Relaxation and Spectra in Condensed Phases

by

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Abstract

In this thesis, various problems in the quantum theory of relaxation are considered. We first discuss the dynamics of low temperature tunneling in condensed phases. With the aid of a variational unitary transformation, we are able to study the limits of both weak and strong coupling of the tunneling system to the environment. Next we discuss the physical implications of the standard Redfield equations when perturbation theory is carried out to fourth order. We then apply similar techniques to the study of the spin-boson problem. Here, various methods of approximate resummation are used to calculate the mean position of a tunneling particle coupled to a fluctuating quantum environment. The next section deals with a theoretical attempt to explain recent hole burning experiments in a low temperature polymer glass. The last section deals with the nonperturbative theory of pure dephasing.

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Chapter 1

Introduction

The relaxation properties of a small quantum system coupled to a heat bath provide the foundation for much of modern spectroscopy. For instance, the Bloch equations, which describe the relaxation of two quantum levels in the presence of a dissipative environment, are highly successful in the description of phase and energy relaxation in both nuclear magnetic resonance and the optical spectroscopy of chromophores. In order to provide a microscopic description of the relaxation properties of such systems, one must start with a Hamiltonian that models the relevant features of the system, the bath and the interaction between them. For a two level system interacting with a generic bath, the Hamiltonian takes the form

$$H = H_{TLS} + H_{bath} + V_{TLS-bath},$$

(1.1)

where the most general form of $V_{TLS-bath}$ is

$$V_{TLS-bath} = (|e\rangle\langle e| - |g\rangle\langle g|)\dot{V}_{pd} + |e\rangle\langle g|\dot{V}_{pr} + \text{c.c.}$$

(1.2)

Here, the $\dot{V}$ terms are pure bath operators, $|e\rangle, |g\rangle$ are the excited and ground states of the isolated system, and "c.c." denotes complex conjugate. $\dot{V}_{pd}$ causes phase relaxation ("pure dephasing"), while the $\dot{V}_{pr}$ term induces energy relaxation.

Once the Hamiltonian is specified, equations of motion for the system variables
of interest must be found. Starting with the density matrix of the entire system plus bath,
\[ \rho(t) = \exp(-iH^t t)\rho(0), \] (1.3)
where \( H^X O = [H, O] \) (i.e. the commutator of the Hamiltonian with an operator), a reduced density operator for the system may be defined
\[ \sigma(t) = \text{Tr}_b \rho(t). \]

Calculation of the reduced density matrix elements provides the quantities necessary for a description of the relevant physical observables. For instance, in the case of the Hamiltonian (1-1), the line shape function
\[ I(\omega) = I_{Rd} \int_0^\infty dt e^{-i\omega t} \langle \mu(0)\mu(t)\rangle, \] (1.4)
is essentially (in the Condon approximation) the Fourier transform of the off-diagonal density matrix element \( \sigma_{eg}(t) \). In the case of two state electron transfer (modeled by the spin-boson Hamiltonian), the mean position of the tunneling particle is given by \( \sigma_{ee}(t) - \sigma_{gg}(t) \), and is thus governed by the digonal elements of the reduced density matrix.

Starting from equation (1-3) and the assumption that the system and bath are initially uncorrelated, the equation for the reduced density matrix of the system may be expressed in the interaction picture as
\[ \sigma(t) = \text{exp}_{T^+}(-i \int_0^t \dot{V}^e(\tau)d\tau) \sigma(0), \] (1.5)
where \( T^+ \) denotes a positive time-ordering and \( \langle ... \rangle \) denotes a thermal average over the bath. A general method for obtaining equations of motion for the system variables is the use of cumulant expansion techniques that approximately resum the terms that appear in the thermal average in equation (1-4). Under the assumptions of weak coupling and rapid decay of correlations in the bath, a second order cumulant expansion
leads to the well known Redfield equations. In general, it is a difficult task to perform calculations when a second order truncation of the cumulant series is not justified. This thesis is devoted to the calculation of the relaxation properties of a small system coupled to a thermal bath in cases where low orders of perturbation theory are not justified. The methods we employ are higher order cumulant expansions, unitary transformations, and in one case, exact solution.

This thesis is organized as follows: in chapter 2, a tunneling system consisting of four states interacting with a bath of harmonic oscillators is studied. Through the use of a variationally optimized unitary transformation, both the weak and strong coupling limits are studied. In chapter 3, we discuss the physical implications of the fourth order extension of the Redfield equations. In chapter 4, we use various fourth order cumulant expansion methods to study the celebrated spin-boson problem. In chapter 5 we study the problem of spectral hole burning in glasses under the assumptions of strong coupling. In the last chapter we study an exactly solvable model of vibronic line shapes in condensed phases.
Chapter 2

A Study of the Coupling Dependence of Relaxation Rates in a Model of Low Temperature Tunneling Dynamics

2.1 Introduction

The dynamics of a tunneling system interacting with a heat bath of harmonic oscillators has been extensively studied in a model that considers the lowest two levels of a symmetric double-well system, with the coupling taken to be linear in both the system and bath coordinates. [1, 2, 3, 4]. Parris and Silbey [5] treated the more general case of a tunneling system composed of two coupled sets of vibrational levels, thus allowing for excited state dynamics in the double well problem. Here we study in detail a specific case of the problem treated by Parris and Silbey; namely the symmetric double-well system composed of four levels, with tunneling between the upper vibrational levels only (see figure 2.1). In particular, we examine in detail the dependence of the various rates in the problem as a function of the coupling parameters that mediate the system-bath interactions.
We wish to study this simple model for a variety of reasons. First, by providing solutions to the dynamics of the tunneling particle, complete with explicit expressions for the various rates in the problem, we can hope to make contact with experiments probing both the temperature and coupling strength dependence of low temperature systems that contain an interplay between tunneling and vibrational relaxation [6].

Our study may also stand on its own as an example of a simple quantum system with relaxation properties that depend on both tunneling and vibrational dynamics. In this light, our system may be viewed as a quantum tunneling analog of the double-well extensions of Kramers' problem [7, 8]. The classical Kramers problem treats the transport of a Brownian particle over a barrier due to interactions with a heat bath. The problem has approximate analytical solutions in two limiting situations. When the frictional coupling between the particle and the bath is small, thermal equilibration within the well is very slow relative to the dynamics of the particle near the barrier top. When the damping is large, the well is assumed to be in thermal equilibrium, and the rate limiting step in the escape process is the flux near the barrier top. Thus, analytical solutions can be found when there is a clear separation of time scales between thermal well equilibration and escape dynamics near the barrier peak.

Our model contains quantum analogs to classical well equilibration and barrier flux. In our model, intrawell vibrational relaxation mirrors the classical equilibration of the particle in the well, while tunneling between excited vibrational states is analogous to classical barrier flux. Frictional effects are introduced by coupling the particle to a bath of harmonic oscillators. We wish to show the similarities and differences between this simple quantum model and the classical Kramers problem.

Recently, studies have integrated low temperature quantum effects and classical barrier hopping [4, 6, 8, 9]. These “quantum Kramers” problems include tunneling corrections to the classical rate of escape, and show explicitly the crossover between the classical and quantum regimes. In contrast, we focus purely on the quantum dynamics, so that comparisons may be made with the analogous classical problem.
2.2 The Hamiltonian

Our Hamiltonian may be written as \((\hbar = 1)\)

\[
H = \sum_q \omega_q a_q^+ a_q + \Omega I_1 + J_1 \sigma_{1x} + V_0 \sigma_{0z} + V_1 \sigma_{1z} + V_R,
\]

(2.1)

where

\[
I_1 = |R_1><R_1| + |L_1><L_1|,
\]

(2.2)

\[
\sigma_{1x} = |R_1><L_1| + |L_1><R_1|,
\]

(2.3)

\[
\sigma_{nz} = |L_n><L_n| - |R_n><R_n|; \quad (n = 0, 1),
\]

(2.4)

\[
V_n = \sum_q g_{qn}(a_q + a_q^+); \quad (n = 0, 1).
\]

(2.5)

\(V_R\) is the, as yet, unspecified vibrational relaxation term. Such a Hamiltonian is a four level extension of the spin-boson Hamiltonian [1] that includes vibrational relaxation [4]. Our Hamiltonian models a double-well system consisting of left and right sites. Each site contains two separate vibrational manifolds. The manifolds are linearly coupled to the displacement of the modes of a bath of harmonic oscillators, with a coupling strength \(g_{qn}\), where \(q\) labels the mode of the bath and \(n\) labels the state of the vibrational manifold \((n = 0, 1)\). The energy separation of the manifolds is given by \(\Omega\), which is assumed to be larger than any other energy in the problem, with the exception of the cutoff frequency \((\omega_c)\) of the bath. Tunneling occurs only between excited vibrational levels. Vibrational relaxation is assumed to occur in the vibrational manifolds of a given site only (i.e. the left and right sites are not vibrationally coupled). Fig2.1 shows an energy level diagram of our system.

In order to facilitate the calculation of relaxation rates in the problem, we perform a variational polaron transformation [2] on the Hamiltonian (2.1). The unitary operator

\[
U = \Pi_n U_n; \quad (n = 0, 1)
\]

(2.6)

\[
U_n = \exp[-\sigma_{nz} \sum_q \frac{f_{qn}}{\omega_q}(a_q - a_q^+)].
\]

(2.7)
effects the transformation. We will be concerned with calculating the mean position of the tunneling particle,

\[ \langle Q(t) \rangle = \langle \sigma_{0z}(t) + \sigma_{1z}(t) \rangle. \]  

(2.8)

Since \( \sigma_{0z} \) and \( \sigma_{1z} \) commute with \( U \), we note

\[ \langle Q(t) \rangle = Tr[(\sigma_{0z} + \sigma_{1z})\rho(t)] = Tr[(\sigma_{0z} + \sigma_{1z})(U\rho(t)U^+)]. \]  

(2.9)

We may thus define a reduced density matrix

\[ \sigma(t) = Tr_b[U\rho(t)U^+] \]  

(2.10)

from which the dynamics of the tunneling particle are calculated. The transformation thus defines an appropriate zeroth order Hamiltonian from which perturbation theory can be used.

The variational constants \( f_{qn} \) are chosen to minimize the free energy. In the absence of tunneling and the vibrational relaxation term, the Hamiltonian is diagonalized by the choice \( f_{qn} = g_{qn} \) (since there is no tunneling in the lower vibrational manifold, \( f_n = g_n \)). When the coupling of the tunneling system to the bath vanishes, \( f_{qn} = 0 \). In the general case we expect \( f_{qn} \) to fall between these two limiting values, while providing an upper bound on the free energy.

After switching to a basis

\[ |1> = \frac{1}{\sqrt{2}}(|L_0> + |R_0>), \]  

(2.11)

\[ |2> = \frac{1}{\sqrt{2}}(|L_0> - |R_0>), \]  

(2.12)

\[ |3> = \frac{1}{\sqrt{2}}(|L_1> + |R_1>), \]  

(2.13)

\[ |4> = \frac{1}{\sqrt{2}}(|L_1> - |R_1>), \]  

(2.14)
the transformed Hamiltonian may be written

\[ \hat{H} = \hat{H}_0 + \hat{V} + \hat{V}_R, \]

(2.15)

\[ \hat{H}_0 = (\Omega + j)|3 \rangle \langle 3| + (\Omega - j)|4 \rangle \langle 4| + \sum_n \omega_n a_n^+ a_n, \]

(2.16)

\[ \hat{V} = \Phi(|3 \rangle \langle 3| - |4 \rangle \langle 4|) + \Phi^+|3 \rangle \langle 3| + \Phi|4 \rangle \langle 4|, \]

(2.17)

\[ \hat{V}_R = \gamma|b^+ \rangle \langle 1| + b|3 \rangle \langle 4| + |b^+ \rangle \langle 2| + b|4 \rangle \langle 2|, \]

(2.18)

where

\[ \psi = \frac{1}{2}(\psi_1 + \psi_1^+), \]

(2.19)

\[ \Phi = [\varphi_1 + \frac{1}{2}(\psi_1 - \psi_1^+)], \]

(2.20)

\[ \psi_1 = J \exp[-2 \sum_n \frac{f_{1n}}{\omega_n}(a_n - a_n^+)] - J, \]

(2.21)

\[ J = J \exp\left[-2 \sum_n \left(\frac{f_{1n}}{\omega_n}\right)^2 \coth\left(\frac{\beta \omega_n}{2}\right)\right], \]

(2.22)

\[ \varphi_1 = \sum_n (g_{1n} - f_{1n})(a_n^+ + a_n), \]

(2.23)

\[ f_{1n} = \frac{g_{1n}}{(1 + 2\frac{\omega_n}{\omega_n \coth(\beta \omega_n/2)} \tanh(\beta j))}, \]

(2.24)

and \(b^+\) is an annihilation (creation) operator for the mode of the bath responsible for vibrational relaxation (e.g. an optical mode of the lattice). For our choice of the vibrational relaxation term, \(\hat{V}_R\), we keep only the energy conserving terms, and assume that there is a single mode in resonance with the transition energy \(\Omega\) [10]. To keep the discussion as simple as possible, only one-phonon terms are retained. In a more realistic treatment, multiphonon processes would be included [10]. Note that \(\gamma\) is a coupling strength with units of energy.
The vibrational (one-phonon) part of the Hamiltonian is postulated in a specific form after the unitary transformation is made on the Hamiltonian. Since the thermal average of $\hat{V}_R$ is zero, no modification of the $f_{qn}$ is necessary [2]. Our form for $\hat{V}_R$ will clearly be accurate only in the weak-coupling limit for vibrational relaxation. In the strong-coupling limit, we must view our form of $\hat{V}_R$ as merely suggestive of the physics we are trying to model. Furthermore, the vibrational scattering rates are limited by the vibrational energy splitting $\Omega$. Since these rates must be smaller than $\Omega$ (or else distinct vibrational states could not be resolved), we need not worry about incorrect use of weak coupling equations (Redfield equations) for all physically acceptable values of $\gamma$.

The variational polaron transformation defines a partitioning of the Hamiltonian into “new” unperturbed ($\hat{H}_0$) and interaction ($\hat{V} + \hat{V}_R$) parts. Note, however, that a large part of the original interaction may be contained in $\hat{H}_0$. This partitioning of the Hamiltonian makes the use of low order perturbation theory on the “new” interaction part possible even in the strong-coupling limit, since much of the “old” interaction is placed into $\hat{H}_0$. In our transformed picture, we note that the tunneling matrix element (2.22) is “renormalized” by a Franck-Condon factor [2], which reduces the tunneling rate between sites.

**2.3 Dynamics**

Standard Redfield theory [11] is used to find equations of motion for the population difference between states of the left and right well:

$$< Q(t) >= s_{0x}(t) + s_{1x}(t), \quad (2.25)$$

$$s_{0x}(t) = < 1|\sigma(t)|2 > + < 2|\sigma(t)|1 >, \quad (2.26)$$

$$s_{1x}(t) = < 3|\sigma(t)|4 > + < 4|\sigma(t)|3 >, \quad (2.27)$$
where $\sigma(t)$ is the time-dependent reduced density operator of the system. Defining

$$s_{0y} = i(\langle 1|\sigma(t)|2 \rangle - \langle 2|\sigma(t)|1 \rangle),$$

(2.28)

$$s_{1y} = i(\langle 3|\sigma(t)|4 \rangle - \langle 4|\sigma(t)|3 \rangle),$$

(2.29)

we find, after invoking the usual Redfield-like approximations [5, 12] (neglecting terms connecting states $|1>, |2>$ to states $|3>, |4>$ due to the rapid oscillation in the phase of such terms, and decoupling the population and the coherence variables) the equations of motion

$$\dot{s}_{0x} = -F_{01}s_{0x} - F_{10}s_{1x},$$

(2.30)

$$\dot{s}_{1x} = -2Js_{1y} - \left(\frac{1}{\tau}\right)s_{1x} - F_{01}s_{0x} - F_{10}s_{1x},$$

(2.31)

$$\dot{s}_{0y} = -F_{01}s_{0y} - F_{10}s_{1y},$$

(2.32)

$$\dot{s}_{1y} = 2Js_{1x} - \left(\frac{1}{\tau}\right)s_{1y} - F_{01}s_{0y} - F_{10}s_{1y}.$$  

(2.33)

The expressions for the rates [4] are given by

$$\frac{1}{\tau} = \Gamma_{pd} + \frac{1}{2}[1 + e^{-2\beta}]\Gamma - \Gamma',$$

(2.34)

$$\frac{1}{\tau'} = \Gamma_{pd} + \frac{1}{2}[1 + e^{-2\beta}]\Gamma + \Gamma',$$

(2.35)

$$\Gamma_{pd} = 2\int_{-\infty}^{\infty} dt <\Phi(t)\Phi(0)>,$$

(2.36)

$$\Gamma = \int_{-\infty}^{\infty} dt e^{2ijt} <\Phi^+(t)\Phi(0)>,$$

(2.37)

$$\Gamma' = \int_{-\infty}^{\infty} dt e^{2ijt} <\Phi(t)\Phi^+(0)>,$$

(2.38)

$$F_{01} = e^{-\beta[H+j]}\Lambda^+ + e^{-\beta[H-j]}\Lambda^-, $$

(2.39)

$$F_{10} = \Lambda^+ + \Lambda^-,$$

(2.40)

$$\Lambda^+ = \frac{\gamma^2}{2}\int_{-\infty}^{\infty} dt <b(t)b^+ > e^{i[H+j]t},$$

(2.41)
\[ \Lambda^- = \frac{\gamma^2}{2} \int_{-\infty}^{\infty} dt < b(t)b^+ > e^{i(\Omega-j)t}. \] (2.42)

Expressions for the vibrational relaxation rates are readily evaluated,

\[ F_{01} = \chi^2 \omega_c \left[ \frac{1}{e^{\beta(\Omega+j)} - 1} + \frac{1}{e^{\beta(\Omega-j)} - 1} \right]. \] (2.43)

\[ F_{10} = \chi^2 \omega_c \left[ \frac{1}{1 - e^{-\beta(\Omega+j)}} + \frac{1}{1 - e^{-\beta(\Omega-j)}} \right]. \] (2.44)

\( \chi \) is a unitless vibrational coupling strength defined through the relationship

\[ \frac{\gamma^2 \rho(\Omega)}{2} = \chi^2 \omega_c, \] (2.45)

where \( \rho(\Omega) \) is the density of states of the bath at frequency \( \Omega \). Note that we have approximated \( \rho(\Omega + j) \) as \( \rho(\Omega) \) since \( \Omega \gg j \).

To proceed further in the determination of the coupling dependence of the various rates, we choose a spectral density of the form

\[ \tilde{J}(\omega) = \frac{\Delta \omega^3}{\omega_c^4} e^{-\omega/\omega_c}, \] (2.46)

where \( \Delta \) is a dimensionless coupling strength. This definition of the spectral density corresponds to that of a three dimensional harmonic solid in the deformation potential approximation [1, 2].

The effective tunneling matrix element, \( j \), can be expressed

\[ j = J \exp \left[ -\frac{2}{\pi} \int_0^\infty \frac{\tilde{J}(\omega) \coth(\beta \omega/2) d\omega}{(\omega + 2j \coth(\beta \omega/2) \tanh(\beta j))^2} \right], \] (2.47)

where \( J \) is the value of the tunneling matrix element in the absence of the bath. For this choice of the spectral density, the behavior of \( j \) is very simple. For small values of \( \Delta \), \( j \approx J \). When \( \Delta \) is large \( j \) decreases to zero exponentially with increasing \( \Delta \).

With the previous definitions, the pure dephasing rate can be expressed as

\[ \Gamma_{pd} = 2j^2 \left[ \int_{-\infty}^{\infty} dt (\cosh(\xi(t)) - 1) \right], \] (2.48)
where
\[
\xi(t) = \frac{4}{\pi} \int_0^\infty d\omega J(\omega) \frac{(\cos(\omega t) \coth(\frac{\beta \omega}{2}) - i \sin(\omega t))}{(\omega + 2J \coth(\frac{\beta \omega}{2}) \tanh(\beta J))^2}.
\] (2.49)

For small \(\Delta\)
\[
\Gamma_{pd} \approx \frac{8J^2 \Delta^2}{\pi^2 \omega_c^4} \int_0^\infty d\omega \omega^6 \mathrm{csch}^2(\frac{\beta \omega}{2})(e^{-2\omega/\omega_c} + 1)
\] (2.50)

For large \(\Delta\), we evaluate (2.48) by expanding about the saddle point \(z = t + i \frac{\beta J}{2} = 0\) in the \((\beta, t)\) plane. Under this approximation, the pure dephasing rate takes the form
\[
\Gamma_{pd} \approx \frac{A e^{-B \Delta}}{\sqrt{\Delta}},
\] (2.51)

where
\[
A = \frac{\omega_c \pi J^2}{\sqrt{2} \int_0^\infty d\omega \omega^3 \mathrm{csch}(\frac{\beta \omega}{2})},
\] (2.52)
\[
B = \frac{4}{\pi \omega_c^2} \int_0^\infty d\omega \omega e^{-\omega/\omega_c} (\coth(\frac{\beta \omega}{2}) - \mathrm{csch}(\frac{\beta \omega}{2})).
\] (2.53)

Note that this rate has a familiar form identical to the hopping rate in the theory of the small polaron [13]. It can easily be shown that in the high temperature limit for the bath \((\beta \omega_c \ll 1)\), the pure dephasing rate has the activated form,
\[
\Gamma_{pd} = A e^{-\epsilon/k_b T},
\] (2.54)

where \(A = \frac{J^2 \pi}{2 \sqrt{2 \omega_c k_b T}}\) and \(\epsilon = \frac{2 \omega_c \Delta}{\pi}\).

We now compute the \(\Delta\) dependence of the rates \(\frac{1}{\tau}\) and \(\frac{1}{\tau'}\). Using the properties of thermal averaging of boson operators over an equilibrium phonon distribution [14], we find
\[
\Gamma = \frac{3\Delta J^3}{\omega_c^2 \pi} e^{-2J/\omega_c} (\coth(\beta J) + 1) + J^2 \int_{-\infty}^\infty dt e^{2iJt} \sinh(\xi(t)).
\] (2.55)

A similar calculation holds for \(\Gamma'\). In the small \(\Delta\) limit,
\[
\frac{1}{\tau} = \frac{2}{3} \frac{1}{\tau'} \approx \frac{2J^3 \Delta}{\omega_c^2 \pi} e^{-2J/\omega_c} (1 + e^{-2\beta J})(\coth(\beta J) + 1).
\] (2.56)
to lowest order in $\Delta$. For large $\Delta$,

$$\frac{1}{\tau} = \frac{1}{2\tau^*} \approx \frac{Ae^{-B\Delta}}{\sqrt{\Delta}},$$

(2.57)

showing the same behavior in this limit as the pure dephasing rate (to lowest order in $\Delta$). We see that in both the small and large $\Delta$ limit, $\frac{1}{\tau} \approx \frac{1}{\tau^*}$. This allows for great simplification in the solution to (2.30-2.33) in these two limits.

First we consider $F \gg j, \frac{1}{\tau}$, i.e. the limit of fast vibrational relaxation. Here we find (assuming $s_{0x}(0) = 1$, and all other initial values are zero)

$$< Q(t) > \approx \tanh\left(\frac{\beta\Omega}{2}\right) \exp\left(-\frac{1}{\tau} \left(\frac{t}{e^{\beta\Omega} - 1}\right)\right) \cos\left(\frac{2Jt}{e^{\beta\Omega} - 1}\right),$$

(2.58)

where we have let the fast transients that establish thermal equilibrium in the left well damp out.

In the limit $J, \frac{1}{\tau} \gg F$ (i.e. slow vibrational relaxation) we find,

$$< Q(t) > \approx \exp(-F_{01}t) \cos\left(\frac{2JF_{01}F_{10}t}{(\frac{1}{\tau})^2 + 4J^2}\right),$$

(2.59)

2.4 Discussion

The two limits considered above provide fertile ground for simple physical interpretation. First we must determine what constitutes the rate of population transfer in each case.

In the limit $F \gg j, \frac{1}{\tau}$, i.e. vibrational relaxation is fast compared to interwell dynamics, our solution exhibits two competing processes. The first is dephasing described by the damping rate $\frac{1}{\tau} (e^{\beta\Omega} + 1)^{-1}$. The second is coherent tunneling with a rate $2J(e^{\beta\Omega} + 1)^{-1}$. In most low temperature situations for which $F \gg j, \frac{1}{\tau}$ (with a spectral density $\tilde{J}(\omega) \sim \omega^3$ and realistic values for the critical frequency, $\omega_c$ and $\Delta \sim O(1)$) $j \gg \frac{1}{\tau}$. Thus we can consider the population transfer to be coherent and governed solely by $j(\Delta)$. This agrees with our intuition; when $F \gg j, \frac{1}{\tau}$, the system essentially starts out with an equilibrium Boltzmann distribution of population in the
left well, and the rate limiting step is the tunneling to the right well.

In the limit of fast interwell dynamics compared to vibrational relaxation, \( j \frac{1}{\gamma} \gg F \), we again find competition between coherent and incoherent population transfer. In this case, however, dephasing is faster, and the rate is essentially given by \( F \), the vibrational scattering rate. This is again indicative of the rate limiting step, which, in this regime, corresponds to vibrational scattering between the ground and excited states by phonons.

The physical processes in two limits discussed above resemble the processes that govern the high and low damping limits in the classical Kramers problem [8]. The similarities, however, are quite vague, due to the fact that there seems to be no simple analog to classical friction in this simple model. In the case of a two-level system coupled to a harmonic bath, it is well known [1, 15] that a macroscopic (Markovian) friction parameter may be related to the coupling strength only when the bath has an ohmic spectral density \( J(\omega) \sim \omega \) for small \( \omega \). In this case, \( \eta \), the macroscopic coefficient of friction, is proportional to \( \Delta \). In our model, the spectral density is “superohmic”, and thus the classical equations of motion for our particle would contain a memory term corresponding to a frequency dependent friction. Furthermore, the introduction of vibrational relaxation (and thus an additional coupling parameter) further hinders the comparison to the classical Kramers problem.

As a simple example, we can construct a model that shows some interesting similarities with the classical treatment. We will interpret the escape rate \( R_{esc} \) as the rate of population transfer as previously discussed. We assume that the bath has an ohmic spectral representation. Further, we assume that the relationship between the macroscopic friction parameter \( \eta \) and the coupling strength \( \Delta \) is valid even when vibrational relaxation is possible. Lastly, as a simple and crude approximation, we assume that the coupling strength to the optical modes is equal to the average coupling strength to the acoustic modes. Thus, \( \chi^2 \approx \Delta \).

In this highly idealized model we find, for small friction \( \Delta \propto \eta \ll 1 \), an escape
rate arising from the vibrational relaxation rate (see eqn (2.43)),

\[ R_{esc} = \Delta \omega_c \left[ \frac{1}{(\exp(\frac{\Omega}{k_b T}) - 1)} + \frac{1}{(\exp(\frac{\Omega}{k_b T}) - 1)} \right] \] (2.60)

For larger values of \( \Delta (\Delta > \pi/4) \) the tunneling matrix element \( \mathcal{J} \) vanishes. The escape rate becomes \( \frac{1}{\tau} (e^{3\Omega} + 1)^{-1} \). Care must be taken in the calculation of \( \frac{1}{\tau} \) due to an infrared divergence in the integral. The result, valid for \( \beta \omega_c \gg 1 \), is [16]

\[ R_{esc} \approx \frac{J^2 \sqrt{\pi}}{2 \omega_c (e^{\frac{3\Omega}{k_b T}} + 1)} (\frac{\pi k_b T}{\omega_c})^{\frac{\Delta}{\pi} - 1} \frac{\Gamma\left(\frac{2\Delta}{\pi}\right)}{\Gamma\left(\frac{2\Delta}{\pi} + \frac{1}{2}\right)}. \] (2.61)

Note that in both cases the rate shows a complex activation, and that the rate increases for small friction, then turns over and goes to zero for large values of friction. In the limit \( \frac{\Omega}{k_b T} \gg 1 \), the escape rate in both the small and large \( \Delta \) limits shows approximate Arrhenius behavior with an activation energy \( \Omega \). This vibrational energy gap is analogous to the barrier height in the classical case. The rate increases linearly with friction for small friction, and goes to zero in a fairly complicated way for large friction. In the low friction, low temperature limit, our result is identical to the "quasiclassical behavior" \( \sim \exp(-\beta \Omega) \Delta \). For larger values of friction and low temperatures, the rate vanishes more quickly than the "quasiclassical" \( \sim \exp(-\beta \Omega) \frac{1}{\Delta} \), although the behavior is qualitatively similar (see Fig.2.2). This can be compared to the classical case [8], where the temperature dependence shows Arrhenius behavior (with a barrier height activation energy), and the rate is proportional to \( \eta \) for small \( \eta \) and to \( \frac{1}{\eta} \) for large \( \eta \). Thus, in this case the ohmic bath quantum model shows similar behavior to the classical model, while for a superohmic bath, the quantum model shows distinct behavior.
Figure 2-1: Energy level diagram of the tunneling part of the Hamiltonian (2.1). \( j \) indicates the tunneling matrix element in the upper \( (n = 1) \) vibrational manifold. \( 2j \) indicates the tunnel splitting of the upper vibrational manifold. \( \Omega \) is the energy difference of the two manifolds. \( \frac{1}{\tau} \) and \( \frac{1}{\tau'} \) are the intramanifold relaxation rates caused by interaction with the phonon bath. \( F_{01} \) and \( F_{10} \) are the intermanifold relaxation rates caused by the interaction with the phonon bath.
Figure 2-2: Behavior of $R_{esc}$ for values of $\Delta > \frac{\pi}{\Omega}$. Solid lines represent $R_{esc}$ and dotted lines represent "quasiclassical" rate $\sim \exp(-\beta \Omega \frac{1}{\Delta})$ normalized to the same starting value. The upper group is for $\beta \Omega = 5$ while the lower group is for $\beta \Omega = 6$. $J$ is taken to be $1 \text{ cm}^{-1}$, $\omega = 100 \text{ cm}^{-1}$, and $\Omega = 50 \text{ cm}^{-1}$. 
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\[ R_{esc} = \frac{2J^2\pi}{\omega_c(e^{\frac{\hbar\omega_c}{k_BT}}+1)} \cos(2\Delta) \frac{(2\pi k_BT)}{\omega_c} \Delta^{-1}. \]

Chapter 3

On the Relaxation of a Two Level System: Beyond the Weak-Coupling Approximation

3.1 Introduction

The study of two quantum mechanical levels coupled to a heat bath of harmonic oscillators has surfaced in numerous areas of chemistry and physics for over thirty years [1, 2, 3, 4]. Much of condensed phase spectroscopy can be reduced to the study of two non-degenerate levels interacting with a bath of independent modes [1, 2]. When second order perturbation theory in the system-bath coupling is used, equations of motions for the reduced density matrix elements (Bloch equations) may be obtained [1, 3, 3, 5]

\[ \dot{\sigma}_{00}(t) = -k_{10}\sigma_{00}(t) + k_{01}\sigma_{11}(t), \quad (3.1) \]

\[ \dot{\sigma}_{11}(t) = k_{10}\sigma_{00}(t) - k_{01}\sigma_{11}(t), \quad (3.2) \]

\[ \dot{\sigma}_{10}(t) = -[i(\omega_0 + \Delta\omega) + 1/T_2]\sigma_{10}(t), \quad (3.3) \]

\[ \dot{\sigma}_{01}(t) = [i(\omega_0 + \Delta\omega) - 1/T_2]\sigma_{01}(t), \quad (3.4) \]
where \( \sigma_{ij}(t) \) are the matrix elements of the reduced density matrix [3] (the density matrix of the "system"), \( k_{10} \) and \( k_{01} \) are the "up" and "down" rate constants, respectively. \( \omega_0 \) is the natural frequency of the two level system, \( \Delta \omega \) is the frequency shift of the system induced by the bath, and \( 1/T_2 \) is the decay rate of the off-diagonal element of the reduced density matrix element. The diagonal elements of the reduced density matrix are referred to as populations, as they measure the probability for the system to be measured in the system states, which are labeled \(|0>\) and \(|1>\). The off-diagonal terms are often called coherences, as they are a measure of the phase coherence between system states. This set of equations is valid for times such that the initial, non-exponential behavior has decayed, and the remaining approach to equilibrium is exponential.

For a wide range of problems, the Bloch equations provide an exceptionally good description of the dynamics of two levels coupled to a dissipative bath. This is especially true in the field of nuclear magnetic resonance, where the equations were introduced [1, 5]. When the standard second order approach is adopted, the equations (3.1-3.4) and the parameters involved have simple, physical interpretations [6, 8]. For example, the equations that govern the time evolution of the populations have the "gain-loss" form typical of the Pauli Master equation [7]. The "up" and "down" rate constants are given by standard, second order golden rule expressions. When the coupling is linear in the coordinate of the bath modes, these expressions can be understood in terms of the absorption and emission of phonons of frequency \( \omega_0 \), i.e. modes of the bath in resonance with the two-level system (TLS). Coupling diagonal in the system states leads to phase relaxation via the modulation of the energy levels of the system by the bath [8]. Coupling that is off-diagonal in the system states lead to both changes in population, and to loss of phase coherence, since the relative phase between system states must change (in an averaged sense) when the populations relax.

A simple derivation shows the relation, at second order [1, 3, 6, 8],

\[
\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2'},
\]

(3.5)
where $1/T_2$ is the rate of total dephasing of the system, $1/T_1$ is the rate of population relaxation, and $1/T'_2$ is the "pure" dephasing rate, caused by adiabatic fluctuations that modulate the system frequency. Such fluctuations tend to destroy the phase coherence, thus rendering a positive pure dephasing rate. This leads to the standard relation,

$$1/T_2 \geq 1/2T_1.$$  

(3.6)

This relation has been of great use in the analysis of spectroscopic experiments, although it is rigorously valid only to second order in perturbation theory.

Recently, there have been studies that transcend second order perturbation theory. Budimir and Skinner performed a fourth order perturbation theory calculation to determine the relaxation properties of a TLS linearly coupled, both diagonally and off-diagonally, to a Gaussian stochastic bath [9]. They showed that at fourth order, the relation (3.5) is not valid, and for some parameters, $1/T_2 \leq 1/2T_1$. Simulations on the same model were performed by Sevian and Skinner[10]. They showed that even for systems that violate the inequality (3.6), the initial non-Markovian behavior is often short compared to the asymptotic, exponential relaxation. Reineker et al., for a different model of bath fluctuations, also showed that the breakdown of the inequality (3.6) is possible [11]. Laird, Budimir, and Skinner (hereafter denoted LBS), performed calculations on a TLS linearly and off-diagonally coupled to a quantum heat bath of harmonic oscillators [12]. Unlike the stochastic studies, their model is valid at finite temperature. They also find that the relaxation properties at fourth order are different than at second order, although the form of the Bloch equations (3.1-3.4) still hold. By using the results of the study of LBS, Laird and Skinner showed that for the particular model that reproduces the interesting stochastic results in the limit of infinite temperature, (the "complex Ohmic-Lorentzian" model), that the inequality (3.6) breaks down at finite temperature as well [13]. Chang and Skinner refined these calculations by discarding the assumption that the density matrix is initially factorized, and included the short time, non-Markovian relaxation behavior in their study [14]. They found once again that the inequality (3.6) can be violated.
Laird, Chang, and Skinner have recently shown that such a breakdown is possible for a "super-Ohmic" model of the heat bath [15].

While much work has been done on the calculational aspects of this problem, little has been done to put the results on a physical foundation. The second order results are useful and meaningful in part because physical interpretation can be found for the processes involved. In the case of a TLS coupled linearly and off-diagonally to a bath of harmonic oscillators, we expect the population relaxation rates to depend on the number of phonons in the bath at a given temperature that have a frequency $\omega_0$. We expect the absence of pure dephasing since the system-bath coupling lacks the ability to cause fluctuations in the system's natural frequency. No such understanding exists at fourth order. In fact, based on our knowledge of second order perturbation theory, many of the fourth order results are surprising. What is the physical meaning of $1/T_2'$ at fourth order? Why can it become negative in some instances (when system-bath coupling constants are complex) and not in others (real system-bath coupling parameters)? Why does the frequency shift of the TLS not agree with the shift inferred from the renormalized energy splitting? How are the fourth-order population shifts to be interpreted? We will attempt in this chapter to interpret the fourth order expressions, and thus answer some of these questions. Along the way, we will touch upon more familiar problems in the theory of quantum relaxation, such as the celebrated spin-boson problem [16, 17, 18, 19, 20, 21, 22, 23, 24].

We will also address the question of experimental measurability of the results obtained in the fourth order calculations of Laird, Budimir, and Skinner. In doing so, we will propose an alternate method of study for the "complex Ohmic Lorentzian" model of Laird and Skinner. Our methods and results will provide a first step in producing a unified view of the dissipative dynamics of a TLS beyond the weak-coupling limit.
3.2 Review of the Problem

LBS considered the Hamiltonian [12],

\[ H = H_{TLS} + H_b + H'; \]  

where \((\hbar = 1)\)

\[ H_{TLS} = \omega_0|1><1|, \]  

\[ H_b = \sum_k (b^+_k b_k + 1/2), \]  

\[ H' = \Lambda|1><0| + \Lambda^+|0><1|, \]  

\[ \Lambda = \sum_k h_k(b^+_k + b_k). \]  

The Hamiltonian consists of the TLS with excited state energy \(\omega_0\), a free, harmonic bath, and a coupling that is off-diagonal in the system states, and linear in the bath normal mode coordinates. The model is confined to coupling constants that are either purely real or purely imaginary.

The dynamics for the total density matrix (system + TLS) are contained in the Liouville equation,

\[ \frac{\partial \rho(t)}{\partial t} = -i[H, \rho(t)]. \]  

A Redfield-type formalism [4] is then used to calculate equations of motion for the bare reduced density matrix, defined by \(\sigma(t) = Tr_b \rho(t)\). By bare we mean that the states used as a basis in the perturbation theory are pure system states, as opposed to “dressed states” that mix system and bath. The initial conditions are taken to be factorized,

\[ \rho(0) = \sigma(0) \otimes \rho^b_{eq} \]

where \(\rho^b_{eq}\) is the equilibrium density matrix of the bath. After transformation to the interaction picture, the equation of motion,

\[ \dot{\sigma}(t) = R(t) \dot{\sigma}(t), \]  

\(3.13\)
\[
R(t) = \sum_n R^{(2n)}(t),
\] (3.14)

where

\[
R^{(2)}(t) = -\int_0^t dt_1 Tr_b[\tilde{L}(t)\tilde{L}(t_1)\rho_b],
\] (3.15)

and

\[
R^{(4)}(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \{Tr_b[\tilde{L}(t)\tilde{L}(t_1)\tilde{L}(t_2)\tilde{L}(t_3)\rho_b] - Tr_b[\tilde{L}(t)\tilde{L}(t_1)\rho_b]Tr_b[\tilde{L}(t_2)\tilde{L}(t_3)\rho_b] \\
- Tr_b[\tilde{L}(t)\tilde{L}(t_2)\rho_b][\tilde{L}(t_1)\tilde{L}(t_3)\rho_b] \\
- Tr_b[\tilde{L}(t)\tilde{L}(t_3)\rho_b]Tr_b[\tilde{L}(t_1)\tilde{L}(t_2)\rho_b]\},
\] (3.16)

is found, and then is projected onto the system states. An equation of the Redfield form results,

\[
\dot{\sigma}_{\alpha\beta} (t) = \sum_{\beta'} e^{i(\alpha-\alpha' - \beta' + \beta') \omega t} R_{\alpha\alpha' \beta \beta'} \tilde{\sigma}_{\beta\beta'} (t),
\] (3.17)

where

\[
R_{\alpha\alpha' \beta \beta'} \equiv \lim_{t \to \infty} (e^{-i(\alpha-\alpha' - \beta' + \beta') \omega t} < \alpha | \{ R(t) | \beta > < \beta' | \} | \alpha' >).
\] (3.18)

Due to the fact that \( H' \) is off-diagonal in the system states, and has zero thermal average, the equations, after transformation back to the Schrodinger picture,

\[
\dot{\sigma}_{00} (t) = R_{0000} \sigma_{00} (t) + R_{0011} \sigma_{11} (t),
\] (3.19)

\[
\dot{\sigma}_{11} (t) = R_{1100} \sigma_{00} (t) + R_{0110} \sigma_{11} (t),
\] (3.20)

\[
\dot{\sigma}_{10} (t) = (-i\omega_0 + R_{1010}) \sigma_{10} (t) + R_{1001} \sigma_{01} (t),
\] (3.21)

\[
\dot{\sigma}_{01} (t) = (i\omega_0 + R_{0101}) \sigma_{01} (t) + R_{0110} \sigma_{10} (t),
\] (3.22)

are found to hold to all orders in the coupling constant. LBS immediately identify
the "up" and "down" rate constants as

\[ k_{10} = -R_{0000}, \quad \text{(3.23)} \]

and

\[ k_{10} = R_{1111} \quad \text{(3.24)} \]

respectively. A rotating wave approximation is made to decouple the coherences in equations (3.21) and (3.22). The identifications

\[ 1/T_2 = -Re \{ R_{1010} \}, \quad \text{(3.25)} \]

and

\[ \Delta \omega = -Im \{ R_{1010} \}, \quad \text{(3.26)} \]

can then be made, relating the dephasing rate and the frequency shift to the relaxation parameters in equation (3.18). The effect of the decoupling of the coherences is detailed in LBS. There it is shown that the definition of 1/T_2 is not effected by such an approximation, while the expression for \( \Delta \omega \) is modified at fourth order. Once the definitions (3.23-3.26) are in place, a perturbative calculation of the rates may be made.

At second order in the coupling strength, the calculation of the "up" rate constant is quite simple. by using equations (3.15) and (3.23), the expression for the "up" rate constant

\[ k_{10}^{(2)} = \lim_{t \to \infty} 2Re \{ \int_0^t dt_1 e^{-i\omega_0 (t-t_1)} C_1(t-t_1) \}, \quad \text{(3.27)} \]

is found. \( C(t-t') \) is the standard harmonic oscillator correlation function,

\[ C_1(t-t') = Tr_b[\rho_b \Lambda(t)\Lambda(t')] = \sum_k |h_k|^2 \{ [n(\omega_k)+1]e^{-i\omega_k(t-t')} + n(\omega_k)e^{i\omega_k(t-t')} \}, \quad \text{(3.28)} \]

and \( n(\omega_k) \) is the Bose factor, giving the thermal occupation of phonons at frequency.
\( \omega_k \). It is convenient to express the rates in the frequency domain. We define

\[
\dot{C}_1(\omega) = \int_{-\infty}^{\infty} e^{i\omega \tau} C_1(\tau) d\tau.
\]  
(3.29)

\( \dot{C}_1(\omega) \) can be expressed as,

\[
\dot{C}_1(\omega) = 2\{\Gamma_1(\omega)[n(\omega) + 1] + \Gamma_1(-\omega)n(-\omega)\},
\]  
(3.30)

where the weighted density of states, \( \Gamma_1(\omega) \), is defined as,

\[
\Gamma_1(\omega) \equiv \pi \sum_k |h_k|^2 \delta(\omega - \omega_k).
\]  
(3.31)

The rate, (3.27), may thus be expressed,

\[
\dot{C}_1(-\omega_0) = 2\Gamma_1(\omega_0)n(\omega_0),
\]  
(3.32)

which, due to the proportionality to the thermal occupation of phonons at \( \omega_0 \), may be interpreted as the absorption of one vibrational quantum of frequency \( \omega_0 \). The rate \( k_{01} \) and thus \( 1/T_1 \), which is defined as \( 1/T_1 = k_{01} + k_{10} \) may be calculated in a similar manner. It is a simple exercise to show that, at second order, \( (1)^{(2)}_{t_0} = \frac{1}{2T_1} \), demonstrating that for the model under consideration, the second order dephasing rate has no contribution from pure dephasing.

The fourth order terms may be calculated by applying equations (3.16),(3.18) and (3.23-3.25). The tedious details are outlined in LBS. At fourth order, a new weighted density of states, \( \Gamma_2(\omega) \) comes into play. This density of states, which arises from terms containing correlation functions \( C_2(t - t') = Tr_b[\rho_b \Lambda(t) \Lambda(t')] \), has the form,

\[
\Gamma_2(\omega) \equiv \pi \sum_k h_k^2 \delta(\omega - \omega_k).
\]  
(3.33)

This density of states gives rise to a correlation function \( \dot{C}_2(\omega) \) with the same form as (3.30), with \( |h_k|^2 \) replaced with \( h_k^2 \). Since the coupling constants are purely real
or purely imaginary by assumption, the density of states $\Gamma_2(\omega)$ is real. Note that $\Gamma_2(\omega)$ may vanish for arbitrarily strong coupling if the coupling constants are chosen to come in pairs in which one coupling constant is real and the other is imaginary, but have equal modulus. This model will be discussed later in the paper.

The fourth order population excitation rate may be expressed in frequency space as,

$$k_{10}^{(4)} = \frac{1}{2\pi} \{ \omega_0^{-1} \hat{C}_2(-\omega_0)[P_2(\omega_0) - P_2(-\omega_0)]$$
$$+ \hat{C}_1^\prime(-\omega_0)[P_1(\omega_0) - P_1(-\omega_0)] + P_1^\prime(-\omega_0)$$
$$[\hat{C}_1(\omega_0) - \hat{C}_1(\omega_0)] - 2\hat{C}_1(-\omega_0)P_1^\prime(\omega_0) \}, \quad (3.34)$$

where

$$P_1(\omega) = \varphi \int_{-\infty}^{\infty} d\omega' \frac{\hat{C}_1(\omega')}{\omega' - \omega}, \quad (3.35)$$

$$\hat{C}_1^\prime(\omega) = \frac{\partial \hat{C}_1(\omega)}{\partial \omega}, \quad (3.36)$$

$$P_1^\prime(\omega) = \varphi \int_{-\infty}^{\infty} d\omega' \frac{\hat{C}_1^\prime(\omega')}{\omega' - \omega}, \quad (3.37)$$

where $\varphi$ denotes Cauchy principal part. The coupling and temperature dependence of this rate expression may be obtained by substituting equations (3.30), (3.31), and (3.33) into (3.34). Note that the zero temperature thermal excitation rate does not vanish in the limit of zero temperature. In fact,

$$\lim_{T \to 0} k_{10}^{(4)} = \frac{2\Gamma_1(\omega_0)}{\pi} \int_0^{\infty} d\omega \frac{\Gamma_1^\prime(\omega)}{\omega + \omega_0}. \quad (3.38)$$

We will return to this result in section (3.3). The total population relaxation rate $(\frac{1}{T_1})^{(4)}$ may be computed simply from the sum of the fourth order "up" and "down" rate constants.

The second order frequency shift may be calculated perturbatively from equation
The result found by LBS is,

\[ \Delta \omega^{(2)} = \left( \frac{1}{2\pi} \right) [P_1(-\omega_0) - P_1(\omega_0)]. \]  

(3.39)

When compared to the “frequency” defined through,

\[ K \equiv e^{-\beta \omega}, \]  

(3.40)

where \( K \) is the equilibrium constant, defined as [3, 12],

\[ K = \frac{\sigma_{i1}(\infty)}{\sigma_{00}(\infty)}, \]  

(3.41)

and \( \sigma_{ii}(\infty) \) is the equilibrium system population in state \( |i> \), LBS found that \( [\omega - \omega_0]^{(2)} \) differs from \( \Delta \omega^{(2)} \). That is, the second order frequency shift is not equal to the frequency shift obtained from the equilibrium constant. This result will be discussed in section (VI).

Finally, LBS calculate the fourth order contribution to \( \left( \frac{1}{T_2} \right)^{(4)} \). As a mathematical means to test the inequality (3.6), LBS define, in analogy to second order perturbation theory,

\[ \frac{1}{T_2} \equiv \frac{1}{T_2} - \frac{1}{2T_1}. \]  

(3.42)

The fourth order contribution to \( \frac{1}{T_2} \) is found to be,

\[ \left( \frac{1}{T_2} \right)^{(4)} = \frac{1}{\pi} \varphi \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2 - \omega_0^2} \left( \partial \omega \frac{\partial}{\partial \omega} [\hat{C}_1(\omega)\hat{C}_1(-\omega)] - \hat{C}_2(\omega)\hat{C}_2(-\omega) \right). \]  

(3.43)

It is to be emphasized that within the context of the calculations performed by LBS, the fourth order definition of “pure dephasing” is a mathematical tool to study the inequality (3.6), and does not have the physical meaning of its second order counterpart. Laird and Skinner study two models for the spectral densities (3.31) and (3.33). In both models, they choose spectral densities that are Ohmic-Lorentzian in form,
i.e.,

\[ \Gamma_i(\omega) \sim \frac{\omega \alpha}{\omega^2 + \alpha^2}. \]  

(3.44)

This type of spectral density reproduces the exponentially damped decay of correlation functions (in the time domain) that are produced by Gaussian stochastic theories. The first model used by Laird and Skinner takes the coupling constants of (3.33) to be real. In this case, \( \hat{C}_1(\omega) = \hat{C}_2(\omega) \). Here, it is found that (3.43) is always positive, so that the inequality (3.6) is never violated. For a model with coupling constants take so that \( \Gamma_2(\omega) \) vanishes (called "complex Ohmic Lorentzian"), Laird and Skinner found that (3.43) can become negative, indicating a violation of (3.6). This model for the coupling is important because it is the physical realization of a spin-1/2 particle in a static longitudinal magnetic field with equal strength but uncorrelated fluctuating magnetic fields in the two transverse directions [1, 9]. With the same "complex" coupling model, Laird, Chang and Skinner have shown that (3.43) may be negative even if the spectral densities are super-Ohmic. These results will be discussed in sections (3.5) and (3.6).

### 3.3 Population Relaxation

We begin by examining closely the fourth order population relaxation terms. Perhaps the most surprising result uncovered by LBS is the fact that the population excitation rate (the "up" rate constant) is non-zero at zero temperature. This result was in fact anticipated by Lindenberg and West [25] in their study of the harmonic oscillator linearly coupled to a quantum heat bath, and by Kassner [26] in his study of correlated initial conditions in the spin-boson problem. All of these studies have shown that there is residual excited state population at \( T = 0 \). The origin of this population is easy to trace in our case. We note that at zero temperature, the equilibrium density matrix of the entire system + bath complex is a projection operator for the ground state, assuming that the ground state may be found. Then [26],

\[ \rho_{eq} = |\psi_g \rangle \langle \psi_g|. \]  

(3.45)
By computing the ground state of Hamiltonian (3.7) to first order in the coupling strength, we find

\[ |\psi_g\rangle = N_0 [1 - \sum_k \frac{\hbar k \sigma_k a_k^\dagger}{(\omega_0 + \omega_k)}] |\Phi_g^0\rangle, \quad (3.46) \]

where \( N_0 \) is a normalization factor, and \( |\Phi_g^0\rangle \) is the ground state of \( H^0 \), consisting of the direct product of the system ground state, and the vacuum state of the bath. The following consequences of the mixing of the system and bath states may be noted:

1) The density matrix, for calculations extending beyond the strict weak coupling limit, has an expansion in powers of the coupling strength [27],

\[ \rho(t) = \rho^{(0)}(t) + \delta \rho^{(1)}(t) + \delta^{(2)} \rho^{(2)} + \ldots \quad (3.47) \]

In a precise treatment, attention must be paid to the various time scales in the problem [28], so that the “time” appearing in equation (3.47) is really a hierarchy of time scales. We will not be concerned with such a treatment here. In our problem, \( \rho^{(2)}(\infty) \) will contain states mixed by \( H' \) at first order in the perturbation. Thus, \( \sigma^{(2)}(\infty) \), obtained by tracing out the bath degrees of freedom, will only contain population in the excited state of the system,

\[ \sigma^{(2)}(\infty) = \left( \frac{1}{\pi} \int_0^\infty \Gamma'(\omega)d\omega \right) |1\rangle\langle 1| \quad (3.48) \]

Note that \( \sigma^{(1)}(\infty) \) is identically zero. By appealing to the properties of the system-bath coupling in the thermodynamic limit, we find that the residual population is \( \mathcal{O}(N^0) \) in magnitude, and thus cannot be neglected [29, 30].

2) Equation (3.46) shows that, due to the mixing of states, bath excitations exist at zero temperature. If we define the total occupancy of phonons, \( N(\omega_0) \), as

\[ N(\omega_0) = \sum_k < a_k^\dagger a_k >, \quad (3.49) \]
then a simple calculation gives,

\[ N(\omega_0) = \frac{1}{\pi} \int_0^\infty \frac{\Gamma'(\omega) d\omega}{(\omega + \omega_0)}, \]  

which is, at this temperature, equal to the equilibrium system population.

We now turn to a discussion of the population excitation rate constant. To see if the rate expression (3.34) is really a fourth order extension of Fermi's Golden Rule, we compute the Fermi Golden Rule rate expression directly [31]

\[ W_{0 \rightarrow 1} = \text{Re} \int_0^\infty d\tau < T_{01}(\tau) T_{10}^\dagger > e^{-i\omega_0 \tau}, \]

where the transition operator is defined \( T \equiv H' + H'GT \), and \( G \) is the zeroth order Green's function. This calculation is confined in Appendix A. Some subtleties arise in the calculation. When properly interpreted, \( W_{0 \rightarrow 1} \) is identical to the expression (3.34) for \( k_{10} \). This confirms that these rates are indeed higher order Fermi Golden Rule expressions.

We may note that cross terms between second order rates and second order populations are contained within the fourth order rate expression. For example, the Bloch equation describing the evolution of the population difference \( P_z(t) \) has the form

\[ \dot{P}_z(t) = -\frac{1}{T_1} [P_z(t) - P_z(\infty)]. \]

For times \( (1/T_1)^{-1} \gg t \gg \tau_b \), where \( \tau_b \) is the correlation time of the bath, a cross term

\[ (1/T_1)^{(2)} P_z^{(2)}(\infty) \]

contributes to the fourth order expression of \( 1/T_1 \). The same argument holds for the individual population transfer rates. This accounts for the appearance of several terms in (3.34). For example, at zero temperature, the "up" rate constant has the same form as the second order expression at finite temperature, with the population of modes \( n(\omega_0) \) replaced by the total number of excited modes \( N(\omega_0) \) (see equations (3.38) and
Thus the rate may be interpreted as the product of the weighted density of states at the resonance frequency times the total number of phonons created with the system excitation.

### 3.4 Application to the Spin-Boson Problem

In this section, we apply the methods used in equations (3.45) and (3.48) to compute some equilibrium properties of the standard spin-boson Hamiltonian [16, 17, 18, 19, 20, 21, 22, 23, 24]. We wish to show that a direct calculation of the zero temperature localization diagram (as well as relaxation rate and line shift expressions) is possible by a simple, static application of Rayleigh-Schrodinger perturbation theory. Our method will reproduce the localization behavior given by the Non-Interacting Blip Approximation (NIBA) [19], which, for the case of Ohmic dissipation, is quantitatively in error as \( t \to \infty \) [21]. A more rigorous analysis, based on mapping the spin-boson model with Ohmic dissipation onto the Ising model with long range interactions, has been carried out by Spohn and Dümcke [22]. We will be content to show that equations (3.45) and (3.48) are deceptively simple, and may be used to extract information that has been obtained previously by more complicated, dynamical means.

We begin with the spin-boson Hamiltonian (in the notation of Aslangul et al [19])

\[
H = -\omega_0 \sigma_x + \sigma_z \sum_k G_k (b_k^\dagger + b_k) + \sum_k \omega_k b_k^\dagger b_k, \tag{3.54}
\]

where, again, \( \hbar \) has been set to one, and \( \sigma_x, \sigma_z \) are standard Pauli matrices defined in the basis \( |L>, |R> \) of “left” and “right” states. This Hamiltonian describes a tunneling system linearly coupled to a bath of harmonic oscillators. The tunneling system can be envisioned as the lowest two levels of a symmetric double well potential. In this picture, the coupling term causes fluctuations in the well depths of the potential. The case of Ohmic dissipation, which is our focus here, is defined by a
Our goal is to compute the degree of localization at $T = 0$, defined by [19],

$$\Sigma(\infty) = \frac{<\sigma_z(\infty)>}{<\sigma_z(0)>}. \quad (3.56)$$

Instead of computing the dynamics of the system, and letting $t \to \infty$, we use equation (3.45) directly, tracing out the bath degrees of freedom, and projecting onto the eigenstates of $\sigma_z$ to compute (3.56). It is simple to show that $\Sigma(\infty)$ is zero until a critical value of the coupling constant $\alpha$. We will simply borrow the result $\alpha_{\text{critical}} = 1$ from previous studies [16]. To find the form of $\Sigma(\infty)$ for coupling constants equal to or greater than $\alpha_{\text{critical}}$, we perform a small polaron transformation on (3.54), defined by [19, 20]

$$\tilde{H} = UHU^\dagger,$$

$$U = \exp\left\{\sum_k \frac{G_k}{\omega_k} (b_k^\dagger - b_k)\right\}. \quad (3.57)$$

The transformed Hamiltonian is given by

$$\tilde{H} = \tilde{H}_0 + \tilde{H}_{\text{int}},$$

$$\tilde{H}_0 = \sum_k \omega_k b_k^\dagger b_k,$$

$$\tilde{H}_{\text{int}} = -\omega_0 (B_+ \sigma_+ + B_- \sigma_-),$$

$$B_+ = \exp\left\{\sum_k \frac{G_k}{\omega_k} (b_k^\dagger - b_k)\right\}. \quad (3.58)$$

For Ohmic dissipation, $<B_+> = 0$. The (left, right) system states are now degenerate, and the interaction term cannot break the degeneracy. A ground state is found by the choice of the initially prepared state, which now mixes with the higher energy states through $\tilde{H}_{\text{int}}$. Choosing the particle to be initially localized in the left well,
the (unnormalized) ground state is given by

$$|\psi_g\rangle = |L\rangle |0\rangle - \omega_0 |R\rangle \sum_{\{n\} \neq 0} \frac{\langle \{n\}|B_+|0\rangle}{\sum_i n_i \omega_i} |\{n\}\rangle,$$

(3.59)

where $|0\rangle$ is the vacuum state of the bath, and $\{n\}$ denotes a set of phonon occupations of the bath. Applying (3.45) and tracing out the bath degrees of freedom, we find,

$$\langle R|\sigma(\infty)|R\rangle = \omega_0^2 \sum_{n \neq 0} \frac{|\langle \{n\}|B_+|0\rangle|^2}{(\sum_i n_i \omega_i)^2}.$$

(3.60)

An explicit calculation of this term is possible, which gives,

$$\langle R|\sigma(\infty)|R\rangle = \omega_0^2 \int_0^\infty dz_1 \int_0^\infty dz_2 e^{-2S} \left\{ \sum_k \frac{4G_k^2}{\omega_k} e^{-\omega_k(z_1+z_2)} - 1 \right\},$$

(3.61)

where

$$S = \sum_k \frac{2G_k^2}{\omega_k^2}.$$

(3.62)

Note that the energy denominators have been rewritten in a Laplace transformed form, which introduces the integrals over $z_1$ and $z_2$. Using the spectral density for the Ohmic bath, and explicitly calculating the integral, the result, valid to second order in $\omega_0$,

$$\Sigma(\infty) = \frac{1}{1 + \left(\frac{\omega_0}{\omega_c}\right)^2 \left\{ \frac{(2\alpha - 1)(2\alpha - 2)}{[(2\alpha - 1)(2\alpha - 2)]} \right\}^{-1}}; \quad \alpha > 1,$$

(3.63)

is obtained. This result is identical to the result found in earlier dynamical studies [16, 19]. The zero temperature relaxation rate and line shift could be calculated in a similar manner, without recourse to standard dynamical techniques. We also note that the method of Spohn and Dümcke is also "nondynamical," in that it does not proceed through the Liouville equation. This method, although much more complicated, is necessary for obtaining the true long time behavior of the Ohmic spin-boson model.
3.5 Dephasing

In the usual second order Redfield approach [3, 4], the relation (3.5) holds. The interpretation of equation (3.5) is simple: The decay of the coherence variable is caused by both energy relaxation (expressed through $T_1$) and the (stochastic) modulation of the system energy levels by the bath (expressed through $T_2$). The pure dephasing rate is positive, since the bath can only increase the rate of phase randomization in the system states. Generally, at second order, the pure dephasing rate is expressed [6],

$$\Gamma_{pd} = \int_{-\infty}^{\infty} d\tau < \{H'_{11}(\tau) - H'_{00}(\tau)\} \{H'_{11} - H'_{00}\},$$

where $H'_{ii}$ is an operator in the bath Hilbert space, obtained by taking the matrix element of the coupling term diagonal in the system state $|i\rangle$ (here $i = 0, 1$). Notice that the correlation function is composed of operators that determine the instantaneous energy fluctuation induced by the bath on the system, in agreement with the discussion above. The Hamiltonian (3.7) contains no diagonal terms in the system-bath coupling. Thus, at second order, the dephasing rate can be expressed solely in terms of $T_1$, i.e. there is no pure dephasing. As discussed in section (3.2), the fourth order dephasing rate deviates from the second order result. If we continue to view pure dephasing processes as those arising from diagonal fluctuations (this is the view expressed by Sevian and Skinner [10]), then (3.5) is violated at fourth order. An alternative view is expressed by LBS. They define

$$\frac{1}{T_2} \equiv \frac{1}{T_2} - \frac{1}{2T_1}$$

as a mathematical means to test the inequality (3.6). The quantity $\left(\frac{1}{T_2}\right)^{(4)}$, expressed in equation (3.43) can become negative for certain parameters in a specific model, signaling the breakdown of the inequality (3.6).

In order to probe the physical meaning of this result, we rely on the observations made in sections (3.2) and (3.6), which dictate that much of the bare rate expressions can be expressed and understood in terms of states that mix system and bath
character. We perform a unitary transformation

\[ \hat{H} = U^\dagger HU \]  

(3.65)

where

\[ U = \exp(S). \]

\( S \) is chosen to diagonalize the Hamiltonian (3.7) to first order by the condition

\[ [H_{TLS} + H_b, S] = -H'. \]  

(3.66)

In the context of the Hamiltonian (3.7), this is referred to as Fröhlich diagonalization [32]. The transformation is given by

\[ S = \sum_k \frac{1}{(\omega_k^2 - \omega_0^2)} \{ \omega_k (b_k - b_k^\dagger) [h_k \sigma_+ + h_k^* \sigma_-] + \omega_0 (b_k + b_k^\dagger) [h_k \sigma_+ - h_k^* \sigma_-] \}. \]  

(3.67)

We will assume for now that the density of states of the phonon bath does not overlap significantly with the energy splitting of the (TLS), so that no divergence problems occur in (3.67) [33]. We will return to this point later in this section. With the transformation (3.65), the effective Hamiltonian, \( \tilde{H} \), may be written

\[ \tilde{H} = H_{TLS} + H_b + \tilde{H}' \]

\[ \tilde{H}' = \sum_{k,k'} \frac{1}{\omega_{k'}^2 - \omega_0^2} \{ A_{k,k'} \omega_{k'} (b_k + b_k^\dagger) (b_{k'} - b_{k'}^\dagger) \]

\[ - B_{k,k'} \omega_0 (b_k + b_k^\dagger) (b_{k'} + b_{k'}^\dagger) \} |1 >> 1|, \]  

(3.68)

where

\[ A_{k,k'} = 2i \text{Im}(h_k h_{k'}^*) \]

\[ B_{k,k'} = 2 \text{Re}(h_k h_{k'}^*). \]
We are now in position to consider the lowest order dynamics of the states

\[ |\tilde{\phi} > = U^* |\phi_0 > . \quad (3.69) \]

For instance, the first order ground state may be calculated by expanding \( U^* \) and applying the expansion to the ground state of \( H_0 = H_{TLS} + H_b \). The state (3.46) is then recovered.

Before rate expressions can be considered, we must remove the secular terms from the potential \( \tilde{V} \). To do this, we place the thermal average of \( \tilde{V} \) into \( H_{TLS} [18] \). This will leave an interaction with zero thermal average, thereby eliminating spurious divergences that might occur in the calculation of rate expressions. We find

\[ < \tilde{V} > = \{-2\omega_0 \sum_k \frac{|h_k|^2}{(\omega_k^2 - \omega_0^2)} \coth \frac{\beta \omega_k}{2} \} |1> <1| . \quad (3.70) \]

If we use the identity

\[ \frac{1}{\omega_k^2 - \omega_0^2} = \lim_{\eta \to 0} \frac{1}{(\omega_k^2 - (\omega_0 - i\eta)^2)} = \varphi \frac{1}{\omega_k^2 - \omega_0^2} - \frac{i \pi}{\omega_0} \delta(\omega_k - \omega_0) \]

to express the diagonal matrix element of \( < \tilde{V} > \) as

\[ < \tilde{V} >_{11} = -\frac{\omega_0}{\pi} \varphi \int_0^\infty \frac{2\Gamma_1(\omega)}{(\omega^2 - \omega_0^2)} \coth \frac{\beta \omega}{2} + 2i\Gamma(\omega_0) \coth \frac{\beta \omega_0}{2} . \quad (3.71) \]

The real part is the second order frequency shift, and the imaginary part is the second order dephasing rate (which is equal to the second order population relaxation rate).

Using the notation in equations (3.30-3.33) and (3.35), these results are seen to be identical to (3.39) and the discussion following (3.32), respectively.

We note from the transformed Hamiltonian (3.68) that the basis of states (3.69) undergoes only pure dephasing. This is not quite correct, however, since the factorized initial conditions in the basis of \( H_0 \) are correlated initial conditions for the states (3.69). This will also lead to population relaxation at fourth order, although we will not pursue this avenue. We now compute the pure dephasing rate of the states...
(3.69) to lowest (fourth) order. We use the Redfield formula (3.64), with the effective potential
\[ \tilde{V} = < \tilde{V} >. \]
The result is
\[
\Gamma_{pd}^{(4)} = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \left[ \frac{(\omega^2 + \omega_0^2)}{(\omega^2 - \omega_0^2)^2} \hat{C}_1(\omega)\hat{C}_1(-\omega) - \frac{1}{(\omega^2 - \omega_0^2)} \hat{C}_2(\omega)\hat{C}_2(-\omega) \right]
= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{d\omega}{(\omega^2 - \omega_0^2)} \left[ \omega \frac{\partial}{\partial \omega} (\hat{C}_1(\omega)\hat{C}_1(-\omega)) - \hat{C}_2(\omega)\hat{C}_2(-\omega) \right],
\]
(3.72)
where we have use the fact that, by assumption, \( \omega_0 \) does not overlap \( \Gamma_1(\omega) \) significantly, so that the integration by parts above is valid. The amazing feature of equation (3.72) is that it is identical in form to the fourth order result (3.43) for the "pure" dephasing \( (\frac{1}{T_2})^{(4)} \) that was introduced solely as a mathematical means to test the validity of the inequality (3.6). We can make the following observations:

1) The fact that (3.72) and (3.43) agree when \( \omega_0 \) does not significantly overlap \( \Gamma_1(\omega) \) (or more precisely \( \hat{C}_1(\omega)\hat{C}_1(-\omega) \)) shows that, in these instances, the inequality (3.6) holds, and \( (\frac{1}{T^2})^{(4)} \) may be interpreted as the pure dephasing of the states (3.69). This means that, in cases where \( \omega_0 \) does not significantly overlap with \( \Gamma_1(\omega) \), the expression (3.43) is derivable from the second order formula (3.64) means that, in these cases, the inequality (3.6) must hold, regardless of the form of \( \hat{C}_1(\omega) \) and \( \hat{C}_2(\omega) \).

2) The strange result (the negativity of (3.43)) is thus a consequence of a resonance phenomena, wherein the result (3.72) is not valid. Heuristically, we may view this behavior as a consequence of the lack of stability of the potential (3.68), which, as a significant number of phonons reach resonance with the TLS, gives rise to "imaginary" modes.

3) The numerical results of Laird and Skinner, and Laird, Chang, and Skinner support the conclusion of point (1). If we plot the high temperature behavior of \( \hat{C}_1(\omega)\hat{C}_1(-\omega) \) (essentially \( \Gamma_1(\omega)^2/\omega^2 \)), we see that the negative dephasing occurs only when there is significant overlap between \( \omega_0 \) and \( \Gamma_1(\omega)^2/\omega^2 \). In figure (3.1) \( \Gamma_1^2(\omega)/\omega^2 \)

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is plotted for the “Ohmic-Lorentzian” density of states \( \Gamma_1(\omega) \propto \frac{\lambda \omega}{(\lambda^2 + \omega^2)} \) for various values of \( \lambda \) and a value of \( \omega_0 \) equal to one. In figures (3.2) and (3.3) the same function is plotted for the super-Ohmic density of states \( \Gamma_1(\omega) \propto \frac{\omega e^{-\omega/\omega_c}}{\omega_c} \) that corresponds to a Debye bath in the deformation potential approximation. A fundamental difference in \( \Gamma_2(\omega)/\omega^2 \) between the two types of spectral functions can be noted. For the Ohmic bath, the overlap of \( \omega_0 \) and a significant concentration of phonons increases in the large bandwidth limit \( \lambda \to \infty \), whereas this overlap is reduced in the super-Ohmic cases. This is due to the fact that Ohmic baths have extensive density of modes at low frequencies, unlike their super-Ohmic counterparts [16]. It is in the large bandwidth limit of the bath that most theories become tractable [20, 34]. Furthermore, in most condensed phase (crystal) systems, the TLS energy is ten to one hundred times smaller than the cutoff frequency of the bath. For these reasons, most previous studies have taken \( \omega_c \gg \omega_0 \).

We may also expect that, for the resonance case in super-Ohmic systems, the method outlined in section (3.2) may not be adequate to describe the experimental situation. This is because the Redfield approach neglects the reaction force of the system on the bath [23, 35]. To make such a thermodynamically consistent calculation tractable, it is often necessary to assume the bandwidth of the bath is larger than any timescale of the system [35, 36]. Otherwise, the dynamics become extremely complicated and the interesting dephasing behavior may be hopelessly buried. When the timescale separation exists, we expect that the methods described in section (3.2) to be adequate. As we have discussed, for super-Ohmic systems this is precisely the regime where (3.6) holds. The question of the effects of the resonance is still open, however we believe that in super-Ohmic systems (which are often the most realistic for condensed phase physical chemistry), the violation of (3.6) may be very difficult to detect.
We now turn to a different approach to the problem considered by LBS. Our shift in focus is necessitated by the following observations:

1) The approach of LBS is valid only for a small range of coupling strengths (coupling strengths for which second order perturbation theory is not sufficient to explain TLS dynamics, and sixth order perturbation theory is unnecessary). We would like to have an analytic method that covers a larger range of coupling strengths, and is flexible enough to handle both the "real" and "complex" coupling models.

2) The interpretation of the physical processes contained in the fourth order theory of LBS is difficult. The interpretation of population relaxation terms is relatively straightforward and is expounded in section (3.3), appendix A, and further in this section. We have already shown how, for the particular Hamiltonian (3.7), the "pure dephasing" rate, $1/T'_2$, can be related to the pure dephasing of states that are mixed at first order in perturbation theory. This correspondence, we believe, is strictly valid only for potentials of the type (3.10), which allow no pure dephasing at second order. Can higher order dephasing processes be given interpretations akin to the interpretation of their second order counterparts in the case of more general coupling?

Consider the Hamiltonian (3.7) with a (perhaps more realistic) modified system-bath coupling [6],

$$H' = |1 > H'_{10} < 0| + |0 > H'_{01} < 1| + |1 > H'_{11} < 1|,$$  \hfill (3.73)

where the terms $H'_{ij}$ are bath operators. This type of coupling appears in the stochastic study of Budimir and Skinner. At finite temperature, the Bloch equations will not be valid at fourth order for such a potential. In fact, at equilibrium, it is simple to show

$$\sigma_{10}(\infty) = Tr_b < 1|exp\{-\beta H\}|0 > = \int_0^\beta d\lambda \int_0^\lambda d\gamma e^{\gamma\omega_0} < H'_{11}(-i\lambda)H'_{10}(-i\gamma) >,$$  \hfill (3.74)

3.6 Variational Procedure

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$$\sigma_{10}(\infty) = Tr_b < 1|exp\{-\beta H\}|0 > = \int_0^\beta d\lambda \int_0^\lambda d\gamma e^{\gamma\omega_0} < H'_{11}(-i\lambda)H'_{10}(-i\gamma) >,$$  \hfill (3.74)
where
\[ H_{ij}(-\epsilon) = e^{iH_0} H_{ij} e^{-iH_0}. \] (3.75)

Thus, in the basis of states defined by \( H_0 \), the equilibrium reduced density matrix of the system is not diagonal. We could choose a basis of states that makes \( \sigma_{10}(\infty) \) vanish, however this seems artificial in light of the fact that even the fourth order calculation is, strictly speaking, a weak coupling calculation, and should be rendered in the eigenstates of \( H_0 \) [27]. The previous point highlights a difficulty of using the "bare" representation even at fourth order. We would like to have a method that incorporates a "dressed" basis that allows for clear physical interpretation of the rate processes.

3) Based on the points (1) and (2), we note that the experimental lineshape may, in fact, be given by
\[ I(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty dt e^{-i\omega t} < \tilde{\mu}(t), \] (3.76)
where \( \tilde{\mu} \) is the dressed dipole operator. Clearly, as shown in connection with the discussion of dephasing and population relaxation much of the bare relaxation rates at fourth order may be expressed in terms of lower order rate expressions involving states that mix system and bath character. The true test of the correct calculation of the lineshape must, in the end, come from experiments.

4) Lastly, the fourth order theory of LBS provides a testing ground for the ability of variational methods to reproduce the exact, perturbative behavior of a small quantum mechanical system coupled to quantum reservoir [20, 37].

The models studied by LBS consist of a real coupling model \( (\Gamma_1(\omega) = \Gamma_2(\omega), \) see equations (3.31) and (3.33)), and a complex coupling model \( (\Gamma_1(\omega) = \Gamma(\omega), \) \( \Gamma_2(\omega) = 0) \). The real coupling model is identical to the standard spin-boson model (see equation (3.54)) in a basis of states,
\[ |0\rangle = \frac{1}{\sqrt{2}}[|L\rangle + |R\rangle], \quad |1\rangle = \frac{1}{\sqrt{2}}[|L\rangle - |R\rangle]. \] (3.77)

We employ the variational polaron transformation, utilized earlier in the study of the
spin-boson problem [20].

\[
U = \exp\{-(|1> < 0| + |0> < 1|) \sum_k \frac{f_k}{\omega_k} (b_k - b_k^+)\},
\]

(3.78)

where \(\{f_k\}\) is a set of variational parameters. In the \(|0>, |1>\) basis, the transformed Hamiltonian is found to be

\[
\tilde{H} = U^* H U = \tilde{H}_0 + \tilde{V},
\]

(3.79)

\[
\tilde{H}_0 = |1> < 1| - |0> < 0| + H_b,
\]

\[
\tilde{V} = \frac{1}{2} (V_+ + V_-) [|1> < 1| - |0> < 0|] + (V_z + V_- - V_+)|1> < 0| + (V_z + V_+ - V_-)|0> < 1|,
\]

where

\[
\tilde{\omega}_0 = \omega_0 e^{-2 \sum_k \frac{f_k^2}{\omega_k} \coth \frac{\tilde{\omega}_k}{2}},
\]

(3.80)

\[
V_+ = V_-^{*} = \frac{\omega_0}{2} \left\{ e^{-2 \sum_k \frac{f_k}{\omega_k} (b_k - b_k^+)} - \frac{\tilde{\omega}_0}{\omega_0} \right\},
\]

(3.81)

\[
V_z = \sum_k (h_k - f_k) (b_k + b_k^+).
\]

(3.82)

We have again identified the renormalized frequency of the system by the removal of the secular term from \(\tilde{V}\). As an illustration of the utility of the dressed picture, we note that

\[
\tilde{b}_k = b_k + \frac{f_k}{\omega_k} \sigma_x,
\]

where \(\sigma_x\) is expressed in the \(|0>, |1>\) basis. If we chose \(f_k\) to minimize the free energy of the system, then we find the implicit equation for the variational constants,

\[
f_k = h_k \{ 1 + \frac{\tilde{\omega}_0}{\omega_k} \coth \frac{\beta \omega_k}{2} \tanh \frac{\beta \tilde{\omega}_0}{2} \}^{-1}.
\]

(3.83)

Thus, at zero temperature we find the second order result

\[
< \tilde{b}_k^\dagger \tilde{b}_k > = \frac{1}{\pi} \int_0^\infty \frac{\Gamma_1' (\omega)}{\omega + \omega_0} d\omega,
\]

(3.84)
in exact agreement with (3.50). Thus the dressed representation is able to account for the number of “bath” excitations present at zero temperature.

Next we show that, for the purpose of calculating relaxation rates, a minimization of the energy of the system is more accurate than a minimization of the free energy, even at finite temperature. Consider the “up” rate constant, calculated from (3.79) by the use of the second order Fermi Golden Rule expression [3],

\[
\Gamma_{0 \rightarrow 1} = \int_{-\infty}^{\infty} dt e^{-i\omega_0 t} < \{ V_z(t) + \frac{1}{2} [V_+(t) - V_-(t)] \} \{ V_z + \frac{1}{2} [V_+ - V_-] \} >
\]

\[
= \int_{-\infty}^{\infty} dt e^{-i\omega_0 t} < \{ V_z(t) - \frac{\omega_0}{2} \sinh \Phi(t) \} \{ V_z + \frac{\omega_0}{2} \sinh \Phi \} >,
\]

(3.85)

where

\[
\Phi = e^2 \sum_{k} \frac{f_k}{\omega_k} (b_k - b_k^\dagger).
\]

We chose the variational constants to minimize the energy of the system, which is the zero temperature limit of (3.83)

\[
f_k = h_k \left\{ 1 + \frac{\tilde{\omega}_0}{\omega_k} \right\}^{-1}.
\]

(3.86)

Note that in this approximation the frequency shift at second order is given by

\[
\Delta \omega^{(2)} = \omega_0 \int_{0}^{\infty} \frac{d\omega}{\omega} \frac{\Gamma_1(\omega) \coth \frac{\omega}{2}}{\omega + \omega_0}.
\]

(3.87)

which differs from the exact result (3.39) by the form of the energy denominator. This error can be viewed as the failure to incorporate a minimization of the energy in both the ground and excited states of the system. An energy minimization of the excited state of the system yields (3.86) with a minus sign in the denominator. In fact, if we heuristically replace \( f_k^2 \) with \( f_k^g f_k^e \) where \( f_k^g \) represents a variational constant (equivalent to (3.86)) for energy minimization in the ground state, and \( f_k^e \) represents a variational constant for energy minimization in the system’s excited state, then (3.39) would be reproduced exactly at second order, as long as it is understood that the principle part of the sum is to be taken (see section (V) for a discussion).
Using (3.86) in (3.85), we calculate terms arising from the lowest order expansion of \( \sinh \Phi \), finding

\[
\Gamma_{0 \to 1}^{[\text{partial}]} = \frac{\pi}{2} \left( 1 + 2 \frac{\omega_0}{\tilde{\omega}_0} + \frac{\omega_0^2}{\tilde{\omega}_0^2} \right) \sum_k |h_k|^2 n(\omega_k) \delta(\omega_k - \tilde{\omega}_0),
\]

where “partial” is used to indicate that terms of fourth and higher order involving \( \Phi^{2n+1} \), \( n \geq 1 \) arising from the expansion of \( \sinh \Phi \) have been omitted. At second order in the coupling we can make the replacement \( \omega_0 = \tilde{\omega}_0 \), and we find

\[
\Gamma_{0 \to 1}^{(2)} = 2\pi \sum_k |h_k|^2 n(\omega_k) \delta(\omega_k - \omega_0) \equiv \hat{C}_1(-\omega_0)
\]

in exact agreement with (3.32). While we expect this agreement based on the fact that at second order we are essentially using bare states, the result is not obvious, in the sense that it depends on the choice of the variational constant. We conclude that the minimization of the system’s energy is more accurate in the calculation of weak coupling rates than a minimization of the system’s free energy, (which would not reproduce (3.32)).

(3.88) may be expanded to fourth order as

\[
\Gamma_{0 \to 1}^{[\text{partial}],(4)} = -\frac{1}{\omega_0} \hat{C}_1(-\omega_0) \Delta \omega_{\text{var}}^{(2)} - \hat{C}_1'(-\omega_0) \Delta \omega_{\text{var}}^{(2)}.
\]

The label “partial” is now included because we have left out some fourth order terms. Note that this is identical to the first two terms of (3.34) where the definition (3.39) of \( \Delta \omega^{(2)} \) has been used (since we are dealing here with the real coupling model, \( P_2(\omega) = P_1(\omega) \)). Thus these terms may be viewed as second order type expressions oscillating about the shifted frequency. This gives explicit support to the claim that resumed, dressed expressions will appear in higher order calculations of bare relaxation rates.

From (3.88) we can find sixth and higher order contributions to the rate constant by simple Taylor expansion of the delta function and the renormalized frequency. Other fourth order terms can be found simply by expanding the \( \sinh \Phi \) term to third order and including all cross products in the correlation function. This will contribute
terms akin to the mixing of first and third order amplitudes as outlined in appendix A. Note, however, that these terms cannot be identical to the remaining terms in (3.39). This is due to the fact that second order rates calculated from (3.76) obey

$$K_{eq} \equiv \frac{\Gamma_{0\rightarrow 1}}{\Gamma_{1\rightarrow 0}} = e^{-3\tilde{\omega}_0},$$

(3.91)

that is, the equilibrium constant defined by the quotient of the dressed rate constants is given by a Boltzmann factor containing the renormalized frequency. This illustrates precisely why the equilibrium constant of (3.91) differs from the equilibrium rate constant defined as the ratio of rates given by equation (3.34) and its "down" rate counterpart at fourth order. The equilibrium constant given by (3.91) is a property of the dressed, not the bare, basis.

We now turn to a calculation of the dephasing properties in the dressed basis. In the transformed picture, the pure dephasing rate may be calculated with second order perturbation theory as

$$\Gamma_{pd} = \frac{\omega_0^2}{2} \int_{-\infty}^{\infty} dt \{ < \cosh \Phi(t) \cosh \Phi > - \frac{\tilde{\omega}_0^2}{\omega_0^2} \},$$

(3.92)

$$= \frac{\tilde{\omega}_0^2}{2} \int_{-\infty}^{\infty} \{ \cosh \xi(t) - 1 \},$$

where

$$\xi(t) = \frac{4}{\pi} \int_{-\infty}^{\infty} d\omega \Gamma_1(\omega) \frac{(\cos \omega t \coth \frac{\theta}{2} - i \sin \omega t)}{(\omega + \tilde{\omega}_0)^2}.$$

(3.93)

Note that the pure dephasing rate is zero at second order, again due to the fact that the second order expansion of the transformed results are really bare results, and should agree with standard second order results in the basis of $H_0$. At fourth order, we find

$$\Gamma_{pd}^{(4)} = \frac{4\omega_0^2}{\pi} \int_{0}^{\infty} d\omega \frac{\hat{C}_1(\omega)\hat{C}_1(-\omega)}{(\omega + \omega_0)^4},$$

(3.94)

where the definition (3.30) has been used for $\hat{C}_1(\omega)$. For the real coupling model, this expression is identical to (3.43) and (3.72) except for the denominator (if the integration by parts in equation (3.72) is valid, see section (3.5)). Again, as in the
discussion of the renormalized frequency, the two expressions would be identical if, in (3.85), we replaced $f_k^2$ with $f_k f_k^p$.

We now discuss how the technique described earlier in this section may be applied to the complex coupling model of (LBS). This model is of importance because it provides a model of dipole with spin-1/2 precessing with Larmor frequency $\omega_0$ around a fixed magnetic field along the z-axis while being perturbed by equal strength but uncorrelated magnetic fields in the two transverse directions [1, 9]. In this model, the spectral density $\Gamma_2(\omega)$ is identically zero, that is

$$\Gamma_2(\omega) = \sum_k h_k^2 \delta(\omega - \omega_k) = 0. \quad (3.95)$$

In the spin-boson language, our Hamiltonian for this complex coupling model may be written

$$H = -\frac{\omega_0}{2} \sigma_x + \sum_k \omega_k (b_k^+ b_k + a_k^+ a_k) + \sigma_z \sum_k |h_k| (a_k^+ a_k) + \sigma_y \sum_k |h_b| (b_k^+ b_k). \quad (3.96)$$

We have written the Hamiltonian in the $|L>, |R>$ basis of (3.77) to show the similarity with the standard spin-boson Hamiltonian of equation (3.54). We have separated the bath into two independent sets of modes that couple with equal strength to orthogonal system operators. This is precisely the physical situation that gives rise to the condition (3.95). Note that in this form, the Hamiltonian (3.96) is nothing more than the pseudo Jahn-Teller system [38, 39]. This insight allows us to chose a dressing transformation from an impressive set of methods that have been applied to this and similar problems. As discussed by Alper and Silbey [39], a transformation of the form (3.78), coupled with second order perturbation theory (as was applied to the real coupling model) accurately accounts for the energy spectrum of the Hamiltonian (3.96). By applying the transformation (3.78) to the Hamiltonian (3.96), and by treating the two sets of modes as independent, i.e.,

$$[a, b^\dagger] = 0$$
for any $a$ and $b$, we can express the Hamiltonian (3.96) in the form (3.79), with the modification

$$V_+ = V_+^* = \frac{\omega_0}{2} \left( e^{-\frac{1}{2} \sum_k \frac{f_k}{\omega_k} (a_k^+ a_k^--) \hat{B} - \frac{\tilde{\omega}_0}{\omega_0} \right)$$

$$\hat{B} = \left( 1_b - \frac{i}{\omega_0} \sum_k |h_k| (b_k^+ + b_k) \right).$$

$1_b$ is the unit operator for the bath. The expressions for $V_z$ and $f_k$ are unchanged.

We find that the pure dephasing for this model

$$\Gamma_{pd} = \frac{\tilde{\omega}_0^2}{2} \int_{-\infty}^{\infty} dt (cosh \xi(t) - 1) + 2 \frac{\tilde{\omega}_0^2}{\omega_0^2} \int_{-\infty}^{\infty} \hat{C}_1(t) \sinh \xi(t) dt. \quad (3.98)$$

Note that the dephasing rate in the complex coupling model can be expressed as the pure dephasing rate of the real coupling model plus an additional term. When expanded to fourth order, an expression similar to (3.43) and (3.72) (with $\hat{C}_2(omega)$) is found. In both the real and complex coupling models, the dephasing rate at fourth order is greater than the population relaxation rate, in contrast to results found with the bare perturbation theory. However, when the energy splitting of the system, $\omega_0$, does not overlap with the bath density of states, the results are essentially identical (with the few modifications discussed in this section). We note in passing that the method used to study the complex coupling model may be used to study other physical systems of interest that have the generalized spin-boson form (3.96) [40].

### 3.7 Conclusion

We briefly recap what has been accomplished in this chapter. We have used the study of a two level system linearly and off-diagonally coupled to a bath of harmonic oscillators conducted by Laird, Budimir, and Skinner to highlight several aspects of dynamical calculations that transcend the weak coupling limit. We have clarified the origin and meaning of the finite zero temperature population excitation rate, and have shown the relationship between the population transfer constants calculated by LBS and the standard, fourth-order Fermi Golden Rule expression. The fourth order
"pure" dephasing expression introduced by LBS as a purely mathematical entity, has
been given a physical meaning. In certain instances, this rate has been shown to be
derivable from the second order Redfield expression for pure dephasing, which means
that, in these instances, the expression derived for "pure" dephasing by LBS must
remain positive, rendering $1/T_2 \geq 1/2T_1$. We have briefly discussed the detection
of the violation of the inequality (3.6). Lastly, we have discussed the relationship
between the dynamics of the density matrix calculated in a bare basis (as is done
in LBS). and a dressed basis, defined by a suitable canonical transformation of the
Hamiltonian. This allows for a better understanding of the frequency shift, and rate
constant calculated in (LBS). Lastly, it is shown how a variational method may be
use to handle the various models studied by Laird and Skinner. It is shown that, in
some instances, the results are very similar to the results of (LBS). The approximate
method is easier to implement and more flexible (in terms of extensions beyond fourth
order) than the method of (LBS). but is not able to show a breakdown of the inequality
(3.6).

3.8 Appendix A

The purpose of this appendix is to calculate the population excitation ("up") rate
constant by standard means, and to show the relationship between this expression
and the expression calculated in (LBS).

We begin with the standard definition of the transition rate (equivalent to (3.31))
[31],

$$W_{0\rightarrow1} = \lim_{t \to \infty} \frac{d}{dt} < | 1 \rangle \langle U(t,0) | 0 \rangle |^2 >, \quad (A-1)$$

where the tilde refers to the interaction picture. It can be seen immediately that
for the particular form of $H'$ given in (3.10), the fourth order contributions to (A-1)
consist of the mixing of first and third order amplitudes, while the contribution from
the mixing of the second order amplitudes vanishes.
Computing $W_{0\rightarrow 1}$ to fourth order gives

$$W_{0\rightarrow 1} = -\lim_{t\rightarrow \infty} \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \left\{ e^{-i\omega_0 t} e^{-i\omega_0 t_1} e^{-i\omega_0 t_2} e^{-i\omega_0 t_3} < \Lambda^\dagger(t_3)\Lambda(t_2)\Lambda^\dagger(t_1)\Lambda(t) > 
+ e^{-i\omega_0 t} e^{i\omega_0 t_1} e^{i\omega_0 t_2} e^{-i\omega_0 t_3} < \Lambda^\dagger(t_3)\Lambda(t_2)\Lambda^\dagger(t_1)\Lambda(t_2) > 
+ e^{-i\omega_0 t} e^{i\omega_0 t_1} e^{-i\omega_0 t_2} e^{i\omega_0 t_3} < \Lambda^\dagger(t_3)\Lambda(t_1)\Lambda^\dagger(t_2)\Lambda(t_3) > 
+ e^{-i\omega_0 t} e^{-i\omega_0 t_1} e^{i\omega_0 t_2} e^{-i\omega_0 t_3} < \Lambda^\dagger(t_3)\Lambda(t_2)\Lambda^\dagger(t_1)\Lambda(t) > \right\}. \quad (A-2)$$

Using Wick's theorem [2] to break up the four point correlation functions into products of two point functions, and making the changing of variables $\tau_1 = t - t_1$, $\tau_2 = t_1 - t_2$, $\tau_3 = t_2 - t_3$, we find, (letting $t \rightarrow \infty$)

$$W_{0\rightarrow 1} = -2Re \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \left\{ e^{-i\omega_0 (\tau_1 - \tau_3)} \left[ C_1(\tau_1)C_1^\ast(\tau_3) + C_2(\tau_2)C_2^\ast(\tau_1 + \tau_2 + \tau_3) + C_1^\dagger(\tau_1 + \tau_2)C_1^\ast(\tau_2 + \tau_3) 
+ C_1(\tau_1 + \tau_2)C_1^\ast(\tau_2 + \tau_3) + C_2(\tau_1 + \tau_2 + \tau_3)C_2(\tau_2) + C_1^\dagger(\tau_1)C_1^\dagger(\tau_3) \right] 
+ e^{-i\omega_0 (\tau_1 + \tau_3)} \left[ C_1^\dagger(\tau_2)C_1(\tau_1 + \tau_2 + \tau_3) + C_2(\tau_1 + \tau_2)C_2(\tau_2 + \tau_3) + C_1(\tau_3)C_1^\dagger(\tau_1) 
+ C_1(\tau_1)C_1(\tau_3) + C_2(\tau_1 + \tau_2)C_2(\tau_2 + \tau_3) + C_1(\tau_1 + \tau_2 + \tau_3)C_1(\tau_2) \right] \right\} \quad (A-3)$$

where the notation of equation (3.28) has been used. The first notable feature of this expression is that part of it diverges as $t \rightarrow \infty$. The origin of these divergent terms has been discussed by Zwanzig [30]. In fact, one reason for introducing the "Van-Hove limit" ($\lambda^2 t$ constant, $\lambda \rightarrow 0$, $t \rightarrow \infty$) is to eliminate such terms. These terms arise when a virtual state in the third order amplitude coincides with the initial (real) state from which the transition is made. If we make the restriction that the virtual states are to be distinct from the states physically involved in the transition, then these terms may be neglected. It is interesting to note that the divergent terms have the form

$$- \frac{1}{T_1}^{(2)} \langle \langle 1|\tilde{U}(t,0)|0 \rangle \rangle^2 \quad (A-4)$$

as $t \rightarrow \infty$. Here, $1/T_1$ is the sum of "up" and "down" rate constants, and $\langle \langle 1| <
1|\tilde{U}(t,0)|0 \rangle^2 > is the thermally averaged transition probability for a transition to occur between the ground and excited states of the system.

Even with the removal of the divergent terms, the expression (A-3) appears different from the equivalent expression (equation (3.90)) in LBS. If we evaluate (A-3) in frequency space by using the methods outlined in appendix B of LBS, we find

$$W_0 \rightarrow 1 = \frac{1}{2\pi} \{ \omega^{-1}_0 [P_2(\omega_0) - P_2(-\omega_0)]$$

$$+ \dot{C}'_1(-\omega_0) [P_1(\omega_0) - P_1(-\omega_0)] + P'_1(-\omega_0) [\dot{C}_1(\omega_0) - \dot{C}_1(-\omega_0)]$$

$$- 2\dot{C}_1(-\omega_0) P'_1(\omega_0) \}$$

in the notation of equations (3.29),(3.30), and (3.35-3.37). This result is identical to equation (3.34).

We may ask why the rate calculated by the method outlined in section (3.2) naturally avoids the divergence problems associated with (A-3). To investigate this, we recast the problem by projecting the Liouville equation onto the system states [41]. We find,

$$\dot{\vec{P}}(t) = \vec{K}(t)\vec{P}(t), \quad (A-6)$$

where

$$\vec{P}(t) = \begin{pmatrix} \sigma_{00}(t) \\ \sigma_{10}(t) \\ \sigma_{01}(t) \\ \sigma_{11}(t) \end{pmatrix},$$

$$\vec{K}(t) = \dot{\vec{A}}(t)\vec{A}^{-1}(t)$$

$$\vec{A}(t) = \begin{pmatrix} G_{0000}(t) & G_{0010}(t) & G_{1000}(t) & G_{1001}(t) \\ G_{0010}(t) & G_{0011}(t) & G_{1010}(t) & G_{1011}(t) \\ G_{0100}(t) & G_{0101}(t) & G_{1100}(t) & G_{1101}(t) \\ G_{0110}(t) & G_{0111}(t) & G_{1110}(t) & G_{1111}(t) \end{pmatrix},$$

and

$$G_{ijkl}(t) = \langle (U^+)^{ij}(t)U_{kl}(t) \rangle .$$

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By noting the form $K(t)$ must take for the Bloch equations to hold, we find, as $t \to \infty$

$$\dot{A}(t) = B A(t) \quad \text{(A-7)}$$

where

$$B = \begin{pmatrix}
-k_{10} & 0 & 0 & k_{01} \\
0 & -\{\frac{1}{T_2} + i(\omega_0 + \Delta \omega)\} & 0 & 0 \\
0 & 0 & -\{\frac{1}{T_2} - i(\omega_0 + \Delta \omega)\} & 0 \\
k_{10} & 0 & 0 & -k_{01}
\end{pmatrix}.$$

Note that at orders higher than fourth, the matrix $B$ must be modified to incorporate the coupling of coherences. From (A-7), we find the implicit equation for the "up" rate

$$k_{10} = \frac{1}{T_1} < |< 1|\tilde{U}(\infty, 0)|0 >|^2 + \frac{d}{dt} < |< 1|\tilde{U}(\infty, 0)|0 >|^2 >. \quad \text{(A-8)}$$

The noteworthy feature of equation (A-8) is that the rate explicitly contains terms canceling the divergence associated with unrestricted summation over virtual states. We also note that (A-7) provides a much easier evaluation of the rate expression than the method of LBS since no commutators are involved. In fact, (A-3) and (A-8) shows that the standard definition ((3.51) or (A-1)) is all that is needed, since the remaining term merely serves to cancel the divergence due to the unrestricted summation over virtual states. We thus could (much more easily) compute $1/T_2$ as

$$\left(\frac{1}{T_2}\right)^{(4)} = Re \left\{ \hat{G}_{0011}^{(4)} \right\}.$$ 

(A-9)
Figure 3-1: $\Gamma_1^2(\omega)/\omega^2$ for "Ohmic-Lorentzian" density of states $\Gamma_1(\omega) = \frac{A\omega}{(\omega^2 + \lambda^2)}$. The value of $A$, which has units of frequency, is taken to be 1 $cm^{-1}$. $\omega_0$ is taken to be 1 $cm^{-1}$. The values of $\lambda$ (in units of $cm^{-1}$) are: (a) .6, (b) 1, (c) 1.47, (d) 2. For $\frac{A}{\omega_0} > 1.4679$, $(\frac{1}{T^2})^{(4)}$ becomes negative.
Figure 3-2: Same plot for the super-Ohmic density of states $\Gamma_1(\omega) = \frac{B\omega^3}{\omega_0} e^{-\omega/\omega_0}$. B is taken to be 1 $cm^{-1}$, $\omega_0$ has the value 1 $cm^{-1}$, and the values of $\omega_c$ (in units of $cm^{-1}$) are: (a) 0.1, (b) 0.15, (c) 0.281.
Figure 3-3: Same plot as (Fig. 2) with the values of $\omega_c$ (in units of $cm^{-1}$) (a) 0.7, (b) 1.006, (c) 2. The function $(\frac{1}{\pi^2})^{(4)}$ is negative for $0.218 > \frac{\omega_c}{\omega_0} > 1.006$. 
Bibliography


Chapter 4

Cumulant Expansions and the
Spin-Boson Problem

4.1 Introduction

The standard spin-boson problem, described by the Hamiltonian [1, 2],

\[ H = \frac{\Delta}{2} \sigma_x + \sum_j \left[ \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left( x_j - \frac{c_j}{m_j \omega_j^2} \sigma_z \right)^2 \right], \]  

(4-1)

has served as a paradigm for the description of dissipative effects in condensed phases. Some experimental realizations of such a Hamiltonian include, e.g., the detection of macroscopic quantum coherence in superconducting quantum interference devices [3, 4], tunneling effects in metallic and insulating glasses [5], electron transfer reactions [6] and the diffusion of light interstitial particles in metals [7]. In each situation, the physical realization of the parameters in the Hamiltonian (4.1) is different. For instance, in metallic glasses at low temperatures the electron-hole pairs at the Fermi level constitute the bosonic bath, while for insulating glasses, tunneling effects are damped by localized and delocalized vibrational modes. Thus, the Hamiltonian (4.1) embodies a wealth of physical situations and has been studied in great detail (see for instance [1, 2] and references quoted therein, or more recently [8, 9, 10]).

In order to study the dynamics of the two-level system coupled to a harmonic bath
as in (4.1), we need a method of “tracing out” the bath or spin degrees of freedom. The bath degrees of freedom can be specified by the spectral density function,

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

(4-2)

which gives the bath density of states weighted by the square of the coupling strength between the two-level system and the bath. In most studies of the spin-boson problem, the spectral density takes the ohmic form [1, 2],

\[ J(\omega) = 2\pi a \omega \exp(-\omega/\omega_c), \]  

(4-3)

where \( \alpha \) is a measure of the coupling strength, and \( \omega_c \) is a frequency cutoff for the bath. We note that in many cases, such as the coupling of a spin degree of freedom to a three dimensional phonon bath in the deformation potential approximation, the spectral density (4.3) is not realistic, and must involve higher powers of \( \omega \).

The usual approach to finding reduced equations for the spin variables of interest involves the use of the functional integral formulation of quantum dynamics [1, 2]. Formally exact equations may be found for the variables

\[ P(t) = \langle \sigma_z(t) \rangle, \]  

(4-4)

and

\[ C(t) = \frac{1}{2} \langle \{\sigma_z(0), \sigma_z(t)\} \rangle, \]  

(4-5)

where \( \langle \ldots \rangle_\beta \) refers to an average with respect to the canonical ensemble of (4-1). The quantity \( P(t) \) describes the population difference in the localized spin states of the Hamiltonian (4.1), given that the particle is initially localized in one well and in thermal equilibrium with the bath. It is the variable of interest in certain physical situations, for example, the electron transfer problem [6]. The quantity \( C(t) \), the symmetrized equilibrium correlation function of the tunneling coordinate, is related to the structure factor for neutron scattering off the tunneling particle, and is of great
significance in various problems, including the antiferromagnetic Kondo problem [11].
For $C(t)$ the long-time behavior at zero temperature is known from the generalized Shibab relation which predicts algebraic decay $C(t) \propto t^{-2}$ [2, 12]. For $P(t)$ the situation is less clear, however some studies have predicted exponential decay as $t \to \infty$ [2, 13]. Despite the importance of $C(t)$, we will focus on the variable $P(t)$ in the following.

The formal path integral expression for $P(t)$ is extremely cumbersome, and a suitable approximation must be implemented to obtain useful information. The so-called “non-interacting blip approximation”, or NIBA [1, 2], is the most commonly used approximation. In this scheme $C(t)$ is entirely determined by $P(t)$, i.e., $C(t) \equiv P(t)$. The NIBA may be obtained from the exact expression for $P(t)$ by invoking a series of physically based approximations. For very low temperatures, these approximations often break down, unless $\alpha$ is very small and only short times are considered. At zero temperature, the NIBA is not justified in the antiferromagnetic Kondo regime $\frac{1}{2} < \alpha < 1$. The NIBA also incorrectly predicts asymptotically algebraic, rather than exponential, decay for the variable $P(t)$. Lastly, NIBA incorrectly predicts that at zero temperature, $C(t) \sim t^{-2(1-\alpha)}$.

Despite these flaws, the NIBA is useful for obtaining quantitative results for $P(t)$ for high temperatures, when the tunneling dynamics is incoherent, and in predicting the qualitative behavior of $P(t)$ for low temperatures. For instance, at zero temperature, the NIBA correctly predicts a crossover from damped oscillations to incoherent decay for the variable $P(t)$ at the point $\alpha = \frac{1}{2}$.

As shown by Aslangul et. al. [14], the NIBA may be obtained by first applying a small polaron transformation to the Hamiltonian (4.1), followed by a second order application of the usual Nakijima-Zwanzig projection operator technique. It has been known for some time that this projection technique, which leads to a master equation of the convolution form, is an order by order resummation of a particular type of cumulants known as “chronologically ordered” cumulants [16, 17, 18, 19, 20]. The use of the “chronological ordering prescription”, or COP, when truncated at second order thus leads to the NIBA.

Interestingly, Aslangul et. al. [15] earlier applied a convolutionless master equa-
tion technique to the study of the zero temperature spin-boson problem. This type of master equation, which can be derived by using a different type of projection operator, involves the summation of a different type of cumulants, known as “partially (time)-ordered” cumulants [21, 17, 18, 19, 20]. This method was probably abandoned for two reasons. First, it incorrectly describes incoherent relaxation for $P(t)$ for all values of $\alpha$. Secondly, it cannot be obtained in a simple manner from the exact path integral expression. The second objection is irrelevant, since it is still possible that such an approximate resummation describes the exact behavior of $P(t)$ well. The first flaw, however, is quite serious. Despite this, the expression obtained from the “partial ordering prescription”, or POP, which naturally resums to an exponential form, may be expected to give a better description of $P(t)$ in the incoherent region. In fact, for values of $\alpha$ greater than $\frac{1}{2}$, but not too large, this method describes weakly stretched exponential relaxation, which closer approximates the true exponential decay of $P(t)$ than does the algebraic behavior predicted by NIBA. Furthermore, as will be demonstrated in this paper, recent simulations of Egger and Mak [22] show that the POP method more accurately captures the deep decay of $P(t)$ at zero temperature for $\alpha > \frac{1}{2}$ than does the COP (NIBA) method, even before the algebraic behavior of the NIBA is manifested.

It is well known that by choosing a particular ordering in a truncated cumulant expansion, we are implicitly assuming different statistical properties for the relevant bath operators. The first purpose of this chapter is to specify these statistical properties for the case of the spin-boson problem at zero temperature. Using this “stochastic” type intuition, we then discuss various cumulant ordering schemes and their associated descriptions of the behavior of $P(t)$ at $T = 0$. This chapter is organized as follows: In Sec. 4.2 we first present a new derivation of the exact expression for $P(t)$ that allows for clear specification of the statistical properties of the bath. For this purpose, orthogonally to the conventional approach, we first integrate out the spin degrees of freedom exactly. In Sec. 4.3, we briefly discuss the COP and POP methods. We then turn to a recently introduced new cumulant method, the “non-crossing” cumulants [23, 24, 25]. Lastly, in Sec. 4.4, we compare the methods
4.2 Moment Expansion

We begin with an explicit expression for $P(t)$ through fourth order in $\Delta$. We could, if we wished, obtain these terms from the exact path integral expression for $P(t)$, however, we believe that the method used in this section most clearly shows the connection to the stochastic methods upon which the cumulant expansions are based. In effect, our method offers another route to the formal expression of Ref. [1, 2].

We begin with the Hamiltonian (4.1) in the form,

$$H = H' + \frac{\Delta}{2} \sigma_z, \tag{4-6}$$

$$H' = \sum_k \omega_k b_k^\dagger b_k - \sigma_z \sum_k g_k (b_k^\dagger + b_k) + \sum_k \frac{g_k^2}{\omega_k}. \tag{4-7}$$

The quantity we wish to calculate is $P(t)$ which is defined as

$$P(t) = \langle \sigma_z (t) \rangle = Z^{-1} \text{Tr} \left( \exp(iHt) \sigma_z (0) \exp(-iHt) \pi^+ \exp(-\beta H') \pi^+ \right) \tag{4-8}$$

where

$$Z = \text{Tr} \left( \pi^+ \exp(-\beta H') \pi^+ \right),$$

$$\sigma_z = |L\rangle \langle L| - |R\rangle \langle R|,$$

$$\sigma_x = |L\rangle \langle R| + |R\rangle \langle L|,$$

$$\pi^+ = \frac{1}{2} (1 + \sigma_z),$$

and $\beta$ is the inverse temperature. We now diagonalize (4.6) in the spin manifold with the use of a transformation employed by Shore and Sander [26, 27] in their study of...
the self-trapping of an exciton coupled to phonons, namely,

\[ U = \frac{1}{\sqrt{2}} \left( \begin{array}{cc} 1 & -1 \\ \phi & \phi \end{array} \right), \]  

(4-9)

where

\[ \phi = (-1)^{\sum_k b_k^\dagger b_k} = \exp \left( i\pi \sum_k b_k^\dagger b_k \right). \]

The operator \( \phi \) is seen to be the parity operator for the bath modes. In the transformed picture, we can express

\[ P(t) = -\tilde{Z}^{-1} \text{Tr} \left( \exp(i\tilde{H}t)\sigma_z(0) \exp(-i\tilde{H}t)\tilde{\pi}^+ \exp(-\beta\tilde{H})\tilde{\pi}^+ \right). \]  

(4-10)

where

\[ \tilde{H} = \frac{\Delta}{2} \phi\sigma_z + \tilde{H}', \]  

(4-11)

\[ \tilde{H}' = \sum_k \omega_k b_k^\dagger b_k + \sum_k g_k (b_k^\dagger + b_k) + \sum_k \frac{g_k^2}{\omega_k}, \]  

(4-12)

\[ \tilde{\pi} = \frac{1}{2} (1 - \sigma_z), \]  

(4-13)

and \( \tilde{Z} \) is now defined with respect to \( \tilde{H}' \) and \( \tilde{\pi}^+ \).

We now perform the trace over the spin degrees of freedom in (4.10), leaving

\[ P(t) = \text{Re} [G(t)], \]  

(4-14)

where

\[ G(t) = \text{Tr}_b \left( \exp(iH_+ t) \exp(-iH_- t) \exp(-\beta\tilde{H}) \right) / \text{Tr}_b (\exp(-\beta\tilde{H}')), \]  

(4-15)

with

\[ H_{\pm} = \pm \frac{\Delta}{2} \phi + \tilde{H}'. \]

This trace over the bath degrees of freedom is most easily performed in the small
polaron representation, defined by the transformation

\[ U = \exp(\xi), \]  
\[ \xi = \sum_k \frac{g_k}{\omega_k} (b_k - b_k^\dagger). \]  

(4-16) \hspace{1cm} (4-17)

In this picture, we may express \( G(t) \) as

\[ \langle \exp_{\rightarrow}(i \int_0^t d\tau \eta(\tau)) \exp_{\leftarrow}(i \int_0^t d\tau \eta(\tau)) \rangle_B, \]  
where

\[ \eta(t) = \frac{\Delta}{2} \exp[-\xi(t)] \phi \exp[\xi(t)], \]  
and

\[ \xi(t) = \sum_k \frac{g_k}{\omega_k} (b_k e^{-i\omega_k t} - b_k^\dagger e^{i\omega_k t}). \]  

(4-18) \hspace{1cm} (4-19) \hspace{1cm} (4-20)

The averaging (denoted by \( \langle \ldots \rangle_B \)) is over the canonical ensemble of harmonic oscillators, (i.e., \( \rho_B = \exp(-\beta \sum \omega_k b_k^\dagger b_k) / \text{Tr}_b \exp(-\beta \sum \omega_k b_k^\dagger b_k) \)), and \( \exp_{\rightarrow} (\exp_{\leftarrow}) \) denotes a time ordered exponential with latest time to the right (left). From this point on, all averaging will be with respect to this ensemble, and we will drop the subscript “\( B \)”. Since the spin degree of freedom has been removed, our method allows us to focus on the bath operators that arise in the expansion of \( P(t) \). Using the following properties of the parity operator,

\[ \phi \exp[\xi(t)] = \exp[-\xi(t)] \phi, \]

and

\[ \phi^2 = 1, \]

we can show, through fourth order in \( \Delta \), the moment expansion for \( P(t) \),

\[ P(t) = 1 + \int_0^t dt_1 \int_0^{t_1} dt_2 m_2(t_1,t_2) + \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 m_4(t_1,t_2,t_3,t_4) + ..., \]  

(4-21)
where the moments $m_i$ equal

\begin{align}
m_2(t_1, t_2) &= -\Delta^2 \text{Re} \langle B_-(t_1)B_+(t_2) \rangle, \quad (4-22) \\
m_4(t_1, t_2, t_3, t_4) &= \frac{\Delta^4}{4} \text{Re} \left[ \langle B_-(t_1)B_+(t_2)B_-(t_3)B_+(t_4) \rangle \\
&+ \langle B_-(t_2)B_+(t_1)B_-(t_3)B_+(t_4) \rangle \\
&+ \langle B_-(t_3)B_+(t_1)B_-(t_2)B_+(t_4) \rangle \\
&+ \langle B_-(t_4)B_+(t_1)B_-(t_2)B_+(t_3) \rangle \right], \quad (4-23)
\end{align}

and

$$B_\pm(t) = \exp[\pm 2\xi(t)]. \quad (4-24)$$

Note that $m_{2n-1} = 0$. In this paper, we shall only use the first two nonvanishing moments, although it is a simple matter to execute the expansion to an arbitrary order. From (4-21)–(4-23) we conclude that $P(t)$ is entirely determined by the statistical properties of the bath operators $B_\pm(t)$ with respect to the canonical state of the bath. Note that the operators $B_\pm$ always appear in pairs. In order to specify the statistics obeyed by the operators $B_\pm$, we now calculate the second and fourth moment of the $B_\pm$’s. It is a simple matter to show that

$$\langle B_-(t_1)B_+(t_2) \rangle = \exp[-iQ_1(t_1 - t_2) - Q_2(t_1 - t_2)], \quad (4-25)$$

where

$$Q_1(t_1 - t_2) = 4 \sum_k \left( \frac{g_k}{\omega_k} \right)^2 \sin(\omega_k(t_1 - t_2)), \quad (4-26)$$

and

$$Q_2(t_1 - t_2) = 4 \sum_k \left( \frac{g_k}{\omega_k} \right)^2 \left[ 1 - \cos(\omega_k(t_1 - t_2)) \right] \coth(\beta \omega_k/2). \quad (4-27)$$

Furthermore, by using the relation $e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]}$ and $\langle e^{\kappa b^\dagger} e^{-\kappa b} \rangle = e^{-|\kappa|^2}$ for $[A, B]$, $\kappa$ being c-numbers, one can also show that the operators $B_\pm$ have the following "statistical" property,

$$\langle B_-(t_1)B_+(t_2)B_-(t_3)B_+(t_4) \rangle =$$

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This property can be extended to an arbitrary number of $B_\pm$ pairs. This gives a type of "Wick" theorem for the operators $B_\pm$, and demonstrates the underlying reason why only the functions $Q_1$ and $Q_2$ appear in the exact path integral (see Eqs. (4-17) to (4-22) in Ref. [1]). It can now be explicitly checked that the expression (4-21) is identical to the exact path integral expression, at least through the fourth moment. Note that the property (4-28) is different than the statistical properties held by commonly used stochastic processes such as Gaussian, two-state-jump, or Gaussian random matrix processes. We will return to this point in the next section.

The moment expansion itself is not a very useful scheme for describing dynamics, because an arbitrary truncation of the expansion leads to secular terms that grow with time. We next resort to schemes that provide partial (approximate) resummations of the moment expansion to all orders. Such schemes are the cumulant expansions that will be introduced in the next section.

### 4.3 Cumulant Expansions

We now discuss the various ordering prescriptions which allow for partial resummation of the expansion (4.21). Each ordering method leads to a unique type of master equation [24]. We note that, when carried out to infinite order, all of the ordering techniques give the same (exact) result. When truncated at a finite order, however, the results are different. In simple stochastic situations, when the temperature of the bath is infinite and the generator for time evolution (the Liouville operator) commutes with itself for all times, i.e., $[L(t), L(t')] = 0$, the use of a particular truncated cumulant expansion implies a knowledge of the stochastic properties of the bath functions. In simple cases, truncation of the cumulant expansion in the “correct” ordering prescription can lead to exact results that may be obtained in the “incorrect” ordering prescription only at infinite order. In the quantum case described by the Hamiltonian (4.1), where $[L(t), L(t')] \neq 0$, truncation of a cumulant expansion at
finite order in any ordering prescription will never lead to exact results due to the
non-commutivity of the Liouvillian at different times [28, 29, 30]. It is precisely this
non-commutivity that leads to the variety of time-orderings of the operators $B_\pm$ in
the expression (4-23) for $m_4$. Despite this fact, the statistical properties of the bath
operators still dictate the choice of an ordering prescription that provides the most
rapid convergence of the cumulant series (if such convergence exists) [31].

We begin by discussing the chronological ordering prescription, or COP. In this
prescription, a master equation of the form (see for instance [20, 17, 18, 19, 24])

$$\frac{dP(t)}{dt} = \int_0^t K^{COP}(t, \tau)P(\tau) \, d\tau$$

is obtained. This equation may be expressed in the form

$$\frac{dP(t)}{dt} = \sum_{n=2}^{\infty} \int_0^t d\tau_1 \cdots \int_0^{\tau_{n-2}} d\tau_{n-1} \gamma_n(t, \tau_1, \cdots, \tau_{n-1})P(\tau_{n-1}). \quad (4-30)$$

The COP cumulants, $\gamma$, are obtained from the moments by a recursion relation [24].
In the present case this yields

$$\gamma_{2n-1} = 0,$$

$$\gamma_2(t, \tau_1) = m_2(t, \tau_1),$$

$$\gamma_4(t, \tau_1, \tau_2, \tau_3) = m_4(t, \tau_1, \tau_2, \tau_3) - m_2(t, \tau_1) m_2(\tau_2, \tau_3), \cdots. \quad (4-31)$$

For the simple case where the stochastic Liouvillian commutes with itself for all
times, all of the COP cumulants $\gamma_n$ vanish for $n \geq 3$ if the stochastic bath functions
have the two-state-jump behavior [20]

$$\langle B(t_1)B(t_2)B(t_3)B(t_4) \cdots \rangle = \langle B(t_1)B(t_2) \rangle \langle B(t_3)B(t_4) \cdots \rangle, \quad (4-32)$$

for $t_1 > t_2 > t_3 > t_4 \cdots$, where $B(t)$ is the stochastic bath function responsible for
system dissipation. If these bath functions have different statistics, it may not be a
good approximation to truncate the series at low orders.

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Returning now to the quantum case of interest in this paper, we find at lowest order, as shown by Aslangul et. al. [14], the NIBA equation for $P(t)$

$$
\frac{dP(t)}{dt} = \int_0^t m_2(t - \tau)P(\tau)d\tau,
$$

(4-33)

where, at $T = 0$, using the ohmic constraint (4-3), along with (4-22), we may express

$$
m_2(t - \tau) = -\Delta^2 Re \frac{1}{[1 + i\omega_c(t - \tau)]^{2\alpha}}.
$$

(4-34)

As shown by Grabert and Weiss [32], the solution to (4-33) with the kernel (4-34) can be given for all $\alpha < 1$ (in the limit $\Delta/\omega_c \to 0$) by the Mittag-Leffler function [33],

$$
P_{NIBA}(y) = E_{2(1 - \alpha)}(-y^{2(1 - \alpha)}),
$$

(4-35)

where $y = \Delta_{\text{eff}}t$ and

$$
\Delta_{\text{eff}} = \Delta [\cos(\pi\alpha)\Gamma(1 - 2\alpha)]^{\frac{1}{2(1 - \alpha)}} \left( \frac{\Delta}{\omega_c} \right)^{\frac{1}{1 - \alpha}}.
$$

(4-36)

This solution shows damped oscillations for $\alpha < \frac{1}{2}$, and incoherent decay for $\alpha \geq \frac{1}{2}$. This behavior has been qualitatively confirmed by Monte Carlo simulation [22].

As mentioned in the introduction, the NIBA cannot give the correct asymptotic decay of $P(t)$ (yielding the algebraic decay $P(t) \propto t^{-2(1 - \alpha)}$ rather than exponential decay), and is unable to account for the depth of the decay in the region $\alpha \geq \frac{1}{2}$, even before the incorrect algebraic behavior sets in. The NIBA is, however, known to work quite well for short times and weak coupling strengths. The analysis given in the last section provides a novel explanation for this fact. For “short” times and “small” values of $\alpha$ the function $m_2(t)$ is a rather broad, weakly decaying function of time. When this is the case, the statistical property (4-28) of the operators $B_\pm$ is approximately of the two-state-jump form (4-32) as far as the integrations over the cumulants $\gamma_{n \geq 3}$ are concerned. This approximate equivalence holds in a stochastic sense, in that all of the four point correlation functions in $m_4$ (see Eq. (4-23)) may
be approximated by \( m_2(t_1, t_2) m_2(t_3, t_4) \). For such times and coupling strengths, the NIBA will be essentially exact, as all COP cumulants for \( n \geq 3 \) will vanish when integrated. We shall not provide precise meaning to the terms “short” or “small”, although their meaning should be clear in the context of the present discussion, and could be quantified without undue labor (in fact “short” and “small” will be coupled in the sense that the effective timescale of oscillation or decay, \((\Delta_{\text{eff}})^{-1}\), depends on \( \alpha \)). Note that the statistical property (4-28) trivially gives two-state-jump behavior for \( \alpha = 0 \), which leads to the correct behavior \( P(t) = \cos(\Delta t) \). While this is obvious, other cumulant techniques (such as those discussed below) do not embody this type of statistics for \( \alpha = 0 \), and cannot give the correct, freely oscillating solution for zero coupling strength upon truncation at second order. The statement (often given in the literature [34]) that NIBA works for weak coupling because it is a perturbative scheme is thus not strictly correct.

The (somewhat heuristically) demonstrated fact that the property (4-28) can resemble two-state-jump behavior under certain circumstances leads one to believe that extending the COP scheme to fourth order would not be useful, since this property is reflected in the vanishing of all COP cumulants higher than the second. Extending the COP method to fourth order does not give a method for computing “interblip” interactions in the language of Ref. [1].

We now turn to the partial ordering prescription, or POP. At second order, this method was applied by Aslangul et. al. [15] to the spin-boson problem at \( T = 0 \). The POP master equation has a convolutionless [20, 24] form

\[
\frac{dP(t)}{dt} = \left( \int_0^t K^{\text{POP}}(\tau) d\tau \right) P(t).
\]

(4-37)

\( K^{\text{POP}}(t) \) may be obtained from the moments

\[
K^{\text{POP}}(t) = \sum_{n=1}^{\infty} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \ldots \int_0^{\tau_{n-1}} d\tau_n \theta_{n+1}(t, \tau_1, \ldots, \tau_n),
\]

(4-38)
where
\[
\begin{align*}
\theta_{2n-1} &= 0, \\
\theta_2(t, \tau_1) &= m_2(t, \tau_1), \\
\theta_4(t, \tau_1, \tau_2, \tau_3) &= m_4(t, \tau_1, \tau_2, \tau_3) - m_2(t, \tau_1) m_2(\tau_2, \tau_3) \\
&\quad - m_2(t, \tau_2) m_2(\tau_1, \tau_3) - m_2(t, \tau_3) m_2(\tau_1, \tau_2), \ldots \\
&\quad \ldots (4-39)
\end{align*}
\]

The POP resummation is exact at second order for the simple case of a classical Gaussian stochastic process. We note that the statistical property (4-28) appears to be very different from the standard Wick theorem for Gaussian processes. We may still expect that the POP method is better suited for the incoherent regime \( \alpha > \frac{1}{2} \) for the following reasons. First, the POP technique resums to an exponential form, which is expected to better capture the long time behavior of \( P(t) \), which is expected to be exponential. In general, the POP method sums (infinitely) more terms than the COP method does. For example, expansion of the second order truncation in the COP gives, to fourth order
\[
P(t) = 1 + \int_0^t dt_1 \int_0^{t_1} dt_2 m_2(t_1, t_2) + \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 m_2(t_1, t_2) m_2(t_3, t_4) + \ldots
\]

whereas the POP gives
\[
P(t) = 1 + \int_0^t dt_1 \int_0^{t_1} dt_2 m_2(t_1, t_2) + \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 m_2(t_1, t_2) m_2(t_3, t_4) \\
+ m_2(t_1, t_3) m_2(t_2, t_4) + m_2(t_1, t_4) m_2(t_2, t_3) + \ldots
\]

Clearly, the extra terms do not insure a more accurate result. For example, for weak coupling strengths, the POP must be carried out to infinite order to obtain coherent behavior. However, in the incoherent regime, the effective timescale, defined by (4-36) is very long, while the decay of the function \( m_2(t) \) is “slow” (algebraic). In this case, we may expect that we must include terms like \( m_2(t_1, t_4) m_2(t_2, t_3) \) that extend over large portions of the integration region. As we will show in the next section, the POP
method seems to capture the behavior of $P(t)$ better than the COP method in the incoherent regime, even before the full asymptotic behavior is displayed.

At second order, $(K^{\text{POP}}(t, \tau) = m_2(t - \tau))$ the POP equation (4.38) may be solved [15],

$$P(t) = \exp \left[ \frac{\Delta^2}{4 \omega_c^2 (\alpha - 1/2)(1 - \alpha)} \left( 1 - \frac{\cos(2(1 - \alpha) \tan^{-1} \omega_c t))}{(1 + \omega_c^2 t^2)^{\alpha-1}} \right) \right].$$

Note that equation (4-40) describes a stretched exponential rather than exponential decay. For values of $\alpha$ that are not too much larger than $\frac{1}{2}$, however, the POP expression should give a better representation of the asymptotic exponential decay of $P(t)$ than the COP (NIBA) expression, which yields algebraic decay asymptotically.

We have now given some motivation for the belief that the COP method (at lowest order) should give a better description of $P(t)$ in the region $\alpha < \frac{1}{2}$ while the POP method should be better in the incoherent region $\alpha > \frac{1}{2}$. We now ask whether there is a summation method that is a “hybrid” of the two methods, in the sense that it can incorporate at low order features of the COP and POP methods. In the theory of stochastic processes, such a technique has recently been developed [23, 24, 25]. This method is based on the summation of “non-crossing” (NC) cumulants (for a precise definition see Refs. [23, 24, 25]). For simple stochastic situations, if the coupling is not too strong, the NC technique (including terms up to fourth order) has been shown to interpolate between the two-state-jump behavior and the Gaussian behavior [24].

The NC description leads to a nonlinear equation of motion for $P(t)$ [24], which at second order, may be expressed

$$\frac{dP(t)}{dt} = M(t),$$

where

$$M(t) = \int_0^t dt_1 \zeta_2(t - t_1)P(t - t_1)P(t_1).$$
To fourth order the master equation for $P(t)$ in the NC scheme reads

$$\frac{dP(t)}{dt} = M(t) + \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \zeta_4(t, t_1, t_2, t_3) P(t - t_1) P(t_1 - t_2) P(t_2 - t_3) P(t_3).$$

(4-43)

As in the previous two case, the NC cumulants, $\zeta$, may be obtained from the moments by a recursion relation [23, 25]. In the present case this yield up to fourth order

$$\zeta_{2n-1} = 0,$$
$$\zeta_2(t, t_1) = m_2(t, t_1),$$
$$\zeta_4(t, t_1, t_2, t_3) = m_4(t, t_1, t_2, t_3) - m_2(t, t_1) m_2(t_2, t_3) - m_2(t, t_3) m_2(t_1, t_2).$$

(4-44)

It is clear that in appearance, the NC cumulants are a “compromise” between the COP and POP cumulants. We note in passing two interesting facts. First, in the stochastic realm, the NC ordering prescription truncated at second order is exact for the case of a stochastic bath modeled by symmetric $(N \times N)$ Gaussian random matrices for the commutator of $\eta(t)$’s. In this case, the “crossing contraction” $m_2(t, t_2) m_2(t_1, t_3)$ vanishes by means of a $\frac{1}{N^2}$ argument for $N \to \infty$. This leads naturally to the equation (4-42) and its systematic generalization (4-43) through the NC cumulants. Eq. (4-42) has first been derived by Kraichnan [36, 37, 38, 39] in the fields of turbulence and fluid dynamics. Our motivation for the application of this method is not based on a stochastic type of reasoning, but on the fact that in simple situations this ordering prescription may combine the benefits of the COP and POP methods.

Before concluding this section, we would like to apply all three ordering prescriptions to the case $T = 0$, $\alpha = \frac{1}{2}$. Here, it is known that the “exact” (in the sense specified in Ref. [1]) result for $P(t)$ is

$$P(t) = \exp \left( -\frac{\pi}{2} \omega_c \left( \frac{\Delta}{\omega_c} \right)^2 \right)$$

(4-45)

in the limit $\frac{\Delta}{\omega_c} \to 0$. Note that in this limit, the second moment becomes $\delta$–correlated.
Using the fact that $P(0) = 1$, it is clear that all three ordering prescriptions give the same result given by (4-45) at second order. Hence, the value $\alpha = \frac{1}{2}$ corresponds to the white noise limit of the bath operators $B_\pm(t)$.

4.4 Results and Conclusions

Before comparing the results of the three ordering methods, we make some comments on the methods discussed in Sec. 4.3. We have shown how three different cumulant methods give rise to different master equations with different properties. We have tried to physically motivate when each approach should have success when applied to the spin-boson problem at zero temperature. Note that in general, the discussion of convergence of each cumulant series is a difficult task. This task is made more difficult by the fact that, at zero temperature, the algebraic decays of the bath correlation functions leave us with no clearly defined relaxation time for the bath. This means that we will rely almost exclusively on physical considerations and comparison with accepted results to determine the success or failure of the methods employed. The case of finite temperature, which can be studied by the same methods employed here, is often easier in this respect. If an exponential correlation time $\tau_b$ can be assigned to the decaying bath correlation functions, than it is possible to consider a systematic expansion in $\Delta_{\text{eff}}\tau_b$ provided that this dimensionless parameter is small. When this is the case, the POP provides the most facile way of systematically summing terms in the parameter $\Delta_{\text{eff}}\tau_b$ [21]. In case of ohmic dissipation and finite temperature $T$, the characteristic correlation time of the $B_\pm(t)$ is given by $\tau_b \sim (2\pi \alpha T)^{-1}$ [1]. This point of view provides a novel explanation for the familiar statement that the NIBA works well in the incoherent tunneling regime $\Delta_{\text{eff}}\tau_b \ll 1$. In a stochastic language, this parameter region corresponds to the narrowing or Markov limit of the $B_\pm$'s. Similarly to the white noise limit mentioned above, one finds that all three cumulants schemes work well already at second order and provide essentially the same behavior,
\[ P(t) \approx \exp[-\Delta_{\text{eff}}^2(T) \tau_b \times t] \text{ with } \Delta_{\text{eff}}(T) \propto T^\alpha [1]. \]

Since we expect the NIBA to be accurate for very weak coupling strengths, we first turn to the case of weak to intermediate coupling strength, \( \alpha = 0.3 \). For coupling strengths in this range, simulations at low temperatures have shown that the NIBA is qualitatively correct in predicting damped oscillations, but may fail in predicting the damping strength. An example of this is given by the simulations of Makarov and Makri [13] which show that for intermediate coupling, NIBA may fail by slightly underestimating the number of oscillations in \( P(t) \). We note, however, that these simulations were carried out for values of \( \frac{\Delta}{\omega_c} \) that are not very small. In Fig. 4.1, we plot the NIBA (second order COP) solution for \( P(t) \) against the solutions obtained from second and fourth order truncations of the non-crossing cumulant method, and the second order POP. Note that, as expected, the second order POP solution for \( P(t) \) fails to produce any oscillations. We expect that for \( \alpha < \frac{1}{2} \) the POP will always be inaccurate at low orders. The second order non-crossing cumulant solution for \( P(t) \), obtained from the Kraichnan-type equation (4-41)–(4-42) is similar to the NIBA solution, although the oscillation in \( P(t) \) is much weaker. The fourth order non-crossing cumulant solution gives a first oscillation which is very similar in magnitude to the NIBA solution, however, it describes one extra weak remnant of an oscillation. This behavior is very similar to the behavior displayed in the exact simulations of Makarov and Makri [13]. Although this example represents only one value of \( \alpha \), similar results may be obtained for all moderately strong values of \( \alpha \) up to \( \alpha = \frac{1}{2} \). Thus, it appears that the non-crossing scheme works well in incorporating (and perhaps improving) the qualities of the COP method for moderate values of \( \alpha \) when \( \alpha < \frac{1}{2} \).

We now turn to the relaxation of \( P(t) \) in the incoherent regime \( \alpha \geq \frac{1}{2} \). Here, the beautiful path integral simulations of Egger and Mak [22] provide a means of comparing the cumulant expansion methods with exact results. In this region, we expect the POP to be most successful, while the NIBA (second order COP) is expected to be worse. Based on experience with simple stochastic situations, we hope, as in the coherent portion of the coupling space, that the non-crossing scheme can capture the essence of the POP in this regime. In Fig. 4.2, we show the decay of \( P(t) \)
calculated by differing ordering prescriptions for $\alpha = 0.6$. It must be noted that the simulations were carried out for long times, but not long enough to show the asymptotic algebraic decay of the NIBA (second order COP) solution of $P(t)$, or the asymptotic exponential decay of the exact solution. Due to this fact, it is somewhat difficult to see that the POP solution is to be preferred over the NIBA solution in the incoherent regime. In support of this claim we note two facts. First, the POP solution better manifests the deep decay of the exact result in the nonasymptotic regime. Secondly, near the point $\alpha = 1/2$, the POP solution will better approximate the exponential decay of $P(t)$ in the asymptotic regime than the NIBA, which predicts $P(t) \sim t^{-2(1-\alpha)}$. The simulations of Egger and Mak end just before this regime is reached. As we had hoped, for $\alpha = 0.6$, the second order non-crossing technique is nearly identical to the POP. Fig.4.3 shows the results for $\alpha = 0.7$. Again, the POP seems to perform the best, while the second order non-crossing scheme overestimates the decay. As in the case of weaker coupling, we see if truncation after fourth order in the non-crossing cumulants can properly correct the second order result. This test is shown in Fig.4.4. While the results appear to show that the non-crossing scheme is converging to a POP-like description of $P(t)$, we again must exercise caution due to the lack of further concrete evidence for this belief. For such large value of $\alpha$, it is quite possible that the cumulant methods break down.

One interesting property displayed in Fig.4.2 and Fig.4.3 is the close agreement between the POP description of $P(t)$ and the exact simulation of $P(t)$ for moderately long times. In Fig.4.3 this behavior occurs for $y \geq 2.5$, while in Fig.4.3, the agreement is less pronounced, but appears to occur for $y \geq 1.6$ (note that there is some scattering in the simulation data for $\alpha = .7$ near $y = 2$ that slightly obscures the apparent agreement). In order to investigate this, we have computed $\int_0^y dy' \int_0^y dy'' K_2^{POP}(y'')$ and $\int_0^y dy' \int_0^y dy'' K_4^{POP}(y'')$ where $K_n^{POP}(t)$ is the $n$-th term in the expansion (4-38). If the integrated second order POP cumulant is of order one for a given time interval, while all other POP cumulants are small when integrated over the appropriate time domain, then we expect the truncation at second order to be a good approximation. While we cannot study all the POP cumulants, we have studied the second and the
fourth. In Fig. 4.5, we compare the properties of the second and fourth POP cumulants for $\alpha = 0.7$. For $y = 1.4$ to $y = 2$ (the boundary of the simulation results of Egger and Mak [22]), we see that the contribution from the second POP cumulant is at least ten times greater than the contribution from the fourth cumulant. This strongly suggests that the agreement of the second order POP method with the exact simulations is no coincidence. In fact, the agreement between (4.41) and the simulation occurs precisely in the interval where the second order cumulant dominates the fourth order cumulant. Since the slopes of the two curves suggest that this behavior continues for some time, we feel there is strong evidence for the somewhat remarkable conclusion that, for significant intermediate times, the decay of $P(t)$ is quantitatively described by a stretched exponential. For longer times, the decay is most likely purely exponential.

We now summarize the results presented in this chapter. We first carried out a new derivation of the moment expansion for the variable $P(t)$ in the spin-boson problem. We then used this derivation to discuss the “statistical” properties of the relevant bath operators. Using the moment expansion, we first discussed the chronological and partial ordering prescriptions that involve different types of cumulants. We discussed the merits and drawbacks of each method. In an effort to combine the merits of the COP and the POP, we applied the non-crossing scheme. Specializing to the case of zero temperature, we tested each method, including fourth order terms when necessary. Our results show that the non-crossing scheme is a promising candidate for combining the virtues of the COP and POP, especially for intermediate values of $\alpha$ on either side of the coherent-incoherent transition value of $\alpha = \frac{1}{2}$. We note that more work should be done to test the validity of this claim. Lastly, we have provided evidence to support the belief that the stretched exponential behavior described by second order truncation of the POP in the incoherent portion of coupling space may in fact be very accurate for intermediate times.
Figure 4-1: Zero temperature plot of $P(y) (y = \Delta_{\text{eff}} t)$ for $\alpha = 0.3$ and $\frac{<e>}{\Delta} = 6$. The dotted line is the second order POP result, the dashed line is the second order non-crossing cumulant result, the dash-dotted line is the NIBA (second order COP) result, and the solid line is the fourth order non-crossing cumulant result.
Figure 4-2: Zero temperature plot of $P(y) (y = \Delta_{eff} t)$ for $\alpha = 0.6$ and $\frac{T}{\Delta} = 6$. The dash-dotted line is the NIBA (second order COP) result, the dashed line is the second order POP result, the solid line is the second order non-crossing cumulant result, and the open circles are the simulation result of Egger and Mak [22].
Figure 4-3: Zero temperature plot of $P(y)$ ($y = \Delta_{\text{eff}} t$) for $\alpha = 0.7$ and $\frac{\Delta}{\alpha} = 6$. The dash-dotted line is the NIBA (second order COP) result, the dotted line is the second order POP result, the solid line is the second order non-crossing cumulant result, and the open circles are the simulation result of Egger and Mak [22].
Figure 4-4: Zero temperature plot of $P(y)$ ($y = \Delta_{\text{eff}} t$) for $\alpha = 0.7$ and $\frac{\alpha}{\Delta} = 6$. The dotted line is the fourth order non-crossing cumulant result, the dashed line is the second order POP result, and the solid line is the second order non-crossing cumulant result. Note the change in the $y$-axis.
Figure 4-5: Relative magnitude of second and fourth cumulant effects in the POP for $\alpha = 0.7$. The dashed line shows $|\int_0^y dy' \int_0^{y'} dy'' K_2^{POP}(y'')|$ and the solid line shows $|\int_0^y dy' \int_0^{y'} dy'' K_4^{POP}(y'')|$. $K^{POP}(t)$ is defined in Eq. (38).
Bibliography


Chapter 5

Spectral diffusion on ultra-long time scales in low temperature glasses

5.1 Introduction

At low temperatures the thermal, acoustic and optical behavior of glasses differs significantly from that of crystalline solids. As examples note the linear temperature dependence of the specific heat, the pronounced absorption of sound even below 1 K, and the anomalous broadening of spectral holes in the homogeneous line of chromophore molecules. It is known now for more than twenty years that phonons cannot account for these observations; instead localized low-energy excitations in the glass are needed. Since the introduction of the standard tunneling model (STM) by Anderson, Halperin and Varma [1] and Phillips [2], and the experimental observation of saturability of ultra-sound by Hunklinger et al. [3] and Golding et al. [4], it is widely accepted that these low-energy excitations are two-level tunneling systems (TLS). Denoting the left and right ground state of the double-well potential by $|L\rangle$
and $|R\rangle$, respectively, the Hamiltonian reads in a Pauli-spin representation

$$H = -\frac{\Delta}{2}\sigma_x - \frac{\epsilon}{2}\sigma_z.$$  \hfill (5-1)

where $\Delta/\hbar$ is the tunneling frequency, $\epsilon$ the asymmetry energy and $\sigma_z = |L\rangle\langle L| - |R\rangle\langle R|$. In the STM the interaction between TLS is neglected, and it is assumed that the tunneling parameters $\Delta$, $\epsilon$ are random variables with distribution

$$P^{(1)}(\epsilon, \Delta)d\epsilon d\Delta = \frac{P_0}{\Delta} d\epsilon d\Delta, \quad \Delta \geq \Delta_{\text{min}},$$  \hfill (5-2)

(with $P_0 \approx 0.6 \times 10^{45}$ J$^{-1}$ m$^{-3}$ in PMMA, a polymer glass). The ensuing constant distribution for the TLS-energy splitting

$$E = \sqrt{\Delta^2 + \epsilon^2}$$  \hfill (5-3)

explains in particular the linear specific heat. Including relaxation of the TLS via the one-phonon process with rate

$$R = \left(\frac{\Delta}{E}\right)^2 R_{\text{max}},$$  \hfill (5-4)

where $(x = E/2k_BT)$

$$R_{\text{max}}(E) = \alpha T^3 x^3 \coth x$$  \hfill (5-5)

and

$$\alpha = \frac{\gamma^2 (2k_B)^3}{2\pi \hbar^4 \varrho v^5},$$  \hfill (5-6)

the model describes most acoustic and optical experiments in glasses satisfactorily. Here, $\gamma$ is the deformation potential energy of the TLS-phonon coupling, $\varrho$ the mass density of the glass, and $v$ the sound velocity.

Recent experiments report a systematic disagreement with the STM. An example is the attenuation of sound below 100 mK. The STM predicts a $T^3$-increase in contradiction with the experimental $T^{(1-2)}$-law. \cite{5, 6} Deviations from the predicted STM
behavior was also observed by Maier, Kharlamov, and Haarer in low temperature hole-burning experiments. [11, 12] They performed hole-burning of a chromophore embedded in PMMA at temperatures around 1 K up to extremely long times (from 10 s to 10 days). They found a logarithmic time-dependence with a crossover to an algebraic behavior after about 3 h. Though the log $t$-behavior is in agreement with the STM, the algebraic behavior is not. The authors could fit their data with an ad hoc ansatz

$$P(\epsilon, \Delta) = P_0 \left[ \frac{1}{\Delta} + \frac{A}{\Delta^2} \right], \quad A = \text{constant}, \quad (5-7)$$

for the TLS-parameter distribution function and the assumption that relaxation occurs via the one-phonon process with the rate (5-4)-(5-6). They motivate the distribution function (5-7) by recent publications focusing on the interaction of TLS in glasses. [13, 14, 15, 16] Indeed, Burin and Kagan [16] have shown, following earlier ideas of Yu and Leggett [14] that pairs of interacting TLS do provide a means of constituting a distribution like the second term in Eq. (5-7) for certain excitations in their energy spectrum. They called TLS which are distributed according to the first term in (5-7) primary TLS, and those distributed according to the second term in (5-7) secondary TLS. The nice feature of their theory is that the distribution of secondary TLS [second term in Eq. (5-7)] is derived from primary TLS which are distributed according to the STM [first term in Eq. (5-7)]. In that sense, Burin and Kagan’s theory stays within the framework of the STM, and includes only excitations which have not been considered in the traditional treatment. So far these ideas have been worked out very qualitatively, and with emphasis on experiments in the millikelvin regime. Hence, the question arises whether they apply to the experiment of Maier et al., i.e., for relaxation processes at 1 K on the time scale between hours and days, or whether an extension of the STM—which would be as phenomenological as the STM—has to be found in order to understand this experiment. It is the purpose of this paper to address this issue by presenting a detailed model that includes TLS-TLS coupling in the manner proposed by Burin and Kagan.

The chapter is laid out as follows: in Sec. 5.2, we analyze the experiment of Maier
et al. [11, 12] and show the achievements and failures of Burin and Kagan’s approach for experiments in the Kelvin regime; in Sec. 5.3 and 5.4, we propose a specific model that combines interacting TLS with strong-coupling effects between TLS and phonons in the framework of the theory of Kassner and Silbey [17]; in Sec. 5.5, we compare the predictions of the new model with the hole-burning data in Ref. [12], and also discuss alternative explanation schemes, which comprise an extension of the STM, and compare with equivalent hole-burning measurements in proteins; finally, in Sec. 5.6, discuss our results and conclude with a short summary in Sec. 5.7. The mathematical details are relegated to three Appendices in order not to obscure the basic ideas.

5.2 Hole-burning at ultra-long times and the Burin-Kagan theory

In Ref. [11, 12] photo-chemical hole-burning in PMMA at 1 and 0.5 K has been performed for extremely long times $t_{\text{max}} = 10^6$ s. The authors found a log $t$-dependence with a crossover to an algebraic behavior after approximately 3 h. The crossover shifts 1 order of magnitude in time from $10^4$ to $10^3$ s, if the temperature is increased by a factor of 2.

A theoretical description of spectral diffusion in glasses was provided by Hu and Walker [7] and Black and Halperin [8]. Reinecke [9], and later Bai and Fayer [10], extended their results to optical experiments. Based on this work the dependence of the hole width $F(t)$ on the waiting time $t$ is determined by

$$P(E, r) = \frac{P_0}{2\sqrt{1 - r}} \left[ \frac{1}{r} + \frac{A}{r^{3/2}E} \right],$$  

where

$$r = R/R_{\text{max}},$$

$$E = \frac{E_{\text{TLS}}}{k_B T}$$
according to the following equation:

\[
\Gamma(t) = \frac{\pi^2}{3h} \langle C \rangle \int_0^\infty dE \, \text{sech}^2 \frac{E}{2k_BT} \int_0^1 dr \, \frac{\epsilon}{E} P(E, r) \times \left(1 - e^{-rR_{\text{max}}t}\right).
\]

(5-10)

Here, \( \langle C \rangle \) is the chromophore-TLS coupling strength. The distribution \( P(E, r) \) directly follows from Eq. (5-7) by using (5-3)-(5-5) and (5-9). With this, we find

\[
\Gamma(t) = \Gamma(t_0) + \frac{\pi^2}{3h} \langle C \rangle P_0 \times \left[k_BT \log \frac{t}{t_0} + A \sqrt{\alpha T^3} \left(\sqrt{t} - \sqrt{t_0}\right)\right]
\]

(5-11)

with

\[
\alpha = 9 \times 10^9 \text{K}^{-3} \text{s}^{-1}
\]

(5-12)

in PMMA.[18] To compare with the experiment, we have included in \( \Gamma(t_0) \) processes which are faster than the shortest experimental time \( t_0 \), for which a hole broadening can be determined. In Ref. 12(a) a fit to the experimental data provided

\[
A/k_B \approx 10^{-7} \text{K}
\]

(5-13)

at 1 and 0.5 K with an error of approximately 10%. Furthermore, the experimental observation of spectral diffusion up to \( t_{\text{max}} \sim 10^6 \text{s} \) suggests

\[
\Delta_{\text{min}}/k_B \lesssim 10^{-8} \text{K}
\]

(5-14)

according to the relation \( t_{\text{max}} \leq 1/R_{\text{min}} = (2k_BT/\Delta_{\text{min}})^2(1/\alpha T^3) \).

Very recently, Burin and Kagan [16] showed that weak TLS-TLS interaction provides ultra-low energy excitations. They added to the Hamiltonian (5-1) an interaction term

\[
H_{\text{TLS-TLS}} = -\frac{1}{4} \sum_{ij} J_{ij} \sigma_i^x \sigma_j^x
\]

(5-15)
where the interaction energy

\[ J_{ij} = \frac{\mu_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|^3} \]  

falls off with distance \(|\mathbf{r}_i - \mathbf{r}_j|\) in a manner typical for a dipole-dipole interaction. They assumed that the angular average of the coupling is zero,

\[ \langle \mu_{ij} \rangle = 0, \]  

(5-17)

and that the TLS-TLS coupling is weak, i.e.,

\[ P_0 U_0 \ll 1, \]  

(5-18)

where \( U_0 \) is set by the variance

\[ \langle \mu_{ij}^2 \rangle = U_0^2. \]  

(5-19)

Such an interaction could be mediated by *virtual phonon exchange* (elastic coupling) or *virtual photon exchange* (electrostatic coupling) between the TLS. In the former case the energy scale of interaction (5-19) is easily found to be

\[ U_0 = \frac{\gamma^2}{\pi g^2}, \]  

(5-20)

which, indeed, provides \( P_0 U_0 \ll 1 \) for all glasses—in PMMA[18]: \( U_0 \approx 1 \text{ eV } \AA^3 \) and \( P_0 U_0 \approx 10^{-4} \). Based on the smallness of \( P_0 U_0 \), Burin and Kagan proposed that the TLS-TLS coupling in glasses is dominated at low temperatures by an *up-down transition*. Such an interaction contains *coherence* because the up transition of one TLS inevitably has to be followed by a down transition of the coupled TLS. After rotating to the eigenbasis \(|0_i\rangle, |1_i\rangle\) of (5-1) by

\[ \sigma_z^i = \frac{\epsilon_i}{E_i} S_z^i - \frac{\Delta_i}{E_i} S_x^i, \]  

(5-21)

\[ \sigma_x^i = \frac{\Delta_i}{E_i} S_z^i + \frac{\epsilon_i}{E_i} S_x^i, \]  

(5-22)
where $S_i^z = |0_i\rangle \langle 0_i| - |1_i\rangle \langle 1_i|$, such an interaction is generated by the

$$-\frac{\Delta_i \Delta_j}{4E_i E_j} J_{ij} S_i^z S_j^z$$

(5-23)

part of (5-15). The eigenstates $|1\rangle \equiv |0_i, 0_j\rangle$, $|2\rangle \equiv |0_i, 1_j\rangle$, $|3\rangle \equiv |1_i, 0_j\rangle$, $|4\rangle \equiv |1_i, 1_j\rangle$ of the Hamiltonian $H_{0,ij} = -(1/2)(E_i S_i^z + E_j S_j^z)$, (cf. Fig. 2), become mixed due to the interaction term (5-23). In the up-down subspace spanned by $|0_i, 1_j\rangle = |0_i\rangle \otimes |1_j\rangle$ and $|1_i, 0_j\rangle = |1_i\rangle \otimes |0_j\rangle$ this pair coupling can effectively be described by a TLS-Hamiltonian of the type (5-1) with $\sigma_z = |0_i, 1_j\rangle \langle 0_i, 1_j| - |1_i, 0_j\rangle \langle 1_i, 0_j|$, $\sigma_x = |0_i, 1_j\rangle \langle 1_i, 0_j| + |1_i, 0_j\rangle \langle 0_i, 1_j|$, and pair asymmetry energy, pair tunneling frequency, and pair level splitting

$$\epsilon_p = E_i - E_j,$$

$$\Delta_p = J_{ij} \Delta_i \Delta_j / 2E_i E_j,$$

$$E_p = \sqrt{\Delta_p^2 + \epsilon_p^2}.$$  

(5-24)

The eigenstates for the coherently coupled pair then read

$$|+\rangle = \sqrt{\frac{1 + \epsilon_p / E_p}{2}} |0_i, 1_j\rangle + \sqrt{\frac{1 - \epsilon_p / E_p}{2}} |1_i, 0_j\rangle,$$

$$|-\rangle = \sqrt{\frac{1 + \epsilon_p / E_p}{2}} |1_i, 0_j\rangle - \sqrt{\frac{1 - \epsilon_p / E_p}{2}} |0_i, 1_j\rangle.$$  

(5-25)

(5-26)

Clearly, the more asymmetric the pair is, i.e., the larger the energy offset $E_i - E_j$ is, the more localized at one TLS is the pair excitation.

Based on the distribution (5-2) of the single TLS tunneling parameters and a uniform spatial distribution of the single TLS in the glass, Burin and Kagan [16] derived the following distribution function for the parameters of coherently coupled pairs

$$P^{(2)}(\epsilon_p, \Delta_p) = \frac{\pi^3}{12} (P_b k_B T)(P_b U_0) \frac{1}{\Delta_p^2} \Theta(\Delta_p - \Delta_{p,\text{min}}),$$

(5-27)

where $\Theta(x)$, the unit step function, is included to emphasize that the distribution

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has a cutoff at small $\Delta_p$. Note that the density of states of the pairs is linearly temperature dependent. Coherent coupling between pairs is destroyed if there is spontaneous decay during the up-down transition. For primary TLS with $E \approx 2k_B T$ this occurs with a rate (5-4), which guided Burin and Kagan to estimate the lower bound (for secondary TLS formed from symmetric primary TLS)

$$\Delta_{p,\text{min}} = \hbar \alpha T^3. \quad (5-28)$$

Comparing (5-27) with (5-7) yields

$$A(T) = \left(\frac{\pi^3}{12}\right) (P_0 U_0) k_B T. \quad (5-29)$$

This looks encouraging; however, after a closer examination, there are several inconsistencies. First, Maier et al. [12] could fit their data with a temperature independent parameter $A$. Burin and Kagan's theory gives $A \propto T$. The 10% variation, which Maier et al.[12] found between the 1 and 0.5 K data, is too weak to account for the linear temperature dependence of the theory. Second, putting in numbers, we find for PMIMA at 1 K: $A(1 \text{ K})/k_B \approx 10^{-4} \text{ K}$ and $\Delta_{p,\text{min}}/k_B \approx 400 \text{ mK}$, which is inconsistent with the experimental values (5-13), (5-14) by several orders of magnitude. Indeed, at 1 K, TLS with $\Delta_{\text{min}}/k_B \sim 0.4 \text{ K}$ can never be responsible for spectral diffusion on the time scale between $10^3$ and $10^6$ s. However, it is possible that very asymmetric primary TLS are responsible for long time spectral diffusion. For very asymmetric TLS, the estimate of Burin and Kagan (28) would be significantly reduced. Hence, though Burin and Kagan's theory predicts the measured time-dependence quite accurately, there arise severe inconsistencies in orders of magnitude and the temperature dependence upon applying their theory at 1 K. It should be mentioned that Burin and Kagan considered only the millikelvin regime, which avoids all these problems.
5.3 The Kassner-Silbey approach for primary and secondary TLS

Though the picture developed by Burin and Kagan is very appealing, it explains only qualitatively the hole-burning data of Maier et al. [11, 12]. The question arises whether a microscopic calculation can yield testable predictions based on the interacting TLS scheme of Burin and Kagan. We carry out calculations based on strong coupling of TLS to phonons with deformation potential $\gamma \approx 1$ eV. This allows for a shifting of the rate distribution towards longer times and indeed brings the “calculated” value of $A$ (see (5.29)) into closer agreement with experiment. Furthermore, the inclusion of strong coupling effects alone gives a reasonable fit to the experiment of Maier et al. for intermediate times (cf. Fig. 5.1).

Let us start with the usual spin-boson Hamiltonian for an ensemble of TLS interacting with phonons via a strain field. In the TLS-eigenbasis the Hamiltonian reads

\begin{equation}
H = -\frac{1}{2} \sum_i E_i S_z^i + \sum_{i,q}(\bar{u}_i S_z^i - u_i S_x^i) c_q^i (b_q + b_{-q}^\dagger)
+ \sum_q \hbar \omega_q b_q^\dagger b_q,
\end{equation}

with

\begin{equation}
c_q^i = i \gamma \left( \frac{1}{2qV\omega_q} \right)^{1/2} e^{iqr_i}
\end{equation}

and

\begin{equation}
u_i = \Delta_i / E_i, \quad \bar{u}_i = \epsilon_i / E_i.
\end{equation}

According to this, the TLS become dressed with clouds of virtual phonons. As a result the coupling between the TLS will also be changed. The assumption traditionally made is that the dressed entities can be considered as weakly interacting. Hence, first order perturbation theory in the dressed states might be sufficient at low temperatures.

Based on this picture, Kassner and Silbey [17] derived a $S_z^i S_z^j$-interaction between
TLS and a reduction of relaxation rates for asymmetric TLS. Compared to Eq. (5-4), they found well below the Debye-temperature of the glass, $T \ll \Theta_D$.

$$R = \left( \frac{\Delta \epsilon}{E} \right)^2 e^{-G(\epsilon/E)^2} R_{\text{max}}, \quad (5-33)$$

where [cf. Eq. (5-6)]

$$G = \left( \frac{\hbar}{8 \pi k_B} \right) \alpha \Theta_D^0. \quad (5-34)$$

It is a peculiar feature of their approach that symmetric TLS have no reduced rates, i.e., $R_{\text{max}}$ is still given by Eq. (5-5), and have zero interaction. It is this very fact which significantly changes the distribution function $P^{(1)}(E, r)$ of single TLS energies $E$ and dimensionless relaxation rates $r = R/R_{\text{max}}$ compared to the STM-result (cf. first term in Eq. (5-8)). According to (5-33)

$$r = \left( \frac{\Delta \epsilon}{E} \right)^2 e^{-G(\epsilon/E)^2} \quad (5-35)$$

(compared to the STM-result $r = (\Delta/E)^2$). With this, Kassner and Silbey derived the new distribution

$$P^{(1)}(E, r) = \frac{P_0}{2r \tilde{u}(r) \{1 + G[1 - \tilde{u}^2(r)]\}} \quad (5-36)$$

where $\tilde{u}(r) = \epsilon/E$ is the inverse function of

$$r(\tilde{u}) = (1 - \tilde{u}^2) e^{-G\tilde{u}^2}. \quad (5-37)$$

The result is a stretching of the distribution in $r$ towards smaller values, i.e., $P^{(1)}(r)$ has an extended tail for such rates. The flaws and merits of the Kassner-Silbey way of handling strong-TLS-phonon-coupling effects have been discussed in Ref. KS. An important point is that a $S^1_z S^1_{\tilde{z}}$-interaction between TLS, as used in Burin and Kagan’s approach, cannot be derived from this approach.

In Appendix A we have generalized Kassner and Silbey’s approach to include coherent coupling between pairs. Our procedure has been as follows. First, we have
eliminated the diagonal \((S'_i^z)\) and off-diagonal \((S^i_z)\) coupling in the Hamiltonian \((5-30)\) by two separate unitary transformations \((A^{-1})\) and \((A^{-6})\). Second, instead of continuing with the full transformed Hamiltonian, we have projected out the one-phonon coupling part in the dressed state basis. This has been achieved by expanding the generated phonon shift operators around their mean value up to the first leading term in \(c_q^i\). This generates one-phonon transition matrix elements in the four-level system of the pair and, more importantly, Debye-Waller factors which renormalize Burin and Kagan’s coherent coupling term \((5-23)\) as

\[
- J_{ij} \Delta_i e^{-G(\epsilon_i/E_i)^2/2} \Delta_j e^{-G(\epsilon_j/E_j)^2/2} / (4E_iE_j) S^i_z S^j_z.
\]

Here,

\[
\frac{1}{4} J_{ij} = \sum_q \frac{c_q^i e_q^j}{\hbar \omega_q},
\]

which is equivalent to \((5-16)-(5-20)\). The pair asymmetry energy and tunneling amplitude read

\[
\epsilon_p = E_i e^{-W_i G \hbar \omega_i^2 / 2} - E_j e^{-W_j G \hbar \omega_j^2 / 2},
\]

\[
\Delta_p = J_{ij} \Delta_i e^{-G \hbar \omega_i^2 / 2} \Delta_j e^{-G \hbar \omega_j^2 / 2} / 2E_iE_j,
\]

with \(W_i = e^{-G \hbar \omega_i^2 / 2}\). One should note that for \(G \gg 1\) the Debye-Waller factor \(e^{-W_i G \hbar \omega_i^2 / 2}\) is practically unity except for nearly symmetric TLS. Since we will be mainly interested in strongly asymmetric TLS, we will always use this simplification hereafter. In Appendix B we calculate the pair parameter distribution function. The result is:

\[
P^{(2)}(\epsilon_p, \Delta_p) = P^{(2)}(\Delta_p) P^{(2)}(\epsilon_p),
\]

with

\[
P^{(2)}(\Delta_p) = \frac{P_0}{\Delta_p^2} e^{-G/2} I_0^2(G/4) \Theta(\Delta_p - \Delta_{p,\text{min}})
\]

and

\[
P^{(2)}(\epsilon_p) = f(\epsilon_p) + f(-\epsilon_p),
\]

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with

\[
f(\epsilon_p) = \frac{A(T)}{1 - e^{-\beta \epsilon_p}} \Theta(E_{\text{max}} - \epsilon_p) \times \log \left( \frac{2}{1 + e^{-\beta \epsilon_p}} \right) - \log \left( \frac{1 + e^{-\beta E_{\text{max}}}}{1 + e^{-3(\epsilon_p + E_{\text{max}})}} \right) \times \left\{ \log \left( \frac{2}{1 + e^{-\beta \epsilon_p}} \right) - \log \left( \frac{1 + e^{-\beta E_{\text{max}}}}{1 + e^{-3(\epsilon_p + E_{\text{max}})}} \right) \right\}.
\]

The parameters \(E_{\text{max}}, \Delta_{p,\text{min}}\) are cutoffs which are set by the requirement of stability for the coupled pairs. \(E_{\text{max}}\) is a cutoff in the energy of the primary TLS, which, as we will see below, is generally a function of the temperature. If \(E_{\text{max}} \gg k_B T\), \(P^{(2)}(\epsilon_p)\) is the sum of a constant and a bell shaped curve centered around \(\epsilon_p = 0\) with a width of \(O(k_B T)\). It can be approximated by

\[
P^{(2)}(\epsilon_p) \approx A(T)[\log 2 + (1 - \log 2) \exp(-\beta^2 \epsilon^2_p/9)]
\]

for all practical purposes. If \(E_{\text{max}} \ll k_B T\), the distribution \(P^{(2)}(\epsilon_p)\) becomes independent of \(\epsilon_p\),

\[
P^{(2)}(\epsilon_p) \approx A(T)E_{\text{max}}(T)/4k_B T.
\]

In the limit \(E_{\text{max}} \gg k_B T\) and \(G, \epsilon_p/k_B T \ll 1\), we find Burin and Kagan's result (5-27). This confirms that their model is valid at ultra-low temperatures for nearly symmetric TLS with weak coupling to phonons. In the limit \(G \gg 1\), the asymptotic expansion of the modified Bessel function, \(I_0(z) \approx e^z/\sqrt{2\pi z}\), \((z \gg 1)\), provides a renormalization of \(P_0\) by a factor \(2/(\pi G)\).

### 5.4 Stability analysis

To determine \(E_{\text{max}}\) and \(\Delta_{p,\text{min}}\), we first neglect the level broadening effect of the phonons. Then, \(E_{\text{max}}\) scales with the glass transition temperature, and \(\Delta_{p,\text{min}}\) is set by the concentration \(N_p\) of pairs in the glass. To determine \(N_p\), we start with estimating the probability for 2 TLS separated by a distance \(r\) to form a pair to \(P(r) \approx P_0U_0/(8\pi/3)|r|^3\). Then the concentration of pairs in a shell \([V-V/2, V+V/2]\) is given by \(N_p \approx \int V^{3/2} P(r)dr\), where \(n = P_0k_B T\) is the number of thermal TLS.
This yields
\[ N_p = \frac{1}{2} (P_0 T) (P_0 U_0) \log 3, \] (5-48)
which in three dimensions is independent of the volume \( V \) due to the \( |r|^{-3} \)-law of interaction. The maximum volume \( V_\ast = (4\pi/3)|r_\ast|^3 \) each of these pairs can occupy is given by \( 1/N_p \) which determines the minimum interaction energy \( J_{\min} = U_0 / |r_\ast|^3 \).

This provides according to Eq. (5-41)
\[ \Delta_{p,\min} = \frac{1}{2} J_{\min} = \frac{\pi}{3} (P_0 U_0)^2 k_B T \] (5-49)
as a reasonable estimation of the lower bound. Indeed, for PMMA, Eq. (5-49) provides \( \Delta_{p,\min}/k_B = 10^{-8} \) K which, at 1 K, corresponds to a maximum relaxation time \( \tau_{\text{max}} = 10^6 \) to \( 10^7 \) s.

Let us now include decoherence effects by phonons. We will not provide a full discussion of the relaxation dynamics in the four-level system of the pair, but instead try to argue more physically. After two unitary transformations (A -1) and (A -6), one finds the Hamiltonian (A -11) as is pointed out in Appendix A. Here, only the term \( \propto S_x \otimes S_y \) allows relaxation within the up-down subspace \( \{|0,1\}, |1,0\} \). The relaxation mechanism is a flip-flop process linked with the emission or absorption of a phonon. The relaxation rate scales with \( (\Delta_p/E_p)^2 \):
\[ R^{(p)} = r_p R_{\text{max}}^{(p)}, \] (5-50)
where
\[ r_p = \left( \frac{\Delta_p}{E_p} \right)^2 \] (5-51)
\[ R_{\text{max}}^{(p)} \approx \alpha T^3 x_p^3 \coth x_p \] (5-52)
and \( x_p = E_p/2k_B T \). We used that \( \alpha_p \approx \alpha \), as discussed in Appendix A. Note that there is no Debye-Waller factor of the Kassner-Silbey type because of the coupling of the phonons to \( \sigma_p^z \) instead of to \( \sigma_p^x \). The coherent coupling is destroyed by spon-
taneous decay during the up-down transition of primary TLS constituting a pair: for instance $|0,1\rangle, |1,0\rangle \rightarrow |0,0\rangle$. Based on this argument, Burin and Kagan estimated $\Delta_{p,\text{min}} = \hbar \alpha T^3$, where $\alpha T^3$ is the decay rate of symmetric, primary TLS with $E = 2k_B T$. Clearly, on a the time scale explored in the experiment of Maier et al., strongly asymmetric TLS dominate the hole width instead of symmetric ones. Note that in constructing $P^{(2)}(\epsilon_p, \Delta_p)$ (Eq. (5.42)), we integrated over values of the energy splittings of the primary TLS less than $E_{\text{max}}(T)$, which have the correct initial population factors to insure the creation of stable pair excitations. We now investigate which primary TLS are able to guarantee stability of secondary TLS at 1 K, i.e., we ask whether the limit $E_{\text{max}}(T) > k_B T$ or $< k_B T$ applies. We first study if secondary TLS may be formed from primary TLS with thermal splittings, $E \sim O(k_B T)$, at 1 K. We need to satisfy three conditions. First, we require

$$E_p/\hbar \geq R(E = 2k_B T), \quad (5.53)$$

where $R(E = 2k_B T) \equiv r \alpha T^3 \leq 1/t$ is the relaxation rate of a primary thermal TLS which has not yet decayed at $t$, i.e., for which (cf. Eq. (5.33))

$$1/r \geq \alpha T^3 t \approx 10^{13} - 10^{16} \quad (5.54)$$

with $t = 10^3 - 10^6$ s. These two requirements guarantee that the secondary TLS is coherent on the timescale where deviations from logarithmic spectral diffusion is seen. Furthermore, if secondary TLS are responsible for the spectral line broadening after $10^3$ s, the pair rate must satisfy $R^{(p)} t = 1$. This provides the relation $(\Delta_p/E_p)^2 = 1/\alpha T^3 t x_p^3 \coth x_p$. Using this relation, multiplying Eq. (5.53) by $1/E_p$ and squaring it, one can now easily check that Eq. (5.54) always implies Eq. (5.53).

With respect to the stability of secondary TLS at 1 K, we conclude: First, from the condition (5.54) we deduce the criterion $r \ll 1$, i.e, the primary TLS must be very asymmetric. Second, upon replacing $\Delta_p = J r$ [cf. Eq. (5.41)] and noting that
\[ \frac{J}{2k_B T} > \sqrt{\Delta T^3 t} \approx 10^6 - 10^8. \]  

(5-55)

Hence, according to \( J = U_0/d^3 \) and \( U_0 \approx 10^4 \text{ K A}^3 \), the relevant TLS are separated by a distance \( d \lesssim 1 \text{ Å} \). Note that these estimates are highly approximate. In particular, we have approximated the rate at which coherence in a secondary TLS is destroyed by the relaxation rate of a primary TLS, without consideration of the true rates that govern the coupled four level system. However, we may still conclude that at 1 K, it is unlikely that primary TLS with thermal splittings can form pairs, unless they sit extremely close to each other. This fact suggests a natural cutoff, \( \Delta_{\text{max}}(T) \), in the energy splittings of the primary TLS that comprise the secondary TLS existing at 1 K. This cutoff is motivated by the above stability criteria, and can change the temperature dependence of \( P^{(2)}(\epsilon_p) \) in Eq. (5-44) and of the hole width in general. We will return to this point in the next section. According to this, the distribution \( P^{(2)}(E_p, r_p) \) reads

\[
P^{(2)}(E_p, r_p) = P^{(2)}(r_p)P^{(2)}(E_p, \tilde{r}_p)
\]

(5-56)

where

\[
P^{(2)}(r_p) = \frac{P_0 e^{-G/2} \Gamma_0^2 (G/4)}{2r_p^{3/2} \sqrt{1 - r_p}} \Theta(r_p - r_{p,\text{min}}),
\]

(5-57)

and

\[
P^{(2)}(E_p, \tilde{r}_p) = \frac{A(T)}{|E_p|(1 - e^{-\beta E_p})} \times
\]

\[
\times \left\{ \log \left( \frac{2}{1 + e^{-\beta E_p}} \right) - \log \left( \frac{1 + e^{-\beta \Delta_{\text{max}}}}{1 + e^{-\beta (r_p E_p + \Delta_{\text{max}})}} \right) \right\}
\]

\[
+ \ (E_p \rightarrow -E_p),
\]

(5-58)

with \( 0 < E_p \leq \Delta_{\text{max}}(T), \tilde{r}_p = \sqrt{1 - r} \), and \( A(T) \) given by Eq. (5-29).
5.5 Comparison with experiment

We now calculate the broadening of a spectral hole in the inhomogeneous line due to spectral diffusion induced by single TLS and pairs. According to the standard theory [7, 8, 9, 10, 11], the experimentally observed line broadening, \( \Delta \Gamma(t) \equiv \Gamma(t) - \Gamma(t_0) \), can be written as

\[
\Delta \Gamma(t) = \int_0^\infty dE \, \text{sech}^2 \left( \frac{E}{2k_B T} \right) \times \int_0^1 dr \left( \bar{u}(r) P^{(1)}(E, r) + \sqrt{1 - r} P^{(2)}(E, r) \right) \times \left( e^{-r R_{\text{max}t_0}} - e^{-r R_{\text{max}t}} \right) \quad (5-60)
\]

where \( P^{(1)}(E, r) \) and \( P^{(2)}(E, r) \) is given by (5-36) and (5-56), respectively. To calculate these integrals, we replace the last factor by the step function, which restricts the \( r \) integration to the interval \([1/R_{\text{max}t}, 1/R_{\text{max}t_0}]\). This gives

\[
\Delta \Gamma(t) = \Delta \Gamma^{(1)}(t) + \Delta \Gamma^{(2)}(t), \quad (5-61)
\]

where

\[
\Delta \Gamma^{(1)}(t) = \frac{\pi^2}{3h} \langle C \rangle P_0 k_B T \log \frac{1 - \bar{u}^2(1/\alpha T^3 t_0)}{1 - \bar{u}^2(1/\alpha T^3 t)} \quad (5-62)
\]

is the contribution of the primary TLS to the spectral hole width. To calculate the pair contribution \( \Delta \Gamma^{(2)}(t) \), we consider the limits \( E_{\text{max}}(T) \gg k_B T \) and \( \ll k_B T \), separately.

5.5.1 The limit \( E_{\text{max}}(T) \gg k_B T \)

Remember, in this limit coherently coupled pairs can be built by thermal primary TLS. We find from Eq. (5-60)

\[
\Delta \Gamma^{(2)}(t) = \frac{\pi^2}{3h} e^{-G/2} I_0^2(G/4) \langle C \rangle P_0 \times \times A(T) \sqrt{\alpha T^3} \left( \sqrt{t} - \sqrt{t_0} \right). \quad (5-63)
\]
Putting Eqs. (5-61)-(5-63) together provides an equation which is very similar to the result (5-11). However, this equation is based on the microscopic picture of phonon-mediated TLS-TLS interaction. There are two regimes where the function \( \tilde{u}(1/\alpha T^3 t) \) can be determined analytically: (i) short-time limit: \( \alpha T^3 t \ll e^G \) which gives \( \tilde{u}^2(1/\alpha T^3 t) \approx \frac{1}{1+G} \log(\alpha T^3 t) \); (ii) long-time limit: \( \alpha T^3 t \gg e^G \) which gives \( \tilde{u}^2(1/\alpha T^3 t) \approx 1 - e^G/\alpha T^3 t \). In Ref. 12(b), Maier and Haarer have fit their data with only the first term in (5-61). By numerical inversion of Eq. (5-37), they could find good agreement on intermediate time scales up to 200 – 300 min. We have illustrated this in Fig. 5.1. The values for the fit parameters \( G \) and \( P_0(C) \) are 32 and 6 \( \times \) 10\(^{-5} \), respectively. With this value for \( G \), the crossover from the short- to the long-time behavior happens after ca. 150 min; Eqs. (5-12) und (5-34) yield a Debye-temperature of \( \Theta_D = 108 \) K, which is in reasonable agreement with literature data for PMMA. It is in part due to the success of the Kassner-Silbey theory at intermediate times that we have adopted the strong coupling approach as our dynamical starting point. For times larger than 300 min, Maier and Haarer attributed the deviations of the theory from the experimental data the contribution of interacting TLS. If this is true, we should find agreement between theory and experiment when including the second term in (5-61). In Fig. 5.2 we have plotted \( \Delta \Gamma(t) \), Eqs. (5-61)-(5-63), together with the experimental data of Ref. [12] for 1 K (upper curve) and 0.5 K (lower curve). We used the same value for \( G \) as in the previous plot, and have optimized the TLS-TLS coupling parameter, \( P_0 U_0 \), and the TLS-chromophore coupling parameter, \( P_0 \langle C \rangle \), to find best agreement for the 0.5 K data. The result is \( P_0 U_0 = 2.5 \times 10^{-6} \) and \( P_0 \langle C \rangle = 4 \times 10^{-5} \). The upper curve shows the prediction of the theory for the 1 K data. The parameter value for \( P_0 U_0 \), which fits the 0.5 K data, is by a factor 25-35 smaller than the literature value.[18] However, we see that a superposition of a \( \log t \)- and a \( t^{0.5} \)-term can be interpreted as an effective \( t^{0.38} \)-power law on the experimental time scale as seen by Maier et al. Hence, under the assumption that primary TLS with thermal energy splitting can form stable secondary TLS at 1 K, we find \( \Delta \Gamma^{(2)} \propto T^{5/2} \), giving a temperature dependence that is too strong compared with the experimental observation which indicates \( \Delta \Gamma^{(2)} \propto T^{3/2} \), at least in fitting the data at
the two temperatures, 0.5 K and 1 K. This can clearly be seen by the prediction of the theory for the data in Fig. 5.2.

5.5.2 The limit $E_{\text{max}}(T) \ll k_B T$

We have noted in the previous section that it is very unlikely that thermal primary TLS can form stable pairs at 1 K. If we impose a minimum separation distance between primary TLS (say 5 Å), then a natural energy cutoff enters due to the stability requirements outlined in the previous section. If we assume that this cutoff $E_{\text{max}}$ satisfies the condition

$$E_{\text{max}}(T) \ll k_B T,$$

then we can estimate $E_{\text{max}}(T)$ from the conditions considered in Sec. IV. Specifically, from $Rt \sim 1$, $R^{(p)}_t \sim 1$, $x_p/\sqrt{x_p^3 \coth x_p} \sim 1$, and $r = \Delta_p/J$,

$$\left( \frac{E_{\text{max}}(T)}{2k_B T} \right)^3 \coth \left( \frac{E_{\text{max}}(T)}{2k_B T} \right) \sim \frac{J_{\text{max}}}{2k_B T \sqrt{\alpha T^3 t}}.$$ (5-65)

where $J_{\text{max}} = U_0/d_{\text{min}}^3$. This shows that $E_{\text{max}}(T) \sim T^{-1/4}$, which significantly alters the temperature dependence of the hole width. If the above condition is met, then

$$P^{(2)}(E_p) \approx A(T) E_{\text{max}}(T)/4k_B T \sim T^{-1/4},$$ (5-66)

and

$$\Delta \Gamma^{(2)}(t) \approx \frac{\pi^2}{6\hbar} e^{-G/2} I_0(G/4) \langle C \rangle P_0 (\sqrt{t} - \sqrt{t_0}) \times \sqrt{\alpha T^3} A(T) \left( \frac{E_{\text{max}}(T)}{2k_B T} \right)^2.$$ (5-67)

In the regime where $E_{\text{max}}(T) \ll k_B T$, this expression is essentially temperature independent. Thus, the stability requirements imply an interesting thermal breakup of the secondary TLS.
5.6 Discussion

For very low temperatures ($E_{\text{max}}(T) \gg k_B T$), the majority of asymmetric TLS are stable even if constructed from asymmetric primary TLS that have energy splittings on the order of $k_B T$, leading to the strong temperature dependence depicted in Fig. 5.2. We have argued that at higher temperatures, a crossover should occur where the temperature dependence should become weaker, as secondary TLS become less stable. Therefore, it is qualitatively consistent with this picture that the observed temperature dependence at $\sim 1$ K is weaker than that shown in Fig. 5.2. Such arguments require further “slowing down” of the temperature dependence. This is indeed seen experimentally at 2 K. [20] Hannig et al. are able to fit their data with essentially the same value of $A$ at 0.5 K and 1 K, and a value of $0.3 \times A(T = 0.5$ K) at 2 K. Eventually, the entire TLS picture should break down at some temperature in the range 1-10 K. A clear test of the validity of this picture would be to see if the stronger temperature dependence emerges at lower temperatures. Such experiments are difficult to conduct at ultra-low temperatures, due to slow equilibration effects.

We may also note that the discrepancy between the “derived” and literature values of $P_0 U_0$ can be explained by the thermal breakup of secondary TLS demanded by stability criteria. As the temperature is raised, the primary TLS must lie closer together to form a stable secondary TLS at long times. The probability of finding two neighboring primary TLS a very close distance apart is small, which effectively decreases the “derived” value of $P_0 U_0$. Note that there is also a reduction in $\Delta \Gamma^{(2)}(t)$ due to the factor $(E_{\text{max}}/2k_B T)^2$ (see Eq. (5-67)). Thus, at least qualitatively, it is indeed possible that a picture based on coupled TLS can account for all the properties currently observed in long-time spectral diffusion experiments.

So far we have shown the pros and cons of applying the idea of coupled pairs to hole-burning experiments on ultra-long time scales at 1 K. Here we propose an interesting experiment which, although difficult to perform, would provide a conclusive test of the coupled TLS hypothesis. A crucial observation is that the exponent of the power law depends on the dimensionality of the glassy probe. For example, the expo-
nent would be systematically smaller if the primary TLS were confined to (quasi)-two dimensions, while the interaction between them still varies as $1/|r|^3$. This would result in a distribution function $P(\Delta_p) \propto \Delta_p^{5/3}$ (from $P(\Delta_p) \propto P(J) = P(|r|)|r|(|d|r|/dJ|$ and $J \propto |r|^{-3}$, $P(|r|) = \text{constant}$) and therefore in a $t^{1/3}$-power law. The experiment we suggest has already been performed, albeit not for the purpose that we discuss here and not on a time scale up to $10^6$ s. The hole-burning experiment by Orrit et al. [21] on an ionic dye in a Langmuir-Blodgett monolayer lying on a three-dimensional substrate is an experiment of the type we proposed above—the TLS dynamics is restricted to two dimensions whereas sound waves and strain are not affected by the interface between the amorphous layer and the bulk. Indeed, Orrit et al. [21] have observed spectral diffusion which could be explained by Pack and Fayer [22] using the standard tunneling model. From this perspective it seems promising to extend Orrit’s experiment to longer times and look whether a power law weaker than the three-dimensional result $t^{0.5}$ could be observed.

There are, however, reasons to be skeptical of the picture we have outlined. A number of approximations have been invoked that render only a semiquantitative description of the experimental results. These approximations include the reduction of the primary TLS to an effective secondary TLS, and the use of relaxation rates for uncoupled TLS to discuss decoherence effects for coupled secondary TLS. These approximations, especially the first one, may not be valid at temperatures near 1 K. Clearly, one has to think about alternative explanations. A simple idea would be to attribute the deviation from the standard log $t$-behavior to a nonequilibrium state of those TLS which relaxes on these long time scales. Indeed, recent experiments by Friedrich et al. [23] have proven that spectral diffusion in glasses under nonequilibrium conditions results in a nonlogarithmic time evolution of the hole width. However, the data in Maier’s experiment were obtained after letting the sample relax at the measurement temperature for a longer period than the later data recording period. Hence, one expects that all relaxation processes shorter than this waiting time occur under equilibrium conditions.

It is interesting to compare the glass results with equivalent experiments on pro-
teins. Hole-burning experiments on proteins show almost no hole broadening up to three hours, followed by a nonlogarithmic hole broadening regime. [24] A new type of temperature-cycle hole-burning experiments[25] leads to the conclusion that the excess broadening of the hole in the protein cannot be interpreted in the framework of the STM. Hence, one might speculate that in both glasses and proteins, the interaction of TLS becomes important at long time scales. An alternative conclusion avoids the notion of interacting TLS altogether. Perhaps the energy landscape of glasses is not too different from that of proteins, and also shows features of organization at high barriers. Recall that the experiments of Maier et al. were carried out in PMMA, which is a polymer glass. Polymer glasses may be expected to have conformations similar to proteins. For example, such “conformational” dynamics may involve side chain motions. The physical picture is that the energy landscape comprises high barriers in addition to constantly distributed lower barriers within each of its basins. The algebraic behavior then results from tunneling through those high barriers, which have to be distributed around a “typical” value $V_0$. This value has to be sufficiently high in order that the onset of the algebraic behavior occurs only after 3 h. A simple model relying on this picture is given in Appendix C. It predicts a temperature and time-dependence of the hole width with an exponent which is slightly weaker than $T^{3/2}$ and $t^{1/2}$, respectively, and a slowly decreasing function of $T$ and $t$. We note that if indeed specific polymer dynamics (like side chain motion) are responsible for deviations from logarithmic spectral diffusion, perhaps a deuterated sample may show different hole broadening behavior.

One is tempted to speculate that these “non-STM like” high barriers arise from the presence of the chromophore in the glassy host[26], because they have not been observed in sound attenuation experiments up to 100 K.[27, 28] Note however, that these experiments were not performed on polymer glasses, and that sound attenuation experiments on PMMA and PS indeed show an additional peak above ca. 50 K.[29] Interestingly, doping a network glass with OH-impurities leads to the same observation [28], which conceivably supports the importance of side chain motion in polymer glasses. Furthermore, in contrast to the glass, the protein probe is not doped by a dye.
Instead part of the protein is chemically changed in order to serve as a chromophore. Thus, it seems that such deviations from standard spectral diffusion behavior are not due to the inclusion of the chromophore into the sample.

One should also note nonlogarithmic line broadening is the typical case because a logarithmic time dependence occurs only in case of a $1/\Delta^n$-distribution for the singular case $n = 1$. Without invoking the physical reasons for deviations from the standard $1/\Delta$ distribution function introduced by Anderson, Halperin and Varma, and of Phillips, we may say that for small values of $\Delta$ (corresponding to long times), the distribution of barriers is not really flat, but instead a smoothly varying function of the parameter $\lambda$ (see Appendix C). That the distribution of barriers in such a model turns out to be a log-normal distribution shows a striking similarity to general systems exhibiting $1/f^\alpha$ noise. [30]

5.7 Conclusions

In this paper we have analyzed the consistency of the conjecture that coupled pairs of TLS dominate spectral diffusion on ultra-long time scales. Because the pairs distribution $P^{(2)}(\epsilon_p, \Delta_p)$ is correlated with the distribution of the primary “STM-like” TLS, we have in a sense pushed the STM as far as possible by looking at these new low energy excitations. We believe that this is an important step, which has to be done before trying to find another extension of the STM for every new experiment. The questions was whether they also apply to the 1 K regime, and, in particular, whether they can provide an explanation of the long-time hole-burning experiment of Maier et al. We find that a picture based on the idea of interacting tunneling systems seems consistent with the experimental data, although we are unable to fit certain aspects of the experiment, such as the temperature dependence, quantitatively. Also, alternative explanations have been presented. These models are, at the moment, at least as speculative as the scenario of coherently coupled pairs. For this reason, we have discussed some possible experimental tests of the theoretical models we have presented. More theory and experiments have to be done to finally evaluate
the role of coupled TLS in glasses, and to understand the origin of nonlogarithmic hole broadening in glasses.
5.8 Appendix A

In this Appendix we generalize Kassner and Silbey’s approach to include coherent coupling between pairs. For this goal we first apply the unitary transformation

\[ U_1 = \exp \left[ \sum_{i,q} \left( \frac{2\bar{u}_i c_q^i}{\hbar \omega_q} (b_q - b_{-q}^\dagger) S_{z}^i / 2 \right) \right] \equiv \prod_i e^{\zeta_i S_{z}^i / 2} \]  

(A-1)

to the Hamiltonian (5-30) which eliminates the diagonal coupling of phonons to \( S_{z}^i \). The transformed Hamiltonian \( H \rightarrow U_1^{-1} H U_1 \) reads with \( S_{\pm}^i = (1/2)(S_{z}^i \pm i S_{y}^i) \): [17]

\[
H = -\frac{1}{2} \sum_i E_i S_{z}^i + \sum_q \hbar \omega_q b_q b_{q}^\dagger - \sum_{i,q} u_{i,q} c_q^i \left( B_{-}^i S_{+}^i + B_{+}^i S_{-}^i \right) - \frac{1}{4} \sum_{i,j} J_{ij} \left( \bar{u}_{i,j} S_{z}^i S_{z}^j - 2 u_{i,j} (B_{-}^i S_{+}^j + B_{+}^j S_{-}^i) S_{z}^i \right),
\]

where

\[
\frac{1}{4} J_{ij} = \sum_q \frac{c_q^i c_{-q}^j}{\hbar \omega_q}, \quad \text{and} \quad B_{\pm}^i = \exp \left[ \pm \sum_q \left( \frac{2\bar{u}_i c_q^i}{\hbar \omega_q} (b_q - b_{-q}^\dagger) \right) \right] \equiv e^{\pm \varphi_i}.
\]

(A-3)

(A-4)

The \( B_{\pm}^i \) are the usual phonon shift operators. Instead of proceeding with the full transformed Hamiltonian, we project out the one-phonon fluctuations around the shifted harmonic oscillators coordinates. This is achieved by expanding \( B_{\pm}^i \equiv \langle B_{\pm}^i \rangle + (B_{\pm}^i - \langle B_{\pm}^i \rangle) = \langle B_{\pm}^i \rangle \pm \varphi_i \), where

\[
\langle B_{\pm}^i \rangle = e^{-G(\zeta_i/E_i)^2/2}, \quad \text{A coherent coupling between pairs}
\]

and neglecting two-phonon terms. Applying Fermi’s Golden Rule to the remaining one-phonon term directly yields the rate (5-33).
is generated by eliminating this term by a second unitary transformation

\[ U_2 = \exp \left[ -\sum_{i,q} \left( 2u_i(B^i_{\pm})c_i^q / \hbar \omega_q \right) (b_q - b_{-q}^\dagger) S_z^i / 2 \right] \]

\[ = \prod_i e^{-\phi_i S_z^i / 2}. \]  

This yields:

\[ H = -\frac{1}{2} \sum_i E_i \tilde{S}_z^i + \sum_q \hbar \omega_q b_q^\dagger b_q \]

\[ - \frac{1}{4} \sum_{i,j} J_{ij} \left\{ \bar{u}_i \bar{u}_j \tilde{S}_z^i \tilde{S}_z^j + u_i \langle B^i_{\pm} \rangle u_j \langle B^j_{\pm} \rangle S_z^i S_z^j \right\} \]

\[ - 2u_i \bar{u}_j \left( \langle B^i_{\pm} \rangle S_z^i - i \varphi_i \tilde{S}_y^i \right) \tilde{S}_z^j \].  

(A -6)

where

\[ \tilde{S}_z^i = S_z^i \cosh \phi_j - i S_y^i \sinh \phi_j, \]  

\[ \tilde{S}_y^i = S_y^i \cosh \phi_j + i S_z^i \sinh \phi_j. \]  

(A -8)

(A -9)

Expanding again around the one-phonon fluctuations around the shifted harmonic oscillator coordinate by replacing \( \tilde{S}_z^i \approx S_z^i \langle D^i_{\pm} \rangle - i \phi_j S_y^i \) and \( \tilde{S}_y^i \approx S_y^i \langle D^i_{\pm} \rangle + i \phi_j S_z^i \), where

\[ \langle D^i_{\pm} \rangle = e^{-G(\Delta_i \langle B^i_{\pm} \rangle / E_i)^2 / 2}, \]  

(A -10)

one finds

\[ H = -\frac{1}{2} \sum_i E_i \langle D^i_{\pm} \rangle S_z^i + \sum_q \hbar \omega_q b_q^\dagger b_q + \frac{i}{2} \sum_i E_i \varphi_i S_y^i \]

\[ - \frac{1}{4} \sum_{i,j} J_{ij} \left\{ \bar{u}_i \langle D^i_{\pm} \rangle \bar{u}_j \langle D^j_{\pm} \rangle S_z^i S_z^j \right\} \]

\[ + u_i \langle B^i_{\pm} \rangle u_j \langle B^j_{\pm} \rangle S_z^i S_z^j - 2u_i \langle B^i_{\pm} \rangle \bar{u}_j \langle D^j_{\pm} \rangle S_z^i S_z^j \]

\[ + 2i u_i \langle B^i_{\pm} \rangle \bar{u}_j \varphi_j S_z^i S_y^j + 2i u_i \langle D^i_{\pm} \rangle \bar{u}_j \langle D^j_{\pm} \rangle \varphi_j S_y^i S_z^j \]

\[ - i \bar{u}_i \bar{u}_j \left( \langle D^i_{\pm} \rangle \phi_i S_y^j S_z^i + \langle D^j_{\pm} \rangle \phi_j S_z^i S_y^j \right) \].  

(A -11)
The only operators which act nontrivially in the up-down subspace \{(|0, 1\rangle, |1, 0\rangle)\} are \(S_z \otimes 1, 1 \otimes S_z, S_z \otimes S_z, S_x \otimes S_y,\) and \(S_y \otimes S_x.\) If we define new pseudo-spin operators for pairs \((i, j)\)

\[
\sigma_z^P = |0_i, 1_j\rangle\langle 1_i, 0_j| + |1_i, 0_j\rangle\langle 0_i, 1_j|,
\]

\[
\sigma_y^P = -i|0_i, 1_j\rangle\langle 1_i, 0_j| + i|1_i, 0_j\rangle\langle 0_i, 1_j|,
\]

\[
\sigma_x^P = |0_i, 1_j\rangle\langle 0_i, 1_j| - |1_i, 0_j\rangle\langle 1_i, 0_j|,
\]

we can project the quoted operators onto the up-down subspace, which yields \(S_z \otimes 1 \rightarrow \sigma_z^P, 1 \otimes S_z \rightarrow -\sigma_z^P, S_x \otimes S_x \rightarrow \sigma_x^P, S_x \otimes S_y \rightarrow -\sigma_y^P,\) and \(S_y \otimes S_x \rightarrow \sigma_y^P.\) If we project the Hamiltonian (A -11) accordingly, we find for each pair

\[
H_{\text{pair}} = -\frac{\Delta_p}{2} \sigma_z^P - \frac{\epsilon_p}{2} \sigma_x^P + i\Delta_p \sigma_y^P \sum_q \frac{2\epsilon_q^p}{\hbar \omega_q} (b_q - b_q^\dagger) + \sum_q \hbar \omega_q b_q^\dagger b_q,
\]

with

\[
\Delta_p = J_{ij} \frac{\Delta_i \Delta_j}{2E_i E_j} \langle B^i_{\pm}\rangle \langle B^j_{\pm}\rangle,
\]

\[
\epsilon_p = E_i \langle D^i_{\pm}\rangle - E_j \langle D^j_{\pm}\rangle,
\]

\[
\epsilon_q^p = c_q^i (\epsilon_i/E_i) - c_q^j (\epsilon_j/E_j).
\]

Applying Fermi’s Golden Rule to the interaction term in (A -15) provides a one-phonon relaxation rate

\[
R_p = \alpha \frac{2E_p}{(2k_B)^3} \coth(E_p/2k_BT).
\]

Here, we have used that the oscillating term in \(c_q^p c_{q}^p\) is small so that pairs and single TLS relax approximately with the same coupling parameter \(\alpha\) provided that \(\epsilon_i/E_i \approx 1.\) Note that because of the coupling of phonons to \(\sigma_y^P\) (instead of \(\sigma_x^P\)), there is no diagonal coupling term \(\propto S_x^P\) as in (5-30) after rotation to the pair-TLS eigenbasis.
5.9 Appendix B

In this Appendix we calculate the distribution function for the pair parameters \( \Delta_p \) and \( \epsilon_p \) of Eqs. (5-40) and (5-41). We note that the single-TLS distribution function for \( u = \Delta / E \) and \( E = \sqrt{\Delta^2 + \epsilon^2} \) reads \( P(E, u) = P_0 / (u \sqrt{1 - u^2}) \). The distribution function for the pair parameter is then given by

\[
P^{(2)}(\epsilon_p, \Delta_p) = \int \frac{dE_1}{1 + e^{-\beta E_1}} \int \frac{dE_2}{1 + e^{\beta E_2}} \times \int_0^1 du_1 \int_0^1 du_2 \int dJ P(E_1, u_1) P(E_2, u_2) P(J) \times \frac{1}{2} \{ \delta(\epsilon_p - E_1 + E_2) + \delta(\epsilon_p + E_1 - E_2) \} \times \delta \left( \Delta_p - \frac{1}{2} J u_1 u_2 e^{-G(1-u_1^2)/2} e^{-G(1-u_2^2)/2} \right).
\]

(B- 1)

The factors \( (1 + e^{\pm \beta E})^{-1} \) account for the thermal occupation of the primary TLS. If the TLS are homogeneously distributed in the glass and interact via a dipolar coupling, \( J = U_0 / |r|^3 \), the distribution function of \( J \) reads for a three-dimensional probe

\[
P(J) = \frac{4\pi U_0}{J^2}.
\]

(B- 2)

Using now that

\[
\int_0^1 du \frac{e^{-u^2 G/2}}{\sqrt{1 - u^2}} = \frac{\pi}{2} e^{-G/4} I_0(G/4),
\]

and

\[
\int_1^1 \frac{dx}{(1 + x)(1 + \mu x)} = \frac{1}{1 - \mu} \left[ \log \frac{2}{1 + y} - \log \frac{1 + \mu}{1 + \mu y} \right],
\]

with \( x = e^{-\beta E}, y = e^{-\beta E_{\text{max}}}, \) and \( \mu = e^{-\beta \epsilon_p} \), one easily finds Eqs. (5-42)-(5-45).
5.10 Appendix C

Here we present an extension of the STM by a Gaussian distribution in the tunneling parameter $\lambda$ centered around the mean value $\lambda_0 \gg 1$:

$$P(\epsilon, \lambda) = P_0 + \frac{P_0 \tilde{A}}{2\sqrt{\pi} \sigma^2} e^{-(\lambda - \lambda_0)^2/2\sigma^2}, \quad (C - 1)$$

where $\tilde{A}$ is a dimensionless constant. A similar model has been used previously by Jankowiak and Small [26] and by Zimdars and Fayer [31]. A combination of both terms is needed in order that the onset of the algebraic line broadening does not occur too early. In the following it will turn out sufficient to reduce the number of parameters by setting

$$\sigma^2 \equiv \lambda_0. \quad (C - 2)$$

The ensuing distribution in $\Delta = \Delta_{\text{max}} e^{-\lambda}$ then reads

$$P(\epsilon, \Delta) = P_0 \left[ \frac{1}{\Delta} + \frac{B \Delta_{\text{max}}^{1-(1/2\lambda_0)\log(\Delta_{\text{max}}/\Delta)}}{\Delta^{2-(1/2\lambda_0)\log(\Delta_{\text{max}}/\Delta)}} \right], \quad (C - 3)$$

where $B = \tilde{A} e^{-\lambda_0/2}/\sqrt{2\pi}\lambda_0$, which has to be compared with (5-7). Here, it is more convenient to define the maximal rate by $R \equiv e^{-2\lambda} R_{\text{max}}$ which gives $R_{\text{max}} \equiv KT x \coth x$. With $\Delta_{\text{max}}/k_B = O(1 \text{ K})$, one finds $K \equiv (\Delta_{\text{max}}/k_B)^2 \lambda \approx 10^{10} \text{ K}^{-1}\text{s}^{-1}$. The distribution function in relaxation rates $R$ and TLS-energies $E$ reads

$$(\epsilon/E) P(E, R) = \frac{P_0}{2} \left[ \frac{1}{R} + \frac{B R_{\text{max}}(R)}{R_{\text{max}}^{1+\nu(R)}} \right], \quad (C - 4)$$

where

$$\nu(R) = \frac{1}{2} - \frac{1}{8\lambda_0} \log(R_{\text{max}}/R). \quad (C - 5)$$

From this expression, it is obvious that an algebraic line broadening $\Delta\Gamma(t) \propto t^\mu$ with an exponent $\mu < 0.5$ occurs for $\lambda_0 \gg \log(KTt)$. The exact calculation reveals

$$\Delta\Gamma(t) = \frac{\pi^2}{3\hbar} P_0(C) k_B T \left[ \log(t/t_0) \right]$$
\[
\Delta \Gamma(t) \propto B T (K T t)^{1/2} \left[1 - \frac{1}{2}\log(K T t)\right].
\]  

(C - 7)

where erfc(x) is the complementary error function. For \( \lambda_0 \gg \log(K T t) \) this gives an algebraic line growth

\[
\Delta \Gamma(t) \propto B T (K T t)^{1/2} - \frac{1}{8\lambda_0}\log(K T t).
\]

From a fit to the data we find \( \lambda_0 = 79.85 \) and \( \tilde{A} = 10^{13} \) [i.e., \( B \approx 10^{-6} \)] with good agreement. Details will be published elsewhere. It is interesting to note that Jankowiak and Small\(^{26(b)}\) could fit the photon echo data of Littau and Fayer [32] and Meijers and Wiersma [33] with two Gaussians centered around \( \lambda_0 \approx 7-10 \) and 16.
Bibliography


Figure 5-1: Hole broadening in PMMA at 1 K (upper curve) and 0.5 K (lower curve) compared with the Kassner-Silbey theory for single TLS. The experimental data are from Ref.12. The two solid lines are $\Delta \Gamma^{(1)}(t)$, Eq. (5-62) for 1 (upper solid curve) and 0.5 K (lower solid curve) with $G = 32 \ (\Theta_D = 108 \ K)$ and $P_0(C) = 6 \times 10^{-5}$. 
Figure 5-2: Same figure as above but now with the contribution of both the single and pair TLS (logarithmic and algebraic part of Eq.(5-61)). The parameters $P_0(C) = 4 \times 10^{-5}$ and $P_0U_0 = 2.5 \times 10^{-6}$ have been optimized to find best agreement with the 0.5 K data; $G = 32$ has been kept fixed. Comparison with the 1 K data clearly shows that the temperature dependence as predicted by Eqs.(5-29) and (5-61) is too strong.
Chapter 6

On the Nonperturbative Theory of Pure Dephasing in Condensed Phases at Low Temperatures

6.1 Introduction

The relaxation of a two level system coupled to a quantum mechanical heat bath has been a topic of great interest in the past decade. One aspect of this subject is the thermal broadening of the zero-phonon line (ZPL) [1, 2], which is intimately connected to the “pure” dephasing of two quantum levels [3]. Such dephasing arises from a system-bath (electron-phonon) coupling that is diagonal in the system states, leading to the decay of the off-diagonal element \( \sigma_{10}(t) \) of the reduced density matrix. The study of this problem was advanced by Osad’ko [4], who provided a nonperturbative expression for the decay of the off diagonal element of the reduced density matrix for two quantum levels coupled quadratically and diagonally to a bath of quantum mechanical harmonic oscillators. Using a different approach, Skinner and Hsu [3] were able to rederive the result of Osad’ko, and then used this result to interpret the experimentally obtained absorption zero-phonon line shapes for dilute impurities in crystals. Good agreement was found in various cases, including the dephasing
induced by acoustic [5], optical [5], and pseudolocal phonons [6]. The derivations of Osad’ko and Skinner and Hsu are correct only in the asymptotic regime $t \gg \tau_b$, where $\tau_b$ is the relaxation time of the bath. As is well known, at low temperatures compared to the phonon frequencies, the bath takes on two distinct time scales [7]. The first is the "mechanical" scale $\frac{1}{\omega_c}$, where $\omega_c$ is the upper cutoff frequency for the bath modes. This is the same time scale that governs the decay of bath correlations at high temperatures, and is usually on the order of 10-100 ps. The second time scale is the quantum-thermal scale $\beta \hbar$, which may become significantly longer than the mechanical time scale at very low temperatures ($T \sim 10mK$ and lower). Since the theories of Osad’ko and Skinner and Hsu are exact only in the limit of times much greater than the larger of the two scales, interesting behavior may be missed at very low temperatures. At such temperatures, the quantum-thermal times scale is on the order of 10 ns or longer, and thus such behavior may be observable by modern spectroscopic techniques, e.g., photon echoes.

We thus wish to investigate the intermediate time effects at very low temperatures in the pure dephasing problem. In doing so, we will introduce a method distinct from that of Osad’ko and Skinner and Hsu that is valid for all times, while remaining formally exact (i.e. nonperturbative). This will allow us to probe the intermediate time regime for very low temperatures, and to assess the relevance of the results, if any, to experiments.

We focus on the case of the Ohmic bath [8]. This is done for several reasons. First, the results for the Ohmic bath are the most interesting. Secondly, while the Ohmic case is often unrealistic for condensed phase optical dephasing experiments at low temperatures, we will argue that the effects uncovered here may indeed manifest themselves in a variety of experimental settings. From a theoretical point of view, little is known about the behavior of quadratic system-bath coupling in the Ohmic case [9]. While the pure dephasing problem is certainly much simpler than other related problems (e.g. the Spin-Boson problem [8]), an exact solution could give insight into the nonlinear effect of an Ohmic bath in more demanding problems. Lastly, we wish to study the Ohmic case because it is a paradigm for the simulation.
of systems with an abundance of low frequency modes, such as liquids, proteins and polymers [10]. The methods we employ are flexible enough to treat any spectral distribution of bath modes. In the next section, we will study the case of linear electron-phonon coupling in some detail. In section 6.3, we will discuss some possible settings where these results may be relevant. In section 6.4, we treat the quadratic electron-phonon coupling. In section 6.5, we conclude.

6.2 Linear Electron-Phonon Coupling

We begin with the Hamiltonian for a two level system coupled linearly to a bath of harmonic oscillators ($\hbar = 1$)

$$H = \omega_0 |1\rangle \langle 1| + H_b + \Delta |1\rangle \langle 1|, \quad (6-1)$$

where

$$H_b = \sum_k \omega_k a_k^\dagger a_k,$$

$$\Delta = \sum_k \hbar \omega_k (a_k^\dagger + a_k),$$

and $|0\rangle, |1\rangle$ are the ground and excited states of the two level system, respectively. In general, such an interaction will not induce relaxation of the reduced density matrix elements, diagonal or off-diagonal. However, if we choose the coupling constants to have an Ohmic distribution [8], i.e.

$$\lim_{\omega \to 0} J(\omega) \sim \omega \quad (6-2)$$

where the spectral density $J(\omega)$ is defined

$$J(\omega) = \pi \sum_k \hbar^2 \omega_k \delta(\omega - \omega_k),$$

then Skinner and Hsu (see also Duke and Mahan [11]) found that the coherence variable of the two level system decays to zero exponentially with a pure dephasing
rate proportional to temperature. We now proceed to solve this model exactly for all times. We assume that the initial value of the density operator takes the factorized form \[ \rho(0) = \sigma(0) \rho_b, \] (6-3)

where

\[ \rho_b = \frac{\exp(-\beta H_b)}{Tr_b[\exp(-\beta H_b)]}. \] (6-4)

It is simple to show that the off diagonal element of the reduced density operator (defined as \( \sigma(t) = Tr_b[\rho(t)] \)) equals

\[ \sigma_{10}(t) = e^{-i\omega_0 t} \sigma_{10}(0) Tr_b[\rho_b \exp\{-i(H_b + \Delta) t\} \exp(iH_b t)]. \] (6-5)

Note that \( H_b + \Delta \) is diagonalized by the unitary shift operator

\[ U = \exp \left[ \sum_k \frac{h_k}{\omega_k} (a_k^\dagger - a_k) \right]. \]

Using the cyclic property of the trace, we find

\[ \sigma_{10}(t) = \exp\{-i(\omega_0 + \sum_k \frac{h_k^2}{\omega_k}) t\} Tr_b \left[ U(t) U^\dagger \rho_b \right], \] (6-6)

where

\[ U(t) = \exp \left[ \sum_k \frac{h_k}{\omega_k} (a_k^\dagger e^{i\omega_k t} - a_k e^{-i\omega_k t}) \right]. \] (6-7)

Combining the shift operators, and using the expression for the thermal average of the exponential of a linear combination of bosonic raising and lowering operators we find,

\[ \sigma_{10}(t) = \exp[-i\{\bar{\omega}_0 t + \frac{2}{\pi} \int_0^\infty d\omega J(\omega) \sin(\omega t)\}] \exp[-\frac{2}{\pi} \{ \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} (1-\cos(\omega t)) \coth(\beta \omega/2) \}], \] (6-8)

where we have combined the polaron shift \( \frac{1}{\pi} \int_0^\infty d\omega J(\omega) \) and the bare frequency \( \omega_0 \) into the renormalized frequency \( \bar{\omega}_0 \). Using the spectral density \( J(\omega) = \alpha \omega e^{-\omega/\omega_c} \) we find,
for low temperatures compared to the bath [13] (i.e. $\beta \omega_c \gg 1$),

$$\sigma_{10}(t) = \left(\frac{1}{1 + \omega_c^2 t^2}\right)^{\alpha/\pi} \left[\frac{(\pi t/\hbar)}{\sinh(\pi t/\hbar)}\right]^{2\alpha/\pi} \exp(-i(\omega_0 t + (\frac{2\alpha}{\pi})\tan^{-1}(\omega_c t))), \quad (6.9)$$

where the $\hbar$ has been reinserted for dimensional convenience. For $t > \beta \hbar$ the dephasing is exponential with a rate constant

$$\frac{1}{T_2} = \frac{2\alpha \pi}{\beta \hbar}$$

as discussed by Skinner and Hsu [3]. However, for times $\frac{\beta \hbar}{\pi} > t \gg \frac{1}{\omega_c}$ we find that the coherence variable decays with the power law

$$|\sigma_{10}(t)| \sim (\omega_c t)^{-2\alpha/\pi}.$$

At zero temperature, after an initial short lived Gaussian decay, the decay of the coherence variable is seen to be algebraic for all times. Thus, pure dephasing may indeed occur at zero temperature, and the low and zero temperature lineshapes will show marked deviations from the usual Lorentzian behavior. For $\beta \omega_c \gg 1$ the lineshape will not be Lorenzian in the wings due to the algebraic decay at short times. At zero temperature, (neglecting the lineshift), the lineshape function may be expressed

$$I(\omega) \sim \int_{-\infty}^{\infty} dt e^{i\omega t} \frac{1}{(1 + \omega_c^2 t^2)^{\tilde{\alpha}}} = \frac{2\sqrt{\pi}}{\omega_c \Gamma(\tilde{\alpha})} \left(\frac{|\omega|}{2\omega_c}\right)^{\tilde{\alpha} - 1/2} K_{\tilde{\alpha} - 1/2} \left(\frac{|\omega|}{\omega_c}\right),$$

where $K_{\nu}$ is a modified Bessel function. Note here that the lineshape shows a singularity at $\omega = 0$ for $\tilde{\alpha} \leq 1/2$ and a singularity in its derivative at $\omega = 0$ for $\tilde{\alpha} > 1/2$. We may conclude, perhaps somewhat imprecisely, that the anomalous dephasing results from an abundance of low frequency modes which are "active" at arbitrarily low temperatures.

We wish to emphasize that pure dephasing at zero temperature is not expected for super-Ohmic baths. Note, however, that algebraic decay may also occur for super-
Ohmic spectral densities. Consider the spectral density

\[ J(\omega) = \alpha \omega^2 e^{-\omega/\omega_c}. \]

For high temperatures compared to the bath, \( \coth(\beta \omega/2) \approx 2/\beta \omega \) and thus

\[ \int_0^\infty \frac{J(\omega)}{\omega^2} \left( 1 - \cos(\omega t) \right) \coth(\beta \omega/2) \approx \frac{\alpha}{\beta} \ln(1 + \omega_c^2 t^2). \]

This gives rise to a coherence decay at high temperatures

\[ \sigma_{10}(t) \sim \frac{1}{(1 + \omega_c^2 t^2)^{\frac{10}{3}}} \]

Which is similar to that of an Ohmic bath at zero temperature. This quadratic spectral density could represent, for example, a two dimensional system (surface) with deformation potential coupling.

These results are essentially the same as those found by Wu, Brown, and Lindenberg [14] for a similar model proposed to study quantum tunneling in excimeric molecular crystals. Our results, however, are analytically exact, and interpolate smoothly between the various decay regimes, while the work of Wu, Brown, and Lindenberg relies on numerical integration and interpolation. The result is also similar to that obtained by Duke and Mahan [11] in their study of the phonon induced broadening of lineshapes in crystals. Similar results are also discussed by Mahan in his work on X-ray spectra in metals [15]. In light of these results, the above may not seem surprising, although within the chemical physics community, the fact that "pure dephasing" may occur at zero temperature in special circumstances seems to be somewhat unappreciated.

### 6.3 Experimental Relevance

Before generalizing the above results to the case of quadratic electron-phonon coupling, we would like to discuss the experimental detection of the phenomena discussed
We have treated an idealized Hamiltonian with a system-bath coupling incapable of causing transitions between the two states of the system. We thus focus on only one aspect of the relaxation process (pure phase relaxation). In general, optical experiments can probe either population decay rates ("T_1" processes probed, for instance, by a three pulse echo experiment) or phase relaxation ("T_2" processes probed by a two pulse echo experiment). The T_2 process will have contributions from both population relaxation induced by perturbations off-diagonal in the system states, and pure phase relaxation, induced by diagonal perturbations [16]. Only in the weak coupling limit are such processes independent [16, 17], giving rise to phase relaxation comprised of noninterfering contributions from population decay and pure dephasing. Thus, our results require that the strength of the diagonal coupling be much stronger than that of the off-diagonal coupling. In this way, we may hope to treat the T_1 processes to lowest order, while treating the pure dephasing nonperturbatively and thus ignore the interference between the two types of relaxation. Ideal experimental situations would choose systems with long excited state lifetimes and weak non-adiabatic coupling, etc. so that T_1 effects are kept as small as possible. Since the pure dephasing contribution does not extrapolate to zero at zero temperatures, the T_2 process will not reach a lifetime limited value. Such effects may indeed be noticeable at very low temperatures. Lastly, parameters such as \( \omega_c \) and \( \alpha \) must take on values appropriate for experimental detection. By this, we mean that these parameters must conspire to maintain a decay slow enough to be observable in the time window of \( \sim 1\text{ps} \) to \( \sim 1\mu s \).

The interesting aspect of the pure dephasing behavior occurs in the time interval \( \frac{1}{\omega_c} \ll t < \beta \hbar \). This time domain will be accessible experimentally for \( T \leq 10mK \). Such temperatures are indeed experimentally reachable, but factors such as inhomogeneous heating effects make these experiments somewhat difficult to perform [18].

Lastly, we would like to briefly sketch some condensed phase systems for which the Ohmic constraint (6.2) is valid. The first is the case studied by Duke and Mahan [11], namely dilute impurity spectra in a piezoelectric crystal. Certain semiconductors
such as CdS have the property that an electric field is produced when the crystal is squeezed, and vice versa. This gives rise to an electron-phonon coupling that is proportional to the amplitude of the phonon field. This amplitude dependent coupling, combined with the density of states for Debye (long wavelength) phonons, gives rise to an Ohmic-type coupling [1, 19]. Thus an electronic transition at an impurity site in a piezoelectric crystal may be crudely described by the Hamiltonian (6.1) combined with the constraint (6.2). One difficulty in this description may be screening effects due to other electrons, which might wash out the algebraic behavior given in Eq. (6.9). However, it may be possible that a very low temperature echo experiment probing an optical transition at an impurity site in a piezoelectric crystal may indeed expose such interesting behavior.

Another situation that naturally gives rise to the Ohmic constraint (6.2) is the relaxation of tunneling systems in metallic glasses at low temperatures [20]. Here the Ohmic friction arises from the excitation of electron-hole pairs near the Fermi surface. Consider the standard Spin-Boson problem,

$$H_{SB} = \left( \frac{\Delta_0}{2} \right) \sigma_x + \left( \frac{\epsilon_0}{2} \right) \sigma_z + \sum_k \omega_k a_k^\dagger a_k + \sum_k h_k (a_k^\dagger + a_k) \sigma_z, \quad (6-10)$$

which is thought to govern the dynamics of tunneling systems at low temperatures in glasses (metallic as well as insulating). For the case of a metallic glass, the bosonic bath excitations are electron-hole pairs, giving rise to an Ohmic spectral density [20, 21]. We may diagonalize the spin portion of (6.10) simply, leaving

$$\tilde{H}_{SB} = (E/2) \sigma_z + [(\Delta_0/E) \sigma_x + (\epsilon_0/E) \sigma_z] \sum_k h_k (a_k^\dagger + a_k), \quad (6-11)$$

where

$$E = \sqrt{\Delta_0^2 + \epsilon_0^2}. \quad$$

In general, the parameters $\Delta_0$ and $\epsilon_0$ have a distribution of values. Tunneling is observed at very low temperatures only for the few tunneling systems for which the effects of the bias are weak. In such cases, due to the large density of states of the
electron-hole pairs at the Fermi level in metallic glasses, the $T_1$ rate is often so large that all phase coherence is lost before an echo can be produced [20]. It may be possible, however, to "tune" the bias, so that the diagonal coupling is stronger than the nondiagonal coupling. Such a bias may be produced by a static external field. In fact, this possibility has been proposed as a way of initially preparing localized tunneling states [22]. If $\Delta_0/E$ is small enough, $T_1$ processes may be suppressed, and we may hope to see the effect of the algebraic loss of phase coherence. Even with the suppression of tunneling, however, the large cutoff energy of the bath, and the large diagonal coupling strength would make observation of this effect difficult [20]. In any event, the search for such behavior is worthwhile since it would reveal dramatic behavior induced by Ohmic coupling.

Ohmic type dephasing may also occur in confined geometries, or in special cases where coupling to the strain field is much stronger in one direction than the others. Recently, Kikas et.al. [23] have proposed a novel explanation of some anomalous impurity spectra in low-temperature insulating glasses. They have noticed that the low temperature spectral holes for chlorin dopant photoproduct states in several different glasses show a peculiar, non-Lorentzian shape. They explain this by postulating that a local defect ("planar crack") caused by dopant phototransformation, induces quasi-one dimensional electron-phonon coupling. This behavior is essentially given by the Ohmic model outlined in section 2. There are some problems with the explanation of Kikas et.al. The first is their use of a zero temperature calculation to explain the product spectra at 5K. There is also no direct evidence for the "crack" formation. Thus, while the work of Kikas et.al. would provide an interesting example of Ohmic dephasing, the evidence is not convincing enough at this time to draw any firm conclusions.

6.4 Quadratic Electron-Phonon Coupling

We now turn to a study of the effect of quadratic electron-phonon coupling on pure dephasing when an abundance of low frequency modes of the bath are present. Again,
we use the Ohmic bath as a model. We will use the Hamiltonian studied by Skinner and Hsu [3] (again setting $\hbar = 1$)

$$H = \omega_0|1\rangle\langle 1| + H_b + \Delta|1\rangle\langle 1|,$$

with

$$H_b = \sum_k \omega_k a_k^\dagger a_k,$$

$$\Delta = \frac{W}{2} \phi^2,$$

and

$$\phi = \sum_k h_k (a_k^\dagger + a_k).$$

We note that the linear electron-phonon term has been neglected, and a particular form of the quadratic term has been used. Neither of these assumptions are necessary. We neglect the linear term simply to focus on the nonlinear effect. As we will see, this term could easily be included in our study. The form of the coupling is chosen to make contact with the work of Skinner and Hsu. In fact, we will show that our method is somewhat better adapted than the method of Skinner and Hsu for treating more general quadratic electron-phonon coupling terms [24].

There have been two previous nonperturbative theories of the pure dephasing of a two level system coupled quadratically to a bath of harmonic oscillators. Osad’ko [4] used an integral equation approach to find a nonperturbative expression for the off diagonal reduced density matrix element in the limit $t \to \infty$. Skinner and Hsu found the expression [3]

$$\sigma_{10}(t) = \sigma_{10}(0) \exp(-i\omega_0 t) \langle F(t) \rangle,$$

where

$$\langle F(t) \rangle = \left\langle \exp_T \left[ -i \int_0^\infty d\tau \Delta(\tau) \right] \right\rangle.$$

$\Delta(t)$ is the Heisenberg expression for the operator $\Delta$, $T$ is the time ordering opera-
tor, and the brackets represent a thermal average over phonon states. Skinner and Hsu evaluate (6.13) by means of a cumulant expansion. Unlike the linear case, all cumulants contribute in general. In the limit $t \gg \tau_c$, where $\tau_c$ is the characteristic decay time of bath correlations, all cumulants are proportional to time, giving rise to exponential decay of the coherence variable. The resulting dephasing rate is obtained by exactly resuming all the cumulants in this limit. The methods of Osad’ko and of Skinner give identical results.

We recall that, in general, there are two correlation times for the bath at low temperatures. The methods of Osad’ko and Skinner and Hsu are valid only in the time regime $t \gg \text{max}(\frac{1}{\omega_c}, \beta \hbar)$ and thus say nothing about the potentially interesting regime between the mechanical and thermal correlation times. In fact, in the case of linear electron-phonon coupling, these methods are incorrect in predicting that the pure dephasing vanishes as the temperature approaches zero for the Ohmic density of states. It would be interesting to see if similar effects exist when the system-bath coupling is quadratic in the bath coordinates. We thus would like to have a method that reproduces the Osad’ko and Skinner and Hsu results when they are valid, while properly describing the pure dephasing at very low temperatures.

Our method is based on a powerful but somewhat unappreciated many body technique introduced by Balian and Brezin as a means to generalize Wick’s theorem [25]. This method is useful for evaluating the thermal average of exponential quadratic phonon operators. The method has been used, for example, by Friesner et.al. [26] in their study of multimode resonance Raman line shapes. The details of the procedure are outlined in Refs. 26 and 27. We begin with the expression for $\langle F(t) \rangle$ in the form

$$\langle F(t) \rangle = \text{Tr}_b[\rho_b \exp(iH_b t) \exp(-i(H_b + \Delta) t)].$$

Where $\rho_b$ is the equilibrium phonon density matrix given in Eq. (6.4). It is the function $\langle F(t) \rangle$ which governs the pure dephasing in Eq. (6.13). Instead of casting this thermal average as a time ordered integral, and calculating the resulting cumulant series, we recast the thermal average as a matrix determinant, thereby effectively sum-
ming all cumulants for all times. The basics of the method of Balian and Brezin are as follows. Any exponential quadratic operator of creation and annihilation operators is first put in the form \( \mathcal{G} = \exp \frac{1}{2} \alpha S \alpha \), where \( \alpha \) is a 2N dimensional vector of boson creation and annihilation operators \( \alpha = (a_1, \ldots, a_N, a_1^+, \ldots, a_N^+) \) and \( S \) is a symmetric matrix. Such an operator is represented by the matrix

\[
[\mathcal{G}] = \exp \tau S, \tag{6-15}
\]

with

\[
\tau = \begin{pmatrix}
0 & 1 \\
-1 & 0
\end{pmatrix}. \tag{6-16}
\]

Here \( 0 \) is the NxN null matrix, and \( 1 \) is the NxN unit matrix. Any product of exponential quadratic operators \( \mathcal{G}_3 = \mathcal{G}_1 \mathcal{G}_2 \) is represented by the matrix \([\mathcal{G}_3] = [\mathcal{G}_1][\mathcal{G}_2]\). It is then possible to show (see Refs. 26 and 27 for details) that the trace of \( \mathcal{G} \) can be written

\[
\text{Tr} \mathcal{G} = \left[ (-1)^N \det ([\mathcal{G}] - 1) \right]^{-1/2}. \tag{6-17}
\]

With this technology, the dephasing function \( \langle F(t) \rangle \) can be expressed

\[
\langle F(t) \rangle = \left( \frac{\det([\rho][\theta_1][\theta_2] - 1)}{\det([\rho] - 1)} \right)^{-1/2}. \tag{6-18}
\]

where \([\theta_1]\) is the matrix representation of the operator \( \exp(iH_b t) \), \([\theta_2]\) is the matrix representation of the operator \( \exp(-i(H_b + \Delta) t) \), and \([\rho]\) is matrix the representation of the density operator.

The method just described is an alternate nonperturbative approach to the quadratic pure dephasing problem. There are two advantages of this method. First, it is valid \textit{for all times}, and not just in the asymptotic regime (as are the methods of Osad'ko and Skinner and Hsu). Secondly, the factorized initial conditions (6.3) need not be used. This second point is generally irrelevant in the time regime for which the method of Skinner and Hsu is valid. However, it may be of extreme importance at short times. The disadvantage of the method is that it requires the input of a finite number of
bath modes, which means that the bath never reaches equilibrium, causing phase recurrences [28]. Thus, we must test the domain of validity by varying the number of modes in the bath, and comparing the results to the previous nonperturbative theory.

We choose an Ohmic bath by selecting frequencies from a flat distribution of values in the interval \((0, \omega_c)\), and choosing coupling constants [5]

\[
h_k = \sqrt{\frac{\omega_k}{2N}}.
\]

Note that the high frequency cutoff function is now taken to have a sharp step function form. This will only have consequences in the inaccessible time regime \(t \sim \frac{1}{\omega_c}\). Our choice of the normalization for the coupling constants requires that [5] \(-1 \leq W \leq \infty\). Negative values of \(W\) correspond to the case for which "soft modes" are present.

We first test the new method by comparing the results with the nonperturbative result of Skinner and Hsu. In their treatment, the asymptotic decay of the coherence variable is given by \(|\sigma_{10}(t)| = \exp(-\frac{1}{T_2}t)\), where [2, 3, 5]

\[
\frac{1}{T_2} = \int_0^\infty \frac{d\omega}{4\pi} \ln \left[ 1 + \frac{4n(\omega)(n(\omega) + 1)W^2J(\omega)^2}{(1 - W\Omega(\omega))^2 + W^2J(\omega)^2} \right],
\]

\[
\Omega(\omega) = \frac{2}{\pi} \int_0^\infty d\nu J(\nu) P \left( \frac{1}{\omega^2 - \nu^2} \right).
\]

\(J(\omega)\) was defined in Eq. (6.2), and \(P\) stands for Cauchy principle part. For this calculation, \(J(\omega)\) takes the form \(J(\omega) = \frac{\pi}{2\omega_c} \omega\) for \(0 < \omega < \omega_c\) and is zero for all other values of \(\omega\).

Fig. 6.1 shows the plot of \(\ln |\sigma_{10}(t)|\) vs. time for \(W = .3, \beta = .1, \) and \(\omega_c = 95\). Time is measured in units where \(\hbar = 1\). The new method is seen to be in excellent agreement with the result of Skinner and Hsu for time intervals that depend on the number of bath modes employed. After a certain time, recurrence of phase destroys the apparent thermodynamic behavior. Fig. 6.2 shows one such large scale recurrence. For all temperatures \(\beta \omega_c \leq 10\), the results of Skinner and Hsu were confirmed. In this temperature range, for any coupling strength, the timescale for nonexponential behavior is very short \((t_{\text{nonexp}} \sim O(\frac{1}{\omega_c}))\). After such short transients, exponential
decay of the coherence variable results with a rate described by Eq. (6.19). Thus in
this temperature regime, the result of Skinner and Hsu is valid. Fig. 6.3 shows the
excellent agreement between the matrix technique and the method of Skinner and
Hsu for a variety of temperatures and coupling strengths. It is interesting to note
that the appearance of the logarithmic term in Eq (6.19) is not accidental. Its origin
can be traced to the matrix expression (6.17), written in the form

\[ \text{Tr} G = \exp\left[-\frac{1}{2} \sum_k \ln(1 - \lambda_k)\right], \]

where \( \{\lambda_k\} \) are the eigenvalues of the exponential quadratic operator. In the limit
of a continuous bath spectrum and asymptotically long times the eigenvalues of the
matrix product in Eq. (6.18) are related to the argument of the logarithmic term in
Eq. (6.19).

For \( \beta \omega_c \gg 1 \) we may expect the methods of Osad'ko and Skinner and Hsu to
break down, as they do in the linear coupling case. This is indeed the case. An
example of this behavior is shown in Fig.6.4. Here, 50 modes were used to simulate
the bath, which is a sufficient number to produce accurate results in the time interval
studied. The figure shows the results of a simulation with \( W = -1 \) and \( \beta \omega_c = 665. \)
For times \( t \gg \frac{1}{\omega_c} \) the decay of the coherence variable is nonexponential. The behavior
is qualitatively similar to the algebraic behavior in the linear case (Eq.(6.9)). This
behavior becomes more pronounced as the temperature is lowered, and the interval
\( \frac{1}{\omega_c} < t < \beta \hbar \) becomes larger. Note that the deviation from exponential behavior is
weaker for quadratic as opposed to linear electron-phonon coupling. This behavior is
more pronounced for negative values of \( W \). However, in many glassy and crystalline
environments "soft modes" are prevalent, thus giving hope that the nonexponential
decay of the coherence variable may be detectable at very low temperatures, perhaps
in one of the settings described in section 6.3. The reason for the qualitative differ-
ences in the dephasing behavior between positive and negative values of the coupling
\( W \) is unclear. It must be noted that the simulations are difficult to perform at low
temperatures due to the fact that the timescale \( \beta \hbar \) becomes long and more bath
modes must be employed to achieve accurate results. However, as the (accurate) simulation results displayed in fig. 6.4 show, the signature of the temperature independent nonexponential decay is clear. This leads one to expect such decay persists for arbitrarily low temperatures.

As briefly mentioned before, similarities exist between the results of section 6.2, and Mahan's work on the X-ray spectra of metals [14]. It is also interesting to note the similarity between our method for treating the quadratic dephasing problem based on the field theoretic method of Balian and Brezin, and the matrix method of Combescot and Nozieres, which provides an exact solution to the Mahan, Nozieres, and DeDominicis (MND) theory of the X-ray spectra of metals [29]. In this method, the "core-hole" Green's function (analogous to \( \langle F(t) \rangle \)) is calculated by a matrix method that employs a finite number of conduction electrons to simulate thermodynamic behavior.

To conclude this section, we note that our method can easily handle any type of quadratic system-bath coupling (through the input of the matrix \([\theta_2]\) in Eq.(6.18)) and any quadratic initial condition. Lastly, the addition of an extra linear term in the bath portion of the system-bath coupling may be handled in a manner discussed by Friesner et. al. [26].

6.5 Conclusion

We briefly recap what has been accomplished in this paper. We have shown that, in certain cases, the nonperturbative methods of Osad'ko and Skinner and Hsu fail to describe the behavior of the pure dephasing of a two level system. These anomalies occur at very low temperatures when the heat bath has an abundance of low frequency modes, as in the Ohmic case. We have developed exact methods capable of handling the low temperature dynamics for all times. Such dynamics may show marked deviations from the expected exponential behavior for experimentally accessible times. The detection of this behavior has also been discussed. It is hoped that some aspects of this behavior may be uncovered in future experiments.
Figure 6-1: Plot of $\ln |\sigma_{10}(t)|$ vs. $t$ in units where $\hbar = 1$, $\beta = .1$ and $W = .3$. The cutoff frequency of the bath is taken to be $\omega_c = 95$. Dashed line is from (6.18) with a twenty mode bath. Dash-dot line is from (6.18) with 50 mode bath, solid line is the Skinner-Hsu result (6.19). The time domain for which (6.18) and (6.19) agree depends on the number of bath modes employed. Eventually, the non-ergodic nature of the finite mode simulations is manifested in deviations from the result (6.19). The fact that the dashed and dash-dot lines do not directly overlap with the solid line at short times may be attributed to correct short time evolution described by (6.18) and not (6.19). In these cases, such differences are negligible.
Figure 6-2: Plot of the decay of $|\sigma_{10}(t)|$ vs. $t$ ($\hbar = 1$) from (6.18). $\beta = .1$ and $W = .1$. The cutoff frequency of the bath is taken to be $\omega_c = 95$. 20 bath modes were employed. A large scale phase recurrence can clearly be seen.
Figure 6-3: Plot of $|\sigma_{10}(t)|$ vs. $t$ ($\hbar = 1$) for several values of $\beta$ and $W$. Solid lines correspond to Skinner-Hsu result (6.19), while broken lines correspond to (6.18) with 20 bath modes employed. The set with the dash-dot line corresponds to $\beta = .04$, $W = .5$, the set with the dotted line corresponds to $\beta = .027$, $W = .6$, and the set with the dashed line corresponds to $\beta = .01$, and $W = .3$. The cutoff frequency of the bath is taken to be $\omega_c = 95$. 

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Figure 6-4: Low temperature evolution of $\ln |\sigma_{10}(t)|$ vs. $t(\hbar = 1)$. The dashed line is a 50 mode simulation with $\beta = 7$, $W = -1$ and the cutoff frequency of the bath taken to be $\omega_c = 95$. The dash-dot line is the linear electron-phonon expression (6.9) shown for reference with $\beta = 7$ and $2\alpha/\pi = .0785$. The solid line, also for reference, gives exponential decay that matches dash-dot line asymptotically.
Bibliography


[18] Temperatures below 1mK have been reached in experiments on glasses, see, for example, P. Esquinazi, R. König, and F. Pobell, Z. Phys. B.-Condensed Matter, 87, 305, (1992).


