seen here. Only the delayed dissipation treatment gives this good agreement. The relaxation shown in the markovian limit is much too rapid.

5.5 Conclusions

We have studied the dissipative dynamics of a two state system coupled to a reservoir, however the method laid out in this chapter can be used in systems with more states. Here we have calculated the reduced density matrix for the evolution of the frustrated T-mode vibration of an adsorbate on a metal surface. The system began in the excited state, and the relaxation over time was calculated. Our calculated relaxation times are in good agreement with experiment.

We have repeated the calculations using the markovian and instantaneous dissipation limits. Each limit gives the correct results at long times, but the short time dynamics
are only properly described by the delayed dissipation method. The instantaneous limit appears to be invalid in this case, giving results that exceed 1 (100% population).

There are two trends shown in the results. Increasing the temperature decreases the oscillations, and leads to a faster relaxation to equilibrium. Increasing the coupling strength has a similar effect. The markovian limit, which shows no oscillations and a very fast relaxation, will be the most useful in high temperature/large coupling situations. However, when these criteria are not met, or when detailed short time dynamics are important, the delayed dissipation treatment is required.

Table 5-1. Frequencies and coupling parameters

<table>
<thead>
<tr>
<th></th>
<th>Na/Cu</th>
<th>CO/Cu</th>
<th>CO/Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_0$</td>
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<td>$1.448 \times 10^{-4} au^{-1}$</td>
<td>$2.183 \times 10^{-4} au^{-1}$</td>
</tr>
<tr>
<td>$\omega_D$</td>
<td>$1.013 \times 10^{-3} au^{-1}$</td>
<td>$1.013 \times 10^{-3} au^{-1}$</td>
<td>$7.283 \times 10^{-4} au^{-1}$</td>
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<td>$p$</td>
<td>$2.31 \times 10^{-7} au^{-2}$</td>
<td>$6.44 \times 10^{-8} au^{-2}$</td>
<td>$1.10 \times 10^{-8} au^{-2}$</td>
</tr>
<tr>
<td>$q$</td>
<td>$-5.80 \times 10^{-5} au^{-1}$</td>
<td>$1.58 \times 10^{-5} au^{-1}$</td>
<td>$3.98 \times 10^{-6} au^{-1}$</td>
</tr>
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</table>

Figure 5-1. Upper: Real part of $C(t)$ for CO/Cu(001) at 150K, 300K, and 450K. Lower: Imaginary part of $C(t)$ for CO/Cu(001) at 150K.
Figure 5-2. Population of the ground state ($\rho_{00}$) for CO/Cu(001) at 150K and 300K.
Figure 5-3. Population of the ground state ($\rho_{00}$) for Na/Cu(001) at 150K and 300K.
Figure 5-4. Population of the ground state ($\rho_{00}$) for CO/Pt(111) at 150K and 300K
Figure 5-5. Population of the ground state ($\rho_{00}$) for CO/Cu(001) at 150K for normal coupling strength and at 0.8 times the coupling strength
Figure 5-6. Population of the ground state ($\rho_{00}$) for CO/Cu(001) at 150K for normal coupling strength and at 1.2 times the coupling strength.
Figure 5-7. Population of the ground state ($\rho_{00}$) for CO/Cu(001) at 150K using delayed dissipation, the instantaneous dissipation limit, and the Markoff limit.
Figure 5-8. Real part of the quantum coherence $\rho_{01}$ for CO/Cu(001) at 150K (solid line) and 300K (dashed line)
Figure 5-9. Imaginary part of the quantum coherence $\rho_{01}$ at short times for CO/Cu(001) at 150K and 300K (upper) and long times (lower)
CHAPTER 6
ELECTRONIC AND VIBRATIONAL RELAXATION

6.1 Introduction

In the previous chapter, we studied the dissipative dynamics of adsorbates on metal surfaces, considering only two vibrational states in a single electronic state. For that model considered, there are no couplings between states. In this chapter, we explore what happens when more vibrational states are considered, which does lead to couplings. We also consider two electronic states, which adds electronic dissipation to our equations, allowing for electronic relaxation. This also allows us to add a laser pulse to cause excitation from the ground state to an excited electronic state. Here we will consider only the system CO/Cu(001). Previous work on this system\textsuperscript{7,8,39} has included only electronic dissipation; here we consider vibrational dissipation as well.

6.2 Model Details

Adding a light pulse to the system requires consideration of the interaction between the pulse (L) with the primary region and with the reservoir. We now have the hamiltonian

\[
\hat{H}(t) = \hat{H}_0 + \hat{H}_{PL}(t) + \hat{H}_{RL}(t),
\]

where \(\hat{H}_0\) was our hamiltonian in the absence of a pulse, and \(\hat{H}_{PL}\) and \(\hat{H}_{RL}\) are the interaction of the regions with light, which in the dipole approximation are

\[
\hat{H}_{PL}(t) = -\hat{D}_P \mathcal{E}_P(t),
\]

\[
\hat{H}_{RL}(t) = -\int d^3r \mathcal{E}_{ext}(t) \hat{P}_R,
\]

where \(\hat{D}_P\) is the electric dipole of the primary region and \(\hat{P}_R\) is the dipole per unit volume in the reservoir. The external field is described by \(\mathcal{E}_{ext}\), and \(\mathcal{E}_P\) is the local value inside the primary region.

To describe the electronic states, we divide the system into a primary region which includes the adsorbate and adjacent metal atoms, and the reservoir, which includes the
rest of the system as shown in Figure 6-2. This model has been used previously for studies of photodesorption. Here, we will restrict the distance from the surface to the adsorbate, $Z$, to its equilibrium value in the ground excited state, $Z_g$. The angles $\theta$ and $\phi$ are set to zero.

### 6.3 Primary Region

The parameters for the primary region come from a ZINDO parameterization. This is a semiempirical method, which is applicable to transition metals. There are two versions of ZINDO: ZINDO/1 is used for calculating ground state properties, such as bond distances, and ZINDO/S is used for calculating excited electronic state properties. Six copper atoms were included, and ZINDO/1 calculations were carried out for the ground electronic state. The results were then rescaled to fit available experimental results for the equilibrium distance from the surface to the adsorbate, as well as the binding energy. The electronic excited state was parameterized using ZINDO/S calculations, along with the transition dipole between the electronic states.

The ground and excited state potentials are

$$V_g(Z, x, \theta, \phi) = V^0_g(\theta)e^{-2\alpha_g(\theta)}\left[\sqrt{x^2+(Z-\gamma d_{\text{CO}})^2} - Z_g(\theta) + \gamma d_{\text{CO}}\right]$$
$$- 2V^0_g(\theta)e^{-\alpha_g(\theta)}\left[\sqrt{x^2+(Z-\gamma d_{\text{CO}})^2} - Z_g(\theta) + \gamma d_{\text{CO}}\right] + \frac{1}{2}M_{\text{CO}}\Omega_g(Z) x^2,$$  \(6-4\)

$$V_e(Z, x, \theta, \phi) = \Delta V_e + V^0_e(\theta)e^{-2\alpha_e(\theta)}\left[\sqrt{x^2+(Z-\gamma d_{\text{CO}})^2} - Z_e(\theta) + \gamma d_{\text{CO}}\right]$$
$$- 2V^0_e(\theta)e^{-\alpha_e(\theta)}\left[\sqrt{x^2+(Z-\gamma d_{\text{CO}})^2} - Z_e(\theta) + \gamma d_{\text{CO}}\right] + \frac{1}{2}M_{\text{CO}}\Omega_e(Z) x^2,$$  \(6-5\)

where $V^0_{g,e}(\theta)$ are potential well depths, $\alpha_{g,e}(\theta)$ are the widths of the wells, $\gamma = M_O/(M_C + M_O)$, with $M_O, M_C,$ and $M_{\text{CO}}$ are the masses of oxygen, carbon, and carbon monoxide. The C-O bond distance is $d_{\text{CO}}$, here taken to be constant; $Z_{g,e}(\theta)$ is the equilibrium distance from the center of mass of CO to the copper surface. The frequency of the frustrated translation is $\omega_{g,e}$. The potentials were found to be only weakly dependent on $\phi$, and its contribution here has been neglected.
Note that many of these parameters have a dependence on the angle $\theta$; in what follows we will write these parameters without the theta, which is assumed to be zero, so that $V^0_g = V^0_g(\theta = 0)$.

Imposing the restrictions $Z = Z_g, \theta = 0$ gives

$$V_g(x) = V^0_g e^{-2\alpha_g \left[ \sqrt{x^2 + (Z_g - \gamma d CO)^2} - Z_g + \gamma d CO \right]}$$

$$- 2V^0_g e^{-\alpha_g \left[ \sqrt{x^2 + (Z_g - \gamma d CO)^2} - Z_g + \gamma d CO \right]} + \frac{1}{2} M CO \Omega_g (Z_g)^2 x^2 \right], \quad (6-6)$$

$$V_e(x) = \Delta V_e + V^0_e e^{-2\alpha_e \left[ \sqrt{x^2 + (Z_g - \gamma d CO)^2} - Z_e + \gamma d CO \right]}$$

$$- 2V^0_e e^{-\alpha_e \left[ \sqrt{x^2 + (Z_g - \gamma d CO)^2} - Z_e + \gamma d CO \right]} + \frac{1}{2} M CO \Omega_e (Z_g)^2 x^2 \right]. \quad (6-7)$$

The dipole is

$$D_P(Z, \theta) = D_0(\theta) Z^2 \left( 1 - \tanh [\eta(\theta)(Z - Z_g(\theta))] \right), \quad (6-8)$$

which becomes a constant

$$D_P = D_0 Z_g^2. \quad (6-9)$$

Dissipation in this model was described in terms of dissipative potentials ($W_{g,e}$), given as

$$W_g(x) = \frac{\hbar}{\tau_g} e^{-2\alpha_g \left[ \sqrt{x^2 + (Z_g - \gamma d CO)^2} - Z_g + \gamma d CO \right]}, \quad (6-10)$$

$$W_e(x) = \frac{\hbar}{\tau_e} e^{-2\alpha_e \left[ \sqrt{x^2 + (Z_g - \gamma d CO)^2} - Z_e + \gamma d CO \right]}, \quad (6-11)$$

with the off-diagonal element

$$W_c(x) = (W_g(x)W_e(x))^{0.5}, \quad (6-12)$$

where $\tau_{g,e}$ are electronic state lifetimes, 5 ps for the ground electronic state, and 50 ps for the excited state. Instead of using these dissipative potentials directly, we use them to
build Lindblad operators\textsuperscript{41,42} for the electronic dissipation

\[
\left( \frac{\partial \rho}{\partial t} \right)_{\text{diss}}^{\text{el}} = -\frac{1}{2\hbar} \left( [W, \rho(t)]_+ - 2W^{0.5}\rho(t)W^{0.5} \right).
\]  

(6–13)

Values of the constants used are shown in Table 6-1. The electronic dissipation is done with the Lindblad operators, while the vibrational dissipation is done using the delayed dissipation treatment outlined in Chapter 5.

These potentials are functions of \( x \) and must be expanded in a harmonic oscillator basis set \( \phi_i(x) \) to include the vibrational states. The potentials for the ground and excited state are cast in matrix form, as

\[
\mathbf{V} = \begin{pmatrix} \mathbf{V}_g & \mathbf{V}_c \\ \mathbf{V}_c & \mathbf{V}_e \end{pmatrix},
\]

(6–14)

where

\[
(V_g)_{ij} = \int dx \phi_i^\ast(x) V_g(x) \phi_j(x),
\]

(6–15)

with a similar expression for \( \mathbf{V}_e \). The coupling between the states depends on the dipole, and the secondary region, discussed later. The Lindblad matrices are

\[
\mathbf{W} = \begin{pmatrix} \mathbf{W}_g & \mathbf{W}_c \\ \mathbf{W}_c & \mathbf{W}_e \end{pmatrix},
\]

(6–16)

with

\[
(W_g)_{ij} = \int dx \phi_i^\ast(x) W_g(x) \phi_j(x),
\]

(6–17)

and similar expressions for \( \mathbf{W}_e \) and \( \mathbf{W}_c \). The equation for the density matrix is then

\[
\frac{d\rho(t)}{dt} = -\frac{i}{\hbar} [\mathbf{V}, \rho(t)] - \frac{1}{2\hbar} \left( [\mathbf{W}_c, \rho(t)]_+ - 2\mathbf{W}_c^{0.5}\rho(t)\mathbf{W}_c^{0.5} \right) - \int_0^t \mathcal{K}(t, t') \rho(t')dt'
\]

(6–18)

where \( \mathcal{K}(t, t') \) is a supermatrix containing all of the elements from Equation 5–8.
6.4 Secondary Region

The secondary region contains the rest of the copper surface. Here we make a two
band approximation, leading to a $2 \times 2$ density matrix. To distinguish it from the density
matrix of the primary region, we will call the secondary region density matrix $\gamma$. The two
states here are the conduction band (c) and the unoccupied band (u), and we consider
only vertical transitions between the two levels.\(^{39}\) We cast the density matrix in terms of
the Pauli matrices,

$$\gamma(t) = \frac{1}{2} I + \sum_{i}^{3} \gamma_{i} \sigma_{i}, \quad \text{(6–19)}$$

with

$$\gamma_{1} = \text{Re}(\gamma_{cu}), \quad \text{(6–20)}$$

$$\gamma_{2} = -\text{Im}(\gamma_{cu}), \quad \text{(6–21)}$$

$$\gamma_{3} = \frac{1}{2}(\gamma_{cc} - \gamma_{uu}). \quad \text{(6–22)}$$

These components evolve in time according to the optical Bloch equations\(^{2,8,77}\)

$$\frac{\partial \gamma_{1}}{\partial t} = \omega_{2} f(t) \gamma_{3} - \frac{\gamma_{1}}{\tau_{\text{coh}}}, \quad \text{(6–23)}$$

$$\frac{\partial \gamma_{2}}{\partial t} = -\omega_{1} f(t) \gamma_{3} - \frac{\gamma_{1}}{\tau_{\text{coh}}}, \quad \text{(6–24)}$$

$$\frac{\partial \gamma_{3}}{\partial t} = (\omega_{1} \gamma_{2} - \omega_{2} \gamma_{1}) - \frac{\gamma_{3} - \tilde{\gamma}_{3}}{\tau_{\text{pop}}}, \quad \text{(6–25)}$$

where $\tau_{\text{coh}}$ is the coherence time, $\tau_{\text{pop}}$ is the population difference decay time, and $\tilde{\gamma}_{3}$ is the
long time equilibrium value of $\gamma_{3}$. These terms are related to the excitation rate, $\kappa_{+}$, the
deexcitation rate, $\kappa_{-}$, and the decoherence rate, $\kappa_{0}$, according to

$$\tau_{\text{coh}} = \frac{1}{2(\kappa_{+} + \kappa_{-} + \kappa_{0})^{-1}}, \quad \text{(6–26)}$$

$$\tau_{\text{pop}} = (\kappa_{+} + \kappa_{-})^{-1}, \quad \text{(6–27)}$$

$$\tilde{\gamma}_{3} = \frac{\tau_{\text{pop}}}{2}(\kappa_{-} - \kappa_{+}). \quad \text{(6–28)}$$
The \( \Omega \) are given by

\[
\begin{align*}
\Omega_1 &= -\frac{2}{\hbar} \text{Re}(d_{cu}^{(el)} E_0), \quad (6-29) \\
\Omega_2 &= \frac{2}{\hbar} \text{Im}(d_{cu}^{(el)} E_0), \quad (6-30)
\end{align*}
\]

where \( d_{cu}^{(el)} \) is the electronic dipole between the bands. The \( f(t) \) term is the laser field envelope, chosen here to be

\[
f(t) = e^{-4(t-t_0)/\tau_p^2} \cos(\omega_0 t), \quad (6-31)
\]

where \( t_0 \) is the center of the pulse, \( \tau_p \) is the width, and \( \omega_0 \) is the frequency. The excitation and deexcitation rates can be calculated from the state to state energy transfer rate, \( R_{tr} \) as

\[
\begin{align*}
\kappa_+ &= g_u R_{tr}, \quad (6-32) \\
\kappa_- &= g_c R_{tr}, \quad (6-33)
\end{align*}
\]

where \( g_{c,u} \) are the density of states of bands \( c \) and \( u \). Values of the parameters used on the optical Bloch equations are given in Table 6-2.

The value of the electric field inside the primary region depends on properties of the secondary region, and is given by

\[
\mathcal{E}_p = -\frac{2N_{el}^*(t)d_{cu}^{(el)} \gamma_2}{|z_s - z_p|^3}, \quad (6-34)
\]

where \( N_{el}^* \) is excited electron density in the metal, given by

\[
N_{el}^* = N_0 + N^*(t), \quad (6-35)
\]

where \( N_0 \) is the number of electrons always available for excitation and \( N^*(t) \) is the number of inflowing electrons. This evolves over time according to

\[
\frac{dN^*(t)}{dt} = S(t)B_s N_0 - K_d(t)N^*(t), \quad (6-36)
\]
where $B_s$ is a parameter related to the size of the S region, $S(t)$ is a source term, and $K_d$ is the rate at which hot electrons decay to the deexcited gas state. This rate is calculated from

$$K_d = \frac{g_{ep}}{\gamma_{el} T_{el}(t)}, \quad (6-37)$$

where $g_{ep}$ is the electron-phonon coupling constant, $T_{el}$ is the electronic temperature, and the electronic specific heat is $C_{el} = \gamma_{el} T_{el}$. The electronic temperature and the lattice temperature, $T_{lat}$, are calculated from the heat diffusion equations$^{22,78}$

$$\frac{dT_{el}}{dt} = \frac{g_{ep} (T_{lat} - T_{el}) + S(t)}{\gamma_{el} T_{el}}, \quad (6-38)$$

$$\frac{dT_{lat}}{dt} = \frac{g_{ep} (T_{lat} - T_{el})}{C_{lat}}, \quad (6-39)$$

where $C_{lat}$ is the specific heat of the lattice. Parameters for the heat diffusion equations are given in Table 6-3.

### 6.5 Unperturbed Dynamics

We first consider the system with no external pulse. The initial state is a Boltzmann thermal distribution. In Figure 6-3 we have the results showing the population of the ground electronic ground vibrational state, along with the coherence between the ground vibrational state and the second excited vibrational state. After 20,000 au, the system settles into a repeating beat pattern. The oscillations are large, and the effects of adding a light pulse would be difficult to determine. This behavior is dictated by the correlation function, which describes the coupling of the medium to the system. In this case, the correlation function is large, indicating a strong coupling. This accounts for the large oscillations. In addition, the correlation function does not decay rapidly; it falls off as time$^{-1}$. This may be the cause of the long-lived oscillations.

### 6.6 Results With a Pulse

To account for the oscillations that occur in the unperturbed case, we run our calculations twice. The first is the unperturbed case, which gives an idea of how long
it takes the system to settle into a repeating pattern. Once that time is known, we run the calculations again, adding the light pulse only after the system has settled. We then subtract the unperturbed population, $\rho^0(t)$, from the populations with the pulse to get the change,

$$\Delta \rho(t) = \rho(t) - \rho^0(t)$$  \hspace{1cm} (6–40)

which shows the overall effect of the pulse.

The pulse is similar to that used in the previous chapter, a gaussian of width 100 fs, fluence of 3.0 mJ/cm$^2$, and frequency 620 nm. In figure 6-4 we see the population differences. The pulse causes an excitation to the excited state, which decays to the ground state. The overall shape of the decay is due to the electronic dissipation. There is a beat pattern of oscillations in the populations; this is due to the vibrational dissipation. The coherences show this beat pattern as well, decaying to zero as the populations return to equilibrium. This same beat pattern is seen in the unperturbed dynamics.

### 6.7 Conclusion

When the correlation function is large and long lived, the system may not settle into a stable thermal equilibrium state. Long-lived oscillations in the populations need to be accounted for, to see the effects of a pulse. In the case of CO/Cu(001), we have added a laser pulse after a long simulation time, then subtracted the results from the no-pulse case in order to see the effects of the pulse. The pulse populates the excited electronic state, which then relaxes to the ground electronic state. The vibrational populations show a beat pattern as they are populated by the pulse and then gradually are depleted by the electronic dissipation.
Figure 6-1. Energy diagram for CO/Cu(001)

Figure 6-2. CO/Cu(001), reprinted with permission from A. Santana and D. A. Micha, Chem. Phys. Lett. 369, 459 (2003)
Table 6-1. Parameters for the ground and excited state potentials

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (atomic units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_g$</td>
<td>$2.68 \times 10^{-2}$</td>
</tr>
<tr>
<td>$V_e$</td>
<td>$4.45 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\alpha_g$</td>
<td>1.52</td>
</tr>
<tr>
<td>$\alpha_e$</td>
<td>2.02</td>
</tr>
<tr>
<td>$Z_g$</td>
<td>4.83</td>
</tr>
<tr>
<td>$Z_e$</td>
<td>5.16</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.572</td>
</tr>
<tr>
<td>$d_{CO}$</td>
<td>2.17</td>
</tr>
<tr>
<td>$M_{CO}$</td>
<td>$5.22 \times 10^4$</td>
</tr>
<tr>
<td>$\omega^T_g$</td>
<td>$1.45 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.572</td>
</tr>
<tr>
<td>$D_0$</td>
<td>$1.12 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Table 6-2. Parameters for secondary region

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (atomic units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{cu}$</td>
<td>0.02</td>
</tr>
<tr>
<td>$g_c$</td>
<td>$20.0 Ry^{-1}$</td>
</tr>
<tr>
<td>$g_a$</td>
<td>$1.0 Ry^{-1}$</td>
</tr>
<tr>
<td>$z_s$</td>
<td>1.0</td>
</tr>
<tr>
<td>$z_p$</td>
<td>4.83</td>
</tr>
<tr>
<td>$\tau_{pop}$</td>
<td>620.1</td>
</tr>
<tr>
<td>$\tau_{coh}$</td>
<td>1157</td>
</tr>
<tr>
<td>$\kappa_0$</td>
<td>$8.959 \times 10^4$</td>
</tr>
<tr>
<td>$R_{tr}$</td>
<td>$3.83 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Table 6-3. Parameters for the heat diffusion equations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (atomic units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_{ep}$</td>
<td>$8.22 \times 10^{-14}$</td>
</tr>
<tr>
<td>$\gamma_{el}$</td>
<td>$3.283 \times 10^{-12}$</td>
</tr>
<tr>
<td>$C_{lat}$</td>
<td>$1.190 \times 10^7$</td>
</tr>
</tbody>
</table>
Figure 6-3. Populations without a pulse of the ground electronic ground vibrational (g0) state, along with the coherence between the ground electronic ground vibrational state and the ground electronic second vibrational state (g02) at 300K.
Figure 6-4. Population differences at 300K with a pulse, for the three vibrational states in the ground electronic state.
CHAPTER 7
ELECTRONICALLY NON-ADIABATIC DYNAMICS OF Ag₃Si(111):H

7.1 Introduction

We now turn our attention to the system of a small cluster of silver atoms on a silicon surface, Ag₃Si(111):H. Here we are interested in electronic and vibrational dissipation as they relate to possible pathways of electron transfer induced by a laser pulse. This pulse may cause a transition directly from the initial state to the final, electron-transferred state. We call this direct excitation. Alternatively, the pulse may cause a transition to an intermediate state, or perhaps a series of intermediate states, which then relax into the electron-transferred state. This is indirect excitation.

In this chapter we consider both direct excitation and indirect excitation with one intermediate state. For indirect excitation, we now have three electronic states, with vibrational relaxation within each state, along with electronic couplings and relaxation between them. The direct excitation case is a two-electronic-state case, similar to that in the previous chapter. However, the correlation function for Ag₃Si(111):H is very different, and the differencing method used previously is not needed.

7.2 Model Details

As in the previous chapter, we will treat electronic dissipation and vibrational dissipation separately. The general equation of motion for the density matrix is

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [\mathbf{H}', \rho] + \left( \frac{\partial \rho}{\partial t} \right)_{el,diss} + \left( \frac{\partial \rho}{\partial t} \right)_{vib,diss}. \quad (7-1)$$

Each of the three terms is defined below. The Hamiltonian $\mathbf{H}'$ contains elements for each state as well as couplings between them. For direct excitation, we expand in a basis of two electronic states, the ground state, $g$, and the final excited state, $e$, so that

$$\mathbf{H}'_{dir} = \begin{pmatrix} H_{gg} & H_{ge} \\ H_{eg} & H_{ee} \end{pmatrix}. \quad (7-2)$$
For indirect excitation, we have a basis of three electronic states, the ground state \( g \), an intermediate excited state \( e \), and the final state \( f \), so that

\[
H'_{\text{indir}} = \begin{pmatrix}
H_{gg} & H_{ge} & H_{gf} \\
H_{eg} & H_{ee} & H_{ef} \\
H_{fg} & H_{fe} & H_{ff}
\end{pmatrix}.
\] (7–3)

The off diagonal elements are the couplings between the states, and will include the effects of the light pulse and any other non-dissipative couplings.

Each electronic state is then expanded in a basis of harmonic oscillator states, \( \phi_{i,v_i} \), where \( i = \{g, e, f\} \) is the electronic state and \( v_i = \{0, 1, 2 \ldots\} \) is the vibrational state. The density matrix is solved in this basis of vibronic states, so that

\[
\rho_{I,J} = \langle \phi_I | \hat{\rho} | \phi_J \rangle,
\] (7–4)

where we use the capital letters \( I \) and \( J \) to denote a vibronic state, so that \( \phi_I = \phi_{i,v_i} \).

The \( g \) electronic state is coupled to the \( e \) and \( f \) states through the light pulse. We use the dipole to calculate the effect of the light pulse \( (l) \) on the system,

\[
\hat{H}^{(l)}_{ij} = -D_{ij}E(t),
\] (7–5)

where \( E(t) \) is the light pulse and \( D_{ij} \) is the dipole between electronic states \( i \) and \( j \). We calculate the full vibronic couplings through the Franck-Condon overlap\(^{79,80}\)

\[
S_{I,J} = \langle i, v_i | j, v_j \rangle,
\] (7–6)

where \( S_{I,J} \) is the overlap between electronic state \( i \) in vibrational state \( v_i \) and electronic state \( j \) in vibrational state \( v_j \). The coupling due to light in the full vibronic basis is then

\[
H_{I,J}^{(l)} = H_{ij}^{(l)} S_{I,J}.
\] (7–7)

The physical parameters of our model are taken from a recent ab initio density functional study\(^{25}\) using periodic boundary conditions\(^{81}\). The model has four layers of
silicon; each layer is $4 \times 6$ atoms. The surface bonds unoccupied by the adsorbed silver cluster are saturated by hydrogen atoms, giving a total composition of Ag$_3$Si$_{96}$H$_{21}$. A picture of the system is shown in Figure 7-1. The transition dipoles ($D_{ij}$) were calculated using Kohn-Sham orbitals generated from augmented plane-wave density functional calculations, using fixed atomic positions. The transition dipoles were then used to calculate the transition oscillator strengths ($f_{ij}$), according to

$$f_{ij} = \frac{2m\omega_{ij}}{\hbar}D_{ij}^2.$$  (7-8)

There are many transitions in this system. Here we choose specific transitions according to two criteria: the transition must have a large oscillator strength and a large change in the electronic population in the silver cluster ($\Delta n$ Ag$_3$). The parameters for the chosen transitions are shown in Table 7-1.

The primary region is the silver cluster, along with the adjacent silicon and hydrogen atoms. We again consider both electronic relaxation and vibrational relaxation of the primary region.

Electronic relaxation is calculated using Lindblad dissipation,

$$\left( \frac{\partial \rho}{\partial t} \right)_{\text{el, diss}} = -\frac{1}{2}[L^\dagger L, \rho]_+ + L\rho L^\dagger,$$  (7-9)

where $[,]_+$ denotes the anticommutator, and $L$ is a matrix derived from the relaxation rates as

$$L_{IJ} = r(I \rightarrow J)^{0.5},$$  (7-10)

where $r(I \rightarrow J)$ is the transition rate from state $I$ to state $J$. The transition rate from the excited state ($e$) to the ground state ($g$), $r(e \rightarrow g)$, is approximated from experiment. Here we have chosen two values for the relaxation time, $\tau_{eg}$, 200 fs and 1 ps. The transition rate is the inverse of the relaxation time, $r(e \rightarrow g) = \tau_{eg}^{-1}$. 

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To get the rate between different vibrational states, we use Franck-Condon factors,

\[ r(e, v_e \rightarrow g, v_g) = r(e \rightarrow g) \frac{S_{ev_e,gv_g}^2}{\sum_{i,j} S_{ev_i,gv_j}^2}. \]  

(7–11)

The reverse rate is calculated by detailed balance, as

\[ r(g, v_g \rightarrow e, v_e) = r(e, v_e \rightarrow g, v_g) e^{\left[-\frac{E(e, v_e) - E(g, v_g)}{2k_bT}\right]}, \]  

(7–12)

where \( E(e, v_e) \) is the energy of the excited electronic state in the \( v_e \) vibrational state, \( T \) is the temperature, and \( k_b \) is the Boltzmann constant. In this case, the energy differences are so large that there are essentially no transitions from the ground state up to the excited state via Lindblad dissipation.

Vibrational relaxation is calculated using delayed dissipation, Equation 2–30. We assume there are no interactions via delayed dissipation across electronic states, meaning the vibrational states in the ground electronic state are coupled to each other, but not to the vibrational states in the excited electronic state, and vice versa.

### 7.3 Correlation Function

We calculate the correlation function according to Equation 5–19. The spectral density coming from the ab initio treatment is shown in Figure 7-4. There is a single large peak near 70 meV that dominates the spectral density. This is in the area of surface vibrations; bulk modes do not couple strongly to the vibrations of the silver cluster.

The correlation function is shown in Figures 7-5 and 7-6. The magnitude of the correlation function is much smaller than that for CO/Cu(001). It also has a nearly gaussian shape, and decays exponentially. This fast decay should lead to shorter lived oscillations.

### 7.4 Direct Excitation

#### 7.4.1 Initial Dynamics

In the case of direct excitation, shown in Figure 7-2, the pulse excites the system directly from the initial ground state to the final state. The final state chosen here has
a strong oscillator strength, as well as a large charge transfer. The minima of the two potentials, \( q_g \) and \( q_e \) are not the same, and the overlap between the states depends on the difference between the two, \( \Delta q \).

We first consider the system without the addition of a light pulse, to determine if there are any initial dynamics which must be accounted for. The initial state is entirely in the ground electronic state, with a thermal distribution of vibrational states, at 300 K. At this temperature, the excited electronic state is not significantly populated. We consider five vibrational states in each electronic state, for a total of ten vibronic states. The populations of the ground state, \( g_0 \), and the coherence between the ground and second excited vibrational state, \( g_{02} \), are shown in Figure 7-7. When there is no pulse, the only driving force is the delayed dissipation. In this case, the dissipation is weak, and has little effect on the population. There is some change in the populations, shown in the upper panel of Figure 7-7, however, the changes are not nearly as strong as in CO/Cu(001), and a differencing method is not required. We can assume the system begins in a stable thermal equilibrium.

### 7.4.2 Photoinduced Dynamics

We repeat the simulation, this time adding a pulse. The pulse parameters are the same as those used in the previous chapters. Because the dissipation is weak, we have also repeated the simulation including the pulse and Lindblad dissipation, but not the delayed dissipation. The total ground and electronic populations are shown in Figures 7-8 and 7-9. The pulse causes a large transfer of population from the ground state to the excited state, which then decays smoothly back to the ground state. This decay is due to the Lindblad dissipation. As the transition rate is decreased (by increasing the time from 200 fs to 1 ps), the decay takes longer. The electronic relaxation dominates the dynamics. There is some change in the populations at early times when delayed dissipation is added, but this effect disappears as time goes on.
In Figure 7-10 we focus on only the highest energy state to see the effects of delayed dissipation. While there is some effect, the population oscillates around the case without delayed dissipation. The other populations show a similar pattern. It may be that these effects are important early in the dynamics, however the light pulse and the electronic relaxation are the dominant factors. In this case, the dynamics are largely captured by including only the electronic dissipation.

The quantum coherence between states e0 and e1 is shown in Figure 7-11. The coherence peaks early, around 2500 au, just as the e state is being populated by the pulse. The coherence has disappeared by 40,000 au.

### 7.5 Indirect Excitation

In the case of indirect excitation, depicted in Figure 7-3, the light pulse excites from the initial ground state (g) to an excited state (e), which then relaxes into the final state (f). This final state is the electron-transferred state. The intermediate excited state has a large oscillator strength, but small charge transfer. The final state couples strongly to the intermediate state, but weakly to the ground state, so there is little direct excitation. The final state has a large charge transfer.

The strong coupling between the g and e states leads to electronic relaxation, which is again treated with the Lindblad form. Here we have chosen to use only the 200 fs rate for the relaxation. The coupling between the g and f states is so small that the relaxation is very slow, and has been neglected in our calculations. The vibrational coupling is treated with delayed dissipation, with no vibrational coupling across electronic states.

The e and f electronic states are are coupled through momentum, as

\[ V_{ef} = -\frac{\hbar^2}{m} \langle e | \frac{\partial}{\partial q} | f \rangle \frac{\partial}{\partial q}, \tag{7–13} \]

where m is the mass of the silver cluster. We need the coupling not just between electronic states, but also the vibrational states, so we expand this expression in terms of harmonic
oscillator states to give
\[
\langle v_e | V_{ef} | v_f \rangle = -\frac{\hbar^2}{m} \sum_{v'_f} \langle e, v_e | \frac{\partial}{\partial q} | f v'_f \rangle \langle v'_f | \frac{\partial}{\partial q} | v_f \rangle.
\] (7–14)

In our notation \( |e, v_e\rangle \) is the \( e \) electronic state in the \( v_e = \{0, 1, 2 \ldots \} \) vibrational state. The first term can be expressed as a Franck-Condon overlap and a coupling factor, \( c_{ef} \), which depends only on the electronic states, to give
\[
\langle v_e | V_{ef} | v_f \rangle = -\frac{\hbar^2}{2} \sum_{v'_f} \langle e, v_e | f v'_f \rangle c_{ef} \langle v'_f | \frac{\partial}{\partial q} | v_f \rangle,
\] (7–15)

The last term can be expressed in terms of the creation and annihilation operators \( a^\dagger \) and \( a \) as
\[
\langle v'_f | \frac{\partial}{\partial q} | v_f \rangle = -\frac{1}{\hbar \sqrt{2}} \langle v'_f | (a^\dagger - a) | v_f \rangle
\]
\[
= -\frac{1}{\hbar \sqrt{2}} (\sqrt{v_f + 1} \delta_{v'_f,v_f+1} - \sqrt{v_f} \delta_{v'_f,v_f-1}).
\] (7–16)

Inserting this into Equation 7–15 gives
\[
\langle v_e | V_{ef} | v_f \rangle = c_{ef} \frac{\hbar}{m} \left( \sqrt{v_f + 1} \langle e, v_e | f v_{f+1} \rangle - \sqrt{v_f} \langle e, v_e | f v_{f-1} \rangle \right),
\] (7–17)

which is the expression used to calculate the coupling. The \( c_{ef} \) term comes from the ab initio study, and is \( 1.764 \times 10^{-4} \) au.

**7.5.1 Initial Dynamics**

We again test the initial equilibrium by considering the system in the absence of a light pulse. We add five vibrational states in the \( f \) electronic state, for a total of fifteen states. The initial state is in a thermal distribution of vibrational states in the ground electronic state at 300 K. The intermediate electronic state is lower in energy than the final electronic state, but is not low enough to be populated at this initial temperature.
The populations at 300 K without a pulse are shown in Figure 7-12. The results are similar to the direct case, with small oscillations that rapidly decay. There is no population in either the $e$ or $f$ states.

### 7.5.2 Photoinduced Dynamics

The pulse used here is the same as for the direct case. We assume that, as before, there are no initial dynamics which must be accounted for. The populations are shown in Figure 7-13, for results with and without delayed dissipation. In each case, the Lindblad dissipation is included. While the delayed dissipation has little effect on the total population of the intermediate state, there is a noticeable increase in the population of the final, charge transferred state. In this case, the electronic dissipation is still the dominant driving force, but the delayed dissipation does have an effect and should be included. Vibrational relaxation enhances the transfer into the final state. The final population of the charge transferred state is about 3.5%. In this model, this population is long-lived, and could lead to surface photovoltage.

### 7.5.3 Memory Time

The delayed dissipation in this model is weak, and its effects decay after a short period of time. This model then is a good test for use of the memory time concept, as detailed in Section 4.4. If our results with a memory time are the same as those obtained using the full memory kernel, then we may be able to use the memory time to speed up our simulations, and overcome some of the computational problems which can arise when large systems or long simulation times are considered.

The memory time approach also changes our initial state. In the previous simulations we begin with the system in a thermal distribution at $t = 0$. In this case, the system is not only in a thermal distribution at time $t = 0$, but it has also been in that state for the duration of $t_{\text{mem}}$. This should change the dynamics for the different states in different ways, depending on whether or not they are initially populated. For the $g$ states, which are all initially populated, we expect the initial oscillations to either disappear, or at
least be reduced. We should see a more stable initial state. For initially unpopulated states, we should see no change in the dynamics. At the beginning of the simulation, there should be no change; the initial population is zero, so any memory terms involving these populations will also be zero. If we have chosen a long enough memory time, we should see no deviations later in the simulation either, since we are only discarding very small values of the memory kernel.

Returning to Figure 7-12, we see that most of the oscillations in the $g_0$ population have largely subsided by 50,000 au. We then take this value for the memory time, $t_{\text{mem}}$, and truncate the memory term as shown in Equation 4–103. We then repeat the simulation with the same parameters as before.

In the absence of a light pulse, we expect more stable initial dynamics. The populations of the $g_3$ and $g_4$ states are shown in Figure 7-14 for the full memory kernel, and using the memory time cutoff. There are some very slight oscillations in the populations when using the memory time, but overall it is much more stable initially than in the full memory kernel case. The initial state of the system more closely resembles a stationary thermal equilibrium.

When a pulse is added, the dynamics should be similar between the two approaches. Results for the $g$ electronic state populations are shown in Figure 7-15, along with the previous results which include the entire memory kernel. The populations of the $g$ states are very similar, although there are some small differences in them. The $g_0$ state has the largest difference, with the memory time approach giving a smaller value at long times. However, these differences are small, and one can consider the memory time approach effective.

The populations of the $e$ and $f$ electronic states are shown in Figures 7-16 and 7-17. These states are not populated initially, so we expect to see no difference in the populations. This is exactly what is seen - the memory time approach gives the same results.
7.6 Conclusions

In the case of Ag$_3$Si(111):H, the correlation function is small, and decays rapidly. This leads to delayed dissipation having little effect on the dynamics. Initially, the system can be considered to be in a stable thermal equilibrium, there is no reason to extend the initial part of the simulation to account for any correlations.

In the case of direct excitation, when a pulse is added, there are transitions to the excited states, then a relaxation dominated by the electronic terms. The vibrational (delayed) dissipation plays a very small role. In the case of indirect excitation, including the delayed dissipation does have an effect on the dynamics - there is an increase in the final population of the final state.

We have also tested our memory time approach and achieved good results. There are some small differences for initially populated states, but the results for initially unpopulated states are the same as those obtained using the full memory kernel. The memory time approach would be very well suited for a system which has relatively few initially populated states, with many initially unpopulated states. This approach can also give an initial state which is close to a stable thermal equilibrium.

<table>
<thead>
<tr>
<th>System</th>
<th>Transition</th>
<th>$\omega$, au</th>
<th>$\Delta E$, au</th>
<th>$f_{ij}$</th>
<th>$\Delta q$, au</th>
<th>$\Delta n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_3$Si</td>
<td>-</td>
<td>$1.0858 \times 10^{-3}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ag$_3^+$Si$^-$</td>
<td>HOMO-4 $\rightarrow$ LUMO+3</td>
<td>$9.9410 \times 10^{-4}$</td>
<td>$7.3965 \times 10^{-2}$</td>
<td>0.1067</td>
<td>$-6.4407 \times 10^{-2}$</td>
<td>0.2816</td>
</tr>
<tr>
<td>Ag$_3$Si$^*$</td>
<td>HOMO $\rightarrow$ LUMO+15</td>
<td>$9.1339 \times 10^{-4}$</td>
<td>$7.2359 \times 10^{-2}$</td>
<td>0.6442</td>
<td>$-3.9081 \times 10^{-2}$</td>
<td>0.0145</td>
</tr>
<tr>
<td>Ag$_3$Si$^+$</td>
<td>HOMO $\rightarrow$ LUMO+12</td>
<td>$1.1270 \times 10^{-3}$</td>
<td>$6.8163 \times 10^{-2}$</td>
<td>0.0036</td>
<td>$-2.3497 \times 10^{-2}$</td>
<td>0.3542</td>
</tr>
</tbody>
</table>

Table 7-1. Parameters for the chosen transitions in Ag$_3$Si(111):H
Figure 7-1. Ag$_3$Si(111):H, reprinted with permission from D. S. Kilin and D. A. Micha, J. Phys. Chem. C 113, 3530 (2009)
Figure 7-2. Energy diagram for $Ag_3Si(111):H$, direct excitation

Figure 7-3. Energy diagram for $Ag_3Si(111):H$, indirect excitation
Figure 7-4. Spectral density of Ag$_3$Si(111):H
Figure 7-5. Real part of the correlation function of $\text{Ag}_3\text{Si}(111)$:H
Figure 7-6. Imaginary part of the correlation function of Ag$_3$Si(111):H
Figure 7-7. The g0 population and g02 coherence without a pulse
Figure 7-8. Total population of the ground and excited electronic states with and without delayed dissipation, $\tau_{el} = 200$ fs
Figure 7-9. Total population of the ground and excited electronic states with and without delayed dissipation, $\tau_{el} = 1$ ps
Figure 7-10. Population of the $e_4$ state, with and without delayed dissipation.
Figure 7-11. Quantum coherence between states $e_0$ and $e_1$
Figure 7-12. Population of the vibrational states of the ground electronic state for the indirect case without a pulse
Figure 7-13. Total population of the ground, excited, and final electronic states with and without delayed dissipation, $\tau_{el} = 200$ fs
Figure 7-14. Populations of the $g_3$ and $g_4$ states without a light pulse, using either the full memory kernel or the memory time.
Figure 7-15. Vibrational populations of the ground electronic state with the full memory (dashed curve) and using a memory time of 50000 au (solid curve)
Figure 7-16. Vibrational populations of the excited electronic state, $e$, with the full memory (dashed curve) and using a memory time of 50000 au (solid curve)
Figure 7-17. Vibrational populations of the final electronic state, $f$, with the full memory (dashed curve) and using a memory time of 50000 au (solid curve)
CHAPTER 8
CONCLUSION

In this work, we have laid out the theoretical framework for studying different forms of energy dissipation in quantum-mechanical systems. We have also developed a numerical method for propagating the integro-differential equations which come out of the theory. We have also shown how this approach may be extended to quantum-classical systems.

We have tested our method on physical systems which include dissipation due to both vibrational and electronic relaxation. Our method also allows for the excitation of the system by a light pulse. These systems have both fast dissipation, and slow (delayed) dissipation. We have seen that the correlation function, which describes the coupling between the primary region and the reservoir, determines the effect of the delayed dissipation.

In the case of adsorbates on metal surfaces, our calculated relaxation times agree well with available experimental results. We have also studied two mechanisms of electron transfer induced by a light pulse in a metal cluster on a semiconductor surface. Both direct and indirect excitation can lead to charge transfer; the indirect excitation case produces a long lived charge transfer state.

8.1 Vibrational Relaxation

Initially, we focused on only vibrational relaxation. We have shown, in the case of a strong coupling to the medium, only the full delayed dissipation treatment can fully describe the dynamics. The instantaneous and markovian limits do give correct equilibrium values, but do not capture the short-time dynamics.

The delayed dissipation may have such a strong effect that there are oscillations at the beginning of the simulation, before any pulse is added. When this is the case, we have used a differencing method to determine the effects of an added pulse. This effect occurs when the correlation function is large and long-lived. When the correlation function is
small and decays rapidly, these initial effects do not appear, and no differencing method is required.

8.2 Electronic and Vibrational Relaxation

Our method is capable of handling different types of dissipation at the same time. We have used a Lindblad formalism to treat electronic dissipation, while treating the vibrational dissipation with a memory kernel. In the systems studied, we have seen that the electronic relaxation tends to dominate the overall dynamics. Including the vibrational relaxation is necessary to obtain the correct long-time results, and to see fine structure in the short-time dynamics.

8.3 Program Development

Our program has been applied to studies of dissipation in quantum mechanical systems, but it is not limited to these. It has been designed to solve integral and integro-differential equations of a general form. In addition, it has been designed to run on systems with parallel processors; we have used both the OpenMP and MPI standards to give the program the widest use on different systems.

The core of the program, which handles the numerical algorithms, is very general, and is kept separate from the modules which handle system-specific functions. This allows for the program to be applied easily to many different systems, with a minimum of recoding.

8.4 Future Work

We have focused on small systems - no more than fifteen states. However, our program is general enough to handle larger systems. Adding more states adds computer time, but this effect can be mitigated somewhat by allowing additional processors to run the code. We can also implement the idea of a memory time, where correlations that occur before a specified time are ignored. This allows the method to scale better, and allow for more states to be considered. Doing so could allow for more complex systems to be studied.
We have also shown how dissipation could be handled in a quantum-classical treatment. The programs which handle dissipation and the quantum-classical treatment are separate; however it should be possible to combine them into one program capable of dealing with dissipation in both quantum and quantum-classical systems.
APPENDIX A  
PROGRAM DETAILS

A.1 Overview

Our program is designed to solve matrix-valued integro-differential equations, using Runge-Kutta integration schemes. It has been applied to Liouville-von Neumann equations, but its use is not limited to these. There are two types of equations considered. The first, which is the more general, is

$$\frac{\partial \rho(t)}{\partial t} = f[t, \rho(t), z(t)]$$  \hspace{1cm} (A–1)

with

$$z(t) = \int_0^t K[t, t', \rho(t')] dt'$$  \hspace{1cm} (A–2)

This must be solved using an explicit method. There is also the linear case, where

$$\frac{\partial \rho(t)}{\partial t} = V(t)\rho(t) + \int_0^t M(t, t')\rho(t')dt'$$  \hspace{1cm} (A–3)

This special case of the first equation can be solved using either an explicit or implicit method.

There are two separate modules of the program. The first, StoreAll.f90, contains the Runge-Kutta propagation code. This module is independent of the system being solved, and should not be altered. The second module, funcs.f90, contains the model-specific details. This section handles the calculation of f and z, and also controls the output format. The program is written completely in Fortran 90.

A.2 Model Specific Functions

The file funcs.f90 contains the following functions and subroutines, all of which are required by the program.

- **init_funcs** This subroutine handles any operations that must happen in the beginning of the simulation. These may include reading parameters, initializing variables, or opening required input or output files.
• **final_funcs** This subroutine is called at the end of the simulation. Possible operations performed here are recording end values or averages, and closing files.

• **rho0** This subroutine sets the initial value of the density matrix, \( \rho(0) \).

• **do_f** This subroutine calculates \( f \) as in equation A–1, where \( t, \rho(t) \) and \( z(t) \) are assumed to be given.

• **do_V** This subroutine calculates \( V \) as in equation A–3. This subroutine is only called when implicit integration is used.

• **do_K** This subroutine calculates \( K \) as in equation A–1, where \( t, t', \) and \( \rho(t') \) are assumed to be given.

• **do_M** This subroutine calculates \( M \) as in equation A–3. This subroutine is only called when implicit integration is used.

• **write_rho** This subroutine is called at the end of each propagation step. It controls the output. In the simplest case, it can record the current \( t \) and \( \rho(t) \) to an output file. However, it could be used for more detailed output if desired. The output files needed should be opened during `init_funcs`, and closed in `final_funcs`.

### A.3 Input And Output Files

The program uses the following input files:

• **PVDRK.in** - this file contains all of the constants required. These include those relevant to the model system, as well as calculation parameters (stepsize, etc.). The constants are enumerated in a simple `variable = value` format.

• **mX.in** - Here 'X' is the order of the integration, for a fourth-order calculation, the program will open `m4.in`. This file contains the parameters for the \( a, b, \) and \( c \) matrices in the Runge-Kutta algorithm. This is only required currently for explicit methods. For implicit methods currently only one fourth-order method is supported, and the constants for it are stored in the program itself.

• Others - it may be required to add additional input files to be read by the system module, `funcs.f90`. For example, in the case of Ag\(_3\)Si(111):H we have also used
nElec.in, which specifies the number of electronic and vibrational states as well as parameters for each state.
REFERENCES


BIOGRAPHICAL SKETCH

Andrew Leathers was born in Lexington, Kentucky. His family would later move to Virginia, where his brother Matthew was born, and a few years later return to Kentucky, settling in Louisville. In 1994, Andrew would begin attending the University of Kentucky, the alma mater of his parents Steven and Marilyn. After his junior year, he became a teaching assistant for the physical chemistry laboratory, and became a research assistant in the field of quantum chemistry under Dr. Roger Grev. He graduated cum laude in 1999 with bachelors degrees in both chemistry and mathematics.

Shortly after graduation, Andrew moved south to Atlanta where he spent a few years working in an environmental laboratory. During this time, he taught himself some basic programming to automate data collection and reporting in the lab. As he learned, he discovered he enjoyed programming, and decided to return to the field of chemistry, with an emphasis on computational work.

In the summer of 2003, he moved south again to Gainesville, Florida to enroll in graduate school and join the Quantum Theory Project at the University of Florida. He took an interest in density matrix theory, and began to work under Dr. David Micha.